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Getting the right answer to a key question concerning molecular wires

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It is shown that the $Cr_5(tpda)_4Cl_2$ molecule has alternating long and short (Cr···Cr) contacts in three compounds, including one in which an evenly spaced chain was recently claimed.

Recently, growing attention has been focused in this laboratory[1] and elsewhere[2] on *molecular compounds*[3] having linear chains of metal atoms in which there are—or may be—bonding contacts between some or all adjacent metal atoms. Even for the simplest case of only two metal atoms[4] the question of metal–metal bonding has been, and in some cases still is, problematical. Even more challenging problems arise with the more recently discovered compounds in which there are three[1a–f,2a–e] or more[1d,2f–h] metal atoms, that is with the *molecular wire* molecules, as we call them.

It is, of course, self-evident that here, as anywhere else in chemistry, a true understanding of electronic structures is possible only when the correct molecular structures are known. Thus, while it is obviously important to pursue the chemistry necessary to make molecular wire molecules, we assert that 'the key question concerning molecular wire molecules' is: how are the metal atoms spaced along the chain direction? This is a more subtle question than might have been expected.

Even for only three metal atoms, there are two possibilities, symmetrical and unsymmetrical:

M——M——M
M—M·········M

For compounds with a $Co_3(dpa)_4^{2+}$ core,† both of these structures occur and, indeed, as we recently showed,[5] the 'same' molecule, $Co_3(dpa)_4Cl_2$, may give a mixture of two types of crystals from the same solution (in which there are only symmetrical molecules[6]), one type containing symmetrical molecules and the other unsymmetrical molecules. We have also shown that there is a similar situation with $Cr_3(dpa)_4^{2+}$ species.[7]

For five metal atoms, at least three possible arrangements may be considered:

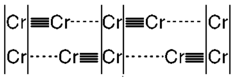
(a) M——M——M——M——M
(b) M—M·········M—M·········M
(c) M—M·········M·········M—M

We have reported the first preparation and structural characterization of the $Cr_5(tpda)_4Cl_2$ molecule,[8] and the chain of five Cr atoms was shown to have alternating Cr to Cr distances, as in pattern (b) above. Thus, to a rough approximation, there are two Cr–Cr quadruple bonds and one isolated Cr^{II} atom at the end, the latter accounting for the magnetic moment of 4.2 μ_B. We may also recall that the compound $[Cr_4(DpyF)_4Cl_2][PF_6]_2$† has the Cr atoms grouped into two Cr_2 quadruple bonds.[1d]

A recent publication[9] claims to have obtained the $Cr_5(tpda)_4Cl_2$ molecule in arrangement (a), that is, with a more or less evenly spaced arrangement of the five metal atoms. This paper also gives a lengthy discussion of the electronic structure of such an evenly-spaced Cr_5 chain. If this structure were correct it would implicate a duality of structure in Cr_5^{10+} chains similar to that for Co_3^{6+} chains, that is, sometimes evenly spaced and sometimes with alternating short and long distances.

In fact, however, this structure is incorrect and only the (b) type structure is found in each of three different crystalline forms of the $Cr_5(tpda)_4Cl_2$ molecule, namely, the one we reported,[8] the one which has just been reported in ref. 9,[9]‡ and a third‡ one that we have also characterized. The key results for all three are collected in Table 1. There is no doubt that the $Cr_5(tpda)_4Cl_2$ molecule consistently has a structure with alternating Cr–Cr distances, Cr≡Cr···Cr≡Cr···Cr, and the claim made[9] for evenly spaced metal atoms is erroneous.

The mistake made in the previous report of the $Cr_5(tpda)_4Cl_2•2Et_2O•4CHCl_3$ structure is obvious in Fig. 1 of ref. 9. The displacement ellipsoids of two of the inner Cr atoms look like rugby balls or American footballs. This is because at each of these positions (as well as the other three) there are two Cr atoms owing to an end-to-end disorder of the molecules:



On the other hand, when this structure is refined correctly,‡ with disordered alternately-spaced Cr_5 chains, all thermal displace-

Table 1 Cr–Cr distances (Å) in three crystal forms of $Cr_5(tpda)_4Cl_2$, M

	Cr(1)–Cr(2)	Cr(2)–Cr(3)	Cr(3)–Cr(4)	Cr(4)–Cr(5)
$M·CH_2Cl_2$[8]	2.578(7)	1.901(6)	2.587(6)	2.031(6)
$M·2Et_2O·4CHCl_3$	2.598(3)	1.872(2)	2.609(2)	1.963(3)
$M·Et_2O$	2.661(3)	1.862(3)	2.644(3)	1.931(3)

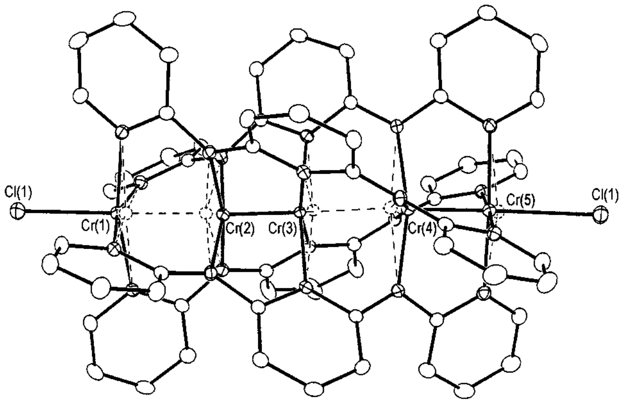


Fig. 1 The $Cr_5(tpda)_4Cl_2$ molecule as it is found in the compound $Cr_5(tpda)_4Cl_2•2Et_2O•4CHCl_3$. The four alternating Cr–Cr distances are listed in Table 1. Atoms are shown as their thermal displacement ellipsoids at the 30% probability level.

ment ellipsoids behave properly, as shown in Fig. 1, and the residuals are reduced. In the other two crystalline forms the same disorder exists and we took account of it in each of our refinements.

There was another problem with the previously reported structure. The electronic structure analysis[9] thereof led to a prediction of two unpaired electrons. This cannot be reconciled with an observed effective magnetic moment of 4.2 μ_B. This value is consistent with the correct structure, as we previously pointed out.[8] The lengthy molecular orbital analysis of the erroneous structure is also invalid.

Based on the results reported here, we would venture to say that a Cr_7 molecule of this ilk would also be expected to have strongly alternating Cr–Cr distances. However a recent report[10] shows a structure with approximately even spacing and pronounced prolate shapes for the Cr atom thermal ellipsoids.

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Notes and references

† dpa is the anion of di(2-pyridyl)amine; tpda is the dianion of tripyridyldiamine; DpyF is the di(2-pyridyl)formamidinate anion.

‡ *Crystal data*: $Cr_5(tpda)_4Cl_2 \cdot 2Et_2O \cdot 4CHCl_3$. For the correct solution of this structure: formula $C_{72}H_{68}Cl_{14}Cr_5N_{20}O_2$; M_w = 2001.76, monoclinic, space group $C2/c$, T = 213 K, a = 28.417(1), b = 13.9755(2), c = 24.8327(7) Å, β = 122.780(3)°, V = 8291.6(4) Å^3, Z = 4, μ = 1.144 mm^{-1}, 22906 reflections collected, 7260 independent, R_{int} = 0.059, final residuals $R1$ = 0.047, $wR2$ = 0.102 [$I > 2\sigma(I)$]; $R1$ = 0.056, $wR2$ = 0.111 (all data).

$Cr_5(tpda)_4Cl_2 \cdot Et_2O$. Formula $C_{64}H_{54}Cl_2Cr_5N_{20}O$; M_w = 1450.17; tetragonal, space group $I4/m$, T = 213 K, a = 10.7234(7), c = 26.663(4) Å, V = 3066.0(5) Å^3, Z = 2, μ = 1.008 mm^{-1}, 9543 reflections collected, 1892 independent, R_{int} = 0.051, final residuals $R1$ = 0.060, $wR2$ = 0.144 [$I > 2\sigma(I)$]; $R1$ = 0.074, $wR2$ = 0.164 (all data). The complex and the included solvent in this structure are quite disordered in the high-symmetry space group $I4/m$; the disorder persists even when the structure is refined in a lower symmetry group. CCDC 182/1424. See http://www.rsc.org/suppdata/cc/1999/2461/ for crystallographic files in .cif format.

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3 The term *molecular compounds* is emphasized because it distinguishes the discrete molecules we are interested in from a host of previously known substances in which linear chains of metal atoms arise *in the solid state only* by stacking of flat molecules (*e.g.* $K_2Pt(CN)_4Br_{0.3}$ or $Pt(NH_3)_4PtCl_4$) or by formation of μ-X bridged chains of octahedra (*e.g.* $NbCl_4$).

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