Structure of a Linear Unsymmetrical Trinuclear Cobalt(II) Complex with a Localized Co^{II}–Co^{II} Bond: Dichlorotetrakis[μ_3-bis(2-pyridyl)amido]tricobalt(II)

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The synthesis and X-ray crystal structure of a linear unsymmetrical trinuclear cobalt(II) complex with a *syn–syn* bis(2-pyridyl)amido ligand, possessing a short, localized Co^{II}–Co^{II} bond and a spin crossover square-pyramidal Co^{II} ion, is described.

Polynuclear metal chain complexes have received considerable interest because of their spin interactions and the nature of the metal–metal bonding.[1] This bis(2-pyridyl)amido ligand has several possible configuration for coordination. The *syn–syn* configuration has been found in trinuclear complexes (M = Cu^{II}, Ni^{II}),[2,3] the *anti–anti* configuration in many bidentate chelate complexes,[4–6] and the *anti–syn* configuration exists in the dimer of free ligand. We report here the synthesis and structure of a quadruply bridged linear trinuclear cobalt(II) complex with a *syn–syn* configuration of the bridged ligand, which binds unsymmetrically with trinuclear cobalt(II) ions. This complex possesses a short, localized Co–Co bond [2.290(3) Å], rather than a delocalized three-centred bond, and a spin crossover square-pyramidal Co^{II} ion.

$$3CoCl_2 + 4Na^+dpa^- \rightarrow [Co_3(\mu_3\text{-}dpa)_4Cl_2] + 4NaCl \quad (1)$$

High-temperature reaction of anhydrous $CoCl_2$ with Na^+dpa^- (1.5 mol. equiv.), where dpa = dipyridylamido anion, prepared *in situ* from Hdpa and Na^+BuO^- in butanol, afforded $[Co_3(dpa)_4Cl_2]$ (eqn 1) in low yield.† The IR spectrum is almost the same as that of the previously reported Ni^{II} complex, which is characterized by lines at 1606 (s), 1594 (s), 1550 (m), 1470 (vs) and 1430 (vs) cm^{-1} with the absence of lines due to N–H stretching mode in the 3300 cm^{-1} region.[3,7] The observed electronic spectrum, measured in CH_2Cl_2 solution, shows absorption maxima at 322 (ε 1.12 × 10^5), 568 (ε 2.28 × 10^3), 1362 nm (ε 1.72 × 10^2 dm^3 mol^{-1} cm^{-1}) and a shoulder about 400 nm.

The structure of $[Co_3(dpa)_4Cl_2]$ is shown in Fig. 1 (along the Co–Co axis).‡ The three Co^{II} ions and two chloride ions are collinear. The *syn–syn* conformation of the four dipyridylamido ligands allows each nitrogen atom to coordinate with a separate cobalt ion. Our structure is essentially isostructural with that of $[M_3(dpa)_4Cl_2]$ (M = Ni^{II}, Cu^{II}). A comparison with this structure appears in Table 1.

The feature of the cobalt trimer that distinguishes it from the nickel and copper trimers is the unsymmetrical bonding formation, which divides the trimer into a diamagnetic dimer Cl–Co^{II}N$_4$–Co^{II}N$_4$ chromophore and a spin crossover Co^{II}N$_4$–Cl chromophore. The dimer chromophore exhibits a short Co^{II}–Co^{II} distance [2.290(3) Å], and a long Co–Cl bond [2.432(4) Å] and short Co–N bonds (1.96, 1.90 Å), consistent

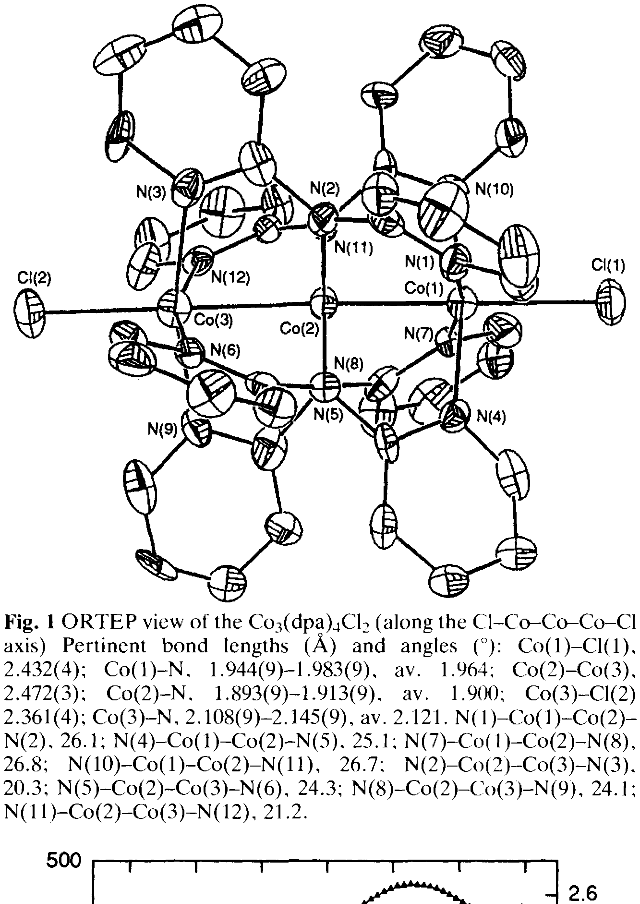


Fig. 1 ORTEP view of the $Co_3(dpa)_4Cl_2$ (along the Cl–Co–Co–Co–Cl axis) Pertinent bond lengths (Å) and angles (°): Co(1)–Cl(1), 2.432(4); Co(1)–N, 1.944(9)–1.983(9), av. 1.964; Co(2)–Co(3), 2.472(3); Co(2)–N, 1.893(9)–1.913(9), av. 1.900; Co(3)–Cl(2) 2.361(4); Co(3)–N, 2.108(9)–2.145(9), av. 2.121. N(1)–Co(1)–Co(2)–N(2), 26.1; N(4)–Co(1)–Co(2)–N(5), 25.1; N(7)–Co(1)–Co(2)–N(8), 26.8; N(10)–Co(1)–Co(2)–N(11), 26.7; N(2)–Co(2)–Co(3)–N(3), 20.3; N(5)–Co(2)–Co(3)–N(6), 24.3; N(8)–Co(2)–Co(3)–N(9), 24.1; N(11)–Co(2)–Co(3)–N(12), 21.2.

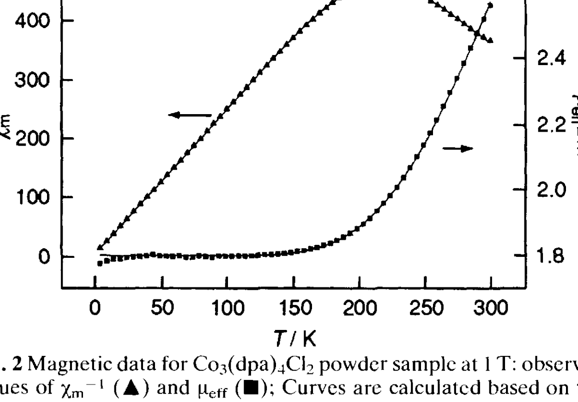
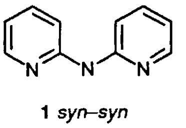
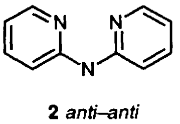


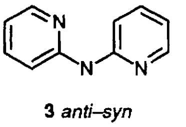
Fig. 2 Magnetic data for $Co_3(dpa)_4Cl_2$ powder sample at 1 T: observed values of χ_m^{-1} (▲) and μ_{eff} (■); Curves are calculated based on the equation $\mu_{eff}^2 = [150\gamma x C\mu_E^2 + 25\{\gamma x(5-\gamma)^2 - 20(2-\gamma)^2\}\exp\{-(E/\varsigma + 5\gamma/6)x\} + 2\{5\gamma x(11+2\gamma)^2 + 88(2-\gamma)^2\}\exp\{-(E/\varsigma + \gamma/3)x\} + 9\{35\gamma x(3+\gamma)^2 + 36(2-\gamma)^2\}\exp\{-(E/\varsigma - \gamma/2)x\}] \times (72\gamma x[2C + \exp\{-(E/\varsigma + 5\gamma/6)x\} + 2\exp\{-(E/\varsigma + \gamma/3)x\} + 3\exp\{-(E/\varsigma - \gamma/2)x\}])^{-1}$ where μ_E = 1.757 BM, $\gamma = -1.5$, ς = 540 cm^{-1}, $x = \varsigma/kT$, E = 1638 cm^{-1}, C = 0.0405.



1 *syn–syn*



2 *anti–anti*



3 *anti–syn*

Table 1 Structural comparison of bond lengths/Å in $[M_3(dpa)_4Cl_2]$ complexes (M = Co^{II}, Ni^{II},[3] Cu^{II} [2])

	Co		Ni	Cu
M–Cl	Co(1)–Cl(1) 2.432(4) Co(3)–Cl(2) 2.361(4)		2.325(3)	2.465(1)
M–M	Co(1)–Co(2) 2.290(3) Co(3)–Co(2) 2.472(3)		2.443(1)	2.471(1)
M–N (of pyridine)	Co(1)–N Co(3)–N	1.96(1) 2.12(1)	2.10(1)	2.05(2)
M–N (of amido)	Co(2)–N	1.90(1)	1.89(1)	1.96(2)

with full pairing of the electrons in a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ MO scheme.[8] It is closely related to diamagnetic $Co_2(triaz)_4$(triaz = di-*p*-tolyltriazenato) [Co–Co distance, 2.265(2) Å], which lacks an axial chloride ligand.[9] In the spin crossover square-pyramidal $Co^{II}N_4Cl$ chromophore, the mean Co–N distance, 2.121, and Co–Cl distance, 2.361(4) Å, are consistent with those normally found in a square-based pyramidal cobalt(II) structure.[10] The Co–Co distance between the spin crossover chromophore and low-spin dinuclear chromophore is 2.472(3) Å, which is comparable with the M–M distances in the Ni and Cu trimers. The magnetic moments of the complex, shown in Fig. 2, are considered intermediate between those expected for high- and low-spin cobalt(II). Qualitatively similar curves were observed for $[Co(terpy)_2]X_2$ and a ^2E-$^4T_1$ cross-over was proposed.[11] Our complex has ΔE value 1638 cm^{-1} between ^2E and $^4T_1$.

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Footnotes

† $[Co(H_2O)_6]Cl_2$ (0.48 g, 2.0 mmol) and dipyridylamine (dpaH, 0.51 g, 3.0 mmol) were placed in a Erlemyer Flask, to which naphthalene (7.2 g) was added. The whole mixture was heated (*ca.* 160–180 °C) for 10 min to remove water. Then n-butanol (3 ml) was added to the heated mixture, and heating was continued until n-butanol was almost completely evaporated. A solution of sodium n-butoxide [Na(0.07 g), n-BuOH (20 ml)] was added dropwise. Heating was continued until the remaining n-butanol was evaporated completely. After the mixture was cooled, with n-hexane was added to wash out naphthalene. The solid remaining was extracted with CH_2Cl_2 and recrystallized from CH_2Cl_2/n-hexane solution. Dark red–green crystals were obtained (yield 2–5%).

‡ Crystal data for $[Co_3(dpa)_4Cl_2]\cdot(CH_2Cl_2)_2H_2O$: tetragonal, space group $I4$, $a = 27.295(6)$, $c = 12.313(5)$ Å, $V = 9173(4)$ Å^3, $D_m = 1.61$, $D_c = 1.614$ g ml^{-1}, $Z = 8$; CAD4 diffractometer with graphite-monochromated Mo-Kα radication, psi scan absorption correction was made; 3308 unique reflection ($2\theta < 45°$) were measured and 2601 with $I > 2\sigma(I)$ were used in the refinement. Refinement of positional and anisotropic thermal perameters for all non-hydrogen atoms (578 variables) converged to $R = 0.049$ and $R_w = 0.039$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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