SHORT PAPER

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Synthesis of novel mononuclear and dinuclear cobalt(III) complexes with cyanamide derivative ligands

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Several new mononuclear and dinuclear cobalt(III) complexes of the type *trans*-[Co(py){(DO)(DOH)pn}pcyd]PF_6 and [{Co(py)((DO)(DOH)pn)}$_2$(μ-dicyd)][PF_6]$_2$ where (DO)(DOH)pn = N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione-2-imine-3-oxime) have been prepared.

Keywords: mononuclear and dinuclear cobalt (III) complexes, cyanamide derivatives

Electronic and magnetic materials based on coordination complexes, composed of metal centres connected by the bridging ligands of some description, are of interest *e.g.* for their potential as molecular wires and switches. Our previous studies on dinuclear ruthenium complexes showed that the magnitude of metal–metal superexchange coupling could be controlled by the nature of both spectator and bridging ligands as well as the outer-coordination sphere.[1–3] In this study, we report a novel dinuclear system in which the degree of metal–metal coupling is remarkably affected by the nature of the metal ion. This new family, together with the previous studies on the Ru-complexes, permit an examination of factors controlling the magnitude of the superexchange interaction.

To fully understand metal-metal coupling through a bridging ligand, at the first step, a series of mononuclear complexes of the type *trans*-[Co(py){(DO)(DOH)pn}L]PF_6 where (DO)(DOH)pn = N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione-2-imine-3-oxime) and L = monoanion of phenylcyanamide(pcyd$^-$) derivatives and later a dinuclear cobalt(III) complex of the type [{Co(py)((DO)(DOH)pn)}$_2$(μ-dicyd)][PF_6]$_2$, where dicyd^{2-} = 1,4-dicyanamidobenzene dianion, have been prepared.

Experimental

All chemicals and solvents were reagent grade or better and used without further purification. The neutral phenylcyanamide derivatives and their thallium salts, pcyd, 4-Mepcyd, 2-Clpcyd, 1,4-dicyd[4-8] and *trans*-[Co(py)((DO)(DOH)Pn)Cl]PF_6 complex[9] were prepared by literature methods.

UV – vis spectra were measured on a JASCO 7850 spectrophotometer. The spectra were measured in acetonitrile solution at room temperature. The IR spectra (KBr disks) were obtained on a Shimadzu 460 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker DRX-500 MHz AVANCE spectrometer at ambient temperature in chloroform-d. Elemental analysis was performed using an Heraeus CHNO-Rapid elemental analyzer.

Trans-(pyridine)(phenylcyanamido)(N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione-2-imine-3-oxime))cobalt(III)hexafluorophosphate, trans-[Co(py)((DO)(DOH)pn)(pcyd)]PF_6 **(1):** *trans-* [Co(py){(DO)(DOH)pn}Cl]PF_6 (400 mg, 0.72 mmol) and deprotonated phenyl cyanamide (Tl salt) (231 mg, 0.72 mmol) were magnetically stirred in acetonitrile (30 ml) for 4 h while gently heated (30–40°C), after which the colour of the solution was deep red. The reaction mixture was allowed to cool to room temperature and then left in a refrigerator overnight. A white solid (TlCl) was filtered off. The brown microcrystalline product was obtained by ether diffusion into the filtrate (acetonitrile solution of the complex). The product was collected as dark brown fine crystals which were washed with ether and vacuum dried. Yield: 275mg (69%). (Found; C,43.6; H,4.8; N,15.2. $C_{23}H_{29}N_7O_2PF_6Co$ requires C,43.2; H,4.7; N,15.3%). IR (KBr) (ν/cm^{-1});1920 (O-H---O), 1590 (C=N), 1287, 1039 (N-O), 840 (P-F), 2151 (N=C=N).

Trans-[Co(py) {(DO)(DOH) pn} (2-Clpcyd)]PF_6 **(2):** This complex was prepared from 2-chlorophenylcyanamide (Tl salt, 2-ClpcydTl) (256mg,0.72mmol)by using the general procedure described above as brown microcrystals. Yield: 320mg (80%). (Found; C,40.7; H,4.3; N,14.8 $C_{23}H_{28}ClN_7O_2PF_6Co$ requires C,41.0; H,4.2; N,14.6%). IR(KBr) (ν/cm^{-1});1927 (O–H---O), 1591 (C=N), 1282, 1035 (N-O), 840 (P-F), 2158 (N=C=N).

Trans-[Co(py){(DO)(DOH)pn}(4-Mepcyd)]PF_6 **(3):** This complex was prepared from 4-methylphenylcyanamide (Tl salt, 4-MepcydTl) (241mg,0.72mmol), by using the general procedure described above, as brown microcrystals. Yield: 290mg (73%). (Found; C,44.6; H,4.7; N,14.9. $C_{24}H_{31}N_7O_2PF_6Co$ requires C,44.1; H,4.8; N,15.0%). IR (KBr) (ν/cm^{-1});1922 (O–H---O), 1588 (C=N), 1286, 1041 (N-O), 840 (P-F), 2143 (N=C=N).

Trans-μ-(1,4-dicyanamidobenzene)bis[N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione-2-imine-3-oxime))pyridinecobalt(III)]hexafluorophosphate,[{pyCo{(DO)(DOH}pn)}$_2$ (μ-dicyd)][PF_6]$_2$ **(4):** A solution of *trans*-{[Co(py)((DO)(DOH)Pn)Cl]PF_6 (1 g, 2 mmol) in DMF (100 ml) was degassed and under an N2 atmosphere, the tallium salt of 1,4-dicyanamidobenzene (1,4-dicydTl$_2$) (506 mg, 1 mmol) was added. The solution mixture was stirred with slight heating (25–35°C) overnight, during which time its colour changed from deep brown to dark blue. The resulting reaction mixture was left in a refrigerator overnight giving a white solid (TlCl) which was filtered off. Ether (500 ml) was added to the dark blue filtrate, and the solution was again placed in the refrigerator overnight. The resulting precipitate of crude product was filtered off and vacuum dried. The desired dinuclear complex was purified by column chromatography using Sephadex G-150. The loaded column was eluted with a mixture of CH_3CN/DMF (3/1 V/V). The dinuclear complex was precipitated from the eluent by the addition of ether and then recrystallised by ether diffusion into an acetonitrile solution, affording dark blue microcrystals. Yield: 395 mg (40%). (Found; C,40.3; H,4.5; N,16.2. $C_{40}H_{52}N_{14}O_4P_2F_{12}Co_2$ requires C,40.0; H,4.4; N,16.3%). IR(KBr) (ν/cm^{-1});1924 (O–H---O), 1595(C=N), 1281, 1044, (N–O), 842 (P–F), 2135 (N=C=N).

Results and discussion

All the complexes were prepared from the metathesis reaction of *trans*-[Co(py){(DO)(DOH)pn}Cl]PF_6 with the thallium salt of a phenylcyanamide (mononuclear) (Scheme 1) and 1,4-dicyanamidobenzene dianion (dinuclear) (Scheme 2).

The elemental analyses of the complexes were consistent with their formulation, as are the following spectroscopic data.

Electronic spectral data for both mono and dinuclear Co(III) complexes in acetonitrile solution are assembled in Table 1. The absorbtion bands seen in the UV region are assigned to ligand-centred (π→π*) transitions.[10] In comparison to Ru(III) and Co(III) phenylcyanamide complexes,[5,11] the two intense

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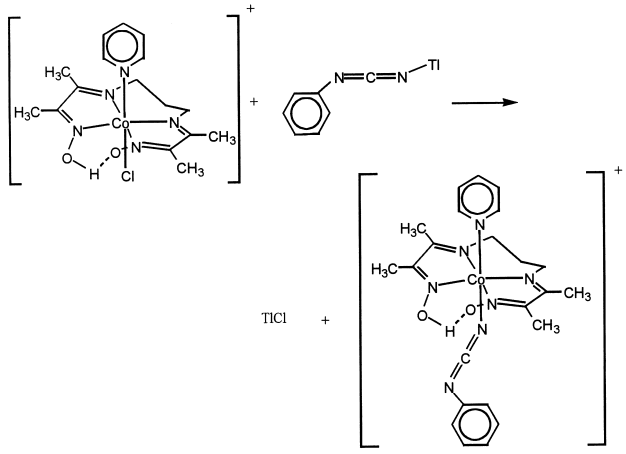
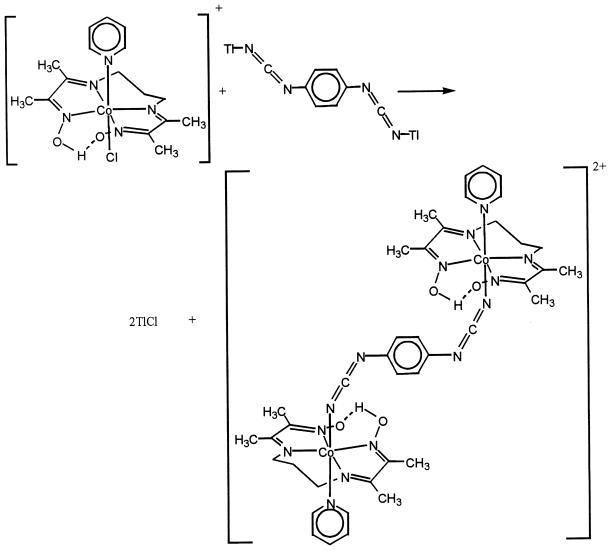


Scheme 1



Scheme 2

absorption bands in the visible region (350–570 nm) are assigned to ligand-to-metal charge transfer (LMCT) with a minor contribution to band intensity due to underlying ligand field transitions. These two LMCT bands are associated with a Co(III)-cyanamide chromophore. The reason for this is the solvent dependence of charge-transfer energy on solvent polarity which is a well- known phenomenon.[12,13] For the mono and dinuclear complexes, changing the solvent from acetonitrile and DMSO shows an increase in solvent polarity and causes the low-energy LMCT bands to shift to higher energy. This behaviour is consistent with ground-state stabilisation of the complexes' permanent dipoles by the solvent.

These two LMCT transitions arise from two nondegenerate pairs of nonbonding electrons (π_{nb}) that are delocalised in the cyanamide moiety.[8] Since the t_{2g} orbitals in Co(III) are full, therefore the LMCT bands originate from the ligand π orbital to a metal eg* (σ^*) orbital ($\pi \rightarrow \sigma^*$).[12]

The IR spectra of the six complexes show similar absorption patterns in the 1800–400 cm^{-1} region, indicating the existence of (DO)(DOH)pn as the common equatorial ligand.[14] The O–H stretching vibration of the (DO)(DOH)pn ligand appears at about 1900 cm^{-1} for all six complexes. The presence of a strong absorption band around 840 cm^{-1} in all the complexes, which is assigned to ν(P–F), demonstrates the existence of PF_6^- as a counter ion in mono and dinuclear complexes.

The IR data for the free phenylcyanamide ligand (neutral and TI salt) have been reported elsewhere.[6-8] These ligands have a sharp and intense absorption band around 2100 cm^{-1} which is assigned to ν(N=C=N). When a phenylcyanamide ligand coordinates to a transition metal ion, ν(N=C=N) is shifted to higher energies.[15,16] The presence of only one sharp and intense absorption band for the cyanamide stretching frequency in the dinuclear complex **4** provides evidence that both cyanamide moeties on the phenyl ring of the bridging ligand (1,4-dicyd) are equivalent in the solid state. When the cyanamide moeties are inequivalent, multiple ν(N=C=N) bands are observed.[15] In mononuclear complexes **1–3**, a small positive shift in ν(N=C=N) is observed, as the electron-withdrawing ability of the substituents on the phenyl ring increases.

The ^{1}H NMR spectral data of complexes **1–4** in chloroform-d were collected, and relevant chemical shifts of the O–H---O signals, equatorial methyl signals, pyridine and phenylcyanamide signals are reported in Table 1.

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Table 1 Spectral data of complexes **1–4**

Complex	UV-vis(CH_3CN,nm),(logε)		^{1}H NMR [$(CD_3)_2SO$, ppm]			
	$\pi \rightarrow \pi^*$	LMCT	O–H---O	C–N=C-CH_3 O-N=C-CH_3	C_5H_5N	Phenyl protons
1	238(4.66)	450(3.89) 537(3.83)	19.31(1H,s)	2.39(3H,s) 2.28(3H,s)	7.28(2H,t) 7.71(1H,t) 8.01(2H,d)	6.40(1H,t) 6.61(2H,d) 6.93(2H,t)
2	239(4.31)	441(3.81) 519(3.78)	19.27(1H,s)	2.40(3H,s) 2.30(3H,s)	7.28(2H,t) 7.70(1H,t) 8.02(2H,d)	6.72(1H,d) 6.86(1H,t) 6.94(1H,t) 7.02(1H,d)
3	242(4.50)	456(3.61) 545(3.67)	19.30(1H,s)	2.43(3H,s) 2.35(3H,s)	7.29(2H,t) 7.72(1H,t) 8.07(2H,d)	6.51(2H,t) 6.87(2H,t)
4	261(4.90)	485(4.12) 590(4.22)	19.21(2H,s)	2.59(6H,s) 2.44(6H,s)	7.31(4H,t) 7.75(2H,t) 8.10(4H,d)	6.46(4H,s)

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