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A remarkable Cr(III) organometallic compound formed by an unprecedented rearrangement of a formamidinate anion

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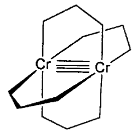
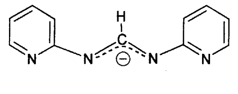
In addition to a quadruply bonded dichromium(II,II) compound of unusual structure, we have obtained a dinuclear, antiferromagnetically coupled, Cr^{III} complex $[Cr_2(\mu\text{-}OMe)_2(\eta^3\text{-}N,C,N'\text{-}H_2DpyF)_2Cl_2\cdot MeOH$, $H_2DpyF = CH(NH\text{-}pyridyl)_2]$ containing a transformed formamidinate group in which the central carbon atom has changed from sp^2 to sp^3 hybridization and Cr–C bonds have been formed; details of the crystal structure of the organometallic compound are given here.

The use of formamidinate ligands of the type RNC(H)NR and ArNC(H)NAr to bridge M_2^{n+} dinuclear units (M = various transition metal atoms, n = 4, 5, and 6) has been intensively studied.[1] Typically, paddlewheel structures, **I**, have been obtained. More recently there has been wide interest in creating longer chains of metal atoms.[2] Thus we decided to use amidinate ligands with more than two N atom donors. One such ligand is the anion of *N,N′*-di(2-pyridyl)formamidine, HDpyF, **II**, where the two Ar groups are 2-pyridyl groups. In this way chains of three and four collinear chromium(II) atoms, **III**, were obtained.[3]

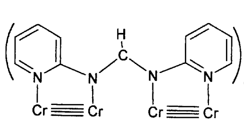
After we recently found that dimolybdenum compounds of the DpyF ligand have many coordination isomers in solution,[4] we have carried out the reaction of $CrCl_2$ with LiDpyF in THF in the molar ratio of 1:2. This reaction affords the dinuclear species of Cr_2^{4+} as an unsymmetrical yellow isomer of the type **IV** as the major product.[5] During the work-up process, the solvent from the reaction mixture was removed under vacuum and the solid residue, which also contained LiCl, was washed with methanol, a solvent in which **IV** is not significantly soluble but LiCl is. We noticed that upon the addition of very dry methanol, a deep red solution was produced above the solid **IV**. After filtration, the red methanol solution was layered with diethyl ether and red crystals of $Cr_2(\mu\text{-}OMe)_2(\eta^3\text{-}N,C,N'\text{-}H_2DpyF)_2Cl_2\cdot MeOH$ were obtained in low yield.†



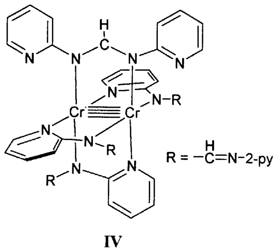
I



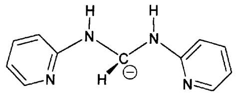
II



III



IV



V

The structure‡ consists of two very similar but crystallographically independent molecules, one of which is shown in Fig. 1. It comprises an edge-sharing bioctahedral (ESBO) dichromium unit with two methoxy groups defining the shared edge. The Cr_2O_2 unit is planar in accordance with lying on a crystallographic inversion center. A chlorine atom on each chromium atom is *cis* to the methoxy groups. The other three coordination sites comprising a face of each octahedron are occupied by a carbon atom and two nitrogen atoms of a tridentate ligand derived from what was the usual form of the DpyF anion, **II**. The carbon atom is *trans* to the chlorine atom. The DpyF ligand has been transformed to the monoanion, **V**. Binding to the chromium atoms no longer occurs in the usual way, by bonds to the amidinate N atoms, but instead through the two pyridyl N atoms and the central C atom. Thus there are two fused five-membered rings with the N atoms *trans* to the methoxy groups. The methoxy bridges are but slightly asymmetric with Cr–O distances of 1.971(2) and 1.984(2) Å. They are very similar to those found in Cr^{III}–O(H)–Cr^{III} units of hydroxo-bridged amine complexes[6] and in some other compounds with $Cr(\mu\text{-}OMe)_2Cr$ cores[7] where they are in the narrow range of 1.95–1.99 Å. The Cr–N distances of 2.086(2) to 2.101(2) Å are also as expected.[8]

The Cr–C distances of 2.059(3) and 2.068(3) Å in the two nonequivalent molecules are within the normal range of 2.04–2.13 Å. The Cr–Cl distances of 2.4653(8) Å are more

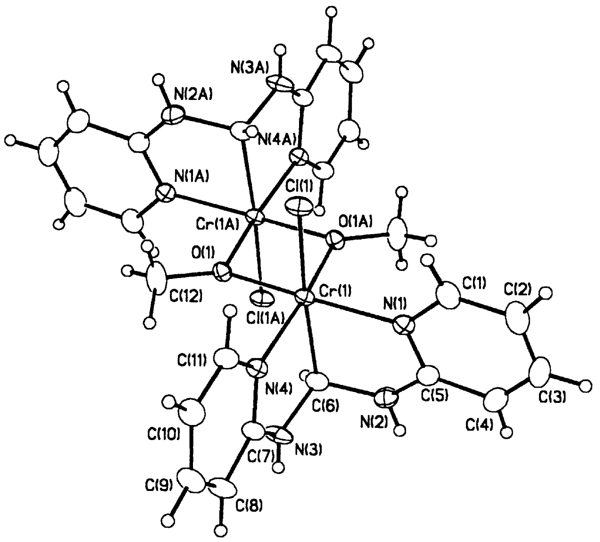


Fig. 1 Plot of one of the independent molecules in $Cr_2(\mu\text{-}OMe)_2(\eta^3\text{-}N,C,N'\text{-}H_2DpyF)_2Cl_2\cdot MeOH$. Hydrogen atoms refined during the X-ray diffraction study are shown as arbitrarily sized circles. Selected distances (Å) and angles (°) are Cr(1)···Cr(1A) 3.0751(8), Cr(1)–C(6) 2.059(3), C(6)–N(2) 1.444(4), C(6)–N(3) 1.455(4); N(2)–C(6)–N(3) 111.0(2), N(2)–C(6)–Cr(1) 108.8(2), N(3)–C(6)–Cr(1) 108.7(2), N(2)–C(6)–H(6) 105(2), N(3)–C(6)–H(6) 110(2).

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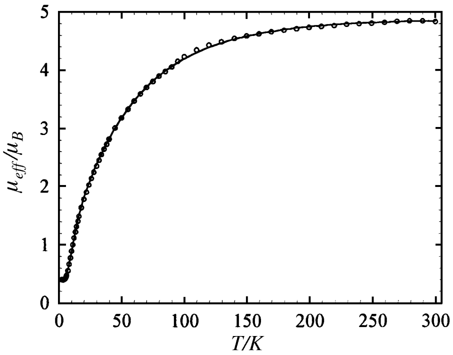

Fig. 2 Temperature dependence of the effective magnetic moment. The solid line is the best fit obtained with a dimer model of $S = 3/2$ magnetic spins (1% of an $S = 3/2$ paramagnetic impurity was taken into account to reflect the residual paramagnetism a low temperature).

difficult to compare with previous results because the presence of halide ions in six-coordinate Cr^{III} organometallic compounds is rare.[9] However, a comparison can be established with *fac*-Cl_3Cr(1,5-diamino-3-azapentane), a coordination compound which has three Cr–N distances varying from 2.08(1) to 2.11(1) Å and three Cr–Cl distances varying from 2.303(7) to 2.332(7) Å.[10] Clearly the Cr–Cl distances in the present case are significantly longer, by more than 0.13 to 0.16 Å. A large *trans* effect for carbon atoms in Cr^{III} organometallic compounds has previously been documented.[11]

All hydrogen atoms were found and refined. In the crystal there is extensive intermolecular hydrogen bonding involving pairs of nonequivalent molecules and also the interstitial methanol molecules. Thus, it is not surprising that the crystalline compound is stable towards exposure to oxygen and moisture.

The most remarkable feature of this compound is the transformation that occurs at the sp^2 methine C atom of the DpyF anion, **II**, whereby the hybridization is changed to sp^3 at the methanide C atom upon hydrogen atom capture by the inner N atoms giving the monoanion **V**. In **II**, the N–C(H)–N unit is typically planar with short C–N distances of 1.31–1.33 Å,[1,12] but in **V** those distances increase to 1.433(4)–1.455(4) Å. These are also *ca.* 0.1 Å longer than those of the corresponding N–$C_{pyridyl}$ bonds. Also consistent with the presence of a methanide group in **V** are the bond angles around the central C atom (including those involving the C–H bond) which are very close to those expected for a tetrahedral atom. Thus the internal consistency of all the structural data supports beyond any doubt the formulation given here.

To our knowledge this is an unprecedented transformation of a formamidinate group (although many other transformations are known[13]) with concomitant formation of a stable Cr(III) organometallic compound. Only one additional report exists of a transformation of an sp^2 C atom in a formamidinate to an sp^3 C atom. This was observed when dimerization of two formamidinate anions was induced by a tantalum compound giving the dianion PhNC(H)N(Ph)*C*(H)(NPh)$_2$,[13] but here the *C* atom has four bonds and is thus unable to bind to metal atoms.

Finally, magnetic measurements (Fig. 2)§ show antiferromagnetic coupling of the two chromium atoms through the methoxy bridges. The fitting of the data using an $S = 3/2$ dimer model[7,14] leads to an exchange interaction, J, of -18 K and a g value of 2.04. This is consistent with the magnetic behavior of other dinuclear Cr^{III}-organometallic compounds.[15]

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Notes and references

† For $Cr_2(\mu\text{-}OMe)_2(\eta^3\text{-}N,C,N'\text{-}H_2DpyF)_2Cl_2\cdot MeOH$: Anal. Calc. For $Cr_2C_{25}H_{32}N_8O_3Cl_2$: C, 44.98; H, 4.83; N, 16.79. Found: C, 44.52; H, 4.79; N, 16.51%. The process whereby the product is formed is not clear yet but a balanced equation can be written as follows:

$$2CrCl_2 + 4LiDpyF \xrightarrow[\Delta]{THF} \xrightarrow{4MeOH}$$

$$Cr_2(\mu\text{-}OMe)_2(\eta^3\text{-}N,C,N'\text{-}H_2DpyF)_2Cl_2 + 2LiCl + 2LiOMe + 2HDpyF$$

In three runs by two different people yields of 5–10% were obtained.

‡ *Crystal data*: $C_{25}H_{32}Cl_2Cr_2N_8O_3$, $M = 667.49$, monoclinic, space group $P2_1/c$, $a = 15.507(2)$, $b = 9.7562(6)$, $c = 19.920(2)$ Å, $\beta = 98.597(7)°$, $V = 2979.8(5)$ Å^3, $Z = 4$, $T = 213$ K, $\mu = 0.95$ mm^{-1}, 15663 measured/4711 independent reflections, R(int) = 0.056. The final $wR(F^2)$ were 0.093 ($I > 2\sigma$) and 0.098 (all). The positions of all H atoms were clearly indicated in the final difference Fourier maps. CCDC 182/1882. See http://www.rsc.org/suppdata/cc/b0/b007813l/ for crystallographic files in .cif format.

§ Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL, from 1.8 to 300 K at 1000 G on a finely divided polycrystalline sample. Data were corrected for the sample holder and for the diamagnetic contributions estimated from Pascal's constants.[16]

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