Structure of a Linear Unsymmetrical Trinuclear Cobalt(II) Complex with a Localized CoII-CoII Bond: Dichlorotetraakis[μ3-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-Co bond and a spin crossover square-pyramidal CoII ion, is described.

Polynuclear metal chain complexes have received considerable interest because of their spin interactions and the nature of the metal-metal bonding. This bis(2-pyridyl)amido ligand has several possible configurations for coordination. The syn-syn configuration has been found in trinuclear complexes (M = CuII, NiII), the anti-anti configuration in many bidentate chelate complexes, 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 CoII ion.

3CoCl2 + 4Na+dpa- -> [Co3(μ3-dpa)4Cl4] + 4NaCl (1)

High-temperature reaction of anhydrous CoCl2 with Na+dpa- (1.5 mol. equiv.), where dpa = dipipyridlamido anion, prepared in situ from Hdpa and Na+BuO- in butanol, afforded [Co3(dpa)4Cl4] (eqn 1) in low yield. The IR spectrum is almost the same as that of the previously reported NiII 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. The observed electronic spectrum, measured in CH2Cl2 solution, shows absorption maxima at 322 (ε = 1.12 × 10⁴), 568 (ε = 2.28 × 10⁴), 1362 nm (ε = 1.72 × 10⁴ dm³ mol⁻¹ cm⁻¹) and a shoulder about 400 nm.

The structure of [Co3(dpa)4Cl4] is shown in Fig. 1 (along the Co–Co axis). The three CoII ions and two chloride ions are collinear. The syn-syn conformation of the four dipipyridlamido ligands allows each nitrogen atom to coordinate with a nickel and copper trimer is the unsymmetrical bonding formation, which divides the trimer into a diamagnetic dimer.
with full pairing of the electrons in a $\sigma_2\pi^2\delta_2\delta^{*}2\pi^{*4}$ MO scheme. It is closely related to diamagnetic Co$_2$(triaz)$_4$(triaz = di-p-tolyltriazaneto) [Co–Co distance, 2.265(2) Å], which lacks an axial chloride ligand. In the spin crossover square-pyramidal Co$^{II}$N$_4$CI 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. 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 $2E$–$4T_1$ crossover was proposed. Our complex has an $\Delta E$ value at 1638 cm$^{-1}$ between $2E$ and $4T_1$.

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Footnotes

† [Co(H$_2$O)$_6$]Cl$_2$ (0.48 g, 2.0 mmol) and dipyridylamine (dpaH, 0.51 g, 3.0 mmol) were placed in a Erlenmeyer 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. The mixture was cooled, with n-hexane was added to wash out naphthalene. The solid remaining was extracted with CH$_2$Cl$_2$ and recrystallized from CH$_2$Cl$_2$/n-hexane solution. Dark red-green crystals were obtained (yield 2–5%).

‡ Crystal data for [Co(dpa)Cl$_3$](CH$_2$Cl)$_2$H$_2$O: 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 cm$^{-3}$. 2 CAD4 diffractometer with graphite-monochromated Mo-Kα radiation, psi scan absorption correction was made; 3308 unique reflection ($20 < 45$°) were measured and 2601 with $I > 2.0$ (I) were used in the refinement. Refinement of positional and anisotropic thermal parameters 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.

References