CRYSTAL STRUCTURE OF $[Co_2(\mu\text{-}dmg)_2(\mu\text{-}dmg\,H)(dmg\,H)(P\phi_3)]$ 1/2 $dmg\,H_2$ 1/2 CH_3OH: A CRYSTAL CONTAINING VARIOUS FORMS OF *dmg* LIGAND***

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The crystal structure of $[Co_2(\mu\text{-}dmg)_2(\mu\text{-}dmg\,H)(dmg\,H)(P\phi_3)]\cdot 1/2\,dmg\,H_2\cdot 1/2\,CH_3OH$ has been determined by single crystal X-ray diffraction. The title complex crystallizes in triclinic space group $P\bar{1}$ with $a=10.859(3)$, $b=13.299(3)$, $c=15.247(3)$Å, $\alpha=98.52(2)$, $\beta=99.26(2)$, $\gamma=97.80(2)°$ and $Z=2$. The agreement indices are $R(F)=0.062$ and $R_w(F)=0.085$ for 5231 observations and 515 variables. Both cobalt atoms have an oxidation state of 3+ and are both six-coordinated; one Co(III) atom is bonded to a phosphorous atom of triphenylphosphine, four nitrogen atoms of two planar ligands, dmg^{2-} and $dmg\,H^-$, and one oxygen atom of another dmg^{2-} ligand. The other Co(III) atom is coordinated by four nitrogen atoms of two *cis* nonplanar ligands, dmg^{2-}, $dmg\,H^-$, and two oxygen atoms of the other dmg^{2-} and $dmg\,H^-$ ligands. There are three N-O bridged ligands namely two dmg^{2-} and one $dmg\,H^-$ between two Co(III) atoms. A free molecule of $dmg\,H_2$ and a molecule of CH_3OH are also found in the crystal lattice. The structure interestingly demonstrates the possible various forms of *dmg*, not only on their charge but also in different conformations upon coordination.

Schrauzer and Windgassen[1] reported the synthesis of the diamagnetic [Co(II)$(dmg\,H)_2L$], L=py, $P\phi_3$, complexes and proposed the dimeric structure of the five-coordinate cobaloximes (II) through a metal-metal bond. Since the Co(II)-Co(II) bond is rare and has only been found in soft ligand complexes, *e.g.*, $[Co_2(NCCH_3)_{10}]^{4+}$ [2], $[Co_2(CN)_{10}]^{6-}$ [3], and $[Co_2(C_4H_2N_4)_4]$ [4], in order to verify the presence of the metal-metal bonding an attempt at growing the single crystal of $[Co(dmg\,H)_2L]$ complexes was made. The actual single crystals obtained had a composition of $Co_2(dmg\,H)_{4.5}(P\phi_3)$ rather than $Co_2(dmg\,H)_4(P\phi_3)_2$. Nonetheless, the structure of this complex turned out to be very interesting and the result is presented here.

EXPERIMENTAL SECTION

Crystals of the title complex were obtained by mixing of $[Co(dmg\,H)_2(H_2O)_2]$ and triphenylphosphine (1:1 ratio) under nitrogen atmosphere in the methanol solution and letting them stand for two days. A Chunky crystal with $0.2\times0.3\times0.7$ *mm* dimension was measured with a CAD-4 diffractometer. D_m was measured by flotation. No absorption correction. $2\theta_{max}=50°$ ($-13\leq h\leq 13$, $-15\leq k\leq 15$, $0\leq l\leq 18$). Unit cell parameters were obtained by least-square refinement of 25 reflections ($21°<2\theta<32°$). Three standard reflections were monitored throughout the measurement; there was no significant variation. 7396 unique reflections were measured, 5231

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*** *dmg* is the general abbreviation for this class of ligand, including neutral free ligand $dmg\,H_2$, monoanion $dmg\,H^-$, and dianion dmg^{2-}

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with $I>2\sigma(I)$. Agreement indices are $R=0.062$, $R_w=0.085$, $S=2.876$ based on F, with $w=1/[\sigma^2(F_o)+0.0002\,F_o^2]$. The two cobalt atoms were located from Patterson map, subsequent Fourier syntheses based on these heavy atoms revealed the positions of the nonhydrogen atoms of the dimeric complex. Disorder methanol molecule and H atoms were found on difference Fourier synthesis and were not refined with the other parameters. The final refinement was completed using an anisotropic temperature factor on all the nonhydrogen atoms. Two peaks were found in final difference Fourier with densities of 1.5 and 0.94 $e/Å^3$ around methanol molecule which is only half occupied and the rest are less than 0.6 $e/Å^3$. Atomic scattering factors were calculated by analytical form using the coefficients in International Tables for X-ray Crystallography. Programs from NRCC PDP-11 package[5].

RESULT AND DISCUSSION

The unit cell of the structure consists of two binuclear complexes, $[Co_2(\mu\text{-}dmg)_2(\mu\text{-}dmgH)(dmgH)(P\phi_3)]$, one free $dmgH_2$ molecule which is located at the center of inversion, and one methanol solvent molecule which is half occupied in the asymmetric unit. The final positional and thermal parameters of the nonhydrogen atoms are given in Table 1. The bond lengths and angles of this structure are presented in Table 2. The molecular structure of the dimeric complex is shown in Fig. 1. The dimerization is through three N-O bridged ligands. Two interesting features of the crystal structure are worthwhile to emphasize. First, it contains various forms of *dmg* ligand; two tridentate bridged dmg^{2-}, a tridentate bridged $dmgH^-$, a bidentate $dmgH^-$ and a free molecule $dmgH_2$. Second, this is the first structure known to have two *dmg* ligands coordinated to the same metal ion through nitrogen atoms in the cis geometry rather than trans. The following discussion is divided into two parts: identification of various forms of *dmg* ligands and coordination geometry of the dimeric complex.

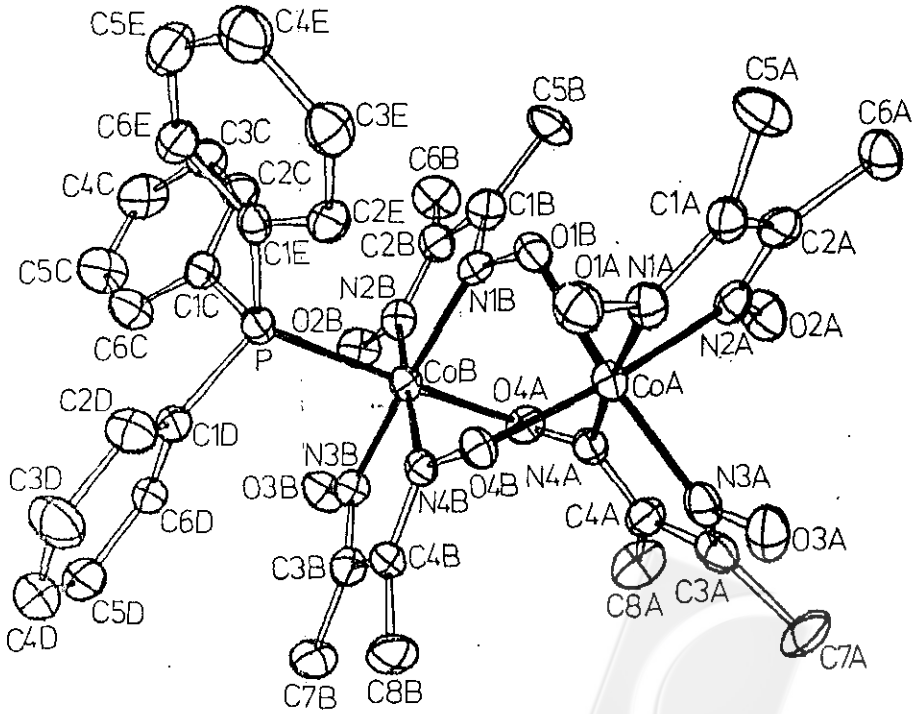


Fig. 1. The Molecular Structure and Labelling Scheme of $[Co_2(dmg)_2(dmgH)_2P\phi_3]$.

Table 1. Positional and Thermal Parameters of $[Co_2(dmg)_2(dmg\,H)_2P\phi_3]\cdot$ 1/2 $dmg\,H_2\cdot$1/2 CH_3OH

Atom	X	Y	Z	Biso	U11	U22	U33	U12	U13	U23
Co A	0.2943(1)	0.3350(1)	0.1389(1)	2.8(0)	3.8(1)	3.0(0)	4.0(1)	0.7(0)	0.9(0)	1.0(0)
Co B	0.1929(1)	0.2301(1)	0.3067(1)	2.8(0)	3.7(1)	3.2(0)	3.8(1)	0.6(0)	1.1(0)	0.5(0)
P	0.3295(2)	0.1471(1)	0.3901(1)	2.9(1)	4.5(1)	3.0(1)	3.4(1)	0.5(1)	0.8(1)	0.6(1)
N1A	0.4600(5)	0.3574(4)	0.1123(4)	3.2(3)	5.1(4)	3.0(3)	4.0(3)	0.9(3)	1.6(3)	0.6(3)
N2A	0.3075(5)	0.4787(4)	0.1335(4)	3.1(3)	3.8(3)	3.5(3)	4.7(3)	1.8(3)	0.2(3)	1.3(3)
N3A	0.2107(5)	0.3078(4)	0.0166(4)	3.1(3)	4.5(3)	3.1(3)	4.2(3)	1.1(3)	1.0(3)	0.9(3)
N4A	0.1229(5)	0.3166(4)	0.1581(4)	3.3(3)	4.5(4)	3.4(3)	4.6(3)	0.9(3)	1.1(3)	1.0(3)
O1A	0.5414(4)	0.2855(3)	0.1065(3)	3.6(3)	4.6(3)	3.2(3)	5.9(3)	0.9(2)	1.4(2)	0.4(2)
O2A	0.2168(5)	0.5300(4)	0.1404(4)	4.7(3)	5.5(3)	4.4(3)	7.9(4)	2.6(3)	1.8(3)	1.8(3)
O3A	0.2699(5)	0.3017(4)	−0.0510(3)	3.9(3)	6.2(3)	4.4(3)	4.1(3)	1.6(3)	1.6(2)	1.5(2)
O4A	0.0821(4)	0.3037(4)	0.2362(3)	3.6(2)	3.6(3)	5.1(3)	4.8(3)	1.5(2)	1.3(2)	1.1(2)
C1A	0.5113(7)	0.4522(5)	0.1179(4)	2.9(3)	5.1(4)	2.6(3)	3.4(4)	0.1(3)	1.3(3)	0.3(3)
C2A	0.4211(7)	0.5216(5)	0.1260(4)	3.2(4)	5.7(5)	2.8(3)	3.6(4)	0.4(3)	1.2(3)	0.5(3)
C3A	0.0899(7)	0.3124(5)	0.0057(5)	3.7(4)	5.1(5)	4.3(4)	4.5(4)	1.4(4)	0.3(4)	0.7(3)
C4A	0.0387(7)	0.3107(6)	0.0872(5)	3.8(4)	4.5(4)	4.9(4)	5.1(5)	0.9(4)	0.7(4)	0.2(4)
C5A	0.6455(7)	0.4863(6)	0.1176(6)	4.2(4)	5.2(5)	3.8(4)	7.1(6)	−0.2(4)	1.6(4)	0.7(4)
C6A	0.4479(8)	0.6345(5)	0.1227(5)	4.3(4)	6.8(6)	2.9(4)	6.6(5)	1.4(4)	1.9(4)	0.9(4)
C7A	0.0146(9)	0.3175(7)	−0.0845(6)	5.7(5)	7.9(7)	8.6(7)	5.1(5)	3.0(5)	0.0(5)	0.9(5)
C8A	−0.0997(8)	0.3000(8)	0.0899(7)	6.5(7)	4.1(5)	11.8(9)	8.8(7)	2.3(5)	0.3(5)	1.8(6)
N1B	0.3094(5)	0.3549(4)	0.3230(4)	2.8(3)	3.7(3)	3.3(3)	3.8(3)	0.8(3)	0.5(3)	0.6(2)
N2B	0.1484(5)	0.3007(4)	0.4118(4)	3.5(3)	3.3(3)	4.9(4)	4.9(4)	1.5(3)	1.4(3)	0.7(2)
N3B	0.0618(5)	0.1152(4)	0.2883(4)	3.2(3)	3.6(3)	4.1(3)	4.5(3)	0.3(3)	1.3(3)	0.9(3)
N4B	0.2226(5)	0.1568(4)	0.1961(3)	2.6(2)	2.8(3)	3.3(3)	3.8(3)	1.2(2)	0.5(2)	1.1(2)
O1B	0.3805(4)	0.3791(3)	0.2638(3)	3.2(2)	4.4(3)	3.6(3)	4.3(3)	0.1(2)	1.0(2)	0.9(2)
O2B	0.0604(5)	0.2612(4)	0.4538(3)	4.7(3)	5.2(3)	6.9(4)	5.9(3)	1.0(3)	2.7(3)	0.5(3)
O3B	−0.0192(5)	0.1028(4)	0.3446(4)	4.7(3)	5.0(3)	6.0(3)	6.7(4)	−0.3(3)	3.2(3)	1.1(3)
O4B	0.3047(4)	0.1928(3)	0.1473(3)	2.8(2)	3.4(3)	3.1(2)	4.4(3)	0.6(2)	1.3(2)	1.0(2)
C1B	0.3018(7)	0.4261(5)	0.3890(5)	3.5(4)	5.8(5)	3.4(4)	4.3(4)	1.0(4)	0.9(4)	0.0(3)
C2B	0.2098(7)	0.3930(6)	0.4424(5)	4.1(4)	5.9(5)	4.5(4)	5.1(5)	2.2(4)	1.2(4)	0.0(4)
C3B	0.0498(7)	0.0478(5)	0.2153(5)	3.4(3)	4.1(4)	4.4(4)	4.4(4)	−0.1(3)	0.8(3)	0.9(3)
C4B	0.1466(6)	0.0713(5)	0.1630(4)	2.8(3)	3.7(4)	3.6(4)	3.5(4)	0.2(3)	0.4(3)	0.5(3)
C5B	0.3737(9)	0.5315(6)	0.4032(6)	5.3(5)	8.5(7)	4.2(5)	7.3(6)	−0.7(4)	1.9(5)	−0.6(4)
C6B	0.1813(10)	0.4612(7)	0.5225(6)	6.6(6)	10.7(8)	6.3(6)	7.9(7)	2.0(6)	3.8(6)	−2.0(5)
C7B	−0.0559(8)	−0.0412(6)	0.1880(6)	4.8(4)	5.5(5)	6.2(5)	6.5(6)	−1.4(4)	1.3(4)	0.5(4)
C8B	0.1588(7)	0.0060(6)	0.0770(5)	4.2(4)	5.8(5)	5.1(5)	4.9(5)	−0.4(4)	1.1(4)	−0.4(4)
C1C	0.3096(7)	0.0096(5)	0.3456(4)	3.3(4)	5.7(5)	2.9(4)	3.8(4)	0.6(3)	0.3(3)	0.4(3)
C2C	0.1981(7)	−0.0547(5)	0.3461(5)	3.7(4)	5.8(5)	3.9(4)	4.5(4)	0.5(4)	0.0(4)	1.0(3)
C3C	0.1834(8)	−0.1600(6)	0.3075(5)	4.6(5)	7.7(6)	4.3(5)	5.6(5)	−0.5(4)	−0.6(4)	1.0(4)
C5C	0.3853(9)	−0.1337(6)	0.2681(7)	5.9(6)	8.4(7)	4.6(5)	9.2(7)	1.9(5)	1.0(6)	−1.8(5)
C6C	0.4017(8)	−0.0296(6)	0.3058(6)	4.7(5)	7.5(6)	3.8(4)	6.5(5)	1.3(4)	0.8(5)	−0.2(4)
C4C	0.2773(9)	−0.1969(6)	0.2686(6)	5.5(6)	8.7(7)	4.0(5)	8.2(7)	1.2(5)	−0.4(5)	−0.7(4)
C1D	0.4964(7)	0.1934(5)	0.3955(4)	3.0(3)	4.8(4)	2.8(3)	4.0(4)	0.8(3)	1.1(3)	0.6(3)
C2D	0.5867(7)	0.1907(6)	0.4705(5)	4.1(4)	5.9(5)	4.9(5)	4.7(5)	0.6(4)	0.5(4)	1.2(4)
C3D	0.7133(8)	0.2232(7)	0.4708(6)	4.7(4)	5.3(5)	6.4(5)	6.1(5)	1.0(4)	−0.6(4)	0.6(4)
C4D	0.7516(7)	0.2575(6)	0.3962(6)	4.5(4)	4.9(5)	5.4(5)	6.9(6)	0.5(4)	0.9(4)	0.0(4)
C5D	0.6632(7)	0.2589(6)	0.3210(5)	4.3(4)	5.5(5)	4.9(5)	5.8(5)	0.6(4)	1.9(4)	0.9(4)
C6D	0.5364(6)	0.2268(5)	0.3206(5)	3.3(3)	3.9(4)	4.2(4)	4.6(4)	1.4(3)	0.7(3)	0.7(3)
C1E	0.3133(7)	0.1583(5)	0.5075(4)	3.4(3)	4.9(4)	4.5(4)	3.4(4)	0.6(3)	1.0(3)	0.9(3)
C2E	0.3507(8)	0.2565(6)	0.5614(5)	4.0(4)	6.1(5)	5.1(5)	4.1(4)	0.1(4)	0.6(4)	0.5(4)
C3E	0.3362(9)	0.2720(7)	0.6510(5)	5.0(5)	8.4(7)	6.8(6)	3.9(5)	0.7(5)	0.8(4)	−0.5(4)
C4E	0.2870(9)	0.1920(8)	0.6879(6)	6.1(6)	8.6(7)	10.5(8)	4.0(5)	−0.6(6)	1.8(5)	0.5(5)
C5E	0.2538(10)	0.0950(8)	0.6365(6)	6.5(6)	9.7(8)	9.8(7)	5.2(5)	−2.2(6)	2.1(5)	2.9(5)
C6E	0.2660(8)	0.0774(6)	0.5455(5)	4.7(5)	7.6(6)	5.7(5)	4.6(5)	−0.9(4)	1.6(4)	1.1(4)
O1F	0.6471(5)	−0.1325(4)	0.0907(3)	4.5(3)	7.5(4)	4.9(3)	4.6(3)	2.5(3)	−0.4(3)	0.7(2)
N1F	0.5678(5)	−0.1071(4)	0.0198(4)	3.3(3)	5.1(4)	3.6(3)	3.8(3)	0.7(3)	1.1(3)	0.6(3)
C1F	0.5410(6)	−0.0162(5)	0.0369(4)	3.0(3)	4.3(4)	3.3(4)	4.0(4)	1.1(3)	1.0(3)	0.5(3)
C2F	0.5908(10)	0.0570(6)	0.1252(6)	5.7(6)	11.6(8)	5.1(5)	5.0(5)	3.5(5)	−1.3(5)	−0.8(4)
O1G	1.0290(0)	0.5380(0)	0.2840(0)	6.3(0)	8.0(0)					
C1G	0.9640(0)	0.4630(0)	0.3100(0)	6.3(0)	8.0(0)					

Table 2a. Bond Lengths (Å) of $[Co_2(dmg)_2(dmg\ H)_2P\phi_3]\cdot 1/2\ dmg\ H_2\cdot 1/2\ CH_3OH$

Atom 1	Atom 2	Length	Atom 1	Atom 2	Length	Atom 1	Atom 2	Length
Co A	N1A	1.901(5)	Co A	N2A	1.912(5)	Co A	N3A	1.896(5)
Co A	N4A	1.919(5)	Co A	O1B	1.948(4)	Co A	O4B	1.932(4)
Co B	P	2.300(2)	Co B	O4A	1.944(4)	Co B	N1B	1.904(5)
Co B	N2B	1.900(5)	Co B	N3B	1.896(5)	Co B	N4B	1.916(5)
P	C1C	1.825(6)	P	C1D	1.818(7)	P	C1E	1.812(6)
N1A	O1A	1.390(6)	N1A	C1A	1.292(7)	N2A	O2A	1.282(6)
N2A	C2A	1.317(8)	N3A	O3A	1.298(7)	N3A	C3A	1.307(9)
N4A	O4A	1.362(7)	N4A	C4A	1.283(9)	O1A	O1AH	0.858(9)
C1A	C2A	1.442(9)	C1A	C5A	1.47 (1)	C2A	C6A	1.500(9)
C3A	C4A	1.44 (1)	C3A	C7A	1.50 (1)	C4A	C8A	1.50 (1)
C5A	C5AH1	0.88 (1)	C5A	C5AH2	1.12 (1)	C5A	C5AH3	1.07 (1)
C6A	C6AH1	0.94 (1)	C6A	C6AH2	1.08 (1)	C6A	C6AH3	1.10 (1)
C7A	C7AH1	1.01 (1)	C7A	C7AH3	1.10 (1)	C7A	C7AH2	1.07 (1)
C8A	C8AH1	0.79 (1)	C8A	C8AH2	1.11 (1)	N1B	O1B	1.325(6)
N1B	C1B	1.297(8)	N2B	O2B	1.327(7)	N2B	C2B	1.295(9)
N3B	O3B	1.335(6)	N3B	C3B	1.298(8)	N4B	O4B	1.334(6)
N4B	C4B	1.292(8)	O2B	O2BH	0.863(9)	O3B	O2BH	1.589(9)
C1B	C2B	1.45 (1)	C1B	C5B	1.48 (1)	C2B	C6B	1.51 (1)
C3B	C4B	1.446(9)	C3B	C7B	1.49 (1)	C4B	C8B	1.498(9)
C5B	C5BH1	0.93 (1)	C5B	C5BH2	1.09 (1)	C5B	C5BH3	1.11 (1)
C6B	C6BH1	0.90 (1)	C6B	C6BH2	1.08 (1)	C6B	C6BH3	1.09 (1)
C7B	C7BH1	0.81 (1)	C7B	C7BH2	1.08 (1)	C7B	C7BH3	1.11 (1)
C8B	C8BH1	1.11 (1)	C8B	C8BH2	1.09 (1)	C8B	C8BH3	1.10 (1)
C1C	C2C	1.39 (1)	C1C	C6C	1.37 (1)	C2C	C3C	1.41 (1)
C2C	C2CH	1.10 (1)	C3C	C4C	1.37 (1)	C3C	C3CH	1.10 (1)
C5C	C6C	1.39 (1)	C5C	C4C	1.35 (1)	C5C	C5CH	1.12 (1)
C6C	C6CH	1.13 (1)	C4C	C4CH	1.07 (1)	C1D	C2D	1.39 (1)
C1D	C6D	1.396(9)	C2D	C3D	1.38 (1)	C2D	C2DH	1.10 (1)
C3D	C4D	1.39 (1)	C3D	C3DH	1.09 (1)	C4D	C5D	1.38 (1)
C4D	C4DH	1.11 (1)	C5D	C6D	1.38 (1)	C5D	C5DH	1.09 (1)
C6D	C6DH	1.12 (1)	C1E	C2E	1.41 (1)	C1E	C6E	1.375(9)
C2E	C3E	1.39 (1)	C2E	C2EH	1.13 (1)	C3E	C4E	1.36 (1)
C3E	C3EH	1.10 (1)	C4E	C5E	1.38 (1)	C4E	C4EH	1.09 (1)
C5E	C6E	1.40 (1)	C5E	C5EH	1.13 (1)	C6E	C6EH	1.16 (1)
O1F	N1F	1.382(7)	N1F	C1F	1.282(8)	C1F	C1F	1.47 (1)
C1F	C2F	1.51 (1)	O1G	C1G	1.29 (1)			

Table 2b. Bond Angle (*deg*) of $[Co_2(dmg)_2(dmg\,H)_2P\phi_3]\cdot 1/2\ dmg\,H_2\cdot 1/2\ CH_3OH$

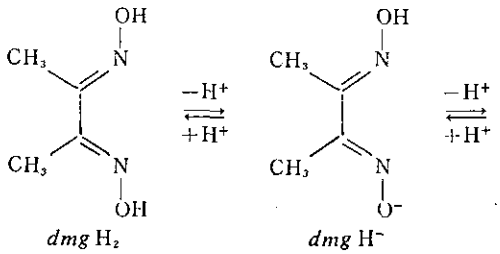
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1A	Co A	N2A	81.5(2)	N1A	Co A	N3A	95.1(2)
N1A	Co A	N4A	175.8(2)	N1A	Co A	O1B	84.3(2)
N1A	Co A	O4B	91.7(1)	N2A	Co A	N3A	88.0(2)
N2A	Co A	N4A	96.0(2)	N2A	Co A	O1B	85.6(2)
N2A	Co A	O4B	172.6(2)	N3A	Co A	N4A	81.4(2)
N3A	Co A	O1B	173.6(2)	N3A	Co A	O4B	95.5(2)
N4A	Co A	O1B	98.9(2)	N4A	Co A	O4B	91.0(2)
O1B	Co A	O4B	90.9(1)	P	Co B	O4A	178.1(1)
P	Co B	N1B	94.9(1)	P	Co B	N2B	92.3(1)
P	Co B	N3B	91.2(1)	P	Co B	N4B	91.4(1)
O4A	Co B	N1B	83.2(2)	O4A	Co B	N2B	87.8(2)
O4A	Co B	N3B	90.7(2)	O4A	Co B	N4B	88.6(1)
N1B	Co B	N2B	81.2(2)	N1B	Co B	N3B	173.3(2)
N1B	Co B	N4B	101.9(2)	N2B	Co B	N3B	95.9(2)
N2B	Co B	N4B	175.0(2)	N3B	Co B	N4B	80.7(2)
Co B	P	C1C	112.5(2)	Co B	P	C1D	115.0(2)
Co B	P	C1E	113.6(2)	C1C	P	C1D	104.3(3)
C1C	P	C1E	106.6(3)	C1B	P	C1E	103.9(3)
Co A	N1A	O1A	126.4(3)	Co A	N1A	C1A	116.5(4)
O1A	N1A	C1A	115.5(5)	Co A	N2A	O2A	123.7(4)
Co A	N2A	C2A	113.5(4)	O2A	N2A	C2A	122.7(5)
Co A	N3A	O3A	123.4(4)	Co A	N3A	C3A	114.1(4)
O3A	N3A	C3A	121.6(5)	Co A	N4A	O4A	127.4(4)
Co A	N4A	C4A	114.9(4)	O4A	N4A	C4A	117.6(5)
N1A	O1A	O1AH	95.5(7)	Co B	O4A	N4A	110.6(3)
N1A	C1A	C2A	111.9(5)	N1A	C1A	C5A	124.6(6)
C2A	C1A	C5A	123.5(5)	N2A	C2A	C1A	115.3(5)
N2A	C2A	C6A	120.2(6)	C1A	C2A	C6A	124.5(6)
N3A	C3A	C4A	113.7(6)	N3A	C3A	C7A	121.6(6)
C4A	C3A	C7A	124.7(6)	N4A	C4A	C3A	113.7(6)
N4A	C4A	C8A	122.3(7)	C3A	C4A	C8A	123.9(6)
C1A	C5A	C5AH1	117.1(9)	C1A	C5A	C5AH2	109.4(8)
C1A	C5A	C5AH3	111.6(8)	C5AH1	C5A	C5AH2	103.0(1)
C5AH1	C5A	C5AH3	107.0(1)	C5AH2	C5A	C5AH3	107.4(8)
C2A	C6A	C6AH1	95.8(7)	C2A	C6A	C6AH2	115.9(8)
C2A	C6A	C6AH3	116.2(7)	C6AH1	C6A	C6AH2	111.1(9)
C6AH1	C6A	C6AH3	109.0(1)	C6AH2	C6A	C6AH3	107.8(8)
C3A	C7A	C7AH1	102.6(8)	C3A	C7A	C7AH3	113.6(8)
C3A	C7A	C7AH2	115.2(8)	C7AH1	C7A	C7AH3	107.0(1)
C7AH1	C7A	C7AH2	109.0(1)	C7AH3	C7A	C7AH2	108.0(1)
C4A	C8A	C8AH1	95.0(1)	C4A	C8A	C8AH2	112.1(9)
C8AH1	C8A	C8AH2	111.0(1)	Co B	N1B	O1B	124.3(3)
Co B	N1B	C1B	116.2(4)	O1B	N1B	C1B	118.5(5)
Co B	N2B	O2B	124.1(4)	Co B	N2B	C2B	116.1(4)
O2B	N2B	C2B	119.8(5)	Co B	N3B	O3B	126.4(4)
Co B	N3B	C3B	116.9(4)	O3B	N3B	C3B	119.6(5)
Co B	N4B	O4B	125.0(3)	Co B	N4B	C4B	115.8(4)
O4B	N4B	C4B	118.8(5)	Co A	O1B	N1B	113.3(3)
N2B	O2B	O2BH	104.3(8)	N3B	O3B	O2BH	102.2(5)

Table 2b. Bond Angle (*deg*) of $(Co_2(dmg)_2(dmg\,H)_2P\phi_3]\cdot 1/2\,dmg\,H_2\cdot 1/2\,CH_3OH$ (Continued)

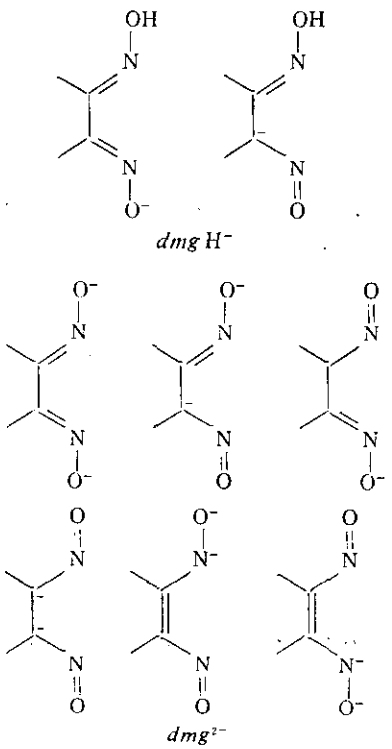
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Co A	O4B	N4B	110.5(3)	N1B	C1B	C2B	112.9(6)
N1B	C1B	C5B	122.7(6)	C2B	C1B	C5B	124.3(6)
N2B	C2B	C1B	113.5(6)	N2B	C2B	C6B	122.6(7)
C1B	C2B	C6B	123.7(6)	N3B	C3B	C4B	112.6(5)
N3B	C3B	C7B	122.7(6)	C4B	C3B	C7B	124.6(6)
N4B	C4B	C3B	113.8(5)	N4B	C4B	C8B	121.6(5)
C3B	C4B	C8B	124.6(5)	C1B	C5B	C5BH1	119.3(9)
C1B	C5B	C5BH2	112.2(8)	C1B	C5B	C5BH3	110.7(9)
C5BH1	C5B	C5BH2	104.0(1)	C5BH1	C5B	C5BH3	103.0(1)
C5BH2	C5B	C5BH3	106.5(9)	C2B	C6B	C6BH1	94.0(8)
C2B	C6B	C6BH2	114.7(9)	C2B	C6B	C6BH3	114.7(9)
C6BH1	C6B	C6BH2	112.0(1)	C6BH1	C6B	C6BH3	112.0(1)
C6BH2	C6B	C6BH3	109.0(1)	C3B	C7B	C7BH1	101.0(1)
C3B	C7B	C7BH2	115.1(8)	C3B	C7B	C7BH3	113.8(8)
C7BH1	C7B	C7BH2	111.0(1)	C7BH1	C7B	C7BH3	108.0(1)
C7BH2	C7B	C7BH3	107.0(1)	C4B	C8B	C8BH1	115.2(7)
C4B	C8B	C8BH2	109.4(7)	C4B	C8B	C8BH3	110.0(7)
C8BH1	C8B	C8BH2	108.0(9)	C8BH1	C8B	C8BH3	107.1(9)
C8BH2	C8B	C8BH3	106.8(9)	P	C1C	C2C	120.4(5)
P	C1C	C6C	120.0(5)	C2C	C1C	C6C	119.5(6)
C1C	C2C	C3C	119.0(7)	C1C	C2C	C2CH	119.0(7)
C3C	C2C	C2CH	122.1(8)	C2C	C3C	C4C	120.2(7)
C2C	C3C	C3CH	120.2(9)	C4C	C3C	C3CH	119.6(8)
C6C	C5C	C4C	120.3(8)	C6C	C5C	C5CH	119.8(9)
C4C	C5C	C5CH	119.9(8)	C1C	C6C	C5C	120.6(7)
C1C	C6C	C6CH	118.8(7)	C5C	C6C	C6CH	120.6(8)
C3C	C4C	C5C	120.4(7)	C3C	C4C	C4CH	120.0(1)
C5C	C4C	C4CH	119.0(1)	P	C1D	C2D	121.6(5)
P	C1D	C6D	119.5(5)	C2D	C1D	C6D	118.8(6)
C1D	C2D	C3D	120.0(6)	C1D	C2D	C2DH	119.4(8)
C3D	C2D	C2DH	120.6(8)	C2D	C3D	C4D	120.6(7)
C2D	C3D	C3DH	119.7(9)	C4D	C3D	C3DH	119.7(9)
C3D	C4D	C5D	119.9(7)	C3D	C4D	C4DH	120.9(8)
C5D	C4D	C4DH	119.1(8)	C4D	C5D	C6D	119.7(6)
C4D	C5D	C5DH	120.3(8)	C6D	C5D	C5DH	120.0(8)
C1D	C6D	C5D	121.0(6)	C1D	C6D	C6DH	120.1(8)
C5D	C6D	C6DH	118.9(8)	P	C1E	C2E	117.0(5)
P	C1E	C6E	123.9(5)	C2E	C1E	C6E	119.0(6)
C1E	C2E	C3E	120.3(6)	C1E	C2E	C2EH	119.5(7)
C3E	C2E	C2EH	120.2(8)	C2E	C3E	C4E	120.4(7)
C2E	C3E	C3EH	120.8(9)	C4E	C3E	C3EH	118.8(8)
C3E	C4E	C5E	119.7(7)	C3E	C4E	C4EH	119.3(9)
C5E	C4E	C4EH	120.9(9)	C4E	C5E	C6E	121.1(7)
C4E	C5E	C5EH	119.7(8)	C6E	C5E	C5EH	119.2(9)
C1E	C6E	C5E	119.4(7)	C1E	C6E	C6EH	119.4(8)
C5E	C6E	C6EH	121.2(8)	O1F	N1F	C1F	113.3(5)
N1F	C1F	C1F	115.7(5)	N1F	C1F	C2F	123.9(6)
C1F	C1F	C2F	120.4(5)	O2B	O2BH	O3B	169.0(1)

Identification of Various Forms of *dmg* Ligands

The neutral ligand $dmg\,H_2$ contains two dissociable protons, it could be dissociated to $dmg\,H^-$ and dmg^{2-} anion according to the following:



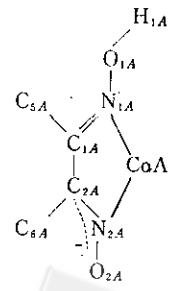
Several possible resonance forms could be written for $dmg\,H^-$ and dmg^{2-} as follows



Due to the different degrees of contribution of various resonance forms, the bond patterns (bond lengths of N-O, C-N *etc.*) of $dmg\,H_2$, $dmg\,H^-$, and dmg^{2-} will be different. The bond lengths of N-O and C-N are expected in the order of $dmg^{2-}<dmg\,H^-<dmg\,H_2$ and $dmg^{2-}>dmg\,H^->dmg\,H_2$ respectively. Therefore these bond lengths could be used to differentiate the various types of *dmg* molecules in the complex. In addition, the location of hydrogen atom can also serve the purpose.

Table 3 presents the summary of bond lengths for *dmg* ligands in this structure and other similar complexes. This structure contains a free ligand, $dmg\,H_2$ molecule; its N_{1F}-O_{1F} and N_{1F}-C_{1F} bond distances are 1.382(7) and 1.282(8) Å *respectively, similar to those in free* $dmg\,H_2$ molecule, 1.410(3) and 1.288(3) Å[6]. This bond pattern can be considered as localized double bond arrangement. The other bond patterns of *dmg* molecules fall into two types: one has the N-O, C-N bond distances around 1.34 and 1.29 Å and is considered a small degree of π-delocalizations, the other has the N-O, C-N bond lengths around 1.29 and 1.31 Å as large degree of π-delocalization.

The bond lengths of N_{1A}-O_{1A}, 1.390(6) Å, and C_{1A}-N_{1A}, 1.292(7) Å in **1** has localized double bond arrangement and those of N_{2A}-O_{2A}, 1.282(6), and C_{2A}-N_{2A} 1.317(8) Å, has large degree of double bond delocalization. One hydrogen atom is located around O_{1A} with H_{1A}-O_{1A} 0.86 Å and 0.48 e/Å^3 so this part of the ligand is consistent with $dmg\,H^-$:



1

Similarly, the other *dmg* molecule around CoA in **2** has bond lengths of N_{3A}-O_{3A}, 1.298(7) Å, and C_{3A}-N_{3A}, 1.307(9) Å, representing a large degree of delocalization

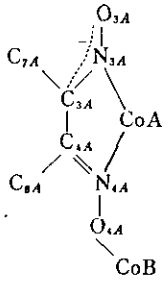
Table 3. Selected Bond Leng ths for *dmg* Ligands and Their Complexes

Compound	M-N	M-L	M-L′	O-N	*dmg*[a] N-C	C-C	Ref.
dmg H_2	—	—	—	1.410(3)	1.288(3)	1.474(3)	6
$Na_2(dmg)8H_2O$	—	—	—	1.388(3)	1.298(3)	1.478(4)	6
$Cu(dmg\ H_2)Cl_2$	1.994(8)	2.246(3) (Cl)	—	1.374(12)	1.293(11)	1.488(15)	6
$Cu(dmg\ H_2)Br_2$	2.003(7)	2.378(2) (Br)	—	1.382(10)	1.279(9)	1.478(12)	6
$(Cu(dmg\ H)_2)_2$	1.952(4)	2.301(3)	—	1.379(5) 1.338(5)	1.281(6) 1.299(7)	1.491(7)	7
$Ni(dmg\ H)_2$	1.89	—	—	1.37	1.23	1.53	8
$Co(dmg\ H)_2LL'$ [b]							
L=Cl, L′=$P\phi_3$	1.89 (1)	2.277(4)	2.327(4)	1.34 (1)	1.30 (2)	1.48 (2)	9
L=Cl, L′=NH_3	1.890(5)	2.251(1)	1.965(4)	1.346(6)	1.282(8)	1.483(8)	9
L=CH_3, L′=$P\phi_3$	1.891(5)	2.026(6)	2.418(1)	1.357(7)	1.314(9)	1.456(9)	10
L=CH_3, L′=py	1.897(5)	1.998(5)	2.068(3)	1.352(7)	1.307(7)	1.482(10)	11
L=i-C_3H_7, L′=2-NH_2py	1.894(4)	2.097(6)	2.194(4)				12
$[Co_2(dmg)_2(dmg\ H_2)P\phi_3]\cdot 1/2\ dmg\ H_2$ Co_A	1.907(5)	1.948(4) (O)	1.932(4) (O)				
Co_B	1.904(5)	1.944(4) (O)	2.300(2) (P)				
in *dmg* H_2				1.382(7)	1.282(8)	1.47 (1)	
in *dmg* $N_{1A}N_{2A}$ 1A				1.390(6)	1.292(7)	1.442(9)	This work
2A				1.282(6)	1.317(8)		
in *dmg* $N_{3A}N_{4A}$ 3A				1.298(7)	1.307(9)	1.44 (1)	
4A				1.362(7)	1.283(9)		
in *dmg* $N_{1B}N_{2B}$ & $N_{3B}N_{3B}$ B				1.330(7)	1.296(9)	1.45 (1)	

[a] Average values of Chemically equivalent bond are reported.

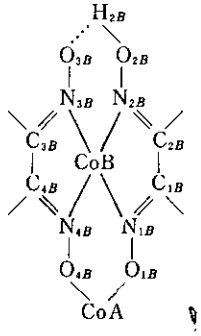
[b] A very large number of this type of complexes has been structurally characterized, the $Co(dmg\ H)_2$ unit appears to be unaffected by axial ligands.

but those of N_{4A}-O_{4A}, 1.362(7), and C_{4A}-N_{4A} distance, 1.283(9) Å, shows only small degree of delocalization. No hydrogen atoms were found around the oxygen atoms. This *dmg* O_{4A} is coordinated to CoB atom, as molecule is consistent with μ-dmg^{2-}:



2

Around the CoB atom, there are two *dmg* ligands in the trans geometry similar to other bis *dmg* complexes[7,12], *e.g.*, $[Ni(dmg\ H)_2]$[9]. The four N-O distances are between 1.325(6) and 1.335(6) Å, and the four C-N distances are between 1.292(8) and 1.297(8) Å representing a small degree of delocalization. One hydrogen atom was found around O_{2B} with H_{2B}-O_{2B} 0.86 Å and 0.38 e/Å^3. O_{4B} and O_{1B} of the two *dmg* molecules are coordinated to CoA ion. Therefore, the two *dmg* molecules are believed to be one μ-$dmg\ H^-$ and one μ-dmg^{2-}.



3

Coordination Geometry of Dimeric Complex

Thus the dimeric complex contains two μ-dmg^{2-}, one μ-$dmg\,H^-$ and one $dmg\,H^-$; in order to balance the charge, both cobalt ions have to be trivalent. It has triagonal distorted octahedral geometry around CoA ion similar to that of $Co(en)_3$. The CoA-N distances vary from 1.896(5) to 1.919(5) Å, and CoA-O distances, 1.948(4) to 1.932(4) Å. It is consistent with the low spin Co(III) complex[9~12]. But around CoB ion, it has tetragonal distorted octahedral geometry, with a μ-$dmg\,H^-$ and a μ-dmg^{2-} ligand forming an equatorial plane; a triphenylphosphine and μ-dmg^{2-} through O_{4A} atom act as axial ligands. The CoB-N distances vary from 1.896(5) to 1.916(5) Å, CoB-P, 2.300(2) Å, to CoB-O_{4A}, 1.932(4) Å, are also consistent with the low spin Co(III) complex. All the bond parameters of triphenylphosphine are normal and will not be discussed here.

CONCLUSION

This structure interestingly demonstrates all the possible types of *dmg* molecule; their charge and various conformations upon coordination are also illustrated. Three types of bond patterns were found in this structure; localized double bond arrangement and small degree and large degree of double bond delocalization. The first one is observed when OH group of *dmg* molecule is weakly (or not) hydrogen bonded. The second is observed when the *dmg* molecule is strongly hydrogen bonded or the oxygen atom of deprotonated *dmg* molecule is coordinated to a metal ion. The last one is observed when oxygen atom of the deprotonated *dmg* molecule is weakly (or not) hydrogen bonded.

This study may also explain that the complexes[1], $[Co(dmg\,H)_2L]$, could be diamagnetic with $[Co(III)(dmg)(dmg\,H)L]$ instead of $[Co(dmg\,H)_2L]$, which was only identified[1] by elemental analysis. Of course, the dimerization of $[Co(II)(dmg\,H)_2L]$ through a metal-metal bond is still possible and further studies are underway.

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