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A chain of five chromium(II) atoms: a desired compound with an undesired, unsurprising, but important structure

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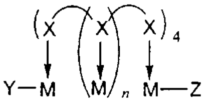
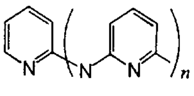
Received 12th October 1998, Accepted 16th December 1998

Reaction of the dilithium salt of tripyridyldiamine, Li_2tpda, and $CrCl_2$ in THF gave the pentachromium compound $Cr_5(tpda)_4Cl_2 \cdot CH_2Cl_2$ in which the metal atoms were arranged in a linear fashion with localized quadruple bonds $Cr{\equiv}Cr \cdots Cr{\equiv}Cr \cdots Cr$.

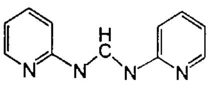
Recently, in this laboratory[1] and in other laboratories,[2,3] there has been much effort devoted to the preparation and study of compounds in which there are linear arrays of metal ions surrounded by four chain ligands that keep adjacent ions within bonding distance of each other. Such molecules may be generically represented by schematic drawing **I**, where Y and Z are axial ligands (not necessarily, but usually, present), X is an atom such as N or O that coordinates the chain ligand to the metal atoms and the number of metal atoms in the chain is $n + 2$. Most of the work to date has been done with the polypyridylamine ligands, **II** (for which the number of metal atoms, $2n + 1$, is always odd), and the metal ions Cr^{II}, Cr^{III},[1c,d] Co^{II} [1a,b,2a] and Ni^{II}.[3a] Compounds with Cu,[3b] Ru[2b] and Rh[2b] are also known. All of the work so far on chromium complexes has come from this laboratory.[1c–e] We have also examined a compound employing the ligand **III** which supports a chain of four Cr^{II} atoms.[1e] It has been found that there is a strong, although not always realized, tendency for adjacent pairs of Cr^{II} atoms to interact strongly to form Cr–Cr quadruple bonds, which are characterized by Cr–Cr distances of 1.90–2.10 Å. This is the case in the compound formed with ligand **III**, where the Cr–Cr distances are 2.013(2) Å, 2.726(2) Å and 2.001(2) Å. In the trinuclear molecules, we have found a remarkable variation in Cr–Cr distances, ranging from two equal distances (2.301(1) Å) through intermediate cases where the two distances are a little different (2.199(3) Å and 2.369(3) Å) to extreme cases where one Cr–Cr distance is in the quadruple bond range while the other (*ca.* 2.60 Å) can be considered nonbonding.



I



II



III

We have now prepared and studied a Cr_5 molecule, $Cr_5(tpda)_4Cl_2 \cdot CH_2Cl_2$ (for ligand nomenclature see ref. 2 or experimental footnote).† In view of the possibility for a structure anywhere in the range from essentially similar Cr–Cr bonds throughout to localized Cr≡Cr (quadruple) bonds, three structures appeared possible for this molecule: (1) a highly delocalized symmetrical one, **IV**; (2) a symmetrical one with localized quadruple bonds, **V**; (3) an unsymmetrical one with localized quadruple bonds, **VI**. The type of structure we have found is **VI**.‡ It is shown in detail in Figs. 1 and 2. Distances (Å) in the essentially linear chain, $Cl–Cr \cdots Cr{\equiv}Cr \cdots Cr{\equiv}Cr–Cl$, are, from left to right: 2.499(6), 2.578(7), 1.901(6), 2.587(6), 2.031(6), 2.604(5).

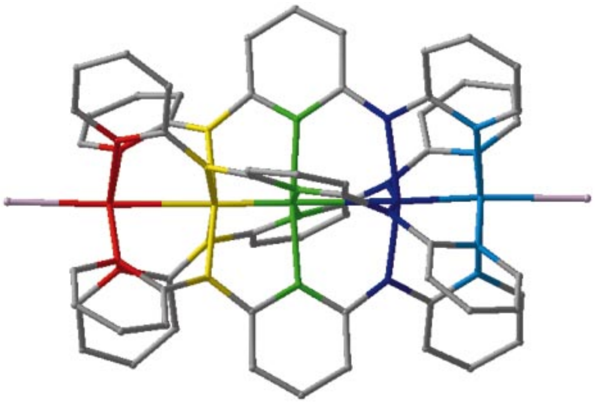


Fig. 1 Side view of the molecule of $Cr_5(tpda)_4Cl_2$.

$$\mathrm{Cr}\overset{a}{=\!=}\mathrm{Cr}\overset{b}{=\!=}\mathrm{Cr}\overset{b}{=\!=}\mathrm{Cr}\overset{a}{=\!=}\mathrm{Cr} \qquad \textbf{IV}$$

$$a \approx b$$

$$\mathrm{Cr}{\equiv}\mathrm{Cr}\text{-}\,\text{-}\mathrm{Cr}\text{-}\,\text{-}\mathrm{Cr}{\equiv}\mathrm{Cr} \qquad \textbf{V}$$

$$\mathrm{Cr}{\equiv}\mathrm{Cr}\text{-}\,\text{-}\mathrm{Cr}{\equiv}\mathrm{Cr}\text{-}\,\text{-}\mathrm{Cr} \qquad \textbf{VI}$$

In the crystal structure the molecules are packed in a disordered fashion such that 68% of the $Cr{\equiv}Cr \cdots Cr{\equiv}Cr \cdots Cr$ chains are oriented in one direction and 32% in the opposite direction. Thus, when this is not taken into account the second and the fourth chromium atoms appear as very prolate ellipsoids. The two differently oriented, superposed chains of 5 Cr atoms were refined as a disordered set, with a restraint added that the chain geometry of the minor orientation was approximately equal to that of the major orientation (in the opposite direction); the fractional occupations were limited only by the requirement that their sum equals one. As always the polypyridylamido ligands form a spiral around the core of metal atoms, as can be seen most clearly in Fig. 2. The average overall twist from one end to the other is 80.7°.

There have already been $M_5(tpda)_4X_2$ type molecules prepared for the metals Co[2c] and Ni.[2c,d] For both of these metals the four M–M distances have been similar, and in the case of cobalt it can be argued, at least superficially, that a net averaged Co–Co bond order of 2.5/4 (see the diagram in ref. 2(*d*)) exists for each of four Co–Co adjacent pairs along the chain. For the nickel compounds, the net average of the Ni–Ni bond orders is necessarily zero and this has been pointed out.[2d] One might remark, in this regard, that this will be true of all Ni_n chains of this kind, regardless of n, which raises the question of why such compounds would be of interest in a quest for “molecular wires”. Would electrical conduction be expected along a chain of metal atoms in which no M–M bonding exists?

For the $Cr_5(tpda)_4Cl_2$ molecule, there existed the possibility

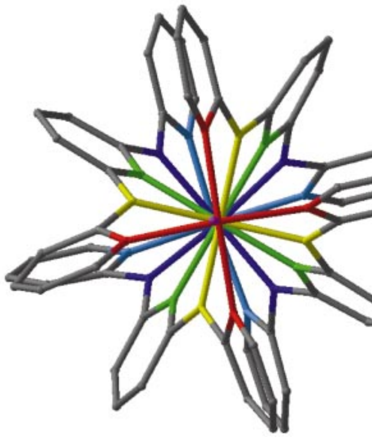


Fig. 2 View of the molecule of $Cr_5(tpda)_4Cl_2$ down the Cr_5 axis. The sum of the torsion angles is 80.7°.

of appreciable Cr–Cr bonding in an (approximately) evenly spaced chain (**IV**), since the average net bond order could have been $10/4 = 2\frac{1}{2}$ per Cr–Cr pair, based on the simple MO picture displayed in ref. 2(*d*). In this case significant "molecular wire" character might have been anticipated, which is why we prepared the compound.

Since the title compound does not contain an evenly-spaced chain of metal atoms we do not expect it to be capable of conduction; it is in this sense that the structure is undesired. However, this structure (or possibly, structure **V**) was not entirely surprising, because we have already observed that the Cr_3 chain in the $Cr_3(dpa)_4X_2$ and $Cr_3(dpa)_4X_2^+$ (dpa = **II**, $n = 1$) compounds readily adopts a highly unsymmetrical structure wherein there is one Cr–Cr quadruple bond and a Cr_4 chain was avoided in favor of a pair of Cr–Cr quadruple bonds.[1e] On the other hand we view the result reported here as important since it shows us that Cr_n chains may be inherently liable to this type of behavior. In view of the great stability of Mo–Mo quadruple bonds, it seems unlikely that symmetrical, uniformly spaced chains of three or more Mo atoms can be obtained, but nevertheless we intend to explore this question directly. Similarly, though it seems unlikely that a Cr_7 chain will be uniformly spaced, we plan to make the $Cr_7(teptra)_4Cl_2$ (teptra = **II**, $n = 3$) compound and find out for certain what structure it will adopt.

Acknowledgements

We are grateful to the Robert A. Welch Foundation for financial support.

Notes and references

† Preparation of $Cr_5(tdpa)_4Cl_2\cdot CH_2Cl_2$. In a 100 mL round bottomed flask tripyridyldiamine, H_2tpda (0.37 g, 1.4 mmol), was dissolved in THF (30 mL). The solution was cooled to −78 °C and methyllithium (2.9 mL) in 1 M THF was added. The reaction mixture was allowed to warm to near room temperature and then transferred *via* cannula to a flask containing anhydrous $CrCl_2$ (0.22 g, 1.80 mmol). After it was stirred for 1 h, the resulting red-brown solution was refluxed overnight to give a brown solid. It was filtered and the solid was extracted with CH_2Cl_2 (30 mL). Crystals of the product were obtained by slow diffusion of hexanes (30 mL) into the CH_2Cl_2 solution. Additional product was obtained from work up of the filtrate. The solvent in the filtrate was removed under reduced pressure. The remaining dark brown solid was partially dissolved in CH_2Cl_2 to give a brown solution. It was filtered and the filtrate was layered with hexanes. Dark-brown crystals from both solutions were collected and washed with hexanes. Yield: 0.16 g, 31%. IR (KBr, cm^{-1}): 1603m, 1577m, 1547m, 1473m, 1453m, 1420s, 1346s, 1300w, 1261w, 1153s, 1005m, 878w, 847w, 770m, 735m, 712w, 645w, 528w, 439w. $\mu_{eff} = 4.2\ \mu_B$.

‡ Crystal data for $Cr_5(tdpa)_4Cl_2\cdot CH_2Cl_2$, $M = 1460.98$. Orthorhombic, space group *Pbca*, $a = 16.8315(5)$, $b = 18.176(1)$, $c = 39.571(3)$ Å, $V = 12106(1)$ Å^3, $D_c = 1.603$ g cm^{-3}, $Z = 8$, $\mu = 1.106$ mm^{-1}. Data were collected (at 213(2) K) on a FAST area detector system. A total of 7177 unique reflections ($2\theta \le 45°$) were measured. The metal atoms are disordered and they were refined successfully as two sets of linear chains of five chromium atoms arranged in a short–long–short–long fashion in two directions with the major orientation of 68% occupancy. Full-matrix least-squares refinement on F^2 for the remaining non-hydrogen atoms (802 variables) converged to $R_1 = 0.102$, $wR_2 = 0.208$ (all data). CCDC reference number 186/1292.

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Communication 8/07928E