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UNEXPECTED SYNTHESIS OF A BINUCLEAR CHROMIUM(III) SALT EXHIBITING N—H···Cl HYDROGEN-BONDING INTERACTIONS

PHILIP W. DYER and **VERNON C. GIBSON***

Department of Chemistry, University Science Laboratories, South Road,
Durham DH1 3LE, U.K.

and

JOHN C. JEFFERY

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

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Abstract—Treatment of $(NH_4)_2Cr_2O_7$ with excess trimethylsilylchloride in the presence of triethylamine and a sacrificial primary amine affords the binuclear chromium salt $[Cr_2Cl_9][Et_3NH]_3$ whose structure reveals N—H···Cl hydrogen-bonding interactions.

Recently, convenient "one-pot" syntheses of molybdenum imido complexes of the type $Mo(NR)_2Cl_2(dme)$ (R = alkyl or aryl; dme = 1,2-dimethoxyethane) have been developed that employ readily available molybdate starting materials.[1,2] The convenience of this approach, and its applicability to large-scale preparations, is of considerable significance since the bis(imido) molybdenum products are utilized as starting materials for the synthesis of technologically relevant olefin metathesis catalysts.[3] We were interested in the possibility of extending this approach to a general synthesis of chromium imido complexes, since to date a synthetic entry into bis(arylimido) chromium chemistry has proved elusive.†

RESULTS AND DISCUSSION

The sequential treatment of ammonium dichromate, $(NH_4)_2Cr_2O_7$, with triethylamine, excess trimethylsilylchloride and 2,6-diisopropylaniline [$ArNH_2$] at room temperature followed by heating at 70°C for 12 h in 1,2-dimethoxyethane (dme), conditions that mimic those used in the preparation of $[Mo(NAr)_2Cl_2(dme)]$, affords an intense red-purple solution. Upon removal of the volatile components under reduced pressure, a copious quantity of an extremely air- and moisture-sensitive dark red paramagnetic solid is obtained whose characterizing data are consistent with the binuclear chromium(III) formulation $[Cr_2Cl_9][Et_3NH]_3$ (**1**). Compound **1** is also obtained when tert-butylamine is used in place of 2,6-diisopropylaniline and is generated in low yield in the absence of any added primary amine. Since no isolable chromium products are obtained when Na_2CrO_4 is used as the source of chromium, it appears that the primary amine functions solely as a proton source, the ammonium counter-ion fulfilling this role in the absence of an alternative source of protons.

Blue-purple plate-like crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of toluene into a dichloromethane solution of **1**. The crystal structure is shown in Fig. 1 and bond lengths and angles are collected in Table 1. The anion possesses a distorted confacial bioctahedral geometry typical of the Group 6 metal

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* Author to whom correspondence should be addressed.

Note added in proof:

† We have recently established a viable synthetic entry into arylimido chromium chemistry via treatment of $(Bu^tN)_2CrCl_2$ with 2,6-diisopropylaniline. See *Polyhedron* 1995, **15–16**, 2455.

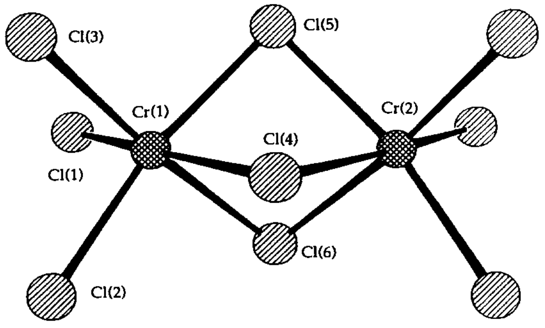

Fig. 1. Structure of the tri-anion of **1**.

enneahalodimetallates,[4] cf. $[Cr_2Cl_9][(n\text{-}C_4H_9)_4]_3$ characterized by Saillant and Wentworth.[5]

Since the report of $K_3W_2Cl_9$ by Olsson[6] in 1914, many other complexes containing the $[M_2X_9]^{3-}$ (M = Cr, Mo, W; X = Cl, Br, I) tri-anion have been reported. Interest in this class of complex has largely centred around the unusual magnetic properties associated with the heavier metal congeners that exhibit varying degrees of metal–metal interaction.[4,7] The molecular structure of **1** reveals a Cr—Cr separation of 3.15 Å which is in close agreement with the value of 3.12 Å determined for $Cs_3Cr_2Cl_9$;[8] no chromium–chromium bond can be inferred. The angles subtended by each of the three bridging chlorine atoms [81.6(1), 81.6(1) and 81.7(1)°] and the average Cr—μCl bond length of 2.407(2)Å are in good agreement with literature values for this anion,[8] and are characteristic of elongation of the bioctahedra along the C_3 axis.

An interesting feature of the X-ray structure of **1** is the presence of hydrogen-bonding interactions between the nitrogen-bound protons of the $[NHEt_3]^+$ cation and four of the terminal chloride ligands [Cl(1), Cl(2), Cl(8) and Cl(9)] (see crystal packing diagram, Fig. 2). These interactions range between 2.21 and 2.68 Å, values typical for N—H···Cl hydrogen bonds.[9] The corresponding Cr—Cl bond lengths of 2.309(2) Å (av) are slightly elongated compared to the remaining two non-hydrogen-bonded terminal chlorides, at 2.288(2) Å (av).

In conclusion, treatment of chromate with primary amines or anilines in the presence of trimethylsilylchloride does not afford chromium imido products, but instead provides convenient access to the $Cr_2Cl_9^{3-}$ anion.

EXPERIMENTAL

General

All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques

Table 1. Selected bond lengths (Å) and interbond angles (°) for **1** with estimated standard deviations in parentheses

Cr(1)—Cl(1)	2.305(2)	Cr(2)—Cl(4)	2.413(2)
Cr(1)—Cl(2)	2.310(2)	Cr(2)—Cl(5)	2.402(2)
Cr(1)—Cl(3)	2.286(2)	Cr(2)—Cl(6)	2.394(2)
Cr(1)—Cl(4)	2.404(2)	Cr(2)—Cl(7)	2.289(2)
Cr(1)—Cl(5)	2.415(2)	Cr(2)—Cl(8)	2.317(2)
Cr(1)—Cl(6)	2.418(2)	Cr(2)—Cl(9)	2.305(2)
Cl(1)—Cr(1)—Cl(2)	92.4(1)	Cl(5)—Cr(2)—Cl(6)	81.8(1)
Cl(1)—Cr(1)—Cl(3)	92.9(1)	Cl(4)—Cr(2)—Cl(7)	174.3(1)
Cl(2)—Cr(1)—Cl(3)	93.8(1)	Cl(5)—Cr(2)—Cl(7)	94.1(1)
Cl(1)—Cr(1)—Cl(4)	172.5(1)	Cl(6)—Cr(2)—Cl(7)	92.8(1)
Cl(2)—Cr(1)—Cl(4)	90.9(1)	Cl(4)—Cr(2)—Cl(8)	89.1(1)
Cl(3)—Cr(1)—Cl(4)	93.6(1)	Cl(5)—Cr(2)—Cl(8)	168.6(1)
Cl(1)—Cr(1)—Cl(5)	94.0(1)	Cl(6)—Cr(2)—Cl(8)	90.2(1)
Cl(2)—Cr(1)—Cl(5)	169.9(1)	Cl(7)—Cr(2)—Cl(8)	94.4(1)
Cl(3)—Cr(1)—Cl(5)	93.6(1)	Cl(4)—Cr(2)—Cl(9)	90.8(1)
Cl(4)—Cr(1)—Cl(5)	81.8(1)	Cl(5)—Cr(2)—Cl(9)	92.9(1)
Cl(1)—Cr(1)—Cl(6)	90.9(1)	Cl(6)—Cr(2)—Cl(9)	172.0(1)
Cl(2)—Cr(1)—Cl(6)	91.1(1)	Cl(7)—Cr(2)—Cl(9)	93.6(1)
Cl(3)—Cr(1)—Cl(6)	173.6(1)	Cl(8)—Cr(2)—Cl(9)	94.1(1)
Cl(4)—Cr(1)—Cl(6)	82.3(1)	Cr(1)—Cl(4)—Cr(2)	81.6(1)
Cl(5)—Cr(1)—Cl(6)	81.0(1)	Cr(1)—Cl(5)—Cr(2)	81.6(1)
Cl(4)—Cr(2)—Cl(5)	81.9(1)	Cr(1)—Cl(6)—Cr(2)	81.7(1)
Cl(4)—Cr(2)—Cl(6)	82.6(1)		

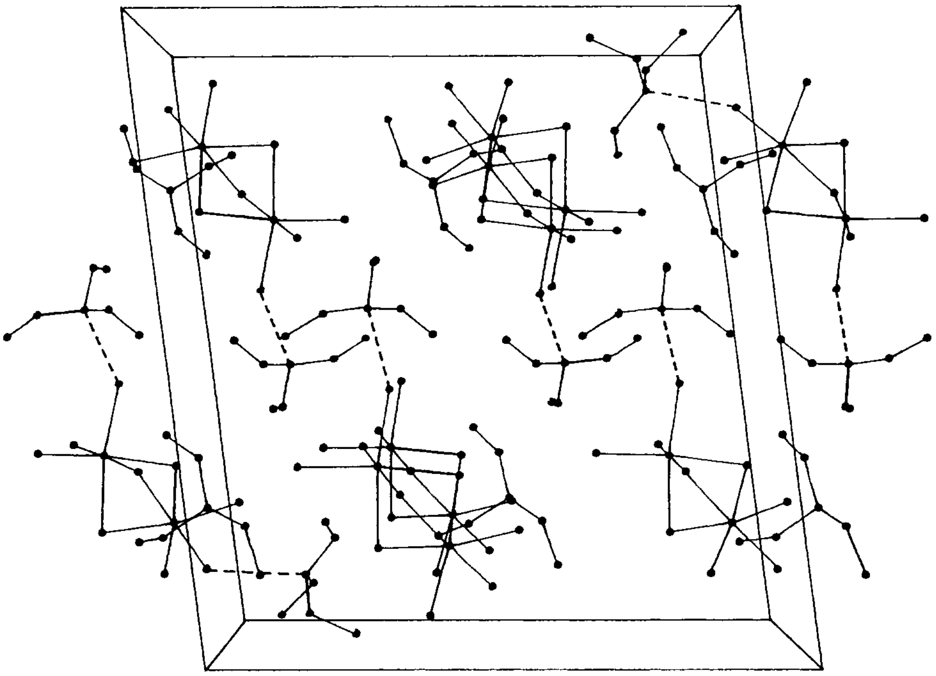

Fig. 2. Crystal packing diagram of **1** showing the hydrogen-bonding interactions (dashed lines).

or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham. IR spectra (Nujol mulls, CsI windows) were recorded on Perkin–Elmer 577 and 457 grating spectrophotometers. $(NH_4)_2Cr_2O_7$ was purchased from Aldrich Chemical Co. and used as received. Me_3SiCl, 2,6-diisopropylaniline and triethylamine were purchased from Aldrich Chemical Co. and distilled prior to use.

Preparation of $[Cr_2Cl_9][NEt_3H]_3$ (**1**)

A suspension of ammonium dichromate, $(NH_4)_2Cr_2O_7$ (1.0 g, 4.0 mmol) in 1,2-dimethoxyethane (30 cm^3) was treated sequentially with triethylamine (4.5 cm^3, 32.3 mmol), chlorotrimethylsilane (8.8 cm^3, 70 mmol) and 2,6-diisopropylaniline (3.0 cm^3, 15.9 mmol) at room temperature. The mixture was then warmed at 70°C for 12 h to give a red-purple solution and a pale residue. The solution was removed by filtration and the residue was washed with dme (2×20 cm^3). Removal of the solvent from the combined filtrates afforded dark red crystalline **1**. Yield 2.1 g (72%). Found: C, 30.2; H, 6.3; N, 5.5. Calc. for $C_{18}H_{48}Cl_9Cr_2N_3$: C, 29.6; H, 6.6; N, 5.8%. IR: 3070w, 1285s, 1265w, 1160w, 1080m, 1040s, 810w(br), 350s(br).

X-ray crystallography

Crystal data for **1**: $C_{18}H_{48}Cl_9Cr_2N_3$, $M = 729.6$, monoclinic, space group $P2_1/c$, $a = 19.100(8)$, $b = 10.270(4)$, $c = 17.342(6)$ Å, $\beta = 96.90(3)°$, $U = 3377(2)$ Å^3, $Z = 4$, $D_c = 1.44$ g cm^{-3}, $F(000) = 1512$, $\mu(\text{Mo-}K_\alpha) = 13.7$ cm^{-1}. Crystal dimensions 0.40×0.60×0.11 mm. Data were measured on a Siemens R3m/V four-circle diffractometer (293 K, Mo-K_α X-radiation, graphite monochromator, $\lambda = 0.71073$ Å). Of the 6110 data collected (Wyckoff ω-scans, $2\theta \leqslant 50°$), 3145 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. An empirical absorption correction was applied using a method based on azimuthal scan data. The data were corrected for Lorentz, polarization and X-ray absorption effects. The structure was solved by conventional heavy-atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C—H 0.96 Å) with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2). Final $R = 0.043$ ($R' = 0.043$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005F^2]$. The final electron density difference synthesis showed no peaks > 0.49 or < -0.43 e Å^{-3}. All calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[10] Scattering factors with corrections for anomalous dispersion were taken from ref. 11. Atom coordinates and additional material comprising of H-atom coordinates, thermal parameters and remaining bond lengths and angles are available from the Cambridge Crystallographic Data Centre.

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