

# A tetranuclear *meso*-helicate

Edwin C. Constable,\* Markus Neuburger, Louise A. Whall and Margareta Zehnder

Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel, Switzerland

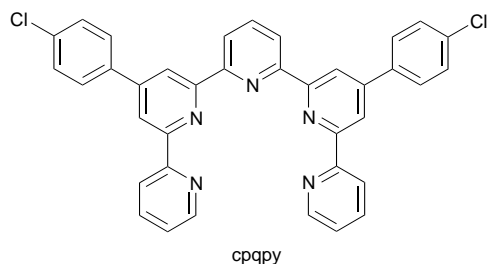
A tetranuclear complex formed from the linking together of two double-helical dicobalt species by acetate bridges has been structurally characterised; the tetranuclear unit consists of two helicates of opposite *P* and *M* chirality.

Oligopyridines and oligopyridine metal-binding domains are a recurrent feature in metallosupramolecular chemistry<sup>1</sup> and it is well-established that the higher oligopyridines can give multiple-helical transition metal complexes.<sup>2</sup> Cobalt has been shown to form both mononuclear helical<sup>3,4</sup> and dinuclear double-helical complexes<sup>5–7</sup> with 2,2':6',2'':6'',2''':6''',2''''-quinquepyridines (qpy), in which the precise structures are defined by reaction conditions and substituents. We have utilised interconversions within cobalt(II) complexes for the specific assembly of heteronuclear helicates.<sup>8,9</sup> In the course of these studies we have further investigated the factors controlling the formation of mononuclear or dinuclear cobalt complexes and now report the formation of a *bis*(double helicate) as a solid state species.

The reaction of cobalt(II) acetate with 4',4''-bis(4-chlorophenyl)-2,2':6',2'':6'',2''':6''',2''''-quinquepyridine (cpqpy) in dry methanol yields an orange solution from which an orange solid of stoichiometry  $\{Co_2(cpqpy)_2(OAc)(PF_6)_3\}$  may be precipitated by the addition of ammonium hexafluorophosphate.† The <sup>1</sup>H NMR spectrum of a solution of this orange product in CD<sub>3</sub>CN revealed one major solution species with 19 paramagnetically shifted resonances [ $\delta$  263, 139, 117, 91, 84, 74, 53, 52, 51.5, 28, 25 (2H), 21, 19, 16 (2H), 7.2, 7 (2H), 5 (2H), –3, –10], as expected for a system in which each of the rings of the cpqpy ligand are non-equivalent. A lower intensity sub-spectrum indicated a system symmetrical about the central pyridine ring of the ligand and corresponded exactly to the mononuclear species  $[Co(cpqpy)(MeCN)_2]^{2+}$  that we have previously characterised.<sup>5,8</sup> Recrystallisation from acetonitrile–diethyl ether gave orange blocks of the major component. In contrast, recrystallisation from damp solvents yielded predominantly the yellow/cream mononuclear compounds we have previously described. Furthermore, an *orange* solution of the isolated orange compound in methanol changed to a *yellow* solution of the mononuclear compound upon treatment with water

and stirring for 30 min at room temperature. The TOF mass spectrum of the orange species exhibited peaks corresponding to  $\{Co_2(cpqpy)_2\}^+$ ,  $\{Co(cpqpy)_2\}^+$ ,  $\{Co_2(cpqpy)OAc\}^+$ ,  $\{Co_2(cpqpy)\}^+$  and  $\{Co(cpqpy)\}^+$ , and these data combined with the <sup>1</sup>H NMR spectrum suggest the formulation of a dinuclear double helix analogous to the cation  $[Co_2(qpy)_2(OAc)]^{3+}$ .<sup>5</sup> The IR spectrum exhibits stretches at 1574 and 1421 cm<sup>–1</sup> that were tentatively assigned to a bridging, chelating or semi-chelating acetate ligand. In view of the uncertainty over the precise nature of these cobalt complexes, we have determined the solid state structure of the major orange component of the reaction of cobalt(II) acetate with cpqpy.

The crystal structure determination revealed the correct formulation of the orange product to be  $[(cpqpy)_2Co_2](\mu-OAc)_2\{Co_2(cpqpy)_2\}[PF_6]_6 \cdot 12MeCN$  and the cationic unit is presented in Fig. 1 together with a stereoview in Fig. 2. Firstly, the predicted dinuclear double-helical species has indeed been formed. The presence of two six-coordinate cobalt(II) centres requires a total of twelve donor atoms, which in  $[Co_2(qpy)_2(OAc)]^{3+}$  are provided by the 10 nitrogen atoms of the double-helical ligand array and a didentate chelating acetate.<sup>5</sup> In this case, instead of a single chelating acetate ligand providing two oxygen donors per double helix, there are two bridging acetate ligands linking two helicates together. The two helicates are related by an inversion centre and so the overall tetranuclear unit comprises one dinuclear unit of *P* and one of *M* chirality (Fig. 3). The end result is an achiral *meso*-helicite consisting of two linked helicates of opposite chirality. We note that this usage differs slightly from the use adopted by Albrect to describe systems in which two metal centres within a dinuclear complex exhibit opposite chirality—in the latter case the *meso* description is certainly correct but it may be argued whether the complexes should now be called helicates. The central

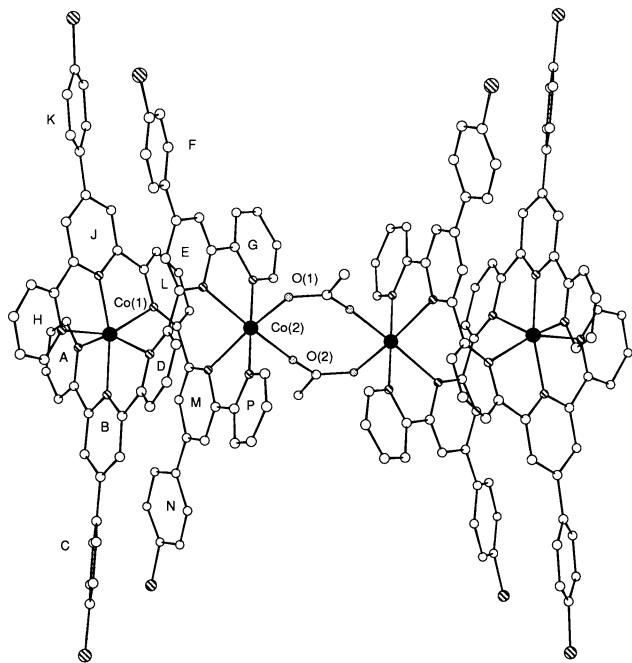


cpqpy

† Selected data for  $[(cpqpy)_2Co_2](\mu-OAc)_2\{Co_2(cpqpy)_2\}[PF_6]_6 \cdot 12MeCN$ : mp > 250 °C, MALDI-TOF mass spectrum: 1338  $\{Co_2(cpqpy)_2\}^+$ , 1278  $\{Co(cpqpy)_2\}^+$ , 785  $\{Co_2(cpqpy)OAc\}^+$ , 728  $\{Co_2(cpqpy)\}^+$ . IR (KBr):  $\nu$  = 1613s, 1574m, 1547m, 1481m, 1450m, 1422m, 1386m, 1247w, 1096m, 1012m, 842vs, 792s, 651w, 558s cm<sup>–1</sup>.

‡ Crystal data for  $[(cpqpy)_2Co_2](\mu-OAc)_2\{Co_2(cpqpy)_2\}[PF_6]_6 \cdot 12MeCN$ : orange block, C<sub>176</sub>H<sub>134</sub>Co<sub>4</sub>N<sub>32</sub>Cl<sub>8</sub>O<sub>4</sub>P<sub>6</sub>F<sub>39</sub>. *M* = 4150.35, triclinic, spacegroup *P*1̄, *a* = 13.868(2), *b* = 15.271(2), *c* = 22.336(4) Å,  $\alpha$  = 87.95(1),  $\beta$  = 89.65(1),  $\gamma$  = 75.39(1)°, *U* = 49 245(9) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 1.51 g cm<sup>–3</sup>, *F*(000) = 2104,  $\lambda$  = 1.541 80 Å,  $\mu$ (Cu-K $\alpha$ ) 5.41 mm<sup>–1</sup>. Intensity data were collected by the  $\omega/2\theta$  scan method (2.52 <  $\theta$  < 66.74°); for a crystal of dimensions 0.22 × 0.24 × 0.32 mm at 223 K; of 12 182 (11 884 independent) reflections measured, 7178 [*I* ≥ 2 $\sigma$ (*I*)] were used in the structure solution. Significant solvent loss occurred over the data collection period (19.47%), even at low temperature. Because of the high decay, absorption corrections were carried out using DIFABS. The structure was solved by direct methods using CRYSTALS [D. J. Watkin, J. R. Carruthers and P. Betteridge, Chemical Crystallography Laboratory, Oxford, UK] to give final *R* and *R*<sub>w</sub> values of 0.0719 and 0.0475, respectively [Chebychev polynomial weighting: J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698].

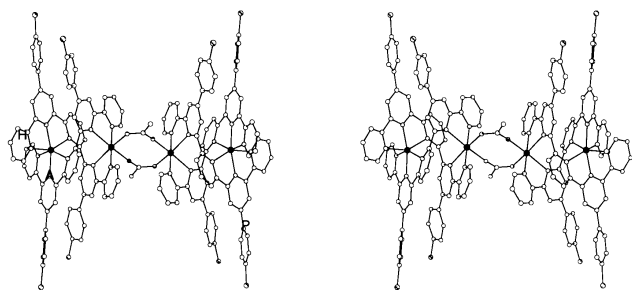
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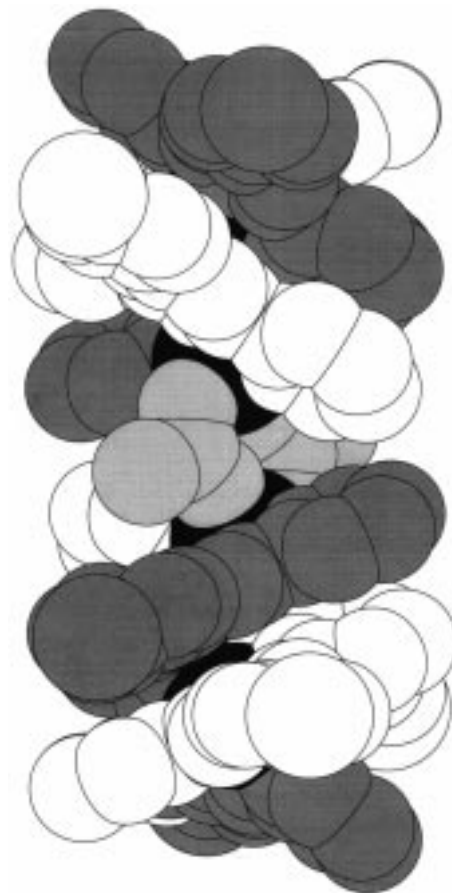
**Fig. 1** The structure of the tetranuclear cation present in  $[(\text{cpqpy})_2\text{Co}_2](\mu\text{-OAc})_2[\text{Co}_2(\text{cpqpy})_2][\text{PF}_6]_6 \cdot 12\text{MeCN}$  showing the numbering scheme adopted for the rings. Selected bond lengths (Å): Co(1)—N(H), 2.195(6); Co(1)—N(J), 2.037(6); Co(1)—N(L), 2.204(6); Co(1)—N(A), 2.180(6); Co(1)—N(B), 2.054(6); Co(1)—N(D), 2.218(6); Co(2)—N(M), 2.207(6); Co(2)—N(P), 2.088(6); Co(2)—N(E), 2.251(6); Co(2)—N(G), 2.108(6); Co(2)—O(1), 2.045(5); Co(2)—O(2), 2.042(6)

Co—O—C—O—Co—O—C—O eight-membered ring is slightly ruffled. The expected  $\pi$ -stacking between the ligand strands is present, with centroid-to-centroid distances of 3.411–3.639 Å observed between the pairs M-B, L-G, P-D and J-E; each pair is approximately coplanar with least squares planes in the range of 4.03–7.35 Å. The chlorophenyl substituents show no interactions with any other aromatic rings. There are also a number of differences from the dinuclear  $[\text{Co}_2(\text{qpy})_2(\text{OAc})]^{3+}$  species previously characterised; the Co(1)—Co(2) distance is considerably greater in the tetranuclear species than in the dinuclear one (4.776 Å *versus* 4.461 Å). This may be traced to changes in the pitch of the helix and the cumulative effect of changes in the dihedral angles between adjacent rings. The Co(1)—Co(1') distance is 4.764 Å. In the case of  $[\text{Co}_2(\text{qpy})_2(\text{OAc})][\text{PF}_6]_3$ , the lattice consists of equal numbers of discrete *P* and *M* helices, whereas with cpqpy, helices of opposite chirality are linked by acetate bridges. The driving force for this behaviour is unclear, and there are no short contacts between the cation and the anions or the lattice solvent molecules.

The similarity of the solution  $^1\text{H}$  NMR spectrum of this complex with those of  $[\text{Co}_2(\text{qpy})_2(\text{OAc})][\text{PF}_6]_3$  and other complexes with substituted qpy ligands that are unam-



**Fig. 2** Stereoviews of the structure of the tetranuclear cation present in  $[(\text{cpqpy})_2\text{Co}_2](\mu\text{-OAc})_2[\text{Co}_2(\text{cpqpy})_2][\text{PF}_6]_6 \cdot 12\text{MeCN}$



**Fig. 3** A space-filling representation of the tetranuclear cation present in  $[(\text{cpqpy})_2\text{Co}_2](\mu\text{-OAc})_2[\text{Co}_2(\text{cpqpy})_2][\text{PF}_6]_6 \cdot 12\text{MeCN}$ , emphasising the opposite chirality of the two dinuclear components.

biguously dinuclear double helicates in the solid state leads us to suggest that the bridging acetates do not persist in solution and that the aggregation is a solid state phenomenon. We are currently extending these studies to co-crystallisation of complexes with chiral oligopyridines.<sup>10,11</sup>

## Acknowledgements

We should like to thank the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung for support.

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Received 17th November 1997; Paper 7/09243A

