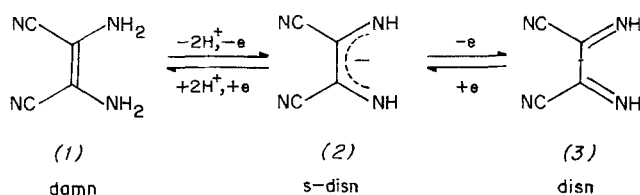# Communication

Syntheses and crystal structures of diiminosuccinonitrile and its iron(II) complex

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A series of metal complexes with diiminosuccinonitrile (disn) *(3)* and diiminosuccinonitrile radical anion (s-disn)

(2), have been described[1–6]. Miles *et al*[1]., have reported the preparation of neutral Ni^{II}, Pd^{II}, and Pt^{II} complexes with *(2)*. Improved synthetic methods for the preparations of the above complexes and the molecular structure of [Pt(s-disn)$_2$] have been reported by Lauher *et al*[2]. We have described the synthesis and reactions of cobalt complexes with *(2)* and the molecular structure of [Co^{III} (CN) (s-disn)$_2$][3]. A series of interesting structures [Ni(s-disn)$_2$], [Co$_2$(s-disn)$_4$], [As(Ph)$_4$] [Co(s-disn)$_2$], [RuCl$_2$(CH$_3$CN)$_2$ (disn)] have been also determined by us[4–6]. The redox-reaction of Cu^{II} with *(1)*, damn, has also been studied[7]. In continuation of previous investigations in this area, we report the syntheses and the crystal structures of α-diimine ligand *(3)* and its iron(II) complexes.

Diiminosuccinonitrile (disn) was synthesized by the oxidation of damn with dichlorodicyanobenzoquinone[8].

Colourless crystals suitable for single x-ray analysis were obtained by sublimation. The structure of disn, *(3)*, is shown in Figure 1[9]. All the non-hydrogen atoms form a least-square plane with the maximum deviations − 0.040 Å for N(1) and 0.047 Å for N(4). The C(1)—N(1) and C(2)—N(2) bonds are double bonds (1.244(3) and 1.241(3) Å, respectively) while the C(3)—N(3) and C(4)—N(4) bonds are triple bonds (1.129(3) and 1.131(2) Å, respectively). The remaining C—C bonds are single bonds.

The reaction of iron(II) perchlorate with disn in alcoholic solution results immediately in the formation of the deep blue tris-(disn) iron(II) complex which is too unstable to isolate. After complex reactions which take a few days addition of Et_2O to the solution leads to the isolation of the blue complex, *(5)*[10].
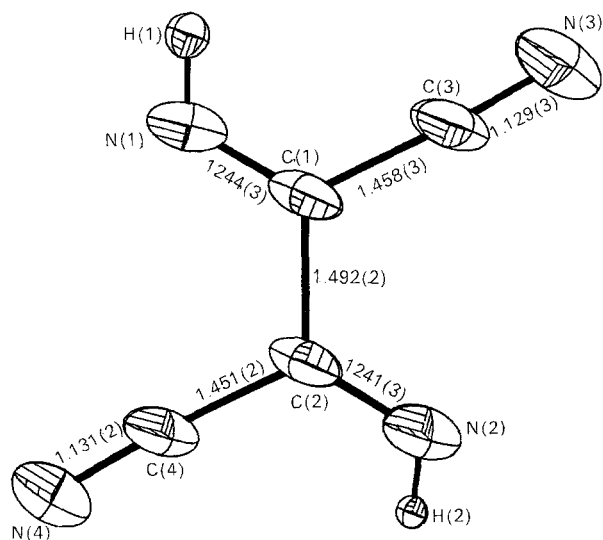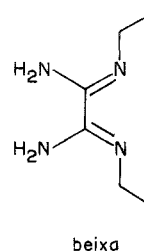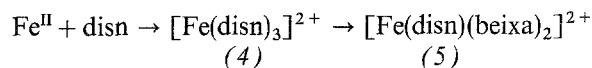
$$Fe^{II} + disn \rightarrow [Fe(disn)_3]^{2+} \rightarrow [Fe(disn)(beixa)_2]^{2+}$$
$$\qquad\qquad\qquad (4) \qquad\qquad\qquad (5)$$

beixa

Suitable single crystals were obtained by slow diffusion of diethyl ether into a ethyl alcohol solution of Fe^{II} (disn)-(beixa)$_2$] (ClO$_4$)$_2$.
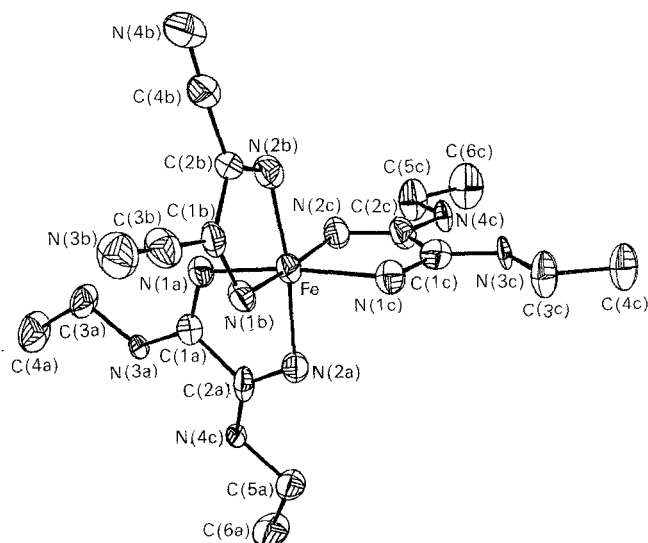

Figure 1. ORTEP plot of *(3)*, unbound disn.

Figure 2. ORTEP plot of the *(5)* [Fe(disn) (beixa)$_2$]$^{2+}$ cation.

Table 1. Bond lengths (Å) and bond angles (°).

Fe—N(1a)	1.966(8)	N(1c)—C(1c)	1.317(14)
Fe—N(2a)	2.005(9)	N(2c)—C(2c)	1.325(14)
Fe—N(1b)	1.871(8)	N(3c)—C(1c)	1.285(13)
Fe—N(2b)	1.873(9)	N(3c)—C(3c)	1.425(15)
Fe—N(1c)	1.985(9)	N(4c)—C(2c)	1.250(14)
Fe—N(2c)	1.989(9)	N(4c)—C(5c)	1.440(15)
N(1a)—C(1a)	1.319(14)	C(1a)—C(2a)	1.478(15)
N(2a)—C(2a)	1.313(13)	C(3a)—C(4a)	1.447(17)
N(3a)—C(1a)	1.286(12)	C(5a)—C(6a)	1.478(17)
N(3a)—C(3a)	1.438(14)	C(1b)—C(2b)	1.435(15)
N(4a)—C(2a)	1.269(13)	C(1b)—C(3b)	1.426(15)
N(4a)—C(5a)	1.424(15)	C(2b)—C(4b)	1.445(16)
N(1b)—C(1b)	1.302(13)	C(1c)—C(2c)	1.492(16)
N(2b)—C(2b)	1.315(14)	C(3c)—C(4c)	1.461(16)
N(3b)—C(3b)	1.109(15)	C(5c)—C(6c)	1.419(18)
N(4b)—C(4b)	1.130(16)		
N(1a)—Fe—N(2a)	79.3(4)	N(1a)—C(1a)—N(3a)	128.8(10)
N(1a)—Fe—N(1b)	91.6(4)	N(1a)—C(1a)—C(2a)	113.9(9)
N(1a)—Fe—N(2b)	92.5(4)	N(3a)—C(1a)—C(2a)	117.3(9)
N(1a)—Fe—N(1c)	166.8(4)	N(2a)—C(2a)—N(4a)	131.0(9)
N(1a)—Fe—N(2c)	92.0(4)	N(2a)—C(2a)—C(1a)	113.3(9)
N(2a)—Fe—N(1b)	95.2(3)	N(4a)—C(2a)—C(1a)	115.7(9)
N(2a)—Fe—N(2b)	171.1(4)	N(3a)—C(3a)—C(4a)	110.8(10)
N(2a)—Fe—N(1c)	90.4(3)	N(4a)—C(5a)—C(6a)	108.2(9)
N(2a)—Fe—N(2c)	90.8(3)	N(1b)—C(1b)—C(2b)	112.0(9)
N(1b)—Fe—N(2b)	81.5(4)	N(1b)—C(1b)—C(3b)	124.7(10)
N(1b)—Fe—N(1c)	97.6(4)	C(2b)—C(1b)—C(3b)	123.3(10)
N(1b)—Fe—N(2c)	173.5(3)	N(2b)—C(2b)—C(1b)	113.4(9)
N(2b)—Fe—N(1c)	98.2(4)	N(2b)—C(2b)—C(4b)	123.9(10)
N(2b)—Fe—N(2c)	93.0(4)	C(1b)—C(2b)—C(4b)	122.7(10)
N(1c)—Fe—N(2c)	79.7(4)	N(3b)—C(3b)—C(1b)	176.5(13)
Fe—N(1a)—C(1a)	117.0(7)	N(4b)—C(4b)—C(2b)	178.8(12)
Fe—N(2a)—C(2a)	116.2(7)	N(1c)—C(1c)—N(3c)	129.2(10)
C(1a)—N(3a)—C(3a)	118.8(8)	N(1c)—C(1c)—C(2c)	114.2(10)
C(2a)—N(4a)—C(5a)	117.1(8)	N(3c)—C(1c)—C(2c)	116.6(9)
Fe—N(1b)—C(1b)	117.2(7)	N(2c)—C(2c)—N(4c)	131.3(10)
Fe—N(2b)—C(2b)	115.8(7)	N(2c)—C(2c)—C(1c)	112.8(10)
Fe—N(1c)—C(1c)	116.4(7)	N(4c)—C(2c)—C(1c)	115.9(9)
Fe—N(2c)—C(2c)	116.8(7)	N(3c)—C(3c)—C(4c)	108.1(10)
C(1c)—N(3c)—C(3c)	119.5(8)	N(4c)—C(5c)—C(6c)	109.1(10)
C(2c)—N(4c)—C(5c)	116.6(9)		

Table 2. Comparison of bond distances (Å) and angles (°) between *(1)*, *(2)*, *(3)* and their metal complexes.

	(1), damn[12]	Ni(s-disn)$_2^{(4)}$	Pt(s-disn)$_2^{(2)}$	*(3)*, disn	*(5)*, [Fe(disn)(beixa)$_2$]$^{2+}$
M—N(1)	–	1.827(4)	1.957(8)	–	1.872(9)
N(1)—C(1)	1.392(8)	1.330(4)	1.323(13)	1.242(3)	1.308(14)
C(1)—C(1)	1.363(6)	1.403(5)	1.416(19)	1.492(2)	1.435(15)
C(1)—C(2)	1.439(7)	1.443(5)	1.415(15)	1.454(3)	1.435(16)
C(2)—N(3)	1.165(10)	1.135(5)	1.123(15)	1.130(3)	1.120(16)
N(1)—M—N(1)	–	84.3(1)	79.1(5)	–	81.5(4)
M—N(1)—C(1)	–	114.6(2)	116.4(7)	–	116.5(7)
N(1)—C(1)—C(1)	124.1(4)	113.2(3)	114.0(6)	120.6(1)	112.7(9)
N(1)—C(1)—C(2)	117.6(3)	124.4(3)	122.6(9)	124.5(1)	124.3(10)
C(1)—C(1)—C(2)	118.1(8)	122.4(3)	123.3(7)	115.0(1)	123.0(10)
C(1)—C(2)—N(3)	179.8(9)	177.8(4)	179.7(13)	175.8(2)	177.6(13)

The results of the x-ray structural analysis of *(5)*, shown in Figure 2[11], indicate that the central iron atom has a trigonally distorted octahedral coordination. The disn ligand is planar with maximum deviation from the least-square plane of 0.035 Å. The extremely short iron-nitrogen(disn) distances (av. 1.872(9) Å, Table 1) indicate very strong binding between the low-spin iron(II) and the disn. Further evidence of the strong Fe—N binding is the

lengthening of the α-diimine bonds. (1.309(14) Å for the disn ligand in the complex and 1.243(3) Å in the free state). It is attributed to back donation from the filled d-orbitals to the π*-orbitals of the α-diimine ligand. The comparison of bond parameters between *(1)*, *(2)*, *(3)* and their metal complexes are tabulated in Table 2. The beixa ligands also form good least-square planes with maximum deviation of 0.042 Å. The four C=N bonds [C(1a)—N(3a), C(2a)—

N(4a), C(1c)—N(3c), and C(2c)—N(4c), av. 1.273(14) Å] are short, consistent with the proposed structure.

It is still not clear that how disn transforms to beixa in the alcoholic solution. We are currently attemping to isolate [Fe(disn)$_3$]$^{2+}$ and clarified the chemical transformation of disn to beixa.

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[9] A colourless crystal of dimensions 0.2 × 0.2 × 0.4 mm was used for data collection. Diffractometer data were collected on a CAD4 diffractometer using graphite-monochromated MoK radiation. Unit cell dimensions were determined from a least squares refinement of 25 reflections (18.20° < 2θ < 24.12°). Formula: C$_4$N$_4$H$_2$, formula weight: 106.05, absorption coefficient: 0.09 mm^{-1}, space group: P cab, $a = 7.535(1)$, $b = 9.865(1)$, $c = 13.428(5)$ Å, V = 998.12 Å^3, Z = 8. Intensity data within 2θ < 60° were collected at various scan speed of 20/16 to 20/3°/s by using the $\omega - 2\theta$ scan techniques, with a scan range calculated according to the expression 0.8 + 0.35 tan θ. The three intensity monitors were checked every 2 hours and fluctucated randomly within 2% over the entire data collection. After data collection, the intensities were reduced to F and σ(F) according to counting statistics, and the weights were assigned as w = 1/σ^2(F) + 0.0001F^2. Of the 1452 unique reflections, 662 having I > 2σ(I), were consider observed. All calculations were carried out on a PDP-11/23 computer, using the NRCC SDP PDP-11 package, MULTAN and the ORTEP from the Enraf-Nonius SDP. Atomic scattering factors were obtained from the international tables for x-ray crystallography (1974). The structure was solved by a direct method using MULTAN with 200 highest E's, 100 smallest E,'s and 3639 σ − 2 phase relationships. The final least-squares cycle with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms, gave R and Rw factors, respectively, of 5.0 and 5.4%. Atomic coordinates, displacement factor coefficients, full lists of bond lengths and angles and lists of Fo/Fc values have been deposited as supplementary data with Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

[10] In the preparation, disn (318 mg in 30 cm^3 EtOH) and Fe(ClO$_4$)$_2$·6H$_2$O (363 mg in 25 cm^3 EtOH) were mixed together. The deep shining blue solution which immediately formed became dark blue gradually. After one to two days, addition of Et$_2$O to the dark blue solution led to the precipitation of blue product *(5)* (50 mg, 8% yield).

[11] A deep blue crystal of dimensions 0.12 × 0.15 × 0.34 mm was used for data collection. Unit cell dimensions were determined from a least-squares refinement of 25 reflections (19.02° < 2θ < 21.4°). Formula: FeN$_{12}$C$_{16}$H$_{31}$Cl$_2$O$_9$, formula weight: 662.02, absorption coefficient: 0.77 mm^{-1}, space group: P 2$_1$/n, $a = 8.519(1)$, $b = 30.270(7)$, $c = 11.701(2)$ Å, $\alpha = 107.02(6)°$, V = 2885.2 Å^3, Z = 4, Intensity data within 2θ < 50° were collected at various scan speed of 20/22 to 20/3°/S by using the $\omega - 2\theta$ scan techniques, with a scan range calculated according to the expression 0.6 + 0.35 tan θ. 4901 unique reflections were measurement, 2397 having I > 3σ(I) were consider observed. All calculations were carried out on a VAX-785 computer, using the NRCC SDP VAX package. The structure was solved by the heavy atom method. The final least-squares cycle with anisotropic thermal parameters for all nonhydrogen atoms and fixed contribution for hydrogen atoms gave R and Rw factors respectively of 8.6 and 6.8%. Other details are the same as in (9).

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