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LETTER

A Dichromium(II) Compound that Avoids Cr–Cr Bond Formation by Adopting a Bizarre Structure: $Cr_2Cl_4(dmpm)_2$

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We have recently prepared and structurally characterized the dichromium(III) compound $Cr_2Cl_6(dmpm)_2$, where dmpm represents $(CH_3)_2PCH_2P(CH_3)_2$ [1]. A major reason for our interest in this compound was to employ it as a precursor to a dichromium(II) compound, $Cr_2Cl_4(dmpm)_2$. We hoped that this molecule would contain a bond between the chromium atoms within a shell of ligands not previously found surrounding a Cr_2^{4+} core, although the analogous, quadruply-bonded $Mo_2Cl_4(dmpm)_2$ is well characterized [2].

Thus, we undertook reaction (1). From a chemical point of view, the experiment was successful.

$$Cr_2Cl_6(dmpm)_2 + 2Na/Hg \longrightarrow Cr_2Cl_4(dmpm)_2 + 2NaCl \qquad (1)$$

A compound of the expected composition $Cr_2Cl_4(dmpm)_2$ was obtained as light blue crystals in about 10% yield. The compound has peaks in the UV–Vis spectrum at 310, 425, 625 nm and is paramagnetic ($\mu_{eff} = 4.54$ BM at 300 K). The compound reacts with methanol according to eqn. (2)

$$Cr_2Cl_4(dmpm)_2 + 2MeOH \longrightarrow Cr_2Cl_4(\mu\text{-}OMe)_2(dmpm)_2 + H_2 \qquad (2)$$

From a structural point of view, however, the result is not what was desired, i.e., a structural analog to $Mo_2Cl_4(dmpm)_2$. It is, in fact, very puzzling. A crystallographic structure determination† gives the results shown in Figs. 1 and 2, with some of the principal dimensions listed in Table 1.

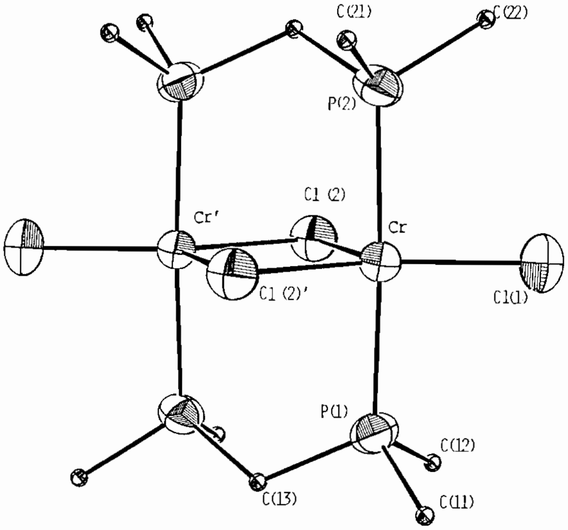

Fig. 1. An overall view of the $Cr_2Cl_4(dmpm)_2$ molecule. Hydrogen atoms are omitted and carbon atoms are represented by arbitrarily small spheres. Cr, Cl and P atoms are represented by their ellipsoids of thermal displacement drawn at the 50% level.

It is clear from Fig. 1 that $Cr_2Cl_4(dmpm)_2$ is entirely unlike the molybdenum compound of corresponding formula, where there is a strong Mo–Mo bond (*c.* 2.13 Å) and no bridging Cl atoms. The Cr–Cr distance is so long, 3.24 Å, it entirely precludes any genuine Cr–Cr bonding. The magnetic moment of about 4.54 BM (for the dinuclear molecule) cannot be given any assured interpretation and we shall attempt to determine the temperature dependence in order to clarify this. The presence of two unpaired electrons on each Cr atom is a possibility.

Although a cursory look at Fig. 1 might suggest that each Cr atom is in a trigonal bipyramidal coordination sphere, with a common Cl···Cl edge, this is far from the case, as Fig. 2 makes clear. So far as we can see, there is no simple analysis of the bonding that is consistent with (let alone predictive of) this extremely irregular structure. Nor will a more sophisticated analysis be easy since we are dealing with an open-shell electron configuration.

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†The compound crystallizes in space group $P2_1/n$ with $a = 8.649(2)$, $b = 12.860(3)$, $c = 11.362(3)$ Å; $\beta = 111.30(1)°$, $V = 1177.5(10)$ Å^3, $Z = 2$. For 147 refined parameters and 2060 unique reflections having $F_o^2 > 3\sigma(F_o^2)$, the structure was refined to $R = 0.050$ and $R_w = 0.063$.

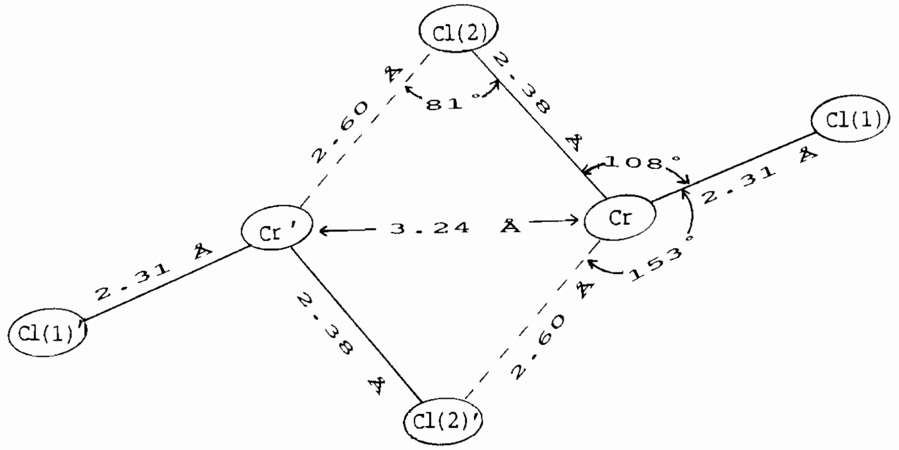

Fig. 2. A drawing of the central Cr_2Cl_4 plane of the molecule, showing the irregular disposition of the Cl atoms about the two Cr atoms.

TABLE 1. Selected distances (Å) and angles (°)

Cr–Cr′	3.237(1)	Cl(1)–Cr–Cl(2)	107.70(4)
Cr–Cl(1)	2.305(1)	Cl(1)–Cr–Cl(2)′	153.36(5)
Cr–Cl(2)	2.379(1)	Cl(2)–Cr–Cl(2)′	98.92(4)
Cr–Cl(2)′	2.595(1)	Cl–Cr–P(av)	89.2(7)
Cr–P(1)	2.488(1)	P(1)–Cr–P(2)	177.12(4)
Cr–P(2)	2.498(1)	Cr–Cl(2)–Cr′	81.08(3)
P–C(av)	1.824(5)	P(1)–C(13)–P(2)′	117.4(2)

The theoretical problem is, however, under continuing scrutiny.

It is well known [3] that practically all quadruply bonded Cr_2^{4+} compounds are of the type where the Cr_2^{4+} unit is bridged by four ligands of the OCO^-, NCO^-, NCN^- or related types. The only exceptions are $[Cr_2(CH_3)_8]^{4+}$, $[Cr(C_4H_8)_4]^{2-}$ and $Cr_2(allyl)$. All other four-coordinate Cr(II) complexes remain stubbornly mononuclear. There have been calculations suggesting that $[Cr_2Cl_8]^{4-}$ with a quadruple bond is capable of existence [4], but all experimental efforts to obtain it have failed†. The concept on which the synthesis of $Cr_2Cl_4(dmpm)_2$ was based was that the introduction of two dmpm ligands arranged so as to tie the Cr atoms together might allow the Cr–Cr bond to persist even though in $[Cr_2Cl_8]^{4-}$ it does not. As the structure reported here shows, this hope has been frustrated. The fact that $Cr_2Cl_4(dmpm)_2$ refuses to adopt a structure with a Cr–Cr bond seems to show rather conclusively that despite theoretical predictions, $[Cr_2Cl_8]^{4-}$ is not capable of existence.

Supplementary Material

Tables of structure factors, anisotropic thermal displacement tensor elements, and complete lists of bond distances and angles are available on request from author F.A.C.

Acknowledgement

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†Many unpublished experiments over many years in this and other laboratories.