Efficient preparation of a linear, symmetrical, metal–metal bonded tricobalt compound; should we believe there is a bond stretch isomer?

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The synthesis in 42% yield of a linear, symmetrical, fully Co–Co bonded [2.3178(9) Å] trinuclear complex $[Co_3(dpa)_4Cl_2]$ [Hdpa = bis(2-pyridyl)amine] is reported, and its crystal structure presented.

While the preparation, characterization and theoretical study of compounds containing strong, short metal–metal (M–M) bonds has become a major field of inorganic chemistry,[1] the study of compounds with linear chains of three or more bonded metal atoms is still in an embryonic state. The first such compound, which contained the $[Ru_3Cl_{12}]^{4-}$ ion, was first reported[2] in 1980 and the phosphine derivatives of this ion were extensively studied[3] in 1989–1991. Only very recently have other M–M bonded linear trinuclear species been reported.[4–7]

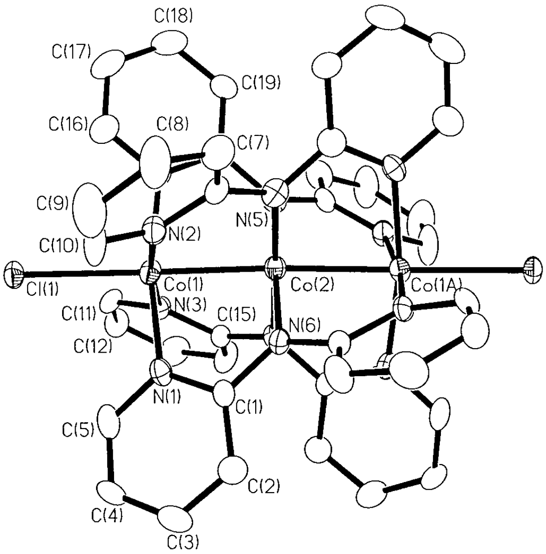

Fig. 1 A side view of the $[Co_3(dpa)_4Cl_2]$ molecule. Selected bond lengths (Å) and angles (°): Co(1)–Co(2) 2.3178(9), Co(1)–Cl(1) 2.520(2), Co(1)–N(av) 1.991, Co(2)–N(av) 1.903; Co(1)–Co(2)–Co(1A) 177.0(1), Cl(1)–Co(1)–Co(2) 178.44(8).

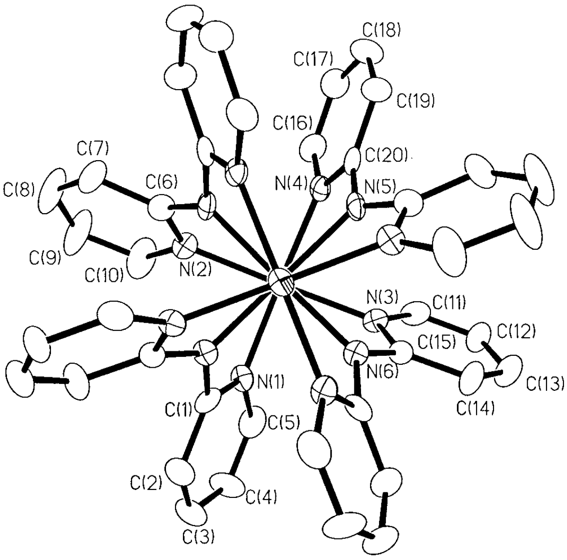

Fig. 2 A view of the $Co_3(dpa)_4$ portion of the molecule looking down the Co_3 axis

One such compound[4] is $[Co_3(dpa)_4Cl_2]$ [Hdpa = bis(2-pyridyl)amine]. The yield quoted was only 2–5% and there were other features (*vide infra*) of the product that caused us concern. Therefore, we decided to look into this matter, beginning with the development of a synthetic method that gives a decent yield.

Our preparative procedure† which has been repeated many times, gives yields on the order of 40%. We have determined the crystal structure‡ of our product, which has the formula $[Co_3(dpa)_4Cl_2]\cdot CH_2Cl_2$, and find it to be significantly different from that previously reported[4] for $[Co_3(dpa)_4Cl_2]\cdot 2CH_2Cl_2\cdot H_2O$. Not only do we find a different space group (*Pnn*2), which is, however, the same space group in which Cu, Ru, and Rh analogues[5,6] crystallize, but we find a rigorously symmetrical molecule as was the case in all other $[M_3(dpa)_4Cl_2]$ compounds.[5–7] Our structure of $[Co_3(dpa)_4Cl_2]$ is shown in Figs. 1 and 2. The Co–Co distances are identical at 2.3178(9) Å as contrasted with values of 2.290(3) and 2.472(3) Å reported for the molecule described in ref. 4.

It is noteworthy that we find $[Co_3(dpa)_4Cl_2]\cdot CH_2Cl_2$ to be crystallographically isomorphous and molecularly isostructural with its symmetric rhodium analogue[5] for which Rh–Rh distances of 2.3920(5) Å were reported. The relationship between the M–M distances in these two isostructural compounds, 2.318 and 2.392 Å for the Co and Rh compounds, respectively, is very similar to that in the $[M_2\{PhNC(Ph)NPh\}_4]$ compounds,[8] where the Co–Co and Rh–Rh distances are, respectively, 2.302(1) and 2.389(1) Å.

One more important observation we made is that the UV–VIS and IR spectra of our compound are the same as those mentioned in ref. 4.

One way to resolve the discrepancy between our structure and that in ref. 4 is to postulate that they are 'bond stretch' isomers, which of course, become identical, one way or the other, in solution. Since all prior claims to this sort of isomerism have turned out to be erroneous (and the whole idea is not credible, anyway) we reject this possibility. There seems no other explanation except to propose that the previously reported structure is in error, although with reported residuals of $R = 0.049$ and $R_w = 0.039$, it is not, *prima facie*, obvious how. We look forward to a full report on the work described two and a half years ago in ref. 4.

Footnotes

† Bis(2-pyridyl)amine (Hdpa, 0.480 g, 2.80 mmol) was placed in a 100 ml round-bottomed flask and dissolved in 16 ml of thf. The solution was cooled to −78 °C, and then 2.0 ml of 1.4 m LiMe was added. The solution immediately turned milky white, but quickly became a clear pale yellow solution upon warming. Anhydrous $CoCl_2$ (0.275 g, 2.12 mmol) was then

added to the reaction from a solid addition tube. The resulting brown solution was refluxed for 5.5 h, and then stirred overnight. After filtration of the mixture, a dark red powder was collected and washed several times with small portions of thf. The powder was dissolved in CH_2Cl_2 and layered with hexanes to yield a large crop of dark green crystals. Additional product was obtained from work-up of the filtrate. The solvent was removed from the filtrate under vacuum, leaving behind a dark residue. The residue was dissolved in 10 ml of CH_2Cl_2, filtered to remove LiCl, and layered with hexanes. Crystals from both solutions were collected, washed with hexanes, and dried under vacuum (0.300 g, 0.296 mmol, 42.3% yield). UV–VIS (CH_2Cl_2): 323, 390(sh), 568 nm.

‡ *Crystal data* for $[Co_3(dpa)_4Cl_2]\cdot CH_2Cl_2$ (-105 °C): orthorhombic, space group *Pnn*2, $a = 12.8145(9)$, $b = 13.955(1)$, $c = 11.1660(9)$ Å, $U = 1996.8(3)$ Å^3, $D_c = 1.685$ g cm^{-3}, $Z = 2$; CAD4 diffractometer with graphite-monochromated Mo-Kα radiation; ψ-scan absorption correction was made; 1449 unique reflections ($2\theta < 45°$) were measured. Full-matrix least-squares refinement on F^2 of positional and anisotropic thermal parameters for all non-hydrogen atoms (287 variables) converged to $R = 0.047$ and $wR_2 = 0.084$ (all data) with the largest peak in difference map $= 0.48(7)$ e Å^{-3}. The absolute configuration was confirmed by the Flack method.[9] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/355.

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