

Tetra- μ -chloro-1:2 κ^4 Cl;1:3 κ^4 Cl-di-methyl-2 κ C,3 κ C-tetrakis(tetrahydrofuran)-1 κ^2 O,2 κ O,3 κ O-chromium(II)-dizinc(II)

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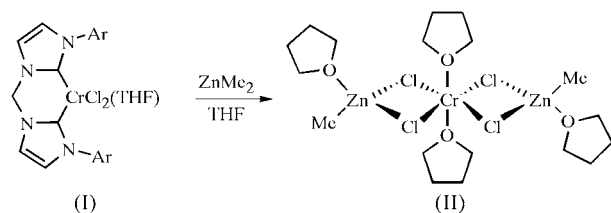
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The title compound, $[\text{CrZn}_2(\text{CH}_3)_2\text{Cl}_4(\text{C}_4\text{H}_8\text{O})_4]$, contains a central distorted octahedral Cr atom, located at an inversion center, bound to two tetrahydrofuran ligands and four chloro ligands that bridge to two symmetry-related tetrahedral Zn atoms. The coordination around zinc is completed by methyl and tetrahydrofuran ligands. This structure is compared with a previously reported complex of vanadium, and their differences in metric parameters are explained.

Comment

We have recently been investigating the organometallic chemistry of chromium supported by a bis(N-heterocyclic) carbene ligand (*L*) (Kreisel *et al.*, 2006). In the hope of synthesizing a stable methyl complex of chromium(II), we reacted ZnMe_2 with the chromium dichloride precursor $\text{LCrCl}_2(\text{THF})$ (THF is tetrahydrofuran), (I). However, isolation of the product gave the title complex, (II), as colorless crystals from THF at 243 K in good yield.



Complex (II) (Fig. 1) is trinuclear, containing an octahedral Cr atom located at an inversion center. The Cr atom is ligated by four bridging equatorial chloro ligands and two axial THF ligands. Furthermore, each pair of bridging Cl atoms is coordinated to a tetrahedral Zn atom, which is also coordinated by methyl and THF ligands. The complex is a congener of a previously reported vanadium complex, $\text{V}(\text{THF})_2[(\mu_2\text{-Cl})_2\text{ZnCl}(\text{PPh}_3)]_2$, (III), making it the second known complex with a $\text{Zn}-(\text{X})_2-\text{M}-(\text{X})_2-\text{Zn}$ motif (Cotton *et al.*, 1985), where *M* is any metal and *X* is any halide.

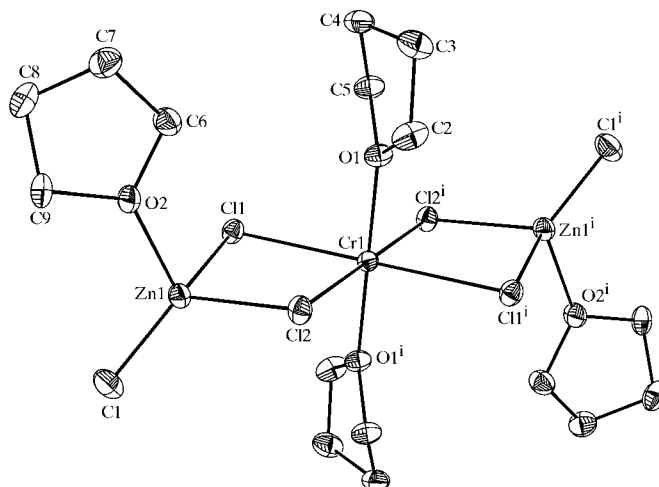


Figure 1

The molecular structure of (II), with ellipsoids depicted at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, 2 - y, -z$.]

The $\text{Cr1}-\text{Cl2}$ bond length in (II) is 2.4576 (5) Å; however, the $\text{Cr1}-\text{Cl1}$ bond length is considerably longer at 2.7149 (6) Å. In the vanadium analog, these bond distances are more similar to each other [2.501 (1) and 2.526 (1) Å]. We propose that the significant lengthening of the $\text{Cr1}-\text{Cl1}$ bond is caused by a Jahn–Teller distortion, which is due to an unpaired electron that occupies either of the degenerate d_{z^2} or $d_{x^2-y^2}$ orbitals of an octahedral complex. Complex (III) does not show this distortion because there are no electrons in these degenerate orbitals. The asymmetry in the bridging $\text{Zn}-\text{Cl}$ distances [2.3105 (5) and 2.3954 (6) Å] may be due to the increased basicity of atom Cl1, which is involved in the Jahn–Teller distortion. A longer $\text{Cr1}-\text{Cl1}$ distance indicates less orbital overlap of the lone pair electrons of the chloro ligand with the Cr atom, suggesting more localization of the electrons in the $\text{Zn1}-\text{Cl1}$ bond. In addition, the acute $\text{Cl1}-\text{Cr1}-\text{Cl2}$ bond angle of 84.33 (2)° reflects the large $\text{Cr}\cdots\text{Zn}$ interatomic separation of 3.481 (6) Å.

Alternatively, one can think of the asymmetric binding of the bridging Cl atoms as a weak $\text{ZnMeCl}(\text{THF})$ adduct of square-planar $\text{CrCl}_2(\text{THF})_2$. Similar cases of apparent distorted octahedral coordination geometries of high-spin Cr^{II} metal centers have been interpreted as square-pyramidal coordination with a weakly coordinated ligand occupying a sixth site (Robertson *et al.*, 2003). In either interpretation of the coordination geometry, the electronic structure should remain the same.

Experimental

A solution of complex (I) (0.210 g, 0.316 mmol) in THF (20 ml) was cooled to 243 K. To the slurry was added ZnMe_2 (0.058 g) and the solution was allowed to warm to room temperature. After stirring overnight, the reaction mixture was filtered, concentrated and cooled to 243 K overnight to yield colorless crystals of complex (II) in 62% yield.

Crystal data

$[\text{CrZn}_2(\text{CH}_3)_2\text{Cl}_4(\text{C}_4\text{H}_8\text{O})_4]$	$V = 660.6 (2) \text{ \AA}^3$
$M_r = 643.02$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.616 \text{ Mg m}^{-3}$
$a = 7.8530 (14) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.8695 (16) \text{ \AA}$	$\mu = 2.63 \text{ mm}^{-1}$
$c = 10.7901 (19) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\alpha = 68.759 (2)^\circ$	Block, colorless
$\beta = 71.741 (2)^\circ$	$0.10 \times 0.06 \times 0.04 \text{ mm}$
$\gamma = 77.434 (2)^\circ$	

Data collection

Bruker APEX diffractometer	7317 measured reflections
ω scans	2938 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	2794 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.779$, $T_{\max} = 0.902$	$R_{\text{int}} = 0.016$
	$\theta_{\max} = 28.2^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.2798P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.36 \text{ e \AA}^{-3}$
2938 reflections	$\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$
134 parameters	
H-atom parameters constrained	

The molecule is located at an inversion center. The heavy-atom bond framework shows significant differences in the component anisotropic displacement parameters along the bonding directions, perhaps because of insufficient absorption corrections. Numerical corrections were unsatisfactory because of indeterminate crystal faces. The results presented represent the best of several attempts at

multi-scan absorption corrections. H atoms were assigned calculated positions ($\text{C}-\text{H} = 0.98$ and 0.98 \AA), with constrained $U_{\text{iso}}(\text{H})$ values of 1.2–1.5 times $U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3045). Services for accessing these data are described at the back of the journal.

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