Synthesis, Characterization, and Chemical Transformation of Di-iminosuccinonitrile Cobalt Complexes; *X*-Ray Crystal Structure of Cyanobis(di-iminosuccinonitrile)cobalt

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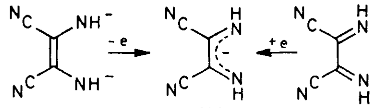
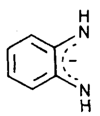
Summary The diamagnetic cobalt(II) complexes [Co($C_4H_2N_4$)$_2$L]$_2$ (L = H_2O or Me_2SO), dimers of bis(di-iminosuccinonitrile)cobalt(II), have been synthesized and transformed to the square-planar Co^{I} complex [Co($C_4H_2N_4$)$_2$]$^-$, and the square-pyramidal Co^{III} complexes [Co(Me)($C_4H_2N_4$)$_2$] and [Co(CN)($C_4H_2N_4$)$_2$]; the structure of the latter unusual compound was determined by single-crystal *X*-ray analysis.

Square-planar transition-metal complexes with unsaturated electron-rich ligands are of considerable interest, owing to their unusual spectroscopic, magnetic, redox, and structural properties.[1–4] An example of this type of ligand, the anion (**1**) of di-iminosuccinonitrile, can be prepared either by the oxidation of the dianion of diaminomaleonitrile or by the reduction of di-iminosuccinonitrile, and is an analogue of the well known ligands (**2**) and (**3**), which undergo reversible electron-transfer reactions.[5] Miles *et al.*,[6] have reported the preparation of neutral Ni^{II}, Pd^{II}, and Pt^{II} complexes with (**1**). We report here the synthesis and reactions of cobalt complexes of the ligand (**1**), and the characterisation by *X*-ray crystallography of the unusual compound [Co(CN)($C_4H_2N_4$)$_2$]$2H_2O$ (**5**).



(1)



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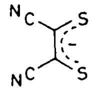

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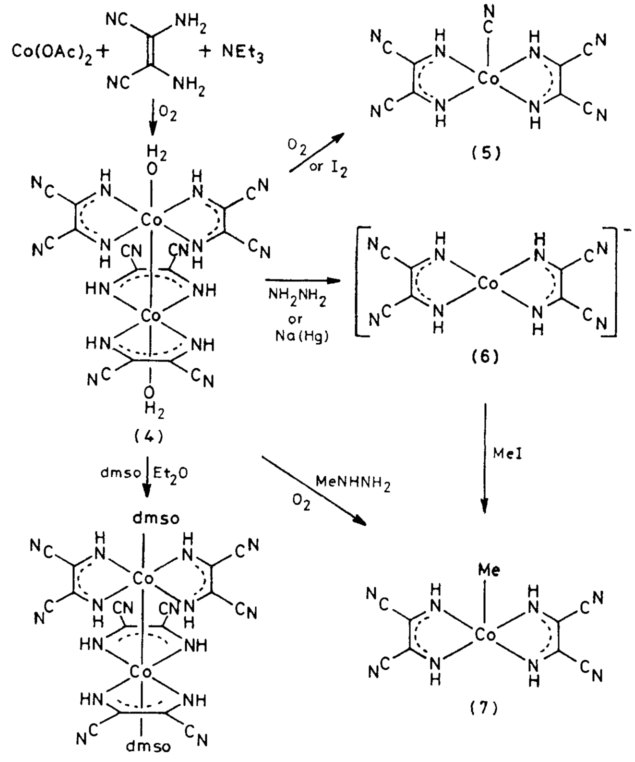

Scheme

The blue Co^{II} complex (**4**) was synthesized by the reaction of diaminomaleonitrile, cobalt(II) acetate, and a base (such as NEt_3) in water–ethanol (50 : 50), followed by air oxidation (Scheme). It is stable in the solid state for months and also stable in dry dimethyl sulphoxide (dmso) solution under nitrogen for a few days. The striking feature of complex (**4**) and the analogous $[Co(C_4H_2N_4)_2(dmso)]_2$ is their diamagnetic properties both in dmso solution and in the solid state. Only a few Co^{II} complexes are known to be diamagnetic and these contain a Co–Co bond: *e.g.*, $Ba_3[Co(CN)_5]_2(H_2O)_{13}$[7] and $[Co_2(CNMe)_{10}]^{4+}$.[8] The rhodium analogue $[Rh(dmg)_2PR_3]_2$ (H_2dmg = dimethylglyoxime) also exists as a dimer with an Rh–Rh bond.[9] Therefore, a dimeric structure with a Co–Co bond is proposed for these complexes. Attempts to grow single crystals suitable for *X*-ray analysis have so far been unsuccessful. Complex (**4**) shows the following spectroscopic data: δ (CD_3SOCD_3) 12·12 (NH); ν_{NH} 3270 and 3300 cm^{-1}, ν_{CN} 2200 cm^{-1}; λ_{max} 625 (10^{-3} ϵ 9·55), 565 (12·7), and 456 (0·802) nm.

Further oxidation of (**4**) in solution leads to the formation of the green complex (**5**); δ 10·18 (NH); ν_{CN} 2100 (Co–CN), 2226, and 2236 cm^{-1}, $\nu_{NH,OH}$ 3090, 3160, 3270, 3460, and 3580 cm^{-1}; λ_{max} 590 (10^{-3} ϵ 6·27), 433 (3·16), and 313 (4·65) nm. It is clear that the free cyanide ligand in this complex originates from the di-iminosuccinonitrile, but the mechanism has not yet been investigated.

The reduction of (**4**) by sodium amalgam or hydrazine in solution gives the orange-brown Co^I complex (**6**); δ 11·74 (NH); λ_{max} 764 (10^{-3} ϵ 2·2), 490sh. (1·8), and 468 nm (2·4), but attempted crystallization with various counter-cations has failed. This diamagnetic cobalt(I) complex undergoes typical nucleophilic reactions of Co^I: it reacts with MeI to give the shiny blue methyl–Co^{III} complex (**7**); δ 12·10 (NH) and 0·39 (Me); ν_{CN} 2230 cm^{-1}, ν_{NH} 3280 cm^{-1}; λ_{max} 655 (10^{-3} ϵ 2·05) and 305 nm (2·34). Complex (**7**) is also formed by the addition of methylhydrazine to a solution of (**4**) followed by bubbling oxygen through the solution.[10]

The structure of the novel complex (**5**) was determined by *X*-ray diffraction. *Crystal data:* $C_9H_4CoN_9,2H_2O$, orthorhombic, space group $Pbc2_1$ (C_{2v}, No. 5), a = 11·589(2), b = 18·314(7), c = 12·734(7) Å; D_m = 1·62, D_c = 1·63 g/cm^3, Z = 8, with two independent molecules in the asymmetric unit. 2521 reflections were measured with Mo-K_α radiation to $\sin\theta/\lambda$ = 0·596. Refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and the positional parameters for hydrogen atoms converged to R = 0·042 and R_w = 0·022.†

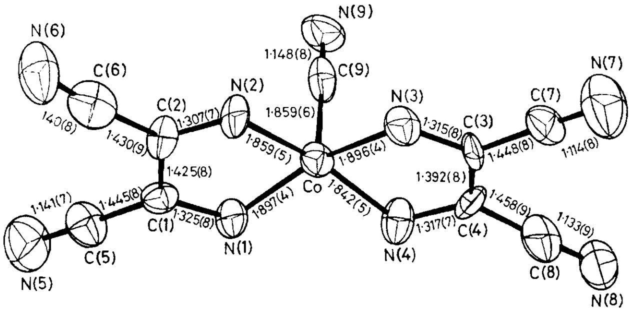

FIGURE. ORTEP plot of one of the independent molecules of complex (**5**).

The structure of one of the independent molecules is shown in the Figure. The Co^{III} atom is bound to cyanide and four nitrogen atoms of the two di-iminosuccinonitrile groups, and is displaced 0·05 Å from the least-squares plane of the four nitrogen atoms. The Co–N bonds are short, ranging from 1·802 to 1·897 Å, and are comparable with low-spin Co^{III}–N distances.[11] The axial Co–C(cyanide) distances, 1·857 and 1·919 Å for the two independent molecules, are also comparable with that for low-spin $[Co(CN)_6]^{3-}$.[12] The interatomic distances within the di-iminosuccinonitrile groups reveal a large degree of delocalization: the average 'C–N' distance, 1·325(8) Å, is significantly longer than observed in isolated co-ordinated imines (1·27 Å) or other α-di-imines (1·29 Å), and comparable with C–N distances (1·323 Å) in $[Pt(C_4H_2N_4)_2]$.[13] The average 'C–C' distance, 1·428(8) Å, is shorter than observed in other α-di-imine structures and is comparable with that in $[Pt(C_4H_2N_4)_2]$ (1·416 Å).[13] The water molecules are weakly hydrogen-bonded between the complexes.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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