

## Chemical Transformations of (2,3,9,10-Tetramethyl-1,4,5,7,8,11,12,14-octa-azacyclotetradeca-1,3,8,10-tetraenato)cobalt(II) Perchlorate

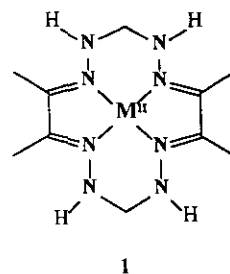
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The monomeric octa-aza bis- $\alpha$ -diimine macrocyclic complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  I, undergoes various reactions on the macrocyclic ligand. Reaction of complex I with triethylamine in double molar proportions, followed by slow aerial oxidation, produces a molecular dimeric complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , III, and a novel Co(I) complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ , IV. Complex III is a staggered cofacial dimer with a cobalt-cobalt bond length 2.86(1) Å. The macrocyclic ligand of the complex contains an  $\alpha$ -diimine function in each five-membered chelate ring, and a three-atom N-C-N delocalized system in each six-membered chelate ring. Complex IV has the 5-5-6-6 chelate arrangement because one  $\alpha$ -diimine moiety is rearranged to a syn-anti configuration. In the structure, the two fused six-membered chelate rings are fully conjugated and the two fused five-membered rings are saturated. However, when complex I reacts with excess triethylamine under the similar conditions, a dimeric complex of another type,  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ , II, was generated, in which one N-N bond of the macrocyclic ligand is broken. Complex IV can be isolated also from the reaction of complex I with excess hydrazine, followed by slow aerial oxidation. When hydrazine in double molar proportions was used, complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNH})]$ , V, which contains a coordinated diazene ligand, was obtained. Only one six-membered chelate ring of complex V is deprotonated and oxidized to form a three-atom N-C-N delocalized system. The structures of octa-aza complexes I-V are determined by X-ray crystallography: I, orthorhombic, *C* mca,  $a = 11.646(4)$ ,  $b = 17.049(3)$ ,  $c = 10.706(3)$  Å,  $Z = 4$ ,  $R = 0.045$ ,  $R_w = 0.047$ , based on 1024 reflections with  $I > 2\sigma(I)$ ; II, monoclinic, *P* 2<sub>1</sub>/*c*,  $a = 9.814(3)$ ,  $b = 22.583(6)$ ,  $c = 14.632(9)$  Å,  $\beta = 98.90(5)^\circ$ ,  $Z = 4$ ,  $R = 0.085$ ,  $R_w = 0.101$ , based on 2033 reflections with  $I > 2\sigma(I)$ ; III, tetragonal, *P* 4/nmm,  $a = 15.614(3)$ ,  $c = 6.498(2)$  Å,  $Z = 4$ ,  $R = 0.081$ ,  $R_w = 0.115$ , based on 340 reflections with  $I > 2\sigma(I)$ ; IV, orthorhombic, *P* bca,  $a = 8.484(1)$ ,  $b = 16.662(3)$ ,  $c = 18.760(2)$  Å,  $Z = 8$ ,  $R = 0.029$ ,  $R_w = 0.024$ , based on 1441 reflections with  $I > 2\sigma(I)$ ; V, monoclinic, *P* 2<sub>1</sub>/*m*,  $a = 7.892(3)$ ,  $b = 11.713(6)$ ,  $c = 9.326(4)$  Å,  $\beta = 108.03(3)$ ,  $Z = 2$ ,  $R = 0.047$ ,  $R_w = 0.056$ , based on 948 reflections with  $I > 2\sigma(I)$ .

### INTRODUCTION

The robust constitution of most synthetic macrocyclic ligands permits modification by diverse chemical transformations, particularly in oxidation and reduction in the coordinated forms.<sup>1</sup> The octa-aza macrocyclic ligand system I is capable of undergoing many facile chemical transformations to produce chelate rings and patterns of unsaturation of various types.<sup>2-9</sup> They include (a) deprotonation from a hydrazine linkage,<sup>3</sup> (b) oxidative dehydrogenation of the saturated C-N linkage to form a C=N imine linkage,<sup>4,7</sup> (c) reduction of the  $\alpha$ -diimine C=N double bond and reoxidation of the ligand to form diazonato chelate rings,<sup>2</sup> (d) nucleophilic attack on C=N double bonds,<sup>2</sup> and (e) further condensation of uncoordinated secondary nitrogen atoms.<sup>8,9</sup>

Several aspects of the octa-aza macrocyclic system are atypical. First, the completely conjugated 14-membered



ring systems that formed by ligand oxidation of the octaaza bis- $\alpha$ -diimine macrocyclic complexes appear to behave as very soft polarizable system with a strong field that is capable of significantly altering the character of coordinated transition metals. Second, the extent of double bond delocalization throughout the octaaza ligand is highly dependent upon the properties of the coordinated metals. Third, the nitrogen atoms of the hydrazine linkage are ambidentate, and

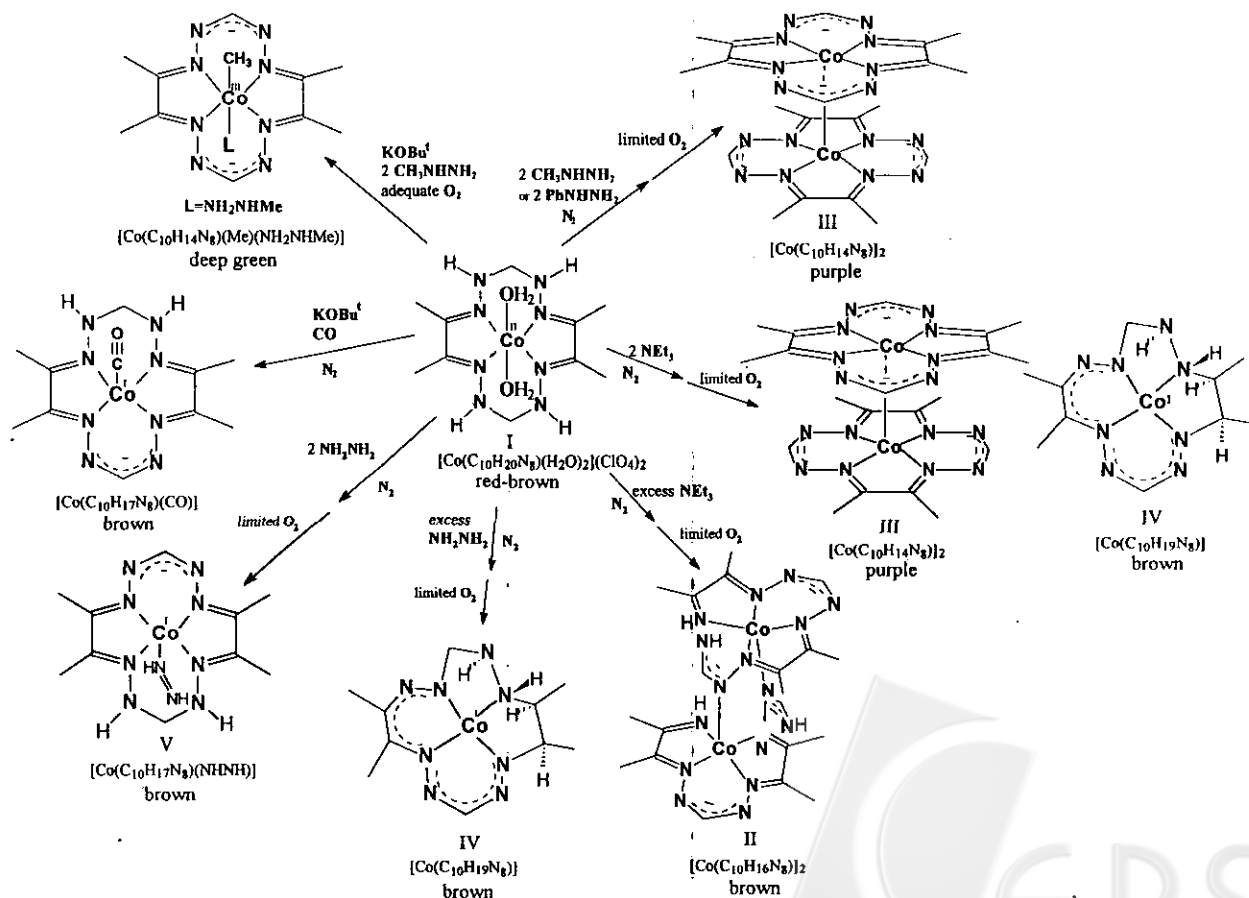
coordination of either nitrogen may occur. Thus, various geometric isomers, depending on whether the 2,3-butanedi-hydrazone has a syn-anti or anti-anti configuration, may be obtained. Fourth, it is possible to systematically alter the degree of saturation and conjugation of the octa-aza macrocyclic system under suitable conditions of reduction and oxidation.

Here we report the reactivity of octa-aza bis- $\alpha$ -diimine cobalt(II) complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ . Under basic or reducing conditions, followed by aerial oxidation, the octa-aza bis- $\alpha$ -diimine macrocyclic complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  readily undergoes varied chemical transformations, as illustrated in Scheme I. The crystal structures of  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ,  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ ,  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ ,  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ , and  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNH})]$  were determined.

## EXPERIMENTAL SECTION

Reagents and solvents were obtained commercially

Scheme I



and were of reagent grade; they were used without further purification. IR spectra of samples in KBr pellets were recorded on a Bio-Rad FTS-40 instrument. Elemental analysis was performed with a Perkin-Elmer 240C CHN elemental analyzer. The UV/VIS absorption spectra were recorded on a Model U-3210 recording spectrophotometer.  $^1\text{H}$  NMR spectra were determined on a Bruker AC-200 spectrometer.

## Synthesis

### $\text{C}_4\text{N}_4\text{H}_{10}$

2,3-butanedi-hydrazone was prepared according to the method of Busch and Bailar.<sup>10</sup>

### $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ , I

The complex was prepared according to the published method for  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)](\text{ClO}_4)_2$ .<sup>11</sup> Aqueous formaldehyde (36%, 0.83 g, 10 mmol) was added to a stirred solution of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.83 g, 5 mmol) in acetonitrile (20 mL) under dinitrogen, to give a red solution. After addition of 2,3-butanedi-hydrazone (1.14 g, 10 mmol), one drop of concentrated perchloric acid was added as catalyst. The solution, which immediately turned deep red-brown, was

stirred for another hour. A degassed solution of diethyl ether was slowly added to the red-brown solution to induce precipitation of the product, which was filtered under dinitrogen (yield about 90%). Suitable crystals for X-ray crystallography were obtained from the saturated solution of  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  when being kept under dinitrogen for several days.

$[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ : red-brown solid; IR (KBr) 3552 and 3464 ( $\text{H}_2\text{O}$ ), 3190 (N-H), 2913 (C-H), 1593 (C=N), 1477, 1432, 1379, 1342, 1297, 1264, 1112 ( $\text{ClO}_4$ ), 628, 487  $\text{cm}^{-1}$ ; UV ( $\lambda_{\text{max}}/\text{nm}$ ,  $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ,  $\text{CH}_3\text{CN}$ ) 242 ( $2.70 \times 10^4$ ), 285 ( $1.22 \times 10^4$ ), 398 ( $5.91 \times 10^3$ ), 561 ( $1.57 \times 10^3$ ); Anal. calcd for  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ : C, 21.99; H, 4.43; N, 20.52; found: C, 21.86; H, 4.59; N, 20.47.

#### A. Reaction of $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ with Triethylamine

##### $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , III, and $[\text{Co}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ , IV

To a solution of  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (1.53 g, 3 mmol) under dinitrogen in acetonitrile (15 mL), a degassed solution of triethylamine (0.61 g, 6 mmol) in acetonitrile (10 mL) was added dropwise. During this period, the solution gradually turned from red-brown to deep blue (about after one molar proportion of triethylamine), and eventually deep blue-purple (about two molar portions of triethylamine). The blue-purple solution was further stirred for 15 min, and then filtered to remove some blue precipitate. The filtrate is sensitive to air; decomposition was observed when much air diffused into the solution. Only a little molecular dioxygen was used for the necessary oxidative dehydrogenation. To modulate the air diffusion, the container was sealed with a serum cap punched by a needle. After standing for one week, the deep blue-purple solution turned deep purple, and deposited two different crystals. The deep purple crystals were identified as  $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  (yield about 30-40%); the red-brown crystals were identified as  $[\text{Co}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$  (yield about 5%).

$[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ : deep purple solid; IR (KBr) 1654 (C=N), 1586, 1527, 1476, 1374, 1289, 1249, 1085, 1000, 853, 655, 626, 561, 477  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 200 MHz)  $\delta/\text{ppm}$  1.16 (24H, s,  $\text{CH}_3 \times 8$ ), 7.76 (4H, s, C-H); FAB (NBA,  $m/z$ ) 610 (dimer), 305 (monomer); UV ( $\lambda_{\text{max}}/\text{nm}$ ,  $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ,  $\text{CH}_3\text{CN}$ ) 299 ( $2.29 \times 10^4$ ), 355 ( $1.42 \times 10^4$ ), 404 ( $1.12 \times 10^4$ ), 535 ( $7.07 \times 10^3$ ), 650 ( $1.69 \times 10^3$ ); Anal. calcd for  $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ : C, 39.35; H, 4.62; N, 36.71; found: C, 39.25; H, 4.83; N, 36.53.

$[\text{Co}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ : brown solid; IR (KBr) 3237 and 3092 (N-H), 2983, 2914 and 2860 (C-H), 1453, 1436 (conjugated C-N, C-C), 1344, 1313, 1248, 1193, 1133, 907, 890, 785, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 200 MHz)  $\delta/\text{ppm}$  1.02 (3H,

s,  $\text{CH}_3$ ) and 1.58 (3H, s,  $\text{CH}_3$ ) (saturated five-membered ring); 2.80 (3H, s,  $\text{CH}_3$ ) and 3.32 (3H, s,  $\text{CH}_3$ ) (for conjugated six-membered ring); 3.39 (2H,  $\text{CH}_2$ ), 4.86 (1H, m, CH), 5.13 (1H, d, CH), 6.43 (s, br, N-H), 9.11 (1H, s, aromatic C-H), 9.62 (1H, t, br, N-H); Anal. calcd for  $[\text{Co}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ : C, 38.71; H, 6.17; N, 36.12; found: C, 38.60; H, 6.23; N, 36.35.

##### $[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ , II

The procedure is similar to that for  $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , but with more than two molar proportions of triethylamine. The blue-purple solution, which gradually turned purple-red, was stirred for 15 min, filtered under dinitrogen and separated into several tubes capped with serum cap and allowed to stand for one week. The solution turned red-brown; red-brown crystals appeared were identified as  $[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$  (yield 40-50%).

$[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ : brown solid; IR (KBr) 3197 (N-H), 1657 (C=N), 1581, 1526, 1457, 1343, 1252, 1117, 992, 660, 624, 561, 504  $\text{cm}^{-1}$ ; FAB (NBA,  $m/z$ ) 614 (dimer), 307 (monomer); Anal. calcd for  $[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ : C, 39.10; H, 5.25; N, 36.47; found: C, 38.87; H, 5.80; N, 36.25.

#### B. Reaction of $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ with Hydrazine

##### $[\text{Co}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ , IV

Excess hydrazine monohydrate (about 12 molar proportion, 1.8 g, 36 mmol) in acetonitrile (10 mL) was added dropwise to a stirred solution of  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (1.53 g, 3 mmol) in acetonitrile (20 mL) under dinitrogen. The solution turned from red-brown to deep blue, then deep purple. On further stirring for 15 min, the solution was filtered under nitrogen and separated into several tubes capped with serum cap and allowed to stand for several weeks. Red-brown crystals were obtained at the bottom of the tube (yield about 40%).

##### $[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNH})]$ , V

Hydrazine monohydrate (2 molar proportions, 0.3 g, 6 mmol) in acetonitrile (10 mL) was added dropwise to a stirred solution of  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (1.53 g, 3 mmol) in acetonitrile (20 mL) in an ice bath under dinitrogen. The resulting solution which turned deep blue immediately was stirred for 15 min. The solution was filtered quickly under dinitrogen; the filtrate was capped with a serum cap with needle hole and left to stand for one week in a refrigerator. The solution turned purple, and lustrous red-brown flaky crystals were obtained (yield about 20%).

With methylhydrazine or phenylhydrazine in double molar proportions under similar conditions, the expected  $[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNCH}_3)]$  or  $[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNPh})]$  were not formed. After the solution was left standing for

several weeks, purple crystals,  $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , were isolated from the purple solution.

$[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNH})]$ : brown solid; IR (KBr) 1608, 1461, 1421, 1364, 1246, 1163, 1106, 1034, 994, 906, 824, 761, 683  $\text{cm}^{-1}$ ; Anal. calcd for  $[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNH})]$ : C, 35.49; H, 5.66; N, 41.42; found: C, 35.35; H, 5.80; N, 41.33.

### X-ray Crystallography

Diffraction measurements were made with a Nonius CAD-4 diffractometer. Lattice parameters were determined from 25 randomly selected high-angle reflections. The space groups were identified from systematic absences. All reflections were corrected for Lorentz, polarization and absorption effects. Absorption corrections were made with the  $\phi$ -scan method. All data reduction and refinement were performed with NRCC-SDP-VAX packages. Structures were solved by direct methods and refined by least-squares cycles; all hydrogen atoms were calculated in idealized positions and included in the calculation of the structure factor. A summary of crystal data appears in Table 1. The coordinates of non-hydrogen atoms are presented in Table 2.

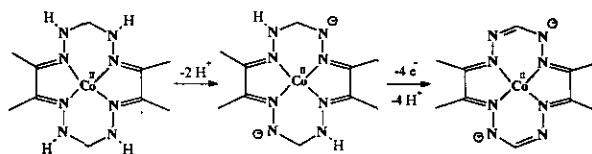
## RESULT AND DISCUSSION

### A. Reaction of $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ with Triethylamine

The initial objective of using triethylamine as base, followed by slow aerial oxidation to extend the unsaturation of the octa-aza bis- $\alpha$ -diimine macrocyclic complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ , I, was to produce the completely conjugated dimeric dihydrooctaaza[14]annulene complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , III. Dark brown crystals of bridged dimeric complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ , II, were isolated. Although double bonds were introduced into the ligand of complex II, one N-N bond of the macrocyclic ligand was broken. According to reaction conditions, only triethylamine and diffused air were involved as reagents to react with complex I. As the purpose of oxidation of the macrocyclic ligand was attained, the factor that destroyed the macrocyclic system may be the excess triethylamine. According to this rationale, complex I reacted with triethylamine in double molar proportions in acetonitrile, followed by slow diffusion (about one week) of molecular dioxygen into the solution to give pillar-shaped deep purple crystals of non-bridged dimeric complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , III. Dark brown rhombic crystals of composition  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ , IV, were isolated from the same reaction.

Formation of the dinuclear complex  $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  requires complicated deprotonation and oxidative dehydro-

genation. The overall reaction involves deprotonation oxidation to form a completely conjugated 16 $\pi$ -electron system of the dihydrooctaaza[14]annulene ligand, as shown below.



The octa-aza bis- $\alpha$ -diimine complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  I, is monomeric, whereas the completely conjugated dihydrooctaaza[14]annulene complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , III, is dimeric. Two effects are pertinent. The "core" size of a highly conjugated macrocyclic system is smaller, the metal can experience stronger tetragonal fields. When the weak field ligand (eg.  $\text{H}_2\text{O}$ ) is detached from the cobalt atom of complex I; the metal may be too large to fit in the plane of a conjugated 14-membered ring and becomes displaced to one side to form a five-coordinate  $d^7$ - $d^7$   $\sigma$  bond. Second, highly delocalized electron systems have more intimate interactions between metal and ligand orbitals, therefore, the d orbitals of a metal ion is more diffuse than usual; and the closed cofacial approach for planar molecules of dihydrooctaaza[14]annulene ligand system is more favorable.

The mononuclear complex  $[\text{Co}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$  has the 5-5-6-6 chelate arrangement because one  $\alpha$ -diimine moiety of 2,3-butanedihydrazine has rearranged to a syn-anti conformation. In the complex, two fused six-membered chelate rings are fully conjugated whereas the two fused five-membered rings are saturated. The overall processes involved removal of a proton and one-electron reduction of  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ .

### B. Reaction of $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ with Hydrazine

Complex IV was isolated as the sole product in the reaction of excess hydrazine with complex I, followed by slow aerial oxidation. When hydrazine in double molar proportions was used, complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNH})]$ , V, that contains a coordinated diazene was obtained. Complex V is similar to a related complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{CO})]$  in which only one six-membered ring of the macrocyclic ligand was oxidized to form a monoanionic ligand.<sup>4</sup> The formation of complex V is the result of deprotonation and one electron oxidation. The product is sensitive to air and easily further oxidized in solution to form the deep purple product  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , III, which then decomposed. Slow diffusion of air enabled the isolation of complex V, which crystallized *in situ*. Hydrazine was oxidized to form a diazene ligand, which acted as an axial ligand for the cobalt atom of

Table 1. Summary of Crystallographic Data of Complexes I-V

Complexes	I	II	III	IV	V
Formula	$[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	$[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)_2 \cdot 2\text{CH}_3\text{CN}] \cdot 5\text{H}_2\text{O}$	$[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)_2] \cdot 5\text{H}_2\text{O}$	$[\text{Co}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$	$[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NH}_2\text{H})] \cdot 2\text{H}_2\text{O}$
Molar mass/g	546.18	695.54	345.20	310.24	374.29
Color	red-brown	brown	purple	brown	brown
Crystal size/mm <sup>3</sup>	$0.35 \times 0.40 \times 0.50$	$0.03 \times 0.20 \times 0.250$	$0.05 \times 0.05 \times 0.50$	$0.20 \times 0.30 \times 0.40$	$0.07 \times 0.22 \times 0.45$
Crystal system	Orthorhombic	Monoclinic	Tetragonal	Orthorhombic	Monoclinic
Space group	C mca	P 2 <sub>1</sub> /c	P 4/mmm	P bca	P 2 <sub>1</sub> /m
a/Å	11.646(4)	9.814(3)	15.614(3)	8.484(1)	7.892(3)
b/Å	17.049(3)	22.583(6)	15.614(3)	16.662(3)	11.713(6)
c/Å	10.706(3)	14.632(9)	6.498(2)	18.760(2)	9.326(4)
β/deg		98.90(5)			108.03(3)
V/Å <sup>3</sup>	2125.7(10)	3203.8(24)	1584.2(6)	2652.2(7)	819.8(6)
Z	4	4	4	8	2
F(000)	1127	1507	728	1367	393
D <sub>calc</sub> /g mL <sup>-1</sup>	1.707	1.442	1.447	1.554	1.516
Radiation (λ/Å)	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107
μ/m <sup>-1</sup>	11.212	10.824	10.999	13.003	10.609
Scan width/deg	$2(0.65 + 0.35 \tan(\theta))$	$2(0.85 + 0.35 \tan(\theta))$	$2(0.65 + 0.35 \tan(\theta))$	$2(0.80 + 0.35 \tan(\theta))$	$2(0.90 + 0.35 \tan(\theta))$
Scan speed/deg min <sup>-1</sup>	2.06-8.24	2.06-3.30	2.06-5.50	2.75-8.24	2.75-8.24
2θ limit/deg	55.0	45.0	50.0	45.0	45.0
hkl range	(0:15)(0:22)(0:13)	(-10:10)(0:24)(0:15)	(0:18)(0:13)(0:7)	(0:9)(0:17)(0:20)	(-8:8)(0:12)(0:10)
No. of unique reflections	1291	4210	799	1724	1130
reflections of obs. (I > 2σ(I))	1024	2033	340	1441	948
No. of refined parameters	82	397	57	249	113
R <sup>a</sup>	0.045	0.085	0.081	0.029	0.047
R <sub>w</sub> <sup>b</sup>	0.047	0.101	0.115	0.024	0.056

<sup>a</sup>R =  $\sum |F_o - F_c| / \sum |F_o|$ <sup>b</sup>R<sub>w</sub> =  $[\sum w(|F_o - F_c|)^2 / \sum w |F_o|^2]^{1/2}$

Table 2. Fractional Atomic Coordinates and B Values ( $\text{\AA}^2$ ) of Complexes I-V

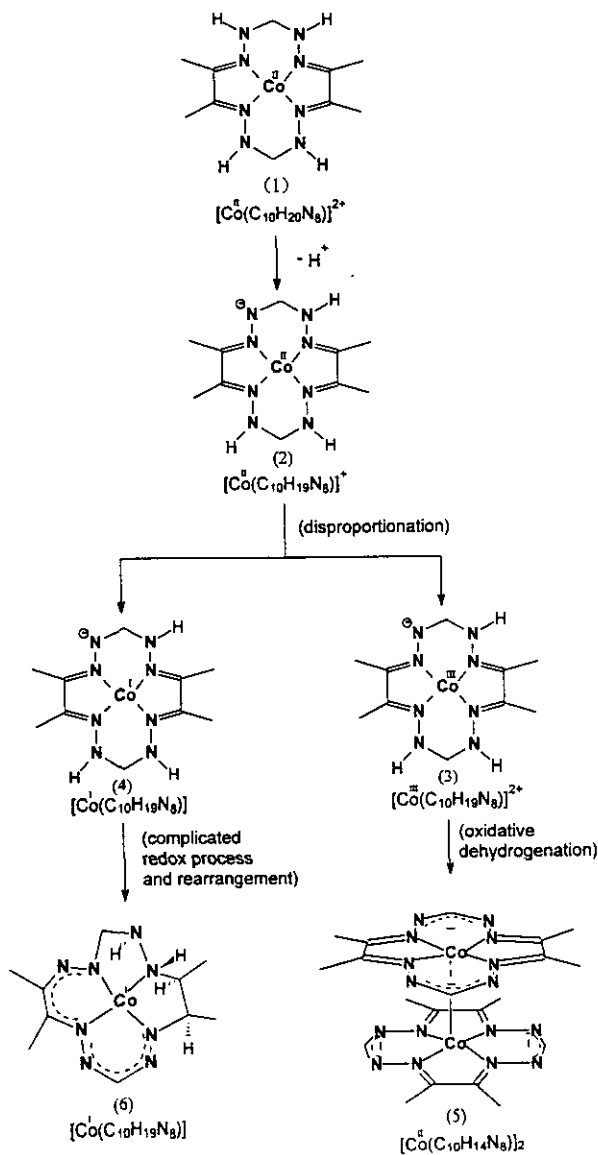
	x	y	z	Beq					
Compound I.									
Co	0	0	0	2.20(3)	C19	-0.042(3)	0.3523(11)	0.4667(14)	5.6(13)
O1	0	-0.04286(23)	0.2034(4)	3.67(17)	C20	0.2075(20)	0.2990(9)	0.3983(14)	3.6(9)
N1	0.1235(3)	0.06717(16)	0.0441(3)	2.50(11)	N18	0.239(5)	0.4790(24)	0.320(3)	19.6(38)
N2	0.1034(3)	0.13749(17)	0.1055(3)	3.15(13)	N19	0.506(6)	0.3988(22)	0.443(4)	24.2(44)
C1	0.2256(3)	0.03899(19)	0.0299(3)	2.65(13)	C21	0.234(4)	0.4898(21)	0.400(3)	13.3(31)
C2	0	0.1765(3)	0.0612(6)	3.23(23)	C22	0.188(8)	0.501(3)	0.473(3)	23.7(61)
C3	0.3336(3)	0.0779(3)	0.0706(4)	3.98(18)	C23	0.503(4)	0.3804(17)	0.353(5)	20.3(55)
C1	1/4	0.31899(8)	1/4	3.62(6)	C24	0.493(5)	0.370(3)	0.253(5)	32.0(69)
O2	1/4	0.4010(3)	1/4	6.9(3)	Compound III.				
O3	0.1220(7)	0.3145(5)	0.2282(12)	8.9(5)	Co	3/4	1/4	0.2803(12)	4.5(3)
O4	0.2695(7)	0.28131(22)	0.1422(4)	11.5(4)	N1	0.8270(10)	0.3371(10)	0.2613(24)	3.0(8)
Compound II.									
Co1	0.10427(23)	0.16683(12)	0.21387(16)	2.38(10)	N2	0.9148(9)	0.3280(8)	0.266(3)	2.9(7)
Co2	-0.10011(22)	0.17350(11)	0.40775(16)	2.21(10)	C1	0.9480(15)	1/4	0.266(5)	3.4(13)
N1	0.0517(17)	0.0872(7)	0.2188(11)	3.5(8)	C2	0.7949(10)	0.4152(10)	0.248(3)	2.5(7)
N2	0.3736(15)	0.1615(8)	0.1636(11)	3.6(8)	C3	0.8515(12)	0.4948(11)	0.243(3)	3.7(10)
N3	0.2623(14)	0.2609(7)	0.1468(10)	3.0(8)	O1	1/4	1/4	0.256(12)	6.7(28)
N4	0.1391(15)	0.2409(7)	0.1711(9)	2.7(7)	O2	0.4265(10)	0.4265	0.261(4)	4.8(8)
N5	-0.0760(13)	0.2001(7)	0.2127(10)	2.4(7)	Compound IV.				
N6	-0.1631(14)	0.1791(7)	0.2692(10)	2.7(6)	Co	0.10848(5)	0.368492(24)	0.042592(23)	2.289(18)
N7	-0.3160(18)	0.1541(9)	0.1349(12)	5.1(9)	N1	-0.0150(3)	0.28185(14)	0.03677(13)	2.37(12)
N8	0.2630(15)	0.1342(8)	0.1827(11)	3.5(8)	N2	-0.0780(3)	0.23713(15)	0.08758(13)	2.84(13)
N9	-0.0537(14)	0.0936(7)	0.4099(10)	3.0(7)	N3	0.0501(3)	0.31470(16)	0.18244(13)	3.19(14)
N10	-0.2570(15)	0.1433(7)	0.4484(10)	2.8(7)	N4	0.1184(3)	0.37078(15)	0.13993(13)	2.61(12)
N11	-0.3651(15)	0.1748(8)	0.4701(11)	3.9(8)	N5	0.2866(3)	0.50824(15)	0.07628(14)	3.41(14)
N12	-0.2486(16)	0.2712(8)	0.4726(11)	3.4(8)	N6	0.2195(3)	0.45897(14)	0.03142(14)	2.81(13)
N13	-0.1313(14)	0.2488(6)	0.4479(9)	2.1(6)	N7	0.1382(3)	0.44268(15)	-0.09079(14)	3.33(14)
N14	0.0747(12)	0.2054(6)	0.4026(9)	1.7(6)	N8	0.1152(3)	0.36242(14)	-0.06006(12)	2.47(12)
N15	0.1667(13)	0.1782(7)	0.3510(9)	2.6(7)	C1	-0.0366(4)	0.25800(20)	0.15429(17)	3.25(17)
N16	0.3316(15)	0.1649(10)	0.4851(10)	4.7(10)	C2	0.1977(4)	0.42718(19)	0.17860(17)	2.98(16)
C1	0.1560(22)	0.0478(9)	0.2160(15)	4.0(10)	C3	0.2741(4)	0.49211(20)	0.14651(17)	3.33(17)
C2	0.2771(25)	0.0746(10)	0.1960(16)	4.6(11)	C4	0.2506(4)	0.48124(18)	-0.04391(18)	3.53(18)
C3	0.3613(18)	0.2196(10)	0.1479(13)	3.5(10)	C5	-0.0293(4)	0.32166(20)	-0.08580(17)	2.87(16)
C4	0.0423(20)	0.2823(9)	0.1707(12)	3.1(9)	C6	-0.0543(3)	0.25163(19)	-0.03561(16)	2.56(14)
C5	-0.0763(17)	0.2593(8)	0.2026(11)	2.2(8)	C7	0.2015(5)	0.41876(21)	0.25840(20)	4.55(20)
C6	-0.2770(18)	0.1557(9)	0.2249(12)	3.1(9)	C8	0.3567(5)	0.55526(22)	0.19084(21)	5.33(22)
C7	-0.1529(21)	0.0571(9)	0.4244(14)	3.6(9)	C9	-0.0228(5)	0.29917(22)	-0.16418(18)	4.24(20)
C8	-0.2689(19)	0.0852(9)	0.4478(14)	3.4(9)	C10	0.0435(4)	0.17622(19)	-0.05145(18)	3.44(18)
C9	-0.3468(21)	0.2321(10)	0.4763(13)	3.6(10)	Compound V.				
C10	-0.0326(19)	0.2885(8)	0.4433(12)	2.6(8)	Co	0.66003(13)	1/4	0.37070(11)	2.37(5)
C11	0.0877(17)	0.2628(8)	0.4149(12)	2.5(8)	N1	0.7595(5)	0.3663(3)	0.5051(4)	2.51(21)
C12	0.2872(20)	0.1603(9)	0.3954(13)	3.4(9)	N2	0.5219(5)	0.3693(4)	0.2634(5)	2.70(19)
C13	0.143(3)	-0.0155(10)	0.2328(21)	6.2(15)	N3	0.8917(6)	0.3559(4)	0.6410(5)	3.38(22)
C14	0.411(3)	0.0447(11)	0.1904(23)	6.9(16)	N4	0.4019(6)	0.3522(4)	0.1179(5)	3.65(22)
C15	0.0624(19)	0.3457(8)	0.1498(13)	3.0(8)	N5	0.8383(8)	1/4	0.2501(7)	4.6(4)
C16	-0.1928(20)	0.2963(10)	0.2152(13)	3.6(9)	N6	0.7873(11)	1/4	0.1013(9)	9.5(8)
C17	-0.1467(24)	-0.0094(11)	0.4126(18)	5.5(12)	C1	0.7089(7)	0.4727(4)	0.4552(6)	2.82(25)
C18	-0.392(3)	0.0535(12)	0.4692(20)	6.4(14)	C2	0.5734(7)	0.4742(5)	0.3143(6)	2.8(3)
					C3	0.7874(8)	0.5779(5)	0.5411(7)	4.1(3)
					C4	0.4943(8)	0.5808(5)	0.2326(7)	4.4(3)
					C5	0.9336(12)	1/4	0.6911(9)	3.9(4)
					C6	0.2971(10)	1/4	0.1124(9)	3.6(4)
					O1	0.9016(5)	0.5078(4)	0.1028(4)	5.09(22)

Beq is the Mean of the Principal Axes of the Thermal Ellipsoid

the complex. Attempts to form similar products, such as  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{CH}_3\text{NNH})]$  and  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{PhNNH})]$ , using methylhydrazine or phenylhydrazine as reagents were unsuccessful, whereas the crystals of dimeric complex III were isolated from the reactions. Therefore, when two six-membered rings were oxidized to form the completely conjugated macrocyclic ligand, the dimeric complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  was obtained.

Formally, the reactions of  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  with triethylamine involve removal of two protons and oxidation of four electrons to form complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , and removal of one proton and reduction of one electron to form complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$ . Both oxidation and reduction were involved in the reaction. In the absence of reducing agent, such as reactions including triethylamine as base, complicated disproportionation occurred. The Co(II) complex may disproportionate to Co(I) and Co(III) species, and Co(III) can act as oxidant to introduce a double bond into the macrocyclic ligand. The process is well established for other low-spin Co(II) complexes, such as cobaloxime(II), which disproportionates in alkaline solution to a mixture of cobaloxime(I) and cobaloxime(III).<sup>12</sup> Similar disproportionation has been reported for the related octa-aza complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{CO})]$ .<sup>4</sup> Scheme II illustrates such a process in which  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)]^{2+}$  (1) was deprotonated to form  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]^+$  (2); and through disproportionation  $[\text{Co}^{\text{III}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]^{2+}$  (3) and  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$  (4) were formed. Anionic intermediates of complexes (2), (3), and (4) are proposed based on the related octa-aza complex  $[\text{Fe}(\text{C}_{10}\text{H}_{19}\text{N}_8)(\text{CO})(\text{CH}_3)]$ , in which only one proton of the octaaza bis- $\alpha$ -diimine macrocyclic ligand was removed to form monoanionic ligand.<sup>3</sup> The intermediate (3) readily undergoes oxidative dehydrogenation reaction to form dimeric complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  (5) with assistance of the central Co(III) metal ion and diffused molecular dioxygen. Complex (4) may be an intermediate to form the product  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$  (6), because the formal oxidation states of both complexes are identical. The complicated geometrical rearrangement and the re-distribution of unsaturation in the macrocyclic ligand are not readily understood. A process in which Co(I) ion acts as reducing agent for the  $\alpha$ -diimine moiety of the macrocyclic ligand can be considered. In that case, the  $\alpha$ -diimine moiety becomes saturated, and the saturated atoms outside the plane of the macrocyclic ligand cause great distortion. To avoid the increasing ring strain due to the distortion, the other uncoordinated nitrogen atoms may coordinate to the central metal ion. Therefore, one  $\alpha$ -diimine moiety may rearrange from the anti-anti to a syn-anti conformation to form a 5-5-6-6 chelate arrangement; intramolecular electronic redistribution occurs con-

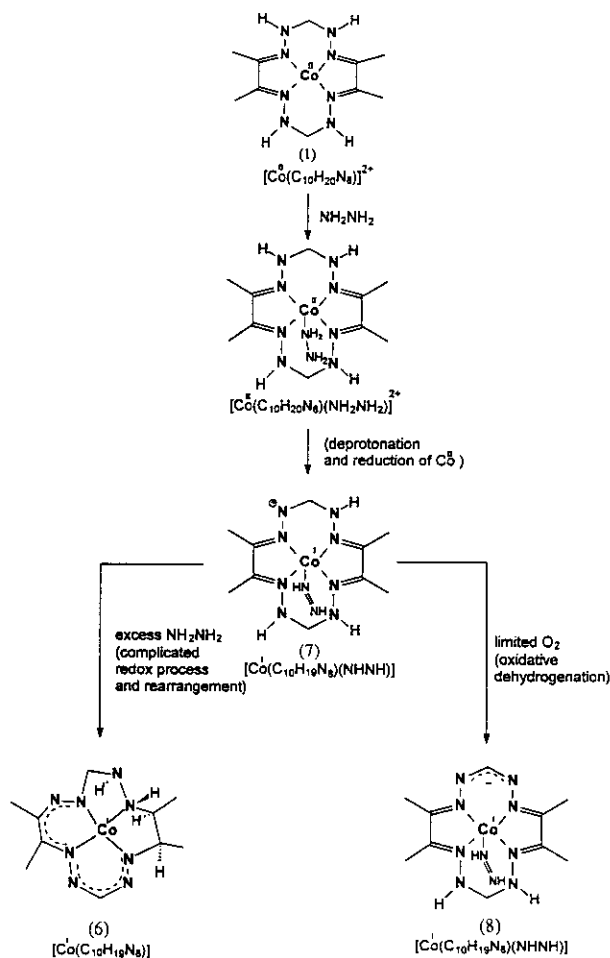
Scheme II



rently.

The reaction processes of complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  with hydrazine are expected to be similar to those described above and are illustrated in Scheme III. As hydrazine can act as reducing agent, coordinating ligand and base, the proposed intermediate  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)(\text{NHNH})]$  (7) may form when  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (1) reacts with hydrazine in double molar proportions. When excess hydrazine was used, the complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$  (6) could be isolated due to its stabilization of the low oxidation state of the octa-aza complex; so rearrangement of the macrocyclic ligand can occur. If hydrazine in only double molar proportions was used in the reaction, the oxidative dehydrogenation reaction would proceed to form complex  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)(\text{NHNH})]$  (8). There was insufficient hydra-

## Scheme III



zine to reduce the macrocyclic ligand, while diffused dioxygen was able to oxidize the ligand. Further oxidation may proceed to form dimeric complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , such as when in  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  reacted with methylhydrazine or phenylhydrazine.

## Structures

 $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  I

The structure consists of a six-coordinate cobalt(II) ion surrounded by four nitrogen atoms of the octa-aza bis- $\alpha$ -diimine macrocyclic ligand with two molecules of water occupying axial sites of the complex. An overview of the molecular geometry is presented in Fig. 1. The two  $\text{CH}_2$  groups of the saturated six-membered chelate rings point upwards on opposite sides of the macrocyclic plane to form a chair-form conformation. Ceulemans et al.<sup>13-15</sup> observed a boat conformation of octa-aza bis- $\alpha$ -diimine Co(II), Ni(II), Cu(II) complexes in the crystalline state. Rapid interconversion between boat and chair conformers of the octa-aza bis- $\alpha$ -diimine macrocyclic ligand in solution is evident.<sup>11</sup>

Thus our report is the first of such a complex crystallized in a chair-form conformation. Interatomic distances and angles for the structure are listed in Table 3. The axially coordinated water is slightly tilted to the coordinated  $\text{N}_4$  plane of the macrocyclic ligand with two  $\text{O}_1\text{-Co-N}_1$  bond angles,  $87.47(11)^\circ$  and  $92.53(11)^\circ$ , due to the steric effect between coordinated water and the  $\text{CH}_2$  group of the saturated six-membered ring.

 $[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$  II

The crystal structure (Fig. 2) shows the original macrocyclic system was destroyed. Scission of one N-N bond of the six-membered chelate ring resulted in two moieties which act as bridge ligand to form the bridged dinuclear dimer  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ . The cobalt atoms exist in square-pyramidal environments, and are displaced  $0.27 \text{ \AA}$  from the plane formed by the four coordinated nitrogen atoms of the macrocyclic ligand. The Co-N distances of the cobalt atoms toward the axial nitrogen atoms, ave.  $2.03(1) \text{ \AA}$ , are greater than the Co-N distances of the cobalt atoms toward the four

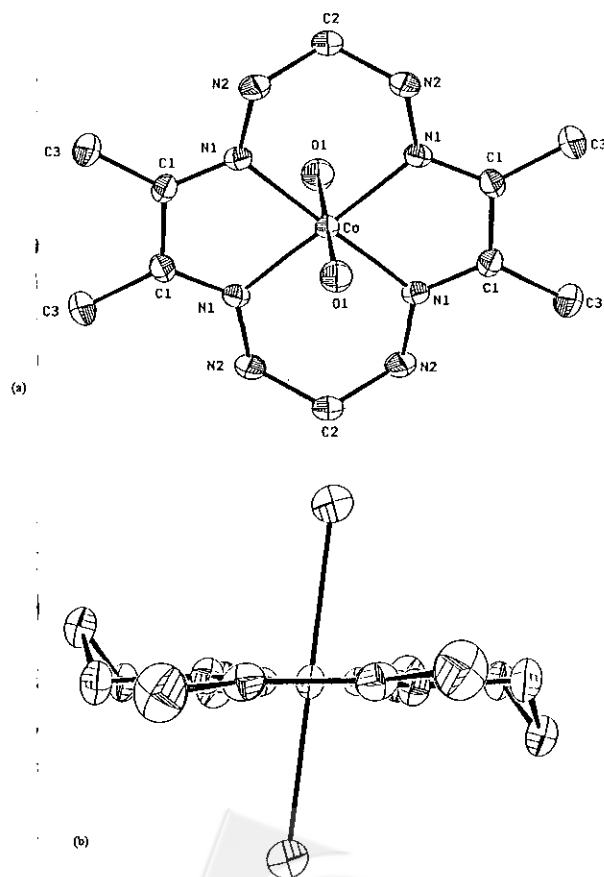


Fig. 1. ORTEP drawing of the  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2]^{2+}$  cation: (a) molecular geometry; (b) side view of the structure, showing the chair-form conformation.



Table 3. Selected Bond Distances and Angles of  $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ 

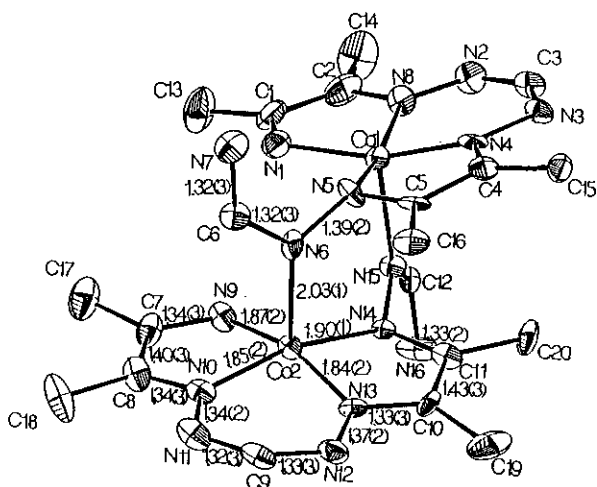
Bond Distances/Å			
Co-O(1)	2.297(4)	N(2)-C(2)	1.455(5)
Co-N(1)	1.898(3)	C(1)-C(1)	1.476(7)
N(1)-N(2)	1.387(4)	C(1)-C(3)	1.487(5)
N(1)-C(1)	1.291(5)		
Bond Angles/deg			
O(1)-Co-O(1)	180.0	Co-N(1)-C(1)	116.35(22)
O(1)-Co-N(1)	87.47(11)	N(2)-N(1)-C(1)	122.2(3)
O(1)-Co-N(1)	92.53(11)	N(1)-N(2)-C(2)	112.3(3)
N(1)-Co-N(1)	180.0	N(1)-C(1)-C(1)	112.7(3)
N(1)-Co-N(1)	98.51(12)	N(1)-C(1)-C(3)	125.4(3)
N(1)-Co-N(1)	81.49(12)	C(1)-C(1)-C(3)	121.9(3)
Co-N(1)-N(2)	120.76(23)	N(2)-C(2)-N(2)	111.7(4)

coordinated nitrogen atoms, ave. 1.86(2) Å, indicating  $\pi$  interactions between cobalt atoms and the coordinated macrocyclic moieties.

Selected bond distances and angles of  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$  are given in Table 4. The average C-N distance 1.33(3) Å and the average N-N distance 1.35(2) Å within the six-membered chelate ring are expected to be similar to those in the complex  $[\text{Co}^{\text{III}}(\text{C}_{10}\text{H}_{14}\text{N}_8)(\text{CH}_3)(\text{NH}_2\text{NHCH}_3)]$ , which contains three-atom N-C-N' segment and delocalized six-membered rings. The average C-N distance of 1.33(3) Å and average C-C distance of 1.41(3) Å within the five-membered chelate rings are expected to be the function of  $\alpha$ -diimine. The terminal part of the broken six-membered rings also has

Table 4. Selected Bond Distances and Angles of  $[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$ 

Bond Distances/Å			
Co(1)-N(1)	1.88(2)	N(12)-N(11)	1.36(2)
Co(1)-N(4)	1.84(2)	N(14)-N(15)	1.41(2)
Co(1)-N(5)	1.92(1)	N(2)-C(3)	1.33(3)
Co(1)-N(8)	1.84(2)	N(3)-C(3)	1.34(3)
Co(2)-N(9)	1.86(2)	N(6)-C(6)	1.31(2)
Co(2)-N(10)	1.86(2)	N(7)-C(6)	1.31(2)
Co(2)-N(13)	1.84(1)	N(11)-C(9)	1.31(3)
Co(2)-N(14)	1.87(1)	N(12)-C(9)	1.32(3)
Co(1)-N(15)	2.02(1)	N(15)-C(12)	1.32(3)
Co(2)-N(6)	2.03(1)	N(16)-C(12)	1.32(3)
N(1)-C(1)	1.36(3)	C(1)-C(2)	1.40(3)
N(4)-C(4)	1.33(3)	C(4)-C(5)	1.42(3)
N(5)-C(5)	1.35(2)	C(7)-C(8)	1.39(3)
N(8)-C(2)	1.36(3)	C(10)-C(11)	1.43(3)
N(9)-C(7)	1.32(3)	C(1)-C(13)	1.46(3)
N(10)-C(8)	1.32(3)	C(2)-C(14)	1.49(3)
N(13)-C(10)	1.33(2)	C(4)-C(15)	1.49(3)
N(14)-C(11)	1.31(2)	C(5)-C(16)	1.45(3)
N(2)-N(8)	1.32(2)	C(7)-C(17)	1.51(3)
N(3)-N(4)	1.39(2)	C(8)-C(18)	1.48(3)
N(5)-N(6)	1.36(2)	C(10)-C(19)	1.49(3)
N(10)-N(11)	1.36(2)	C(11)-C(20)	1.48(3)
Bond Angles/deg			
N(1)-Co(1)-N(5)	96.7(7)	Co(2)-N(14)-C(11)	116(1)
N(1)-Co(1)-N(8)	82.8(7)	Co(1)-N(15)-N(14)	117.9(9)
N(1)-Co(1)-N(8)	94.1(7)	Co(1)-N(15)-C(12)	124(1)
N(4)-Co(1)-N(5)	82.0(6)	Co(2)-N(6)-N(5)	120(1)
N(9)-Co(2)-N(14)	98.7(6)	Co(2)-N(6)-C(6)	125(1)
N(9)-Co(2)-N(10)	81.4(7)	N(1)-C(1)-C(2)	113(2)
N(10)-Co(2)-N(13)	92.9(7)	C(1)-C(2)-N(8)	113(2)
N(13)-Co(2)-N(14)	81.7(6)	C(2)-N(8)-N(2)	115(2)
N(15)-Co(1)-N(1)	97.2(7)	N(8)-N(2)-C(3)	116(2)
N(15)-Co(1)-N(4)	100.3(6)	N(2)-C(3)-N(3)	137(2)
N(15)-Co(1)-N(5)	95.6(6)	C(3)-N(3)-N(4)	115(2)
N(15)-Co(1)-N(8)	99.1(6)	N(3)-N(4)-C(4)	115(2)
N(6)-Co(2)-N(9)	96.5(6)	N(4)-C(4)-C(5)	111(2)
N(6)-Co(2)-N(10)	101.7(6)	C(4)-C(5)-N(5)	114(2)
N(6)-Co(2)-N(13)	102.8(6)	C(5)-N(5)-N(6)	115(1)
N(6)-Co(2)-N(14)	94.3(6)	N(5)-N(6)-C(6)	114(1)
Co(1)-N(1)-C(1)	114(1)	N(6)-C(6)-N(7)	127(2)
Co(1)-N(4)-N(3)	127(1)	N(9)-C(7)-C(8)	114(2)
Co(1)-N(4)-C(4)	118(1)	C(7)-C(8)-N(10)	112(2)
Co(1)-N(5)-N(6)	122(1)	C(8)-N(10)-N(11)	117(2)
Co(1)-N(5)-C(5)	112(1)	N(10)-N(11)-C(9)	116(2)
Co(1)-N(8)-N(2)	128(1)	N(11)-C(9)-N(12)	139(2)
Co(1)-N(8)-C(2)	116(1)	C(9)-N(12)-N(13)	115(2)
Co(2)-N(9)-C(7)	115(1)	N(12)-N(13)-C(10)	115(2)
Co(2)-N(10)-N(11)	127(1)	N(13)-C(10)-C(11)	113(2)
Co(2)-N(10)-C(8)	116(1)	C(10)-C(11)-N(14)	112(2)
Co(2)-N(13)-N(12)	128(1)	C(11)-N(14)-N(15)	117(1)
Co(2)-N(13)-C(10)	117(1)	N(14)-N(15)-C(12)	118(1)
Co(2)-N(14)-N(15)	121(1)	N(15)-C(12)-N(16)	127(2)

Fig. 2. ORTEP drawing of the  $[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$  complex with selected interatomic distances.

the delocalized N-C-N' system with average N-N bond length 1.38(2) Å, both C-N bond lengths 1.32(3) Å and average N-C-N bond angle 126.7°. The planar N-C-N moieties of the broken six-membered rings are rotated about the N-N single bond and coordinated to the cobalt atom of another broken macrocyclic unit with torsion angles C<sub>6</sub>-N<sub>6</sub>-N<sub>5</sub>-C<sub>5</sub> 103.1°, C<sub>11</sub>-N<sub>14</sub>-N<sub>15</sub>-C<sub>12</sub> 87.3°.

### [Co(C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>)<sub>2</sub>], III

The molecular structure of [Co(C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>)<sub>2</sub>] is illustrated in Fig. 3; the packing arrangement of the molecules is presented in Fig. 4; the bond distances and angles are listed in Table 5. There are several notable structural features associated with the dimeric complex. First, the dimer contains a non-bridged Co<sup>II</sup>-Co<sup>II</sup> bond of length 2.86(1) Å. The dihydrooctaaza[14]annulene ligand is essentially planar. The Co atom is displaced 0.12 Å from the plane defined by the four coordinated nitrogen atoms toward the other Co atom of the dimer. The average bond angle Co'-Co-N is 94°. Second, the bond pattern of the completely conjugated macrocyclic ligand contains two α-dimine five-membered chelate rings and two anionic three atoms, N-C-N', delocalized six-membered chelate rings. Third, the two macrocyclic units of the dimer are arranged in a staggered conformation; and the dimer units are packed along the c axis of the unit cell forming Co chains with adjacent dimer units having a cobalt-cobalt distance of 3.64 Å. These aspects are considered further in detail.

Because of the nonbonding repulsion between two macrocyclic units, the σ-bond Co-Co distance in the present dimer exceeds that of [Co<sub>2</sub>(CN)<sub>10</sub>]<sup>6-</sup><sup>16</sup> and [Co<sub>2</sub>(CNCH<sub>3</sub>)<sub>10</sub>]<sup>4+</sup><sup>17</sup> with lengths 2.794(2) Å and 2.74(1) Å, respectively. The distance is also greater than that of eclipsed cofacial dimers of [Co(s-disn)<sub>2</sub>]<sub>2</sub><sup>18</sup> (2.633(3) Å) and [Co(s-pqdi)<sub>2</sub>]<sub>2</sub><sup>19</sup> (2.689(1) Å), in which Co-Co σ-bonds and li-

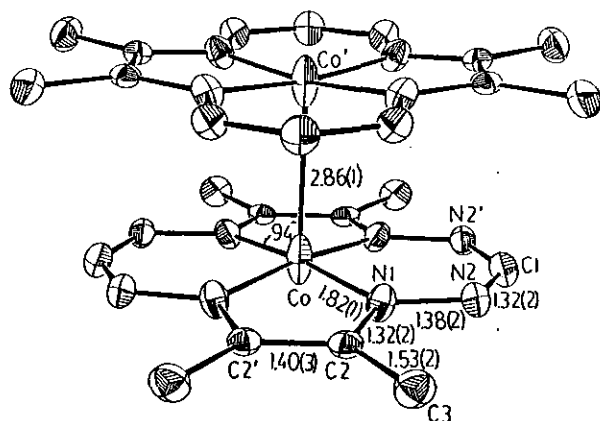


Fig. 3. ORTEP drawing of the [Co(C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>)<sub>2</sub>] dimer with selected interatomic distances.

Table 5. Selected Bond Distances and Angles of [Co(C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>)<sub>2</sub>]

Bond Distances/Å			
Co-N(1)	1.819(12)	C(1)-N(2)'''	1.324(16)
N(1)-N(2)	1.377(21)	C(2)-C(2)'	1.40(3)
N(1)-C(2)	1.322(23)	C(2)-C(3)	1.526(24)
N(2)-C(1)	1.324(16)		
Bond Angles/deg			
N(1)-Co-N(1)''	172.2(8)	N(1)-N(2)-C(1)	119.1(15)
N(1)-Co-N(1)'	82.8(8)	N(2)-C(1)-N(2)'''	133.7(21)
N(1)-Co-N(1)'''	96.7(8)	N(1)-C(2)-C(2)'	112.3(14)
Co-N(1)-N(2)	125.4(12)	N(1)-C(2)-C(3)	122.2(14)
Co-N(1)-C(2)	116.3(12)	C(2)-C(2)-C(3)	125.4(14)
N(2)-N(1)-C(2)	118.3(12)		

gand-ligand attractive pseudo δ-bonds contribute to the bonding. The interplanar separations between least-squares planes defined by symmetry-equivalent atoms N<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and N<sub>2</sub> of the macrocyclic ligand within the dimer are listed in Table 6. The separations are increased when the atoms of

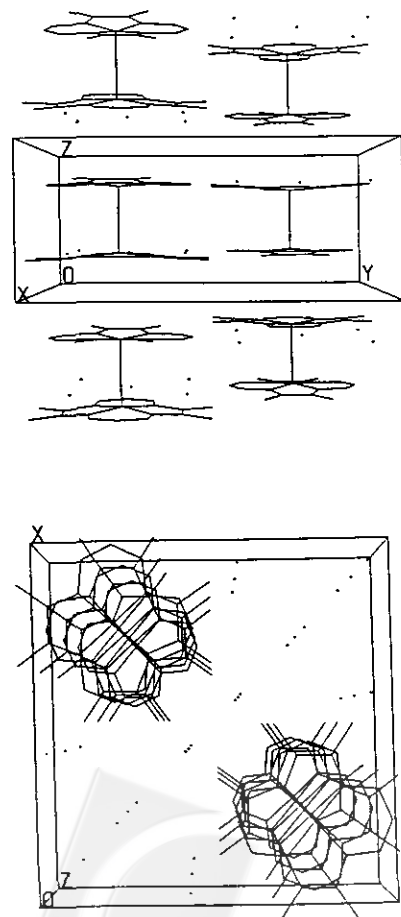
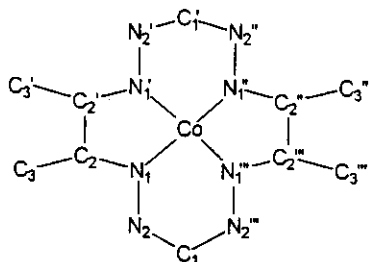


Fig. 4. Two views of three unit cells of [Co(C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>)<sub>2</sub>] illustrating the stacked nature of the dimers.

Table 6. Interplanar Separations within the Dimer  $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2^a$ 

Atoms Defining Plane	Interplanar Separations/Å
$\text{N}_1\text{-N}_1'\text{-N}_1''\text{-N}_1'''$	3.10
$\text{C-}C_2'\text{-}C_2''\text{-}C_2'''$	3.28
$\text{C-}C_3'\text{-}C_3''\text{-}C_3'''$	3.34
$\text{N}_2\text{-N}_2'\text{-N}_2''\text{-N}_2'''$	3.04

<sup>a</sup> The Co-Co bond distance within dimer is 2.86(1) Å, between dimers is 3.64 Å.

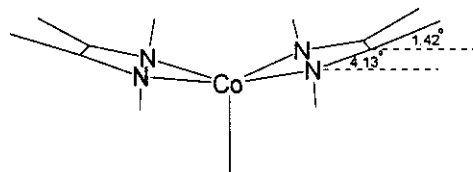


the defining plane are far from the cobalt atom as indicated by separations 3.10, 3.28, 3.34 Å for atoms defining planes  $\text{N}_1\text{-N}_1'\text{-N}_1''\text{-N}_1'''$ ,  $\text{C}_2\text{-C}_2'\text{-C}_2''\text{-C}_2'''$ , and  $\text{C}_3\text{-C}_3'\text{-C}_3''\text{-C}_3'''$ , respectively. These separations are in the repulsive range of a nonbonding interaction. The dihedral angles of various multiple atoms that define planes with the  $\text{N}_4$  donor atom plane are given in Table 7. The planes defined by four atoms of the five-membered chelate rings are tipped by 4.13° relative to the  $\text{N}_4$  donor plane. Obviously the steric effect of the macrocyclic ligands prevent closer approach of the two macrocyclic moieties.

The average C-N and N-N distances in the six-membered rings are 1.32(2) Å and 1.38(2) Å, respectively; the average C-N and C-C distances in five-membered rings are 1.32(2) Å and 1.40(3) Å. Compared with the related octa-aza[14]annulene nickel complex,<sup>6</sup> delocalization in the complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  is less extensive than that observed in the complex  $[\text{Ni}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ . The macrocyclic ligands of the complex  $[\text{Ni}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  are essentially completely delocalized with average C-N and N-N distances in the six-membered rings, 1.336 Å and 1.339 Å, and average C-N and C-C distances in the five-membered rings, 1.357 Å and 1.396 Å. Thus the unsaturation of the complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  is limited to discrete  $\alpha$ -diimine functions of five-membered chelate rings and to a three-atom delocalized system of allylic type, N-C-N', isolated by single N-N bonds of the six-membered chelate rings. The Co-N distance, 1.82(1) Å, associated with completely conjugated octa-aza[14]annulene complex II, is significantly smaller than the Co-N distance of octa-aza bis- $\alpha$ -diimine complex I, 1.898(3) Å. It is attributed to a decreased "core" size as each

Table 7. Angles between the  $\text{N}_4$  Donor Atom Plane and Other Selected Interatomic Distances

Atoms Defining Plane	Angles with the $\text{N}_4$ Plane/deg
$\text{N}_1\text{-C}_2\text{-C}_2'\text{-N}_1'$	4.13°
$\text{C}_3\text{-C}_2\text{-C}_2'\text{-C}_3'$	1.42°
$\text{N}_1\text{-N}_2\text{-C}_1\text{-N}_2''\text{-N}_1'''$	1.03°
$\text{N}_1\text{-Co-N}_1'$	5.17°
$\text{N}_1\text{-Co-N}_1'''$	5.85°



double bond is introduced into the ligand.

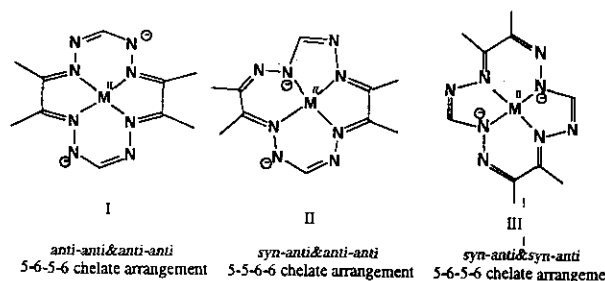
Two factors contribute to repulsive interactions between macrocyclic units of the cobalt dimer — nonbonding repulsion caused by the cofacial approach of the atoms of the macrocyclic ligands, and coulombic repulsion caused by the anionic N-C-N' moieties of the macrocyclic ligands in the eclipsed approach of the macrocyclic units. To minimize most repulsive interactions, the macrocyclic ligands of the cobalt dimer are staggered.

The conformation and degree of delocalization of the dimeric octaaza[14]annulene cobalt complex differ from those of the nickel complex. The two macrocyclic ligands of the dimer  $[\text{Ni}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  are eclipsed and the double bonds of the ligand are completely delocalized. The reasons for the difference between  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  and  $[\text{Ni}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  are unclear. Attractive interaction between two macrocyclic moieties in addition to the metal-metal  $\sigma$ -bond must obviously be present in the nickel complex, but absent from the cobalt complex. The structures of octa-aza[14]annulene complexes,  $[\text{Ni}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  and  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$ , are assumed to consist of metal(II) and dianionic ligand. This electronic arrangement of the complexes gives a formal metal(II)-16 $\pi$ -electron system. This arrangement would result in an anti-aromatic 16 $\pi$  ligand with fixed double bonds. The bond pattern of the macrocyclic ligand of the complex  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  is consistent with an anti-aromatic bonding scheme treated as  $[\text{Co}^{\text{II}}\text{L}^2(16\pi)]$ . If the bonding scheme depicted is valid, the staggered arrangement of the structure becomes plausible. As mentioned above, coulombic repulsion caused by the charge distribution over three-atom linkages of adjacent planes and nonbonding repulsion of atoms of adjacent planes favor a staggered structure. However, the bond pattern of the macrocyclic ligand of the complex  $[\text{Ni}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  is inconsistent with a bonding scheme treated as  $[\text{Ni}^{\text{II}}\text{L}^2(16\pi)]$ . The reason that the  $[\text{Ni}^{\text{II}}$

$(C_{10}H_{14}N_8)_2$  complex forms a fully delocalized macrocyclic system, whereas the  $[Co^{II}(C_{10}H_{14}N_8)_2]$  complex forms a localized conjugated macrocyclic system, is unclear. Different degrees of double-bond delocalization throughout the ligand appear to be related to varied  $\pi$ -backbonding tendencies of nickel and cobalt ions. As full delocalization of the  $[Ni^{II}(C_{10}H_{14}N_8)_2]$  complex occurs over the macrocyclic system, an attractive  $\pi$ - $\pi$  interaction may contribute to the bonding of the two macrocyclic groups to form an eclipsed dimer. In a closely related case, Holm<sup>20</sup> and co-workers synthesized a tetraaza macrocyclic complex  $[Ni(Me_4[14]-hexaenatoN_4)_2](CF_3SO_3)_2$  in which a Ni(II)-stabilized 15 $\pi$ -electron system is delocalized over the 14-membered ring system. The macrocyclic ligands of the dimer are also eclipsed and have a fully delocalized bond pattern.

#### $[Co(C_{10}H_{19}N_8)]$ , IV

There are three possible geometrical isomers of the octaaza[14]annulene complex, I (5-6-5-6 chelate arrangement), II (5-5-6-6 chelate arrangement) and III (5-6-5-6 chelate arrangement).



The three isomers of octa-aza[14]annulene nickel(II) complex were obtained by condensation of 2,3-butanedione,

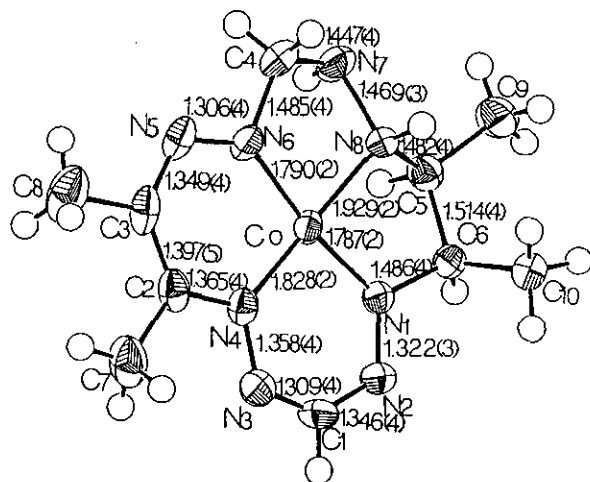


Fig. 5. ORTEP drawing of  $[Co(C_{10}H_{19}N_8)]$  with selected interatomic distances.

hydrazine, and formaldehyde with nickel(II) perchlorate,<sup>21</sup> but the crystal structure of isomer II is not yet reported. The geometrical arrangement of the complex  $[Co^I(C_{10}H_{19}N_8)]$  belongs to isomer of type II. Fig. 5 illustrates the ORTEP drawing of  $[Co^I(C_{10}H_{19}N_8)]$ . Relative to the starting material  $[Co^{II}(C_{10}H_{20}N_8)(H_2O)_2](ClO_4)_2$ , apparently one  $\alpha$ -diimine moiety was rearranged from the anti-anti to the syn-anti configuration to form the 5-5-6-6 chelate arrangement product.

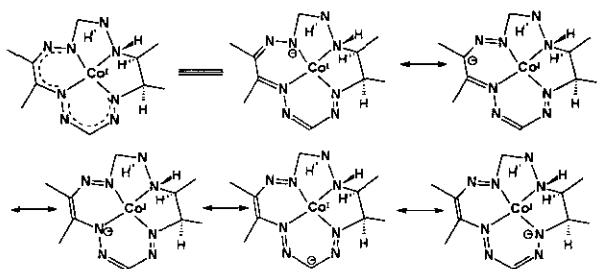
Selected bond lengths and bond angles for  $[Co^I(C_{10}H_{19}N_8)]$  are listed in Table 8. To the two fused six-membered chelate rings, N-N bond lengths 1.322(3), 1.358(4) and 1.306(4) Å, C-N bond lengths 1.346(4), 1.309(4), 1.365(4) and 1.349(4) Å, and C-C bond length of 1.397(5) Å all lie between values for single and double bonds, indicating that moderate conjugation between two fused six-membered rings. In the two fused five-membered

Table 8. Selected Bond Distances and Angles of  $[Co(C_{10}H_{19}N_8)]$

Bond Distances/Å			
Metal-N		fused six-membered rings	
Co-N(1)	1.787(2)	N(1)-N(2)	1.322(3)
Co-N(4)	1.828(2)	N(3)-N(4)	1.358(4)
Co-N(6)	1.790(2)	N(5)-N(6)	1.306(4)
Co-N(8)	1.929(2)	C(1)-N(2)	1.346(4)
fused five-membered rings		C(1)-N(3)	1.309(4)
N(7)-N(8)	1.469(3)	C(2)-N(4)	1.365(4)
C(4)-N(6)	1.485(4)	C(3)-N(5)	1.349(4)
C(4)-N(7)	1.447(4)	C(2)-C(3)	1.397(5)
C(5)-N(8)	1.482(4)	C(2)-C(7)	1.504(5)
C(6)-N(1)	1.486(4)	C(3)-C(8)	1.513(5)
C(5)-C(6)	1.514(4)		
C(5)-C(9)	1.518(5)		
C(6)-C(10)	1.535(4)		
Bond Angles/deg			
N(1)-Co-N(4)	96.0(1)	C(2)-C(3)-N(5)	127.7(3)
N(1)-Co-N(6)	169.0(1)	C(3)-N(5)-N(6)	118.0(3)
N(1)-Co-N(8)	85.1(1)	N(5)-N(6)-C(4)	112.3(2)
N(4)-Co-N(6)	94.3(1)	N(6)-C(4)-N(7)	110.5(3)
N(6)-Co-N(8)	175.3(1)	C(4)-N(7)-N(8)	104.7(2)
Co-N(1)-N(2)	130.4(2)	N(7)-N(8)-C(5)	113.5(2)
Co-N(1)-C(6)	117.5(2)	N(8)-C(5)-C(6)	105.4(2)
Co-N(4)-N(3)	123.5(2)	C(5)-C(6)-N(1)	106.0(2)
Co-N(4)-C(2)	124.6(2)	C(6)-N(1)-N(2)	112.2(2)
Co-N(6)-N(5)	133.1(2)	C(7)-C(2)-N(4)	118.4(3)
Co-N(6)-C(4)	114.5(2)	C(7)-C(2)-C(3)	119.4(3)
Co-N(8)-N(7)	110.4(2)	C(8)-C(3)-C(2)	121.1(3)
Co-N(8)-C(5)	109.0(2)	C(8)-C(3)-N(5)	111.2(3)
N(1)-N(2)-C(1)	114.8(3)	C(9)-C(5)-N(8)	113.5(3)
N(2)-C(1)-N(3)	135.1(3)	C(9)-C(5)-C(6)	114.6(3)
C(1)-N(3)-N(4)	120.0(3)	C(10)-C(6)-C(5)	115.8(3)
N(3)-N(4)-C(2)	111.8(2)	C(10)-C(6)-N(1)	109.5(3)
N(4)-C(2)-C(3)	122.2(3)		

chelate rings, all N-N, C-N and C-C bonds are longer than those of the two fused six-membered rings. The N-N bond of length 1.469(3) Å, C-N bonds of length 1.485(4), 1.447(4), 1.482(4) and 1.486(4) Å, and a C-C bond of length 1.514(4) Å are saturated single bonds. Because of back-bonding between Co(I) and the two fused six-membered rings, the bond Co-N<sub>1</sub>, Co-N<sub>4</sub>, Co-N<sub>6</sub> lengths (1.787(2), 1.828(2) and 1.790(2) Å, respectively) are shorter than Co-N<sub>8</sub> (1.929(2) Å). Torsional angles for four-atom segments of the [Co<sup>I</sup>(C<sub>10</sub>H<sub>19</sub>N<sub>8</sub>)] macrocyclic ligand are listed in Table 9. The two fused conjugated six-membered rings are nearly planar with torsional angles from only 0.5(4)° to 4.8(3)°, whereas the two saturated five-membered rings have torsional angles from 14.0(3)° to 39.8(2)°. The N<sub>7</sub>, N<sub>8</sub>, C<sub>5</sub> and C<sub>6</sub> atoms of the saturated five-membered rings have the chiralities of N<sub>7</sub>-(R), N<sub>8</sub>-(S), C<sub>5</sub>-(S), C<sub>6</sub>-(R), respectively.

The macrocyclic ligand of the complex is a monoanionic ligand containing a 10 π-electron system delocalized between two fused six-membered rings. Six valence isomers are drawn below.



If we suppose that every resonance form has an equal contribution to the π-bonding of the macrocyclic ligand, we can compare the bond pattern of the two fused six-membered rings with the theoretical π-bonding character. In similar coordinated surroundings, the bond N<sub>3</sub>-N<sub>4</sub> (2/5 π character) of length, 1.358(4) Å, is longer than N<sub>1</sub>-N<sub>2</sub> (4/5 π character) of length, 1.322(3) Å; and the bond C<sub>1</sub>-N<sub>2</sub> (1/5 π character) of length, 1.346(4) Å, is also longer than C<sub>1</sub>-N<sub>3</sub> (3/5 π character) of length, 1.309(4) Å. The bond C<sub>2</sub>-N<sub>4</sub> (2/5 π character) of length, 1.365(4) Å, is longer than the bond C<sub>3</sub>-N<sub>5</sub> (1/5 π character) of length, 1.349(4) Å; this effect is attributed to back-bonding interaction between Co(I) and the coordinated C<sub>2</sub>-N<sub>4</sub> moiety.

#### [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)], V

The structure consists of a five-coordinate square pyramidal cobalt(I) ion girded by four nitrogen atoms of the monoanionic macrocyclic ligand and an axial coordinated diazene ligand. An ORTEP plot of the molecule, with the labeling scheme and bond lengths, is presented in Fig. 6. Selected bond distances and angles of complex

Table 9. Torsion Angle/deg for Four-Atom Segments of [Co<sup>I</sup>(C<sub>10</sub>H<sub>19</sub>N<sub>8</sub>)] Macrocyclic Ligand

fused six-membered rings		fused five-membered rings	
C(6)-N(1)-N(2)-C(1)	4.8(3)	N(5)-N(6)-C(4)-N(7)	17.9(4)
N(1)-N(2)-C(1)-N(3)	2.3(2)	N(6)-C(4)-N(7)-N(8)	38.0(2)
N(2)-C(1)-N(3)-N(4)	1.8(1)	C(4)-N(7)-N(8)-C(5)	17.7(3)
C(1)-N(3)-N(4)-C(2)	3.0(4)	N(7)-N(8)-C(5)-C(6)	14.0(3)
N(3)-N(4)-C(2)-C(3)	1.7(4)	N(8)-C(5)-C(6)-N(1)	39.8(2)
N(4)-C(2)-C(3)-N(5)	2.2(2)	C(5)-C(6)-N(1)-N(2)	20.3(4)
C(2)-C(3)-N(5)-N(6)	0.7(2)		
C(3)-N(5)-N(6)-C(4)	3.4(4)		
C(7)-C(2)-C(3)-C(8)	1.7(2)	C(9)-C(5)-C(6)-C(10)	43.8(2)
C(7)-C(2)-N(4)-N(3)	1.4(2)	C(9)-C(5)-N(8)-N(7)	67.7(2)
C(7)-C(2)-C(3)-N(5)	1.8(4)	C(9)-C(5)-C(6)-N(1)	14.6(4)
C(8)-C(3)-N(5)-N(6)	0.5(4)	C(10)-C(6)-C(5)-N(8)	81.8(3)
C(8)-C(3)-C(2)-N(4)	2.0(4)	C(10)-C(6)-N(1)-N(2)	74.8(3)

[Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)] are listed in Table 10. The two six-membered chelate rings of the monoanionic macrocyclic li-

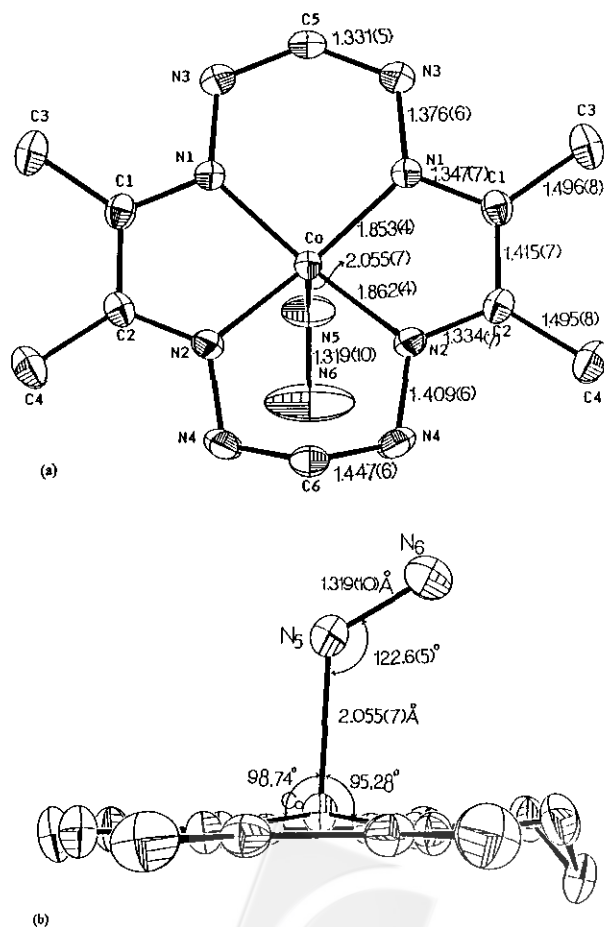


Fig. 6. ORTEP drawing of the [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)] complex: (a) molecular geometry; (b) another view of the structure.

Table 10. Selected Bond Distances and Angles of [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)]

Bond Distances/Å			
Co-N(5)	2.055(7)	N(2)-C(2)	1.334(7)
Co-N(1)	1.853(4)	N(3)-C(5)	1.331(5)
Co-N(2)	1.862(4)	N(4)-C(6)	1.447(6)
N(5)-N(6)	1.319(10)	C(1)-C(2)	1.415(7)
N(1)-N(3)	1.376(6)	C(1)-C(3)	1.496(8)
N(2)-N(4)	1.409(6)	C(2)-C(4)	1.495(8)
N(1)-C(1)	1.347(7)		
Bond Angles/deg			
N(5)-Co-N(1)	98.7(2)	N(4)-N(2)-C(2)	120.9(4)
N(5)-Co-N(2)	95.3(2)	N(3)-C(5)-N(3)	137.6(7)
N(1)-Co-N(1)	94.6(2)	N(3)-N(1)-C(1)	117.3(4)
N(1)-Co-N(2)	82.3(2)	N(2)-N(4)-C(6)	111.0(4)
N(1)-Co-N(2)	166.0(2)	N(2)-C(2)-C(1)	112.2(4)
N(2)-Co-N(2)	97.3(2)	N(2)-C(2)-C(4)	123.7(5)
Co-N(5)-N(6)	122.6(5)	N(1)-N(3)-C(5)	116.1(5)
Co-N(1)-N(3)	126.9(3)	N(1)-C(1)-C(2)	113.0(4)
Co-N(1)-C(1)	115.4(3)	N(1)-C(1)-C(3)	123.2(5)
Co-N(2)-N(4)	121.2(3)	C(2)-C(1)-C(3)	123.8(5)
Co-N(2)-C(2)	115.9(3)	C(1)-C(2)-C(4)	124.1(5)
N(4)-C(6)-N(4)	111.7(6)		

gand are different in that one six-membered ring has allyl-like N-C-N in a delocalized system with C-N bond length 1.331(5) Å, N-N bond length 1.376(6) Å. The other six-membered ring is saturated with C-N bond length 1.447(6) Å, N-N bond length 1.409(6) Å. The torsion angles C<sub>2</sub>-N<sub>2</sub>-N<sub>4</sub>-C<sub>6</sub> and N<sub>2</sub>-N<sub>4</sub>-C<sub>6</sub>-N<sub>4</sub>' of segments of the saturated six-membered ring are 29.3(5)° and 72.9(5)°, respectively. The dihedral angle between plane N<sub>4</sub>-C<sub>6</sub>-N<sub>4</sub>' and the coordinated N<sub>4</sub> donor atom plane is 57.78°. N donor atoms of two types are reflected in Co-N bond distances and α-diimine C=N distances of the macrocyclic complex. The six-membered chelate ring with delocalization of allyl-type has stronger Co<sup>I</sup>-N binding and yields a remarkably small Co-N distance, 1.853(4) Å, compared to the saturated chelate ring for which the length of the Co-N bond is 1.862(4) Å. The two imine functions of the five-membered chelate rings also differ, with bond lengths 1.347(7) Å and 1.334(7) Å, which are greater than those observed in 'pure' α-diimine complex (1.29 Å) and approaching the aromatic C-N distance observed in pyridine (1.35 Å). The C-C bond, of length 1.415(7) Å, is shorter than that observed in other α-diimine structures and also approaches the aromatic C-C distance 1.398 Å. The short Co-N bond and extensive delocalization through α-diimine and three atom N-C-N moieties indicate strong π-backbonding associated with Co<sup>I</sup> and the monoanionic macrocyclic ligand. The pattern of delocalization of

the [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)] complex is similar to that reported for the [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(CO)] complex,<sup>4</sup> whereas delocalization in the macrocyclic ligand of [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)] is somewhat greater than that of [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(CO)]. The average Co<sup>I</sup>-N distance of [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(CO)] is 1.873(2) Å; C-N and C-C distances in the α-diimine chelate rings are 1.335(3) Å and 1.423(5) Å; C-N and N-N distances in the six-membered ring of allyl-like delocalization are 1.335(7) Å and 1.394(3) Å respectively.

The Co(I) ion is displaced 0.225 Å from the plane of the four ligating atoms. The diazene ligand lies in a crystallographic mirror plane that bisects the two six-membered chelate rings of the macrocyclic ligand. The length of the N<sub>5</sub>-N<sub>6</sub> bond is 1.319(10) Å and the bond angle Co-N<sub>5</sub>-N<sub>6</sub> is 122.6(5)°, indicating a trigonal arrangement about N<sub>5</sub>. A comparison of structural parameters of [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)] with those of organometallic "diazo" compounds appears Table 11. Although the crystal structure of a monodentate diazene complex is not yet reported,<sup>22,23</sup> several examples of bidentate diazene complexes are known.<sup>24-35</sup> The N=N distance (1.319 Å) of [Co(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)] is slightly greater than the corresponding distance in [μ-N<sub>2</sub>H<sub>2</sub>{Ru(PPh<sub>3</sub>)(dttdd)}<sub>2</sub>] (where dttdd = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2-)) (1.301(14) Å), but nevertheless much smaller than that of the N-N bond of hydrazine (R<sub>2</sub>N-NR<sub>2</sub>) or hydrazido (NR-NR<sub>2</sub>) complexes, and greater than that of diazenido (NR=NR) complexes. The N-N distance in the corresponding octa-aza methylhydrazine complex [Co<sup>III</sup>(C<sub>10</sub>H<sub>14</sub>N<sub>8</sub>)(CH<sub>3</sub>)(CH<sub>3</sub>NHNH<sub>2</sub>)],<sup>5</sup> 1.441(3) Å, is obviously greater than that in the diazene complex of [Co<sup>I</sup>(C<sub>10</sub>H<sub>17</sub>N<sub>8</sub>)(NHNH)]. To avoid steric interaction between the axial ligand and the macrocyclic ligand, the axial coordinated diazene is opposite the CH<sub>2</sub> group of the saturated six-membered ring, and the terminal of the coordinated diazene lies toward the saturated six-membered ring. This arrangement differs from that of normal saddle-shaped complexes of octa-aza bis-α-diimine, [M<sup>II</sup>(C<sub>10</sub>H<sub>20</sub>N<sub>8</sub>)Cl]<sup>+</sup> (M<sup>II</sup>=Ni<sup>II</sup>, Cu<sup>II</sup>), in which the axial ligand is coordinated at the same side with the CH<sub>2</sub> group of the saturated six-membered rings in the crystalline state.<sup>13-15</sup>

## CONCLUSIONS

Varied ligand oxidation and reduction of an octa-aza macrocyclic system was achieved by varying the proportions of reagents, such as triethylamine, hydrazine, and diffused air. According to our expectation, the monomeric [Co<sup>II</sup>(C<sub>10</sub>H<sub>20</sub>N<sub>8</sub>)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complex is easily oxidized to form a completely conjugated dihydrooctaaza[14]an-

Table 11. Comparison of Structural Parameters of  $[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NH}=\text{NH})]$  with Organometallic "diazo" Compounds

Complexes	M-N-N bond angle/deg	N-N bond length/Å	M-N bond length/Å	reference
(a) <sup>b</sup> $[\text{Co}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NH}=\text{NH})]$	122.6(5)	1.319(10)	2.055(7)	this work
(b) <sup>b</sup> $[\mu\text{-N}_2\text{H}_2\{\text{Cr}(\text{CO})_5\}_2]$	130.5(4)	1.250(25)	2.076(13)	24.25
(c) <sup>b</sup> $[\mu\text{-N}_2\text{H}_2\{\text{Ru}(\text{PPh}_3)(\text{dtd})\}_2]$	129.3(9)	1.301(14)	2.026(5)	26
(d) <sup>b</sup> $[\mu\text{-N}_2\text{H}_2\{\text{Fe}(\text{N}_\text{H}\text{S}_4)\}_2]$	132.2(5)	1.300(7)	1.867(4)	27
(e) <sup>c</sup> $[\mu\text{-N}_2\text{H}_2\{\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)_2\}_2]$	116	1.42	2.24	28
(f) <sup>c</sup> $[\mu\text{-N}_2\text{H}_2\{\eta^5\text{-C}_5\text{Me}_4\text{Bu}^1\text{WI}(\text{CCMe}_3)\}_2]$	131.7(5)	1.410(9)	1.932(7)	29
(g) <sup>d</sup> $[\text{Cp}^*\text{WMe}_4(\eta^2\text{-NHNH}_2)]$	69.2(15), 72.9(14)	1.39(3)	2.12(2), 2.17(3)	30
(h) <sup>e</sup> $[\text{Co}(\text{C}_{10}\text{H}_{14}\text{N}_8)(\text{CH}_3)(\text{NH}_2\text{NHCH}_3)]$		1.441(3)	2.083(2)	5
(i) <sup>a</sup> $[\text{Pt}(\text{PEt}_3)_2(\text{NNC}_6\text{H}_4\text{F})\text{Cl}]$	118.3(20)	1.17(3)	1.975(28)	31
(j) <sup>b</sup> $[\text{Pt}(\text{PEt}_3)_2(\text{HNNC}_6\text{H}_4\text{F})\text{Cl}](\text{ClO}_4)$	125.3(6)	1.235(10)	1.973(7)	32
(k) <sup>c</sup> $[\text{Pt}(\text{PEt}_3)_2(\text{H}_2\text{NNHC}_6\text{H}_4\text{F})\text{Cl}](\text{BF}_4)$	113.2(5)	1.436(11)	2.081(7)	33
(l) <sup>a</sup> $[\text{Rh}(\text{PhP}((\text{CH}_2)_3\text{PPh}_2)_2)\text{Cl}(\text{NNC}_6\text{H}_5)]^+$	125.0(10)	1.17(2)	1.954(8)	34
(m) <sup>a</sup> $[\text{IrCl}_2(\text{o-N}_2\text{C}_6\text{H}_4\text{NO}_2)(\text{CO})(\text{PPh}_3)_2]$	115(3)	1.19(4)	2.05(4)	35

<sup>a</sup> Diazenido(N=NR); <sup>b</sup> Diazene(RN=NR); <sup>c</sup> Hydrazine (R<sub>2</sub>N-NR<sub>2</sub>); <sup>d</sup> Hydrazido(NR-NR<sub>2</sub>); <sup>e</sup> 1,2-Hydrazido(NR-NR)(R signifies an organic group or H).

nulene system; a close cofacial approach of planar molecules forming the non-bridged dinuclear  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  complex occurs. We isolated a monoanionic macrocyclic system stabilized with a diazene ligand,  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{17}\text{N}_8)(\text{NHNH})]$ , in which only one six-membered ring of the octa-aza bis- $\alpha$ -diimine ligand is oxidized. The uncoordinated nitrogen atoms of the hydrazine linkages in the octa-aza macrocyclic system may coordinate to cobalt ion under suitable conditions. Thus, the bridged dinuclear  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_{16}\text{N}_8)]_2$  complex and the intramolecular rearranged  $[\text{Co}^{\text{I}}(\text{C}_{10}\text{H}_{19}\text{N}_8)]$  complex were obtained.

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#### Key Words

Cobalt complexes; Macrocyclic complexes; Diazene complexes; Crystal structures; Metal-metal bonding.

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