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Notes

First Cr(II) Complex with a Tetrahedral $M_4(\mu_4\text{-O})$ Core: $[M_4(\mu_4\text{-O})(\mu\text{-Cl})_6(THF)_4]$

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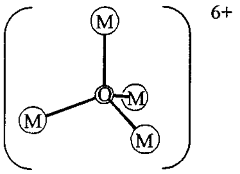
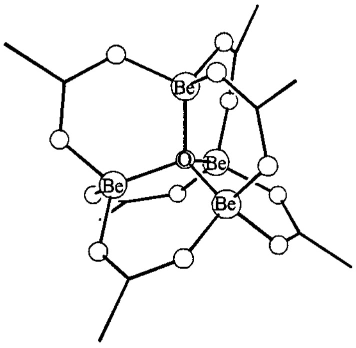
Introduction

The core structure $[M_4O]^{6+}$, with a four-coordinate oxygen atom occupying the center of a tetrahedron of divalent metal atoms, **I**, provides the foundation for two of the classical structures in inorganic chemistry.[1] One of these is exemplified by basic beryllium acetate,[2] **II**, in which an oxygen atom is tetrahedrally surrounded by four beryllium atoms; each beryllium atom is also bound to three additional oxygen atoms from bridging carboxylate groups, so that each beryllium atom has distorted tetrahedral coordination. This type of structure is also known for Co[3] and Zn.[4] Substitution of the acetate groups by other bridging anions is known for complexes of Mn,[5] Fe,[5] Co,[5] and Zn.[5]

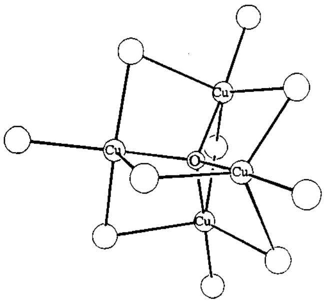


I



II

For copper, the closely related structure $[M_4(\mu_4\text{-O})(\mu\text{-X})_6L_4]$,[6] **III**, is well-known. In this prototypical structure the inner core is similar to that in **II**, but the six carboxylate groups have been replaced by six halide ions (Cl^-, Br^-, I^-). Each metal atom coordinates additionally to a fifth ligand, L, such as another halide ion,[7] an amine,[8] nitrile,[9] or a phosphine oxide.[10] This increases to 5 the coordination number of each metal atom, so that each Cu(II) atom has approximately trigonal-bipyramidal (tbp) coordination. The first example was described in 1966.[11] There are cases when the halide ions are substituted by ligands such as hydroxide,[12] disulfide,[13] diselenide,[14] or alkoxide,[15] but in these there are large deviations from tbp coordination.



III

An essentially regular structure is also known for the magnesium compound $Mg_4OBr_6 \cdot 4Et_2O$.[16] Two examples have also been reported for manganese,[17] in which X = I and L = PPr^n and PMe_2Ph.

We now report the preparation and structural characterization of the first chromium(II) compound with a regular structure of type **III**, in which X = Cl and L = THF.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere using standard glovebox and Schlenk techniques. Solids were handled in a Vacuum Atmospheres drybox with a Dri-Train recirculator. Solvents were distilled prior to use from appropriate drying agents. Starting materials were obtained as follows: $CrCl_2$ was purchased from Strem Chemicals and used as received; 1,3,5-trimethoxyphenyl (HTMP) was prepared as reported elsewhere and recrystallized by sublimation; MeLi (1 M solution in THF/cumene) and Bu^nLi (1.6 M in hexane) were purchased from Aldrich and used as received. Elemental analysis was performed by Canadian Microanalytical Service.

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Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Perkin-Elmer 16PC spectrophotometer using KBr pellets. Solid state susceptibility measurements were performed on a Johnson Matthey magnetic susceptibility balance.

Synthesis. Method A. To a cold solution of 0.025 g (0.6 mmol) of $LiOH \cdot H_2O$ in 40 mL of THF was slowly added 1.12 mL (1.80 mmol) of Bu^nLi in hexane. Then, $CrCl_2$ (0.58 g, 4.7 mmol) was added via a solids addition tube. The grayish starting material immediately reacted to yield a green powder. This was slowly extracted with six portions of 20 mL of hot THF. The product was crystallized from the light green THF solutions after diffusion of a layer of hexanes (6 × 30 mL). Yield of crystalline material: 0.37 g, 36.5%. The product readily oxidized to a dark green-brown powder when exposed to air.

Method B. To a solution of LiTMP at room temperature, prepared in situ by addition of 0.327 g (1.94 mmol) of HTMP and 1.95 mL of slightly hydrolyzed MeLi in 15 mL of THF, was added $CrCl_2$ (0.18 g, 1.46 mmol; ratio Cr:L, 3:4) via a solids addition tube. The initially colorless mixture became dark green and then brown. The mixture was refluxed overnight, and the solution was then allowed to cool. It was then filtered and layered with hexanes. After 2 days, large crystals of two species, green for $[Cr_4(\mu_4\text{-}O)(\mu\text{-}X)_6(THF)_4]$, **1**, and red for $[Cr_2(TMP)_4] \cdot THF$, **2**, were harvested. Yield of **1**: 0.060 g (23% based on Cr). Yield of **2**: 0.070 g (33% based on Cr).

Anal. Calcd for $[Cr_4(\mu_4\text{-}O)(\mu\text{-}X)_6(THF)_4]$, **1**: C, 26.50; H, 4.45. Found: C, 26.39; H, 4.40. IR (cm^{-1}): 2935 (s), 1480 (m), 1063(s), 870(s); these absorptions are due to stretching and bending modes of the THF molecules. Magnetic susceptibility data measurements were made at room temperature on polycrystalline $[Cr_4(\mu_4\text{-}O)(\mu\text{-}X)_6(THF)_4]$. The sample was contained in a glass capillary sealed with a septum, and the experimental susceptibilities were corrected for sample-holder diamagnetism. The diamagnetic contributions from atomic core electrons were applied to the molar susceptibility.

Crystallographic Procedures. Single-crystal X-ray work for **1** was carried out in a Nonius FAST diffractometer at −60 °C, using the program MADNES.[18] The crystal was mounted on the tip of a quartz fiber. The unit cell was calculated via an autoindexing routine. The parameters were later refined using 250 reflections measured over a wide range of 2θ values. Axial photographs corroborated the cell dimensions and established unequivocally the Laue group. The data set was corrected for Lorentz and polarization effects, but no absorption correction was applied. Data were processed and reduced using PROCOR,[19] and the skeleton of the complex was found by direct methods, using the commercial package SHELXTL.[20] After being solved in the correct space group, the structure underwent successive refinement cycles using the program Shelx93.[21] Hydrogen atoms were found in successive Fourier difference maps.

Compound **1** crystallizes in the orthorhombic space group $Pna2_1$, with an entire molecule per asymmetric unit. In the final stages of refinement, 3254 independent reflections were used to minimize the shifts of 308 parameters. All atoms, except hydrogen atoms, were refined with anisotropic thermal parameters. Hydrogen atoms were refined riding on their parent atoms. The final values of R1 and wR2 were 0.039 and 0.106. Two of the THF molecules were found to be disordered. This disorder was modeled as two interlaced rings. Other relevant crystallographic data are provided in Table 1.

Table 1. Crystallographic Data for **1**

empirical formula	$Cr_4O_5Cl_6C_{16}H_{32}$
fw	725.2
space group	$Pna2_1$
a, Å	15.239(3)
b, Å	15.852(3)
c, Å	11.790(2)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	2848(1)
Z	8
T, °C	213(2)
λ, Å	0.710 73
ρ_{calc}, g cm^{-3}	1.658
μ, mm^{-1}	2.071
R^a	R1 (all data) 0.040; ($I > 2\sigma(I)$): 0.039 wR2 (all data) 0.106; ($I > 2\sigma(I)$): 0.103

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

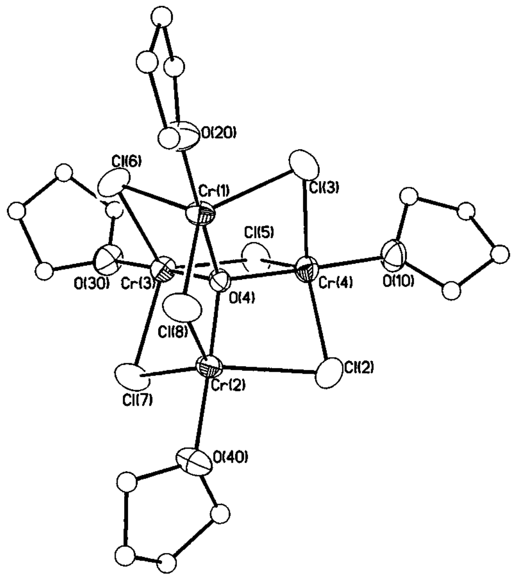

Figure 1. Molecular view of compound **1**. Ellipsoids are drawn at 50% probability level. Two of the THF ligands are disordered; disordered and hydrogen atoms are omitted for clarity.

Complex $[Cr_2(TMP)_4] \cdot THF$, **2**, which cocrystallizes with **1** (method B), crystallizes in space group $P\bar{1}$;[22] its structure will be reported elsewhere.

Results and Discussion

Crystal Structure of $[Cr_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(THF)_4]$. A drawing of the molecular structure is shown in Figure 1; selected bond distances and angles are given in Table 2. There is an oxygen atom coordinated to four chromium atoms and located in the center of a nearly regular tetrahedron. The Cr⋯Cr distances are almost equal but long (>3.1 Å). The Cr−O distances are all ca. 1.96 Å. Each chromium atom is bound to the central oxygen atom, to three bridging chlorine atoms, and to one THF molecule, giving a slightly distorted trigonal bipyramidal

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(22) Crystallographic procedures similar to those described for **1** were used. Data for the new crystallographic form: triclinic, $P\bar{1}$: $a = 11.245(1)$ Å, $b = 11.450(2)$ Å, $c = 17.297(2)$ Å, $\alpha = 101.47(2)°$, $\beta = 93.21(1)°$, $\gamma = 113.47(1)°$. A total of 5039 unique data were collected, from which 4413 with $I > 2\sigma(I)$ were used for the refinement of 496 parameters. An entire molecule was found in the asymmetric unit. In the final refinement cycle, the residuals converged to values of 0.059 (R1) and 0.171 (wR2). There are two interstitial THF molecules per unit cell. This compound is a polymorph of the one previously published in ref 24.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cr_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(THF)_4]$

Cr(1)−O(4)	1.960(4)	O(4)−Cr(1)−O(20)	178.1(2)	Cl(6)−Cr(3)−Cl(5)	123.51(7)
Cr(1)−O(20)	2.042(5)	O(4)−Cr(1)−Cl(8)	85.14(12)	O(4)−Cr(3)−Cl(7)	84.06(12)
Cr(1)−Cl(8)	2.446(2)	O(20)−Cr(1)−Cl(8)	96.81(14)	O(30)−Cr(3)−Cl(7)	95.2(2)
Cr(1)−Cl(3)	2.478(2)	O(4)−Cr(1)−Cl(3)	84.94(12)	Cl(6)−Cr(3)−Cl(7)	119.53(8)
Cr(1)−Cl(6)	2.509(2)	O(20)−Cr(1)−Cl(3)	93.7(2)	Cl(5)−Cr(3)−Cl(7)	114.89(8)
		Cl(8)−Cr(1)−Cl(3)	128.97(7)		
Cr(2)−O(4)	1.946(4)	O(4)−Cr(1)−Cl(6)	84.81(12)	O(4)−Cr(4)−O(10)	178.5(2)
Cr(2)−O(40)	2.044(5)	O(20)−Cr(1)−Cl(6)	94.3(2)	O(4)−Cr(4)−Cl(2)	84.67(12)
Cr(2)−Cl(7)	2.443(2)	Cl(8)−Cr(1)−Cl(6)	120.21(7)	O(10)−Cr(4)−Cl(2)	96.72(14)
Cr(2)−Cl(2)	2.494(2)	Cl(3)−Cr(1)−Cl(6)	108.50(7)	O(4)−Cr(4)−Cl(5)	84.86(12)
Cr(2)−Cl(8)	2.515(2)			O(10)−Cr(4)−Cl(5)	94.8(2)
		O(4)−Cr(2)−O(40)	176.9(2)	Cl(2)−Cr(4)−Cl(5)	123.30(9)
Cr(3)−O(4)	1.966(4)	O(4)−Cr(2)−Cl(7)	85.55(12)	O(4)−Cr(4)−Cl(3)	84.53(13)
Cr(3)−O(30)	2.055(5)	O(40)−Cr(2)−Cl(7)	91.4(2)	O(10)−Cr(4)−Cl(3)	94.2(2)
Cr(3)−Cl(6)	2.460(2)	O(4)−Cr(2)−Cl(2)	84.14(12)	Cl(2)−Cr(4)−Cl(3)	123.84(9)
Cr(3)−Cl(5)	2.462(2)	O(40)−Cr(2)−Cl(2)	97.5(2)	Cl(5)−Cr(4)−Cl(3)	110.29(7)
Cr(3)−Cl(7)	2.482(2)	Cl(7)−Cr(2)−Cl(2)	125.41(9)		
		O(4)−Cr(2)−Cl(8)	83.52(12)	Cr(2)−O(4)−Cr(1)	110.6(2)
Cr(4)−O(4)	1.965(4)	O(40)−Cr(2)−Cl(8)	98.4(2)	Cr(2)−O(4)−Cr(4)	109.9(2)
Cr(4)−O(10)	2.041(4)	Cl(7)−Cr(2)−Cl(8)	122.52(7)	Cr(1)−O(4)−Cr(4)	108.8(2)
Cr(4)−Cl(2)	2.460(2)	Cl(2)−Cr(2)−Cl(8)	109.26(8)	Cr(2)−O(4)−Cr(3)	109.5(2)
Cr(4)−Cl(5)	2.486(2)			Cr(1)−O(4)−Cr(3)	109.1(2)
Cr(4)−Cl(3)	2.489(2)	O(4)−Cr(3)−O(30)	179.2(2)	Cr(4)−O(4)−Cr(3)	108.9(2)
		O(4)−Cr(3)−Cl(6)	86.01(13)		
		O(30)−Cr(3)−Cl(6)	94.6(2)		
		O(4)−Cr(3)−Cl(5)	85.49(12)		
		O(30)−Cr(3)−Cl(5)	94.61(14)		

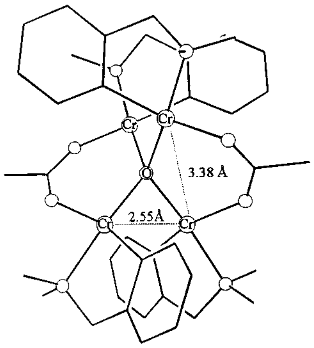
coordination to each metal atom. The equatorial positions are occupied by the chlorine atoms, and the axial ones by oxygen atoms from the THF and the central oxygen atom.

This structure is remarkable in two respects:

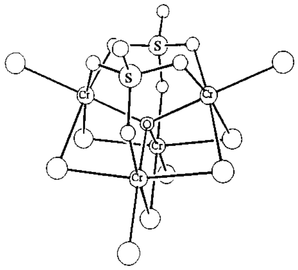
1. Trigonal-bipyramidal pentacoordination in divalent chromium complexes is rare; a search of the Cambridge Crystallographic Data Center revealed only a few examples.[23]

2. This is the first complex of divalent chromium that has a regular type **III** structure.

In a previous paper,[24] we described the structure of a somewhat related product, $[Cr_4(\mu_4\text{-}O)(\eta^2\text{-}C_6H_4\text{-}o\text{-}CH_2NMe_2)_4(\mu\text{-}CH_3COO)_2]$, **IV**. Although the two formulas show similarities, the geometry and arrangement of atoms in the two complexes are very different. The only common feature is the presence of the $[Cr_4(\mu_4\text{-}O)]^{6+}$ core. In structure **IV**, the Cr−O−Cr angles range from 79° to 130°, the Cr···Cr distances are 2.45 and 3.38 Å, and there is an extremely distorted tetrahedral arrangement about each Cr^{II} atom. This kind of highly distorted environment around each metal center can be found also in complexes with a similar $[M_4O]^{n+}$ core, but different oxidation states for the metals (Y[25] or Zr[26]), or in clusters with the same stoichiometry but with mixed-metal centers (e.g., an $FeZr_3(\mu_4\text{-}O)$ compound[27]).



IV



V

Another related structure is found in the anion $[Cr_4(\mu_4\text{-}O)(\mu_3\text{-}SO_4)_2(\mu\text{-}Cl_5)Cl_4]^{3-}$, **V**, in which an oxygen atom is surrounded by four 6-coordinate chromium(III) ions.[28] Some mixed-metal complexes also have such a core.

Synthesis and Properties. This oxo-centered tetranuclear complex is readily oxidized to a dark green-brown powder when exposed to air; such air sensitivity is a common feature for most chromium(II) complexes. The magnetic moment of 8.03 μ_B is consistent with the presence of four Cr(II) atoms strongly coupled through the oxygen atom. Similarly, significant decreases from spin-only values have been observed in $Co_4(\mu_4\text{-}O)(acetate)_6$[3] and copper complexes of type **III**. It has been argued that strong antiferromagnetic coupling is responsible for the observed decrease in the magnetic moments.[29]

The compound is prepared in 36% yield by reaction of $CrCl_2$ and a stoichiometric source of oxide ions:

$$8CrCl_2 + LiOH\cdot H_2O + 3Bu^nLi \xrightarrow{THF} 2Cr_4OCl_6(THF)_4 + 4LiCl + 3Bu^nH$$

The greenish compound is only sparingly soluble in THF at room temperature but more soluble at higher temperature. Thus the solid obtained from the reaction is a mixture of the complex

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and LiCl. Analytically pure samples can be obtained by crystallization from a saturated solution on which hexanes have been layered.

We first obtained this compound serendipitously while reacting $CrCl_2$ and Li(2,4,6-trimethoxyphenyl) (LiTMP) in boiling THF, which has been reported to produce $Cr_2(TMP)_4$.[30] We repeated this reaction four times using conditions similar to those previously reported, but substituting MeLi for Bu^nLi as the deprotonating agent. On each occasion we observed a mixture of crystals. Some of them corresponded to the reddish $Cr_2(TMP)_4$ complex (ca. 30% yield), which we characterized by X-ray crystallography in a new polymorphic form; the second component was $[Cr_4OCl_6(THF)_4]$ (ca. 20% yield).

The LiMe was a commercial solution in THF/cumene, presumably containing LiOH produced by partial hydrolysis. It is well-known that LiOH is quite soluble in THF. When Bu^nLi in hexane, in which LiOH is insoluble, was used to deprotonate HTMP and this mixture was then added to $CrCl_2$ in THF, the only observed product was $Cr_2(TMP)_4$. This would also be a plausible explanation for the previously reported formation of $[Cr_4(\mu_4\text{-}O)(\eta^2\text{-}C_6H_4\text{-}o\text{-}CH_2NMe_2)_4(\mu\text{-}CH_3COO)_2]$.[25]

Our experience may serve as a warning to the users of commercial sources of LiMe, especially when the solvent is THF. One further point is that the possibility that the central oxygen atom could have come from atmospheric oxygen can be ruled out since both $Cr_2(TMP)_4$ and $Cr_4OCl_6(THF)_4$ are readily oxidized to chromium(III) species in the presence of atmospheric oxygen.

Acknowledgment. We are grateful to the National Science Foundation for support.

Supporting Information Available: An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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