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Comparative Structural Studies of the First Row Early Transition Metal(III) Chloride Tetrahydrofuran Solvates

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Abstract

Two compounds of empirical formula $MCl_3(THF)_3$, M = V and Cr, have been characterized by single crystal X-ray studies. The $VCl_3(THF)_3$ molecule, which has a *mer* octahedral stereochemistry, crystallizes in the monoclinic space group $P2_1/c$ with a = 8.847(2), b = 12.861(5), c = 15.134(3) Å, β = 91.94(2)°, V = 1721(1) Å^3 and Z = 4. The V–Cl(1) and V–Cl(2) distances have a mean value of 2.330[3] Å while V–Cl(3) = 2.297(2) Å, The V–O(1) and V–O(2) distances have a mean value of 2.061[8] Å while V–O(3) = 2.102(3) Å. *cis* Cl–V–Cl angles average 92.0[5]° and *cis* O–V–O angles average 86.2[2]°. The isostructural complex, $CrCl_3(THF)_3$, has a crystal structure made up of discrete octahedral *mer*-$CrCl_3(THF)_3$ molecules with the following unit cell dimensions (space group $P2_1/c$): a = 8.715(1), b = 12.786(3), c = 15.122(3) Å, β = 92.15(1)°, V = 1684(1) Å^3 and Z = 4. The Cr–Cl(1) and Cr–Cl(2) distances have a mean value of 2.310[3] Å while Cr–Cl(3) = 2.283(2) Å. The Cr–O(1) and Cr–O(2) distances have a mean value of 2.010[17] Å while Cr–O(3) = 2.077(4) Å. *cis* Cl–Cr–Cl angles average 90.9[4]° and *cis* O–Cr–O angles average 86.1[2]°. The structures of these two octahedral complexes and those previously reported for $ScCl_3(THF)_3$ and $TiCl_3(THF)_3$ are compared and certain general trends are discussed.

Introduction

Tetrahydrofuran complexes of the early transition metal chlorides, which may be prepared by simple, high-yield routes [1], represent very convenient starting materials for the synthesis of numerous inorganic and organometallic compounds. Although several of these complexes have been thoroughly investigated by elemental analyses, electronic spectra, far-infrared spectra and room temperature magnetic moments [2, 3], little structure information based on X-ray crystallography has been reported.

We earlier gave a preliminary report [4] on the structure of $VCl_3(THF)_3$. In the course of preparing a more complete report of that work, we noted that two other such compounds, $ScCl_3(THF)_3$ [5] and $TiCl_3(THF)_3$ [6] have also been studied crystallographically. However, the rather synthetically useful $CrCl_3(THF)_3$ [7] had not been. Since we had available some well formed crystals of the chromium compound, we decided to study its crystallography also.

Experimental

All operations were performed under an atmosphere of argon using standard Schlenk techniques and a double manifold vacuum line. Tetrahydrofuran and hexane were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless cannulae and/or syringes. $VCl_3(THF)_3$ was prepared according to the published procedure [1]. Crystallographic quality crystals were obtained by careful layering of a tetrahydrofuran solution of $VCl_3(THF)_3$ with hexane. X-ray quality crystals of $CrCl_3(THF)_3$ were obtained according to ref. 7.

X-ray Crystallography

General procedures used for data collection have been previously described [8] and the relevant parameters are summarized in Table I for $VCl_3(THF)_3$ and $CrCl_3(THF)_3$. Lorentz and polarization corrections were applied to the data; neither decay nor absorption corrections were necessary.

The vanadium atom of $VCl_3(THF)_3$ was located by Patterson synthesis. Full-matrix least squares refinement and difference Fourier calculations were used to locate the remaining non-hydrogen atoms. All nineteen atoms were refined anisotropically to convergence. The largest peak in a final difference Fourier map had a density of 0.47 e/Å^3.

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TABLE I. Crystal Data

Formula	$VCl_3(THF)_3$		$CrCl_3(THF)_3$
Formula weight	373.62		374.67
Space group		$P2_1/c$	
Systematic absences		$0k0$; $k \neq 2n$ $h0l$; $l \neq 2n$	
a (A)	8.847(2)		8.715(1)
b (A)	12.861(5)		12.786(3)
c (A)	15.134(3)		15.122(3)
β (deg)	91.94(2)		92.15(1)
V (A^3)	1721(1)		1684(1)
Z		4	
D_c (g/cm^3)	1.422		1.478
Crystal dimensions (mm)	0.8 × 0.4 × 0.3		0.5 × 0.5 × 0.4
μ(Mo Kα) (cm^{-1})	10.285		11.441
Data collection instrument		Syntex P$\bar{1}$	
Radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 A)		Mo Kα (λ_α = 0.71073 A)
Orientation reflections, number, range (2θ)	15, 20.2–29.6		15, 14.4–22.2
Temperature (°C)	22		5
Scan method	$\omega - 2\theta$		$\omega - 2\theta$
Data collection range, 2θ (deg)	$4 < 2\theta < 45$		$4 < 2\theta < 50$
Number unique data; total	1780		2447
with $F_o^2 > 3\sigma(F_o^2)$	1690		1835
Number of parameters refined	172		172
R^a	0.053		0.059
R_w^b	0.080		0.086
Quality-of-fit indicator[c]	1.804		1.787
Largest shift/e.s.d., final cycle	0.04		0.1
Largest peak (e/A^3)	0.466		0.454

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2 / N_{obs} - N_{parameters})]^{1/2}$.

TABLE II. Positional Parameters and Their Estimated Standard Deviations for $VCl_3(THF)_3$[a]

Atom	x	y	z	B (A^2)
V	−0.2481(1)	0.26670(8)	0.23623(6)	4.15(2)
Cl(1)	−0.0723(2)	0.3472(2)	0.3321(1)	6.16(4)
Cl(2)	−0.4235(2)	0.1972(2)	0.1346(1)	6.00(4)
Cl(3)	−0.2415(2)	0.1173(1)	0.3194(1)	6.57(4)
O(1)	−0.4195(4)	0.3321(4)	0.3057(2)	5.3(1)
O(2)	−0.0738(4)	0.2194(3)	0.1577(3)	4.82(9)
O(3)	−0.2535(5)	0.4029(3)	0.1594(3)	5.7(1)
C(1)	−0.4171(9)	0.3445(8)	0.4020(4)	8.1(2)
C(2)	−0.569(1)	0.3838(9)	0.4222(5)	10.4(3)
C(3)	−0.6549(8)	0.3993(8)	0.3425(5)	8.3(2)
C(4)	−0.5687(9)	0.3595(9)	0.2695(5)	10.5(3)
C(5)	−0.0674(9)	0.1224(6)	0.1056(5)	7.3(2)
C(6)	0.0875(8)	0.1190(6)	0.0670(5)	6.6(2)
C(7)	0.1399(9)	0.2299(7)	0.0693(6)	9.0(2)
C(8)	0.0721(8)	0.2744(7)	0.1502(6)	9.7(2)
C(9)	−0.235(2)	0.5087(7)	0.1971(6)	13.1(4)
C(10)	−0.267(2)	0.5772(8)	0.1182(7)	13.8(4)
C(11)	−0.237(2)	0.5184(8)	0.0417(6)	14.0(5)
C(12)	−0.270(1)	0.4062(7)	0.0616(5)	9.8(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

It was expected that $CrCl_3(THF)_3$ would be isomorphous with $VCl_3(THF)_3$ when the unit cell parameters for those two compounds were found to be very similar. A Patterson map was consistent with this, so the coordinates of the V, Cl, and O atoms of $VCl_3(THF)_3$ were used for Cr, Cl, and O atoms. Two cycles of least-squares refinement led to $R = 0.243$. All of the carbon atoms were then located in a difference Fourier map. Complete anisotropic refinement was then carried out.

Tables of structure factors and anisotropic thermal parameters are available as supplementary material.

Results

The crystal structures of the vanadium and chromium compounds are isotypic. The atomic positional parameters for each one, along with isotropic-equivalent thermal displacement parameters are listed in Tables II and III, respectively. The two molecular structures are very similar and the atoms have been numbered analogously. Figure 1 shows the qualitative structure of both molecules and defines the atom numbering scheme that they share.

TABLE III. Positional Parameters and Their Estimated Standard Deviations for $CrCl_3(THF)_3$[a]

Atom	x	y	z	B (Å^2)
Cr	−0.2366(1)	0.26427(9)	0.23691(7)	3.08(2)
Cl(1)	−0.0573(2)	0.3400(2)	0.3336(1)	4.56(4)
Cl(2)	−0.4175(2)	0.1941(2)	0.1387(1)	4.51(4)
Cl(3)	−0.2291(3)	0.1137(2)	0.3181(1)	4.77(4)
O(1)	−0.4036(5)	0.3276(4)	0.3059(3)	4.1(1)
O(2)	−0.0667(5)	0.2184(4)	0.1576(3)	3.8(1)
O(3)	−0.2441(6)	0.4014(4)	0.1632(3)	4.0(1)
C(1)	−0.409(1)	0.3268(8)	0.4053(5)	5.8(2)
C(2)	−0.549(1)	0.377(1)	0.4240(6)	9.1(3)
C(3)	−0.6413(9)	0.4003(8)	0.3452(6)	5.7(2)
C(4)	−0.5493(9)	0.367(1)	0.2670(6)	7.5(3)
C(5)	−0.0618(9)	0.1208(6)	0.1093(6)	4.6(2)
C(6)	0.0965(9)	0.1180(6)	0.0680(5)	4.5(2)
C(7)	0.146(1)	0.2321(8)	0.0676(7)	6.3(2)
C(8)	0.0785(9)	0.2766(7)	0.1488(6)	5.9(2)
C(9)	−0.217(1)	0.5057(7)	0.2008(7)	7.5(3)
C(10)	−0.261(2)	0.5798(8)	0.1250(7)	8.8(3)
C(11)	−0.243(2)	0.5189(9)	0.0440(7)	10.9(5)
C(12)	−0.271(1)	0.4069(7)	0.0666(5)	6.7(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

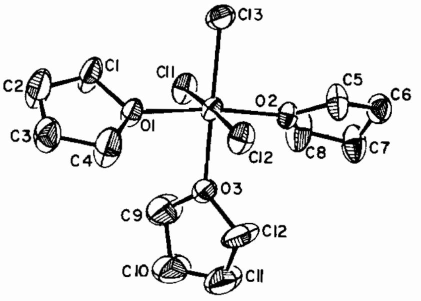

Fig. 1. The molecular structure and atom numbering scheme for both $VCl_3(THF)_3$ and $CrCl_3(THF)_3$ molecules.

TABLE IV. Principal Dimensions of the $MCl_3(THF)_3$ Molecules

	V	Cr
Distances (Å)		
M–Cl(1)	2.333(1)	2.312(2)
M–Cl(2)	2.326(1)	2.307(2)
M–Cl(3)	2.297(1)	2.283(2)
M–O(1)	2.054(3)	1.994(4)
M–O(2)	2.069(3)	2.027(4)
M–O(3)	2.102(3)	2.077(4)
Angles (deg)		
Cl(1)–M–Cl(2)	175.93(6)	178.12(7)
Cl(1)–M–Cl(3)	91.50(6)	90.47(7)
Cl(2)–M–Cl(3)	92.57(6)	91.34(7)
O(1)–M–O(2)	172.2(2)	172.5(1)
O(1)–M–O(3)	85.9(2)	86.5(1)
O(2)–M–O(3)	86.3(2)	86.0(1)
Cl(3)–M–O(3)	179.8(1)	179.6(1)

The two molecules differ in their exact dimensions of course, and Table IV gives important dimensions for both the $VCl_3(THF)_3$ and $CrCl_3(THF)_3$ molecules. Complete lists are available as supplementary material.

Discussion

With the two structures reported here, there are now four $MCl_3(THF)_3$ compounds, with M = Sc, Ti, V, Cr that have been structurally characterized. All have the same meridional molecular structure. Three of them are crystallographically isotypic and the other (Ti) has a closely related crystal structure.

It is interesting to compare these four molecular structures and this can be done with the help of Table V, which gives principal molecular dimensions averaged according to C_{2v} symmetry. As shown in

TABLE V. Selected Bond Distances and Angles for Four $MCl_3(THF)_3$ Compounds

M	M–Cl_{ax}[a]	Average M–Cl_{eq}	M–O_{ax}	Average M–O_{eq}	Cl_{ax}–M–O_{ax}	Average Cl_{ax}–M–Cl_{eq}	Average Cl_{ax}–M–O_{eq}
Sc	2.406(4)[b]	2.418[3]	2.236(8)	2.156[9]	179.5(3)	92.8[3]	96.4[3]
Ti[c]	2.336[5]	2.351[5]	2.183[2]	2.097[6]	176.8[6]	94.0[8]	91.6[4]
V	2.297(2)	2.330[4]	2.102(3)	2.062[8]	179.64(11)	92.0[5]	93.7[1]
Cr	2.283(2)	2.310[3]	2.077(4)	2.01[2]	179.8(1)	90.9[4]	93.9[0]

[a] Cl_{eq} refers to the chlorine atoms *trans* to each other, while Cl_{ax} designates the chlorine atom *trans* to an oxygen atom. Similarly, O_{eq} refers to *trans* oxygen atoms, while O_{ax} indicates the oxygen *trans* to Cl_{ax}. [b] A number in parentheses is an e.s.d. for a given individual value, while a number in square brackets is equal to $[\Sigma_n\Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the i^{th} of n values from the arithmetic mean of the n values. [c] Values given are average values for two independently refined molecules.

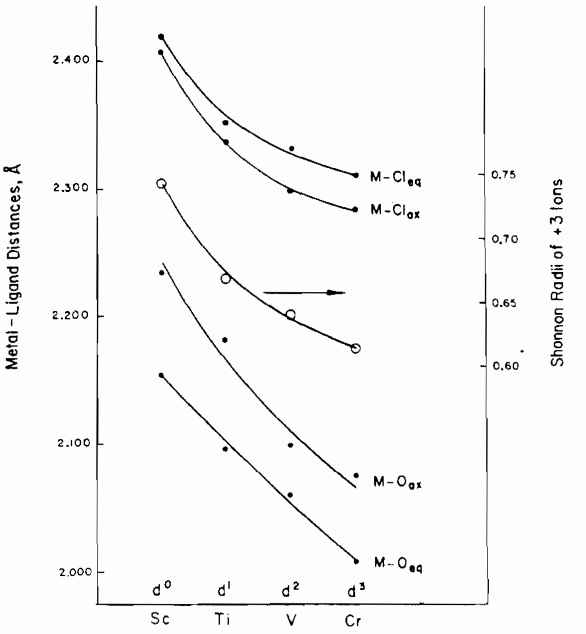

Fig. 2. Plots of the various metal–ligand distances (left ordinate scale) and of the Shannon M^{3+} radii (right ordinate scale).

Fig. 2, the trends in bond lengths among these molecules, in which the number of t_{2g} electrons increases from 0 to 3, are smooth within the experimental errors. No point deviates from the appropriate line by more than one e.s.d. The monotonic downward trends are expected. Also included on Fig. 2 is a plot of the Shannon [9] ionic radii for the four M^{3+} ions. It is interesting that the M–Cl distances track this trend in radii fairly well, whereas the M–O distances fall more steeply. Since the radii were derived from data on binary ionic compounds, the results for the M–Cl distances are to be expected. The fact that the M–O distances fall more steeply than the M–Cl distances may be due to the fact that the oxygen atoms of the THF ligands repel each other less than the Cl^- ligands repel each other, and thus they can approach the metal ions more closely as the latter decrease in size. Smaller repulsive forces between the THF oxygen atoms as compared to those between Cl^- ions are logically to be expected since the oxygen atoms are smaller and uncharged.

Another point of interest in these molecules is the orientation of the THF oxygen atom as it bonds to the metal atom. This can be defined in terms of how far the metal atom lies out of the C–O–C plane. The analogous question is of interest in connection with hydrated metal ions, but unless neutron diffraction data can be obtained so that the H–O–H plane is well defined (and this has been done in only a very few cases [10]) it is not possible to answer it.

TABLE VI. Orientations of THF Molecules Relative to Metal Atoms

Compound	Distances[a] of M from C–O–C Planes (Å)		
	(1)	(2)	(3)
$ScCl_3(THF)_3$	0.032	0.067	0.073
$TiCl_3(THF)_3$	0.134	0.082	0.276
	0.160	0.417	0.209
$VCl_3(THF)_3$	0.232	0.127	0.068
$CrCl_3(THF)_3$	0.249	0.170	0.058

[a] Each distance has an e.s.d. of *ca.* 0.001 Å; (1) and (2) are for THF *trans* to THF while (3) is for THF *trans* to Cl.

In the present $MCl_3(THF)_3$ molecules, we find considerable variation in this feature of the structures, as shown by the results in Table VI. There is no consistent pattern to be found, but rather great variation from molecule to molecule. It is true that for the two compounds whose structures are reported here, the pattern is similar, but it is different in the scandium compound, even though this is isotypic with the vanadium and chromium compounds. In the case of the titanium compound, the two crystallographically distinct molecules differ significantly from each other, and both differ from all the other compounds. We can only conclude that the directionality of the donor function of THF towards these +3 cations is not sharply defined.

Acknowledgement

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Supplementary Material

Tables of observed and calculated structure factors, anisotropic displacement parameters and full list of bond distances and angles for $CrCl_3(THF)_3$ and $VCl_3(THF)_3$ (25 pages). Copies may be obtained from author F.A.C.

References

1 J. P. Fackler, Jr., (ed.), 'Inorganic Syntheses', Vol. XXI, Wiley, New York, 1982, p. 135–140.
2 R. J. Kern, *J. Inorg. Nucl. Chem., 24,* 1105 (1962).

3 G. W. A. Fowles, D. A. Rice and R. A. Walton, *J. Inorg. Nucl. Chem., 31,* 3119 (1969).

4 F. A. Cotton, S. A. Duraj, M. W. Extine, G. E. Lewis, W. J. Roth, C. D. Schmulbach and W. Schwotzer, *J. Chem. Soc., Chem. Commun.,* 1377 (1983).

5 J. L. Atwood and K. D. Smith, *J. Chem. Soc. Dalton Trans.,* 921 (1974).

6 M. Handlowic, D. Miklos and M. Zikmund, *Acta Crystallogr., Sect. B:, 37,* 811 (1981).

7 J. P. Collman and E. T. Kittleman, *Inorg. Synth., 8,* 149 (1966).

8 See for example, A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 18,* 3558 (1979).

9 R. D. Shannon, *Acta Crystallogr., Sect. A:, 32,* 751 (1976).

10 F. A. Cotton, C. K. Fair, G. E. Lewis, G. N. Mott, F. K. Ross, A. J. Schultz and J. K. Williams, *J. Am. Chem. Soc., 106,* 5319 (1984).