

Can crystal structure determine molecular structure?

For $\text{Co}_3(\text{dpa})_4\text{Cl}_2$, yes

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Received 12th August 1999, Accepted 18th August 1999

A tetragonal form of $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ [dpa = anion of bis-(2-pyridyl)amine] with an unsymmetrical chain of three Co atoms is found to crystallize along with its previously reported orthorhombic form that has a symmetrical chain.

In 1994 it was reported¹ that the title compound, $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ [dpa = anion of bis(2-pyridyl)amine], had a molecular structure in which there was a very unsymmetrical linear chain of cobalt atoms with Co–Co distances of 2.270(3) Å and 2.472(3) Å. This appeared to be anomalous in view of the fact that previously analogous molecules containing nickel² and copper,³ and subsequently, those with ruthenium⁴ and rhodium⁴ were all found to have symmetrical chains of metal atoms. This prompted us to reinvestigate the compound, and we found⁵ that it formed crystals, $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$, that were isomorphous (space group *Pnn2*) with those of the copper,³ ruthenium⁴ and rhodium⁴ compounds. In all four *Pnn2* crystals, there is one molecule of solvent per molecule of the trinuclear complex: CH_2Cl_2 for Co, Ru and Rh, and H_2O for Cu.^{3b} At this point it was uncertain what to make of the reported¹ unsymmetrical tricobalt compound, which was said to be $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ and to crystallize in space group *I4*.

This interesting, if confusing, state of affairs was made still more interesting by the next two developments. (1) It was found⁶ that $\text{Cr}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ could be made and that it too, crystallized in space group *Pnn2* with a symmetrical structure.⁷ (2) Another compound, $[\text{Co}(\text{dpa})_2][\text{Co}_3(\text{dpa})_4\text{Cl}_2]$, in which two neutral molecules were co-crystallized, was prepared and found to contain the unsymmetrical $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ molecule,⁸ very similar to that first reported.¹ Most recently, two more crystalline forms of $\text{Ni}_3(\text{dpa})_4\text{Cl}_2$ have been discovered and both of these also contain symmetrical molecules.⁹

At this point, the situation was that for $\text{M}_3(\text{dpa})_4\text{Cl}_2$ molecules with $\text{M} = \text{Cr}, \text{Ni}, \text{Cu}, \text{Ru},$ and Rh , only the symmetrical form was seen, but for Co the molecule had been observed once in symmetrical form and twice in unsymmetrical form. The two cases where it was unsymmetrical were each unique in their unit cell contents, containing, according to the report,¹ three solvent molecules (2 CH_2Cl_2 and H_2O) in one case and the $\text{Co}(\text{dpa})_2$ molecule in the other.⁸ One other paper bearing on the problem reports a DFT calculation¹⁰ on $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ that finds a single, broad potential minimum for the Co_3 chain with the middle Co atom centered, but with the potential well very shallow.

We now report that in our method of preparation^{5,8} for $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$, which we heretofore believed to give only the orthorhombic, *Pnn2*, crystal form of this composition, with symmetrical molecules, one actually obtains a mixture of these orthorhombic crystals with another type, namely a tetragonal form. Both are very dark greenish black and cannot be distinguished by color alone. They are shown in Fig. 1. We have characterized this second form crystallographically.¹¹ These

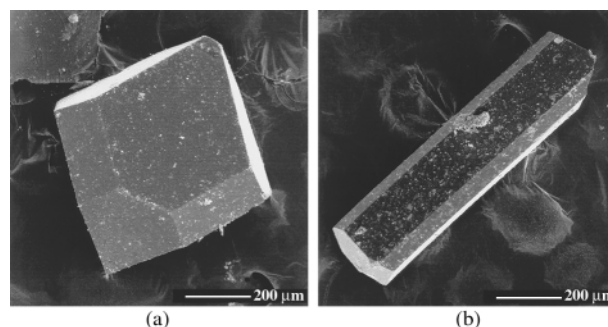


Fig. 1 Scanning electron micrograph of two crystalline forms of $\text{Co}_3(\text{dpa})_4\text{Cl}_4$. (a) Orthorhombic crystal. (b) Tetragonal crystal. They crystallized together from a dichloromethane solution and were separated by hand.

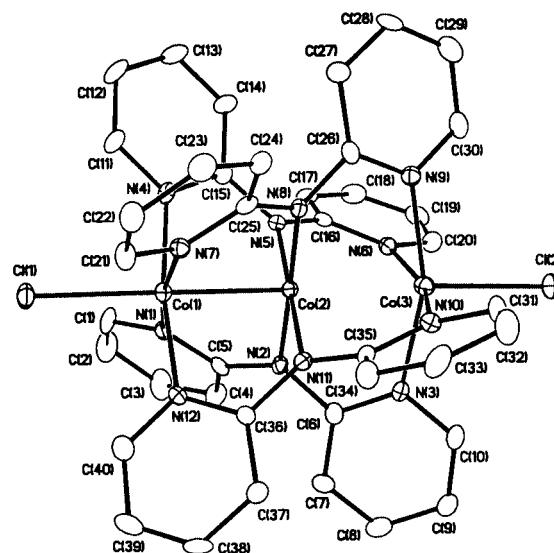


Fig. 2 Perspective view of the molecule of $\text{Co}_3(\text{dpa})_4\text{Cl}_4$ in $\text{Co}_3(\text{dpa})_4\text{Cl}_4 \cdot 2\text{CH}_2\text{Cl}_2$. Atoms are drawn as their ellipsoids at the 40% probability level. Hydrogen atoms are omitted for clarity.

crystals are tetragonal, space group $I\bar{4}$, and they contain the $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ molecules in their unsymmetrical form, as shown in Fig. 2. The composition is $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2$. Table 1 compares the key molecular dimensions of the unsymmetrical molecules as found in the two previous cases,^{1,8} and in this case. There are no significant differences, and with respect to the short and long Co–Co distances, the agreement is particularly good. Thus, even though the reported calculation¹⁰ showed no evidence for a minimum at any specific combination of unequal distances, when the molecule adopts an unsymmetrical form, it

Table 1 Dimensions of unsymmetrical $\text{Co}_3(\text{dpa})_4\text{Cl}_4$ solv. molecules in three crystal forms

	Ref. 1	Ref. 8	This work
Solvent	$2\text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	$[\text{Co}(\text{dpa})_2]$	$2(\text{CH}_2\text{Cl}_2)$
Crystal form	$I4^a$	$P4/n$	$I\bar{4}$
Co(1)–Co(2)	2.290(3)	2.285(1)	2.294(1)
Co(2)–Co(3)	2.472(3)	2.459(1)	2.466(1)
Co(1)–Cl	2.432(4)	2.386(2)	2.432(1)
Co(3)–Cl	2.361(4)	2.353(2)	2.369(2)
Co(1)–N	1.964(av)	1.965(3)	1.973(av)
Co(2)–N	1.900(av)	1.907(3)	1.906(av)
Co(3)–N	2.121(av)	2.125(3)	2.115(av)
Temperature/K	295 ^b	213	213

^a Should be $I\bar{4}$; see text and ref. 1. ^b Reported at the Cambridge Crystallographic Data Centre but not stated in ref. 1.

is always the *same* unsymmetrical form. This poses an interesting problem for further theoretical work.

A powder diffraction pattern from a typical preparation of $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ shows that both the tetragonal and orthorhombic forms are present (and nothing else), with the former making up 10–20%. Both forms, when dissolved in CH_2Cl_2 give the same ^1H NMR spectrum.

The key conclusions to be drawn from these new observations are (1) that the two forms of the molecule are energetically so similar that both can crystallize simultaneously from the same solution in CH_2Cl_2 and (2) any measurement made on a bulk sample (*e.g.* magnetic susceptibility) is of dubious value since the sample is, or at least may be, a mixture of two different substances.

Acknowledgements

We are grateful to the National Science Foundation for financial support.

Notes and references

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- 3 (a) L. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1990, 3835; (b) G. J. Pyrka, M. El-Mekki and A. A. Pinkerton, *J. Chem. Soc., Chem. Commun.*, 1991, 84.
- 4 J. Sheu, C. Liu, I. Chao, C. Wang and S. Peng, *Chem. Commun.*, 1996, 315.
- 5 F. A. Cotton, L. M. Daniels and G. T. Jordan IV, *Chem. Commun.*, 1997, 421.
- 6 F. A. Cotton, L. M. Daniels, C. A. Murillo and I. Pascual, *J. Am. Chem. Soc.*, 1997, **119**, 10223.
- 7 F. A. Cotton, L. M. Daniels, C. A. Murillo and I. Pascual, *Inorg. Chem. Commun.*, 1998, **1**, 1. $\text{Cr}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{C}_6\text{H}_5\text{Me}$ also contains symmetrical molecules, although in this case they lie on general positions, *i.e.*, crystallographically they are not required to be symmetrical.
- 8 F. A. Cotton, L. M. Daniels, G. T. Jordan IV and C. A. Murillo, *J. Am. Chem. Soc.*, 1997, **119**, 10377. In two places in this paper the chemical formula is misstated as $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2$. There is, in fact, only *one* CH_2Cl_2 .
- 9 R. Clérac, F. A. Cotton, K. R. Dunbar, C. A. Murillo, I. Pascual and X. Wang, *Inorg. Chem.*, 1999, **38**, 2655.
- 10 M.-M. Rohmer and M. Bénard, *J. Am. Chem. Soc.*, 1998, **120**, 9372.
- 11 Crystal data: $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2$ (dark green, 213 K), $\text{Co}_3\text{C}_{42}\text{H}_{36}\text{N}_{12}\text{Cl}_6$, $M = 1098.32$, tetragonal, space group $I\bar{4}$, $a = 27.2558(8)$, $b = 27.2558(8)$, $c = 12.2451(7)$ Å, $U = 9096.6(6)$ Å³, $Z = 8$, $D_c = 1.604$ g cm⁻³, Nonius FAST Area Detector System, Mo-K α , $\mu = 1.481$ mm⁻¹, 6115 data with $5875 > 2\sigma(I)$, $R1 = 0.038$, $wR2 = 0.091$ ($I > 2\sigma(I)$) and $R1 = 0.041$, $wR2 = 0.093$ (all data). These unit cell dimensions are similar to the ones published previously.¹ CCDC reference number 186/1621.

Communication 9/06722A