# Notes

## Isolation and Crystal Structure of $[NHMe_3]_2[ZrCl_4(OMe)(MeOH)]Cl$.* The First Example of a Linear Zirconium–Methoxide Bond: Structural and Bonding Implications

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Treatment of $[ZrCl_4(NMe_3)_2]$ with boiling methanol provided colourless needle crystals which were identified by *X*-ray crystallography as the 'mixed' alcohol–alkoxide derivative $[NHMe_3]_2[ZrCl_4(OMe)(MeOH)]Cl$. Crystals are orthorhombic, space group $P2_12_12_1$, $Z = 4$, with $a = 7.192(8)$, $b = 14.578(11)$, $c = 19.343(21)$ Å. 1 717 Above-background reflections were collected on a diffractometer and the structure was refined to $R = 0.065$. In the $[ZrCl_4(OMe)(MeOH)]^-$ anion, the zirconium atom is octahedral being bonded to four chlorine atoms [2.480(4)—2.496(4) Å] in the equatorial plane and to two oxygen atoms in axial positions at distances of 1.847(10) and 2.264(9) Å, identified with the $OMe^-$ and MeOH ligands respectively. The Zr–O–Me angle to the alcohol ligand is 128.6(10) and to the alkoxide 171.4(13)°. This is the first known example of a linear zirconium–methoxide bond. The structural and bonding implications are discussed.

Reactions of $ZrX_4$ ($X$ = Cl, Br, or I) with trimethylamine (L) give the bis-adducts $[ZrX_4L_2]$ which are regarded as monomeric six-co-ordinate species, *cis* for X = Cl or Br, and *trans* for X = I, based on solid-state i.r. spectroscopic data.[1] There is no evidence of reduction to $Zr^{III}$ species as is the case for titanium where $Ti^{IV} \longrightarrow Ti^{III}$ readily occurs in the presence of excess amine, *e.g.* formation of the five-co-ordinate trigonal-bipyramidal complex $[TiBr_3L_2]$.[2]

Our attempts to clarify the *cis–trans* assignment of these $[ZrX_4L_2]$ species by *X*-ray crystallography[1] have been thwarted by their limited solubility in the common suitable organic solvents and also by their tendency to give solvolytic reactions in solvents containing an active hydrogen atom. As an example of the latter we report here an interesting product of a methanolysis reaction.

### Experimental

Treatment of $[ZrCl_4L_2]$ with boiling methanol (Soxhlet extraction) provided colourless needle crystals which were subsequently identified as the 'mixed' alcohol–alkoxide derivative $[NHMe_3]_2[ZrCl_4(OMe)(MeOH)]Cl$ (**1**) (Found: C, 21.2; H, 5.9; Cl, 39.0; N, 6.1; Zr, 20.0. Calc. for $C_8H_{27}Cl_5N_2O_2Zr$: C, 21.3; H, 6.0; Cl, 39.2; N, 6.2; Zr, 20.2%), m.p. 241—245 °C with decomposition.

*Crystal Data.*—$C_8H_{27}Cl_5N_2O_2Zr$, $M = 451.8$, orthorhombic, $a = 7.192(8)$, $b = 14.578(11)$, $c = 19.343(21)$ Å, $U = 2\,028.0$ Å$^3$, $Z = 4$, $D_c = 1.48$ g cm$^{-3}$, $F(000) = 920$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 11.81$ cm$^{-1}$, space group $P2_12_12_1$.

A crystal of approximate size 0.5 × 0.33 × 0.15 mm was mounted on a Stoe Stadi-2 diffractometer and data collected *via* variable-width ω scan. Background counts were 20 s and the scan rate of 0.033° s$^{-1}$ was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 2 064 Independent reflections with $2\theta < 50°$ of which 1 717 with $I > 3\sigma(I)$ were used in the subsequent refinement. The structure was determined by the usual heavy-atom methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to nitrogen were placed in tetrahedral positions. The hydrogen atom bonded to O(12) was located in a difference Fourier synthesis and refined independently. The methyl groups were refined as rigid groups with a common refined thermal parameter. The structure was then refined by full-matrix least squares to $R = 0.065$ ($R' = 0.067$). The weighting scheme used was $w = 1/[\sigma^2(F) + 0.003F^2]$. All calculations were carried out with SHELX 76[3] and some of our own programs on the Amdahl V7 computer at the University of Reading.

Atomic positions are listed in Table 1 and the geometry of the $[ZrCl_4(OMe)(MeOH)]^-$ anion is given in Table 2.

### Results and Discussion

The crystal structure determination of (**1**) has established that the asymmetric unit contains four discrete ions, *viz.* two $[NHMe_3]^+$ cations and the $[ZrCl_4(OMe)(MeOH)]^-$ and $Cl^-$ anions. The $Cl^-$ anion forms a hydrogen bond to each of the three other ions. This arrangement around the chloride anion, together with the atomic numbering scheme are shown in the Figure.

In the $[ZrCl_4(OMe)(MeOH)]^-$ anion the zirconium atom is octahedral, being bonded to four chlorine atoms [distances 2.480(4)—2.496(4) Å] in the equatorial plane and to two oxygen atoms in axial positions at distances of 1.847(10) and 2.264(9) Å, identified with the $OMe^-$ and MeOH ligands respectively. The hydrogen atom on O(12) was clearly resolved in a difference Fourier synthesis and refined successfully; its position is compatible with intramolecular hydrogen bonding to the chloride anion Cl(5).

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* Trimethylammonium tetrachloro(methanol)methoxozirconium(IV) chloride.

*Supplementary data available* (No. SUP 56584, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

**Table 1.** Atomic co-ordinates ( × $10^4$) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Zr | 2 772(2) | 5 226(1) | 1 462(1) | C(22) | 9 395(32) | 6 161(18) | 3 996(16) |
| Cl(1) | 980(7) | 6 692(3) | 1 472(3) | C(23) | 11 185(49) | 7 262(20) | 3 280(11) |
| Cl(2) | 3 998(7) | 3 640(3) | 1 319(3) | C(24) | 10 954(46) | 7 454(15) | 4 541(10) |
| Cl(3) | 915(8) | 4 667(4) | 2 459(2) | C(13) | −1 576(19) | 4 841(15) | 930(9) |
| Cl(4) | 4 099(6) | 5 660(3) | 325(2) | C(14) | 6 006(33) | 6 066(16) | 2 460(9) |
| Cl(5) | 363(5) | 4 273(3) | −699(2) | N(31) | 5 263(26) | 8 655(10) | 1 058(8) |
| O(11) | 4 711(16) | 5 692(9) | 1 980(6) | C(32) | 6 849(43) | 8 109(18) | 1 136(14) |
| O(12) | 359(14) | 4 719(8) | 815(5) | C(33) | 4 241(53) | 8 646(20) | 1 714(12) |
| N(21) | 11 016(22) | 6 781(10) | 3 950(8) | C(34) | 4 218(45) | 8 334(16) | 479(11) |

**Table 2.** Molecular dimensions in the $[ZrCl_4(OMe)(MeOH)]^-$ anion: distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| Zr–Cl(1) | 2.496(4) | Zr–O(11) | 1.847(10) |
| Zr–Cl(2) | 2.490(5) | Zr–O(12) | 2.264(9) |
| Zr–Cl(3) | 2.483(5) | O(11)–C(14) | 1.423(20) |
| Zr–Cl(4) | 2.480(4) | O(12)–C(13) | 1.420(17) |
| Cl(1)–Zr–Cl(2) | 168.20(16) | Cl(4)–Zr–O(11) | 95.56(39) |
| Cl(1)–Zr–Cl(3) | 89.86(18) | Cl(1)–Zr–O(12) | 83.55(32) |
| Cl(2)–Zr–Cl(3) | 88.40(18) | Cl(2)–Zr–O(12) | 84.66(32) |
| Cl(1)–Zr–Cl(4) | 89.27(17) | Cl(3)–Zr–O(12) | 84.81(30) |
| Cl(2)–Zr–Cl(4) | 90.09(17) | Cl(4)–Zr–O(12) | 83.55(29) |
| Cl(3)–Zr–Cl(4) | 168.35(18) | O(11)–Zr–O(12) | 177.5(5) |
| Cl(1)–Zr–O(11) | 94.08(43) | Zr–O(11)–C(14) | 171.4(13) |
| Cl(2)–Zr–O(11) | 97.72(43) | Zr–O(12)–C(13) | 128.6(10) |
| Cl(3)–Zr–O(11) | 96.09(39) | | |

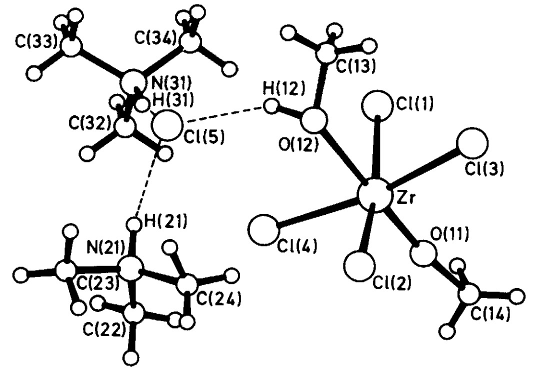

**Figure.** The structure of $[NHMe_3]_2[ZrCl_4(OMe)(MeOH)]Cl$, showing the atomic numbering scheme. Intermolecular hydrogen bonds are shown as dotted lines

**Table 3.** Structures containing M–O–Me angles >150°

| Angle | Ref. | M–O–Me/° | M–O/Å |
|---|---|---|---|
| Re–O–Me | *a* | 168.4 | 1.86 |
| U–O–Me | *b* | 178.3 | 2.04 |
| Ti–O–Me | *c* | 160.6 | 1.75 |
| Nb–O–Me | *d* | 160.3 | 1.88 |
| Ti–O–Me | *e* | 153.3 | 1.80 |
| Ti–O–Me | *f* | 171.0 | 1.77 |
| W–O–Me | *g* | 153.6 | 1.97 |
| Zr–O–Me | *h* | 171.4 | 1.847 |

[a] *trans*-Di-iodo(methoxo)oxobis(triphenylphosphine)rhenium(V)–chloroform (1/1); G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi, and M. Freni, *Inorg. Chim. Acta*, 1983, **72**, 29. [b] Dimethoxotetrakis($\eta^5$-pentamethylcyclopentadienyl)-μ-phosphido-diuranium; M. R. Duttera, V. W. Day, and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 2907. [c] Tetrakis(tetramethoxotitanium); D. A. Wright and D. A. Williams, *Acta Crystallogr., Sect. B*, 1968, **24**, 1107. [d] Bis(pentamethoxoniobium); A. A. Pinkerton, D. Schwarzenbach, L. G. Hubert-Pfalzgraf, and J. G. Riess, *Inorg. Chem.*, 1976, **15**, 1196. [e] $[(MeO)_2Ti(\mu\text{-}CH_2PMe_2CH_2)_2(\mu\text{-}OMe)_2Ti(OMe)_2]$; U. Schubert, D. Neugebauer, and W. Scharf, *J. Organomet. Chem.*, 1981, **206**, 159. [f] Methoxo(5,10,15,20-tetraphenylporphyrinato)titanium(III); ref. 7. [g] Di-μ-(methoxo)-hexamethoxobis(phenylimido)ditungsten; A. J. Nielson and J. M. Waters, *Polyhedron*, 1982, **1**, 561. [h] This work.

Dimensions of the intermolecular hydrogen bonds are Cl(5)···N(21) 3.10(3) Å, Cl(5)···H(21) 2.17 Å, Cl(5)···H(21)–N(21) 165° (symmetry position 1.5 − *x*, 1 − *y*, −0.5 + *z*); Cl(5)···N(31) 3.10(3) Å, Cl(5)···H(31) 2.18 Å, Cl(5)···H(31)–N(31) 163° (symmetry element −0.5 + *x*, 1.5 − *y*, −*z*); Cl(5)···O(12) 2.95 Å, Cl(5)···H(12) 2.354 Å, Cl(5)···H(12)–O(12) 122(6)° (symmetry element *x*, *y*, *z*). The three H···Cl(5)···H angles are 121, 76, and 108°.

With regard to the dimensions of the anion there is a clear and significant difference between the two metal–oxygen distances; indeed the Zr–O(11) bond [1.847(10) Å] is shorter than all other Zr–O bond distances in the Cambridge Data Centre files. Whereas we can find no previous structures containing the Zr–OMe moiety, there are several with a Zr–OBu$^t$ grouping which show the characteristics of an approximately linear Zr–O–C angle and a very short Zr–O distance as a common structural feature: *e.g.* $[(Et_2O)_2Li(\mu\text{-}Cl)_2ZrCl(OCBu^t)_2]$,[4] Zr–O 1.900(6) and 1.889(8) Å, Zr–O–C 166.0(8) and 171.9(6)°; [t-butoxobis($\eta^5$-cyclopentadienyl)zirconio]dicarbonyl($\eta^5$-cyclopentadienyl)ruthenium,[5] Zr–O 1.910(4) Å, Zr–O–C 169.6(4)°; t-butoxo[$\eta^2$-1-(t-butylimino)ethyl]methyl[tris(3,5-dimethylpyrazolyl)hydroborato]zirconium(IV),[6] Zr–O 1.924(6) Å, Zr–O–C 174.4(6)°. Steric effects may be a contributing factor to the expansion of the Zr–O–C angle in these compounds but such factors are not likely to be of much importance for the Zr–OMe group in the present anion.

For means of comparison we also searched the Cambridge Data Centre files for structures containing a transition metal bonded to an –OMe group. Of the 71 examples located, the mean M–O–Me angle was 128.1° and a general pattern emerged that electron-deficient metals $d^n$ ($n$ = 0, 1, or 2) feature large M–O–Me angles, within the range 130—150°, whereas for the later transition metals, angles of *ca.* 120° are normal. Examples where terminal M–O–Me angles are greater than 150° are listed in Table 3. Recent work on methoxo–metal–porphyrin complexes of first-row transition metal elements [M(OMe)(tpp)] (tpp = 5,10,15,20-tetraphenylporphyrinate; M = Ti,[7] Fe,[8,9] or Co[10]) also substantiates this bond length to bond angle correlation. With a decrease in the number of electrons in going from Co to Ti there is a shortening of the M–O bond distances commensurate with multiple-bond formation and a corresponding increase in the M–O–Me angle towards linearity. In particular M = Ti$^{III}$ ($d^1$) has M–O–Me 171° and Ti–O 1.77 Å, the latter reflecting considerable multiple bonding (*cf.* a single Ti–O bond length of *ca.* 2.0 Å)[11] and the very short Ti–O linkage [1.613(5) Å] observed in 2,3,7,8,12,13,17,18-octaethylporphyrinato-oxotitanium(IV).[12]

These structures show that the alkoxide can behave as a 'non-innocent' ligand, *i.e.* it can exist in more than one electronic and structural configuration and hence can act as a variable electron donor. The nitrosyl group (bent *versus* linear) provides a classic example of such an electron donor. In the same context the high oxophilic nature of the early transition metal elements, particularly Ti, Zr, and Hf, can be related to the facility of oxygen donors, especially alkoxo groups, to donate in excess of two electrons to available empty metal orbitals.[13] Such high $\pi$-donor capacity can obviously enhance co-ordinative saturation (18-electron rule).

Three extremes can be identified for M–O–R structures, *viz.* (*a*) a linear M–O–C bond incorporating oxygen *sp* hybridisation (180°) with two filled orthogonal $p_\pi$ orbitals, (*b*) a bent M–O–C bond involving oxygen $sp^2$ hybridisation (120°) with one filled orthogonal $p_\pi$ orbital, and (*c*) an even more bent M–O–C bond with oxygen $sp^3$ hybridisation (109.5°) and zero $p_\pi$ orbital capacity. In the present structure the almost linear Zr–O–C angle is compatible with (*a*) above, *i.e.* overlap of the two filled $p_\pi$ orbitals of oxygen and the empty $t_{2g}$ orbitals of zirconium ($d^0$) provides a linear, triple-bonded ($\sigma^2\pi^4$) zirconium–methoxide linkage. In order to complete a full $t_{2g}$ set of metal orbitals we require two further $\pi$ electrons. These can be formally supplied by the bound solvent MeOH molecule utilising oxygen $sp^2$ hybridisation with one orthogonal filled $p_\pi$ orbital. Of necessity this must involve a bent M–O–C angle based on 120° (the only alternative, oxygen $sp^3$ hybridisation, has zero $\pi$-donor capacity). Thus an electron count for the resulting complex anion gives 6e ($\sigma^2\pi^4$) from $-OMe^-$, 4e ($\sigma^2\pi^2$) from MeOH, and 2e ($\sigma^2$) from each of the four equatorial chloride ions making up an effective 18-electron valence configuration. Note that the Zr–O–C angles [171.4(13) and 128.6(10)°] differ slightly from the ideal but are in general accord with this simple electronic model. There is no evidence of steric influence. The possibility of some $\pi$ contribution from overlap of the metal $t_{2g}$ set and the filled $p_\pi$ orbitals of the equatorial chloride ions cannot be excluded. However, the zirconium–chlorine bond lengths (2.48—2.50 Å) are considerably longer than those in the parent halide (terminal Zr–Cl 2.307 Å)[14] and we suggest that the lengthening in the present instance reflects the structural adaption to $\pi$-donation of ligands in the order $MeO^-$ ($4\pi$) > MeOH ($2\pi$) > $Cl^-$ (minimal $\pi$). The superior $\pi$-donor ability of alkoxide as compared with chloride ion is well established.[13,15] Presumably the reason that $[ZrCl_4(OMe)(MeOH)]^-$ is stable with respect to subsequent 'expected' expulsion of HCl leading to six-co-ordinate species based on $[ZrCl_3(OMe)_2]^-$, *e.g.* dimer formation, $[Zr_2Cl_6(OMe)_4]^{2-}$, or monosolvated species, $[ZrCl_3(OMe)_2(MeOH)]^-$, is that all such species would provide an excess of $\pi$-electron density. One interesting possibility that would achieve a satisfactory 18-electron count is the six-co-ordinate anionic species $[ZrCl_4(OMe)_2]^{2-}$ incorporating both a linear and a bent methoxide group. However we conclude that the formation of the monoanion $[ZrCl_4(OMe)(MeOH)]^-$ represents the energetically most stable (co-ordinatively saturated) species of all those possible when taken in conjunction with a favourable lattice energy enhanced by the hydrogen bonding between the chloride anion and the three remaining ions.

*Possible Mode of Preparation.*— Reactions of alcohols with chlorozirconium(IV) [and chlorotitanium(IV)] result in solvolysis but rarely proceed completely to the direct alkoxide equivalent even in the presence of base as HCl scavenger, equation (1).[16] This ambiguity is evident in the present instance

$$MCl_x + xROH \longrightarrow M(OR)_x + xHCl \qquad (1)$$

where, although a Zr–OMe bond is formed, the product is none of the 'obvious' methanolysis products $[ZrCl_x(OMe)_{4-x}]$ ($x$ = 0, 1, 2, or 3), with or without bound solvent (MeOH) molecules.

The presence of a co-ordinated solvent (MeOH) molecule in tandem with an alkoxide linkage is somewhat surprising but not unknown in early transition metal–alkoxide chemistry.[16] We are unable to provide a plausible reaction scheme since there are almost certainly other reaction products; however there are several points to note. Replacement of L by solvent molecules in the original $[ZrCl_4L_2]$ is more likely to be associative than dissociative based on the known tendency for $Zr^{IV}$ to show co-ordination greater than six. Five-co-ordinate $Zr^{IV}$ species are extremely unlikely. Expulsion of HCl provides a ready proton source for formation of the $[NHMe_3]^+$ cation with free L acting as an 'internal' scavenger. The retention of four chlorines to each $Zr^{IV}$ centre in the product implies $Cl^-$ attack at some stage: replacement of bound solvent MeOH by $Cl^-$ released by the favourable equilibrium $NHMe_3Cl = [NHMe_3]^+ + Cl^-$ in methanolic solution is one possibility.

Following the same approach we have isolated $[NHMe_3]_2[HfCl_4(OMe)(MeOH)]Cl$ as colourless crystals from methanolysis of $[HfCl_4L_2]$ (Found: C, 17.6; H, 5.0; Cl, 32.6; Hf, 33.0; N, 5.2. Calc. for $C_8H_{27}Cl_5HfN_2O_2$: C, 17.8; H, 5.0; Cl, 32.9; Hf, 33.1; N, 5.2%). The compound is isomorphous with its zirconium(IV) counterpart as confirmed by *X*-ray diffraction studies.

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