Journal of Organometallic Chemistry, 265 (1984) 167–173
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STRUCTURAL CHEMISTRY OF BIMETALLIC HYDRIDE COMPLEXES OF TITANIUM AND ALUMINIUM

I. CRYSTAL AND MOLECULAR STRUCTURE OF $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2AlH_2]_2(CH_3)_2NCH_2CH_2N(CH_3)_2C_6H_6$

E.B. LOBKOVSKII, G.L. SOLOVEICHIK,

Institute of New Chemical Problems, Academy of Sciences of the U.S.S.R., Chernogolovka 142432 (U.S.S.R.)

A.I. SISOV, B.M. BULYCHEV*,

Moscow State University, Chemical Department, Moscow 117234 (U.S.S.R.)

A.I. GUSEV and N.I. KIRILLOVA

Institute of Organo-Element Compounds, Moscow 111123 (U.S.S.R.)

(Received October 25th, 1983)

Summary

The structure of a titanium aluminium hydride complex of composition $[(C_5H_5)_2TiAlH_4]_2(CH_3)_2NC_2H_4N(CH_3)_2C_6H_6$ has been determined by X-ray diffraction. The complex forms triclinic crystals with unit cell dimensions $a = 8.406(2)$, $b = 10.117(2)$, $c = 11.269(3)$ Å; $\alpha = 112.01(2)°$, $\beta = 109.25(2)°$, $\gamma = 87.04(2)°$, space group $P\bar{1}$, $Z = 2$ and density $d = 1.21$ g/cm^3. The structure was refined to give a discrepancy index $R = 0.056$. The crystals are composed of centrosymmetric molecules of $(Cp_2TiAlH_4)_2$TMEDA (Cp = η^5-cyclopentadienyl) and molecules of crystal benzene. Two moieties of $Cp_2TiH_2AlH_2$ are linked by a tetramethylethylenediamine molecule (r_{Al-N} 2.11 Å). The aluminium atom is bonded to a titanium atom by a double hydride bridge ($r_{Al-H}b = 1.8$, 1.6 Å, $r_{Ti-H}b = 1.6$ Å), and has trigonal bipyramidal stereochemistry, $[H_4N]$ ($r_{Al-H}t = 1.6$ Å).

Introduction

Up to now, the structures of bimetallic hydride complexes of transition metals and aluminium of type $L_mM(AlH_4)$ have been investigated mainly by indirect methods (IR and ESR spectroscopy) [2–4], in contrast to the thoroughly-studied boron hydride analogues [1]. The only exceptions have been the hydride complexes of yttrium and aluminium that are stabilized by cyclopentadienyl ligands [5]. Even

0022-328X/84/$03.00

these few examples have shown that the structural chemistry of the aluminium and transition metal hydride compounds is much richer, owing to the larger number of coordination possibilities of aluminium than that of the corresponding boron hydrides, which have only the tetrahedral stereochemistry of boron [1]. Of special interest are the structures of the hydride complexes of aluminium and dicyclopentadienyltitanium(III) produced in the systems $(\eta^5\text{-}C_5H_5)_2TiCl_2\text{-}LiAlH_4$ and $(\eta^5\text{-}C_5H_5)_2TiX_2\text{-}LiAlH_4$ which display high catalytic activity in hydrogenation and isomerization of olefins [6,7]. One of these complexes, $(\eta^5\text{-}C_5H_5)TiAlH_4$, is relatively unstable [8]. However, the addition of tetramethylethylenediamine (TMEDA) to an ether/benzene solution of this complex stabilizes the complex and precipitates a compound of formula $[(\eta^5\text{-}C_5H_5)_2TiAlH_4]_2TMEDA \cdot C_6H_6$. The results of the structural studies are presented below.

Results and discussion

Crystals of $(Cp_2TiAlH_4)_2(CH_3)_2NCH_2CH_2N(CH_3)_2 \cdot C_6H_6$ are composed of centrosymmetric, dumbbell-shaped molecules of $Cp_2TiH_2AlH_2(CH_3)_2NCH_2CH_2N(CH_3)_2H_2AlH_2TiCp_2$ (I), with molecules of benzene filling in the gaps between (Fig. 1). The introduction of benzene apparently facilitates the packing of I in the crystal and produces a monocrystalline preparation distinct from the finely-dispersed compound of composition $(Cp_2TiAlH_4)_2 \cdot$ TMEDA which separates from pure ethereal solutions. Toluene also acts as a stabilizer. Heating eliminates crystal benzene and toluene from the molecule without causing decomposition of the hydride framework and splitting of diamine.

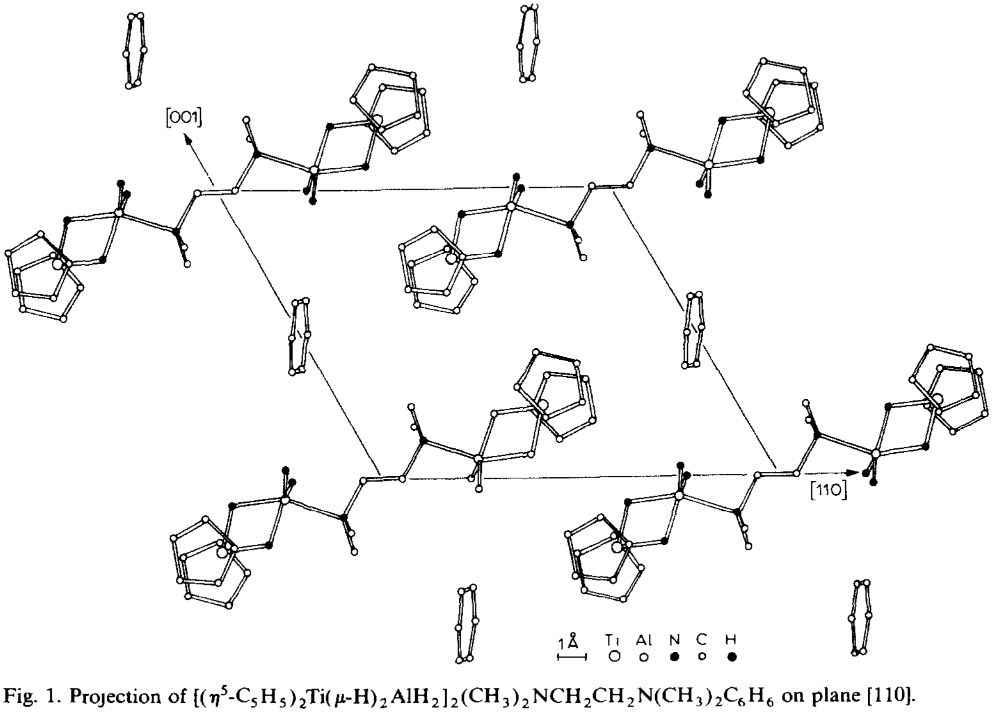


Fig. 1. Projection of $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2AlH_2]_2(CH_3)_2NCH_2CH_2N(CH_3)_2C_6H_6$ on plane [110].

Molecules of I occupy centres of inversion (0,0,0) in the crystal, while the benzene rings lie in the centres (0,0,1/2). The intermolecular distances do not exceed the corresponding Van der Waals contacts.

Two $Cp_2TiH_2AlH_2$ moieties of I are bonded via a bidentate ligand (TMEDA) by donor-acceptor Al ← N bonds (Fig. 2). Titanium coordinates to two planar cyclopentadienyl rings (C_5H_5) (deviation from planarity does not exceed 0.01 Å), forming an inclined sandwich with an angle, φ, of 40.6°. The average Ti–C distance equals 2.36 Å (range of variation: 2.32–2.39 Å) (Table 2). Two bridging hydrogens which bond titanium to aluminium lie in the bisecting plane of the inclined sandwich. The interatomic Ti–Al distance equals 2.788 Å and thus approaches the sum of the covalent radii of the metals (2.62 Å). It is interesting that the same Ti–Al distance is observed in the molecules of $[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$ (2.82 Å) [9] and $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$ (2.79 Å) [10], in which carbon of the C_5H_4 group occupies one of the bridging positions in the cycle $\mathrm{Ti}{<}\begin{smallmatrix}x\\ \\x\end{smallmatrix}{>}\mathrm{Al}$ and hydrogen the other. The fact that the Ti–Al distance is close to the sum of the covalent radii may be explained by weak, direct metal–metal interaction. This, in general, agrees well with the noticeable increase (ESR data) in the spin density of an unpaired electron at aluminium in passing from the chlorine-bridged complex $\mathrm{Ti}{<}\begin{smallmatrix}\mathrm{Cl}\\ \\\mathrm{Cl}\end{smallmatrix}{>}\mathrm{Al}$ (in which the interatomic distance obviously exceeds the sum of covalent radii) to the hydride analogues with $\mathrm{Ti}{<}\begin{smallmatrix}\mathrm{H}\\ \\\mathrm{H}\end{smallmatrix}{>}\mathrm{Al}$ [2]. Nevertheless, up to now we have no direct proof of the formation of a metal titanium–aluminium bond. Without taking the latter into account, the coordination polyhedron of aluminium is a distorted trigonal bipyramid. Nitrogen and bridging hydrogen (1) occupy axial positions, while the second bridging hydrogen (2) and the terminal hydride atoms H(3) and H(4) lie in equatorial positions. The distance Al–axial H, as suggested previously, somewhat exceeds the distance Al–H to the other hydrogen occupying an equatorial position in the bridge $\mathrm{Ti}{<}\begin{smallmatrix}\mathrm{H}\\ \\\mathrm{H}\end{smallmatrix}{>}\mathrm{Al}$. The observed asymmetry of the bridge agrees with the increase in the number of absorption bands $\nu(\mathrm{Ti{-}H^{M}{-}Al})$ observed in the IR spectrum of I, compared with non-solvated $CH_2(C_5H_4)_2TiH_2AlH_2$ [11] in which

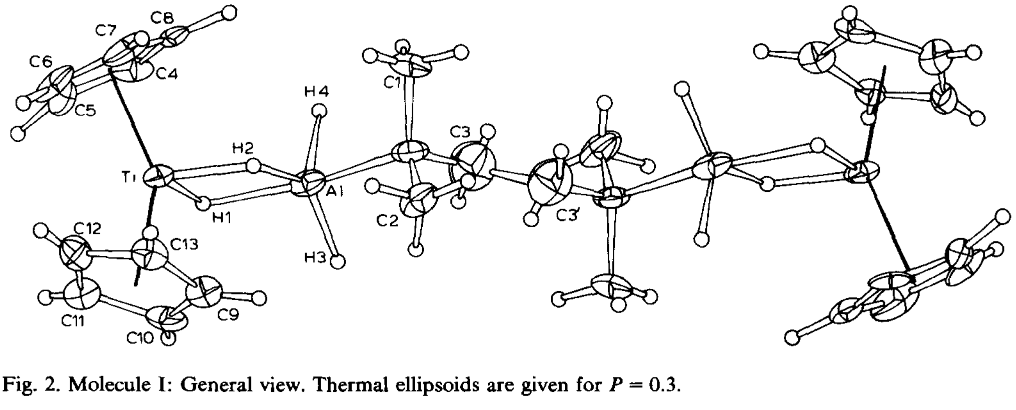


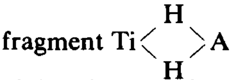
Fig. 2. Molecule I: General view. Thermal ellipsoids are given for $P = 0.3$.

TABLE 1

COORDINATES OF SYMMETRICALLY-INDEPENDENT ATOMS[a]
(For Ti, Al, N, $\times 10^4$; for C and H, $\times 10^3$.)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
Ti	5306(2)	4920(2)	2442(2)	3.7	H(5)	413(15)	104(13)	269(11)	9
Al	2853(3)	2680(3)	649(3)	5.3	H(6)	284(16)	−17(13)	232(11)	8
N	1918(8)	1303(7)	1329(7)	6.0	H(7)	359(14)	5(12)	102(11)	8
C(1)	333(1)	47(1)	188(1)	6.7	H(8)	90(15)	149(13)	288(11)	9
C(2)	123(1)	212(1)	244(1)	6.7	H(9)	54(15)	262(12)	198(11)	9
C(3)	62(2)	38(2)	1(1)	11.2	H(10)	223(15)	277(13)	327(11)	6
C(4)	718(2)	358(2)	137(1)	6.9	H(11)	92(14)	−33(13)	−20(11)	10
C(5)	784(1)	499(2)	202(2)	6.6	H(12)	60(14)	60(12)	−100(11)	10
C(6)	828(1)	533(2)	338(2)	7.0	H(13)	701(14)	319(12)	64(11)	11
C(7)	784(2)	417(3)	363(2)	8.1	H(14)	788(14)	576(12)	154(11)	4
C(8)	715(1)	307(1)	234(2)	7.0	H(15)	861(14)	618(12)	422(11)	8
C(9)	299(1)	600(1)	312(1)	5.2	H(16)	786(14)	408(12)	440(10)	10
C(10)	307(1)	645(1)	211(1)	5.9	H(17)	675(14)	207(12)	227(10)	10
C(11)	462(2)	727(1)	259(1)	6.2	H(18)	214(13)	542(12)	317(10)	12
C(12)	548(1)	729(1)	388(1)	5.7	H(19)	260(14)	630(12)	120(11)	8
C(13)	449(1)	652(1)	423(1)	5.4	H(20)	509(15)	756(12)	209(12)	6
C(14)	147(2)	939(2)	511(2)	8.2	H(21)	640(14)	750(12)	420(11)	10
C(15)	27(3)	913(1)	386(2)	8.3	H(22)	488(14)	649(12)	501(11)	9
C(16)	882(2)	969(2)	376(1)	7.5	H(23)	236(14)	893(13)	522(11)	3
H(1)	407(11)	421(10)	86(9)	0	H(24)	69(14)	850(12)	306(11)	11
H(2)	408(12)	361(10)	226(9)	1	H(25)	794(11)	951(12)	299(11)	9
H(3)	118(12)	304(10)	2(9)	1					
H(4)	365(12)	135(10)	−31(9)	2					

[a] For non-hydrogen atoms $B_{iso}^{eq} = 4/3 \sum_i \sum_j b_{ij} \vec{a}_i \vec{a}_j$ [17].

the fragment  $\mathrm{Ti}\langle{}^{\mathrm{H}}_{\mathrm{H}}\rangle\mathrm{Al}$ is apparently symmetrical. The coordination polyhedron of aluminium is not unique in the structural chemistry of aluminium. As to the hydride hydrogens, only one more compound of aluminium, $(Cp_2YH)_2(AlH_3NEt_3)_2$ [5], reveals them to be in a trigonal bipyramid, $[H_4L]$. In this compound, two hydrogens are bridging and two are terminal; the distance Al–N (2.13 Å) is close to that in I (Table 2).

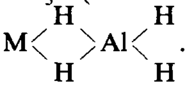
The hydride hydrogens, especially the bridging hydrogens (Table 1), have anomalously small coefficients of thermal vibration. This, in the given case, points not to limited thermal motion of the atoms but rather to excessive electron density on the atoms. And, indeed, the maximum electron densities corresponding to the hydride atoms exceed the peaks of the other hydrogens in molecule 1 by 1.5–2 times. The shift in electron density should apparently be attributed to charge transfer from nitrogen to the electron-deficient system TiH_2Al. This is also expressed in the shortening of the Al–N bond to 2.11 Å, compared with 2.195 Å in $AlH_3 \cdot TMEDA$ possessing trigonal–bipyramidal stereochemistry of aluminium, $[H_3N_2]$ [12]. A pronounced increase in φ in the inclined sandwich, compared with $CpTiBH_4$ (136°) [13], indicating an increase in the electron density on titanium, also agrees with the above. Greater nucleophilicity of the hydride atoms in I presupposes an increase in the ionic contribution in the bonding of two atomic groups, as compared with the covalent boron hydride of dicyclopentadienyltitanium(III). This, however, does not give us the grounds to regard the hydride compounds of titanium and aluminium as ionic aluminium hydrides. The latter are constructed of discrete cations and tetrahedral anions ($[AlH_4]^-$) and are not characterized by the ligand coordination at aluminium [14]. It seems to be more expedient to class $Cp_2Ti(\mu\text{-}H_2)\text{-}AlH_2 \cdot TMEDA \cdot C_6H_6$ with a new type of hydride aluminium compounds, which may be considered derivatives of the donor–acceptor complexes of aluminium hydride of type AlH_3L (the so-called alanes) and covalent aluminium hydrides with the metallocycle  $\mathrm{M}\langle{}^{\mathrm{H}}_{\mathrm{H}}\rangle\mathrm{Al}\langle{}^{\mathrm{H}}_{\mathrm{H}}$.

TABLE 2

MAIN BOND LENGTHS (*d*, in Å)

Bond	*d*	Bond	*d*	Bond	*d*
Ti–C(4)	2.36(1)	Ti–C(9)	2.39(1)	Ti–H(1)	1.63(8)
Ti–C(5)	2.34(2)	Ti–C(10)	2.39(1)	Ti–H(2)	1.60(11)
Ti–C(6)	2.36(1)	Ti–C(11)	2.37(1)	Ti···Al	2.788
Ti–C(7)	2.37(2)	Ti–C(12)	2.32(1)	Ti···CpI [a]	2.04
Ti–C(8)	2.36(1)	Ti–C(13)	2.34(1)	Ti···CpII [a]	2.04
Al–N	2.11(1)	C(4)–C(5)	1.38(2)	C(9)–C(10)	1.39(2)
Al–H(1)	1.80(11)	C(5)–C(6)	1.36(2)	C(10)–C(11)	1.41(2)
Al–H(2)	1.68(8)	C(6)–C(7)	1.40(3)	C(11)–C(12)	1.39(2)
Al–H(3)	1.45(9)	C(7)–C(8)	1.40(2)	C(12)–C(13)	1.41(2)
Al–H(4)	1.65(9)	C(8)–C(4)	1.38(3)	C(13)–C(9)	1.41(1)
N–C(1)	1.52(1)	N–C(2)	1.50(1)	N–C(3)	1.50(1)
(Ti–C)aver.	2.36	(C–C)aver.	1.39	C(3)–C(3)′	1.32
C(14)–C(15)	1.37(3)	C(15)–C(16)	1.31(3)	C(16)–C(14)′	1.36

[a] CpI and CpII are the r.m.s. planes for C(4)–C(8) and C(9)–C(13), respectively.

TABLE 3

VALENCE ANGLES (ω, in °)

Angle	ω	Angle	ω
CpI/CpII [a]	139.4	H(1)-Al-H(2)	66(5)
H(1)-Ti-H(2)	71(5)	H(1)-Al-H(3)	99(5)
N-Al-H(1)	155(3)	H(1)-Al-H(4)	102(5)
N-Al-H(2)	89(4)	H(2)-Al-H(3)	124(5)
N-Al-H(3)	93(5)	H(2)-Al-H(4)	118(4)
N-Al-H(4)	92(4)	H(3)-Al-H(4)	118(4)
Al-N-C(1)	110.1(6)	C(1)-N-C(2)	107.8(7)
Al-N-C(2)	111.3(6)	C(1)-N-C(3)	112.8(5)
Al-N-C(3)	99.5(4)	C(2)-N-C(3)	115.1(5)
C(4)-C(5)-C(6)	107(2)	C(9)-C(10)-C(11)	109(1)
C(5)-C(6)-C(7)	110(1)	C(10)-C(11)-C(12)	107(1)
C(6)-C(7)-C(8)	105(2)	C(11)-C(12)-C(13)	109(1)
C(7)-C(8)-C(4)	108(2)	C(12)-C(13)-C(9)	107(1)
C(8)-C(4)-C(5)	109(1)	C(13)-C(9)-C(10)	108(1)
Ti-H(1)-Al	109(5)	Ti-H(2)-Al	115(5)
C(14)-C(15)-C(16)	120(1)	C(15)-C(16)-C(14)′	120(1)
C(15)-C(14)-C(16)′	119(1)		

[a] CpI and CpII are the r.m.s. planes for C(4)-C(8) and C(9)-C(13), respectively.

The results of X-ray analysis of I confirm the assumptions made on the basis of indirect physico-chemical studies: Al and Ti bond via a double hydrogen bridge [2,15], and the molecule $Cp_2TiH_2AlH_2$ solvates at aluminium in donor-type solvents [15,16]. The data are extremely important from a synthetic point of view, since they pave the way for the stabilization of unstable bimetallic complexes of transition and non-transition metals.

Experimental

Preparation

The complex compound $(Cp_2TiAlH_4)_2 \cdot TMEDA \cdot C_6H_6$ was obtained [16] by mixing stoichiometric quantities of $(Cp_2TiCl)_2$ and $LiAlH_4$ in ether/benzene, followed by the subsequent separation of LiCl and the addition of a calculated amount of TMEDA. Crystals of composition $(Cp_2TiAlH_4)_2 \cdot TMEDA \cdot C_6H_6$ precipitated from the solution. Found: Ti, 14.9; Al, 8.4; H_{act}, 1.4%. Calculated for $[(C_5H_5)_2TiAlH_4]_2[(CH_3)_2N(C_2H_4)N(CH_3)_2]C_6H_6$: Ti, 15.65; Al, 8.82; H_{act}, 1.31%.

Determination of crystal structure

The crystals of the compound are triclinic, with unit cell dimensions $a = 8.406(2)$, $b = 10.117(2)$, $c = 11.269(3)$ Å, $\alpha = 112.01(2)°$, $\beta = 109.25(2)°$, $\gamma = 87.04(2)°$, $V = 836.0(4)$ Å^3, space group $P\bar{1}$, $Z = 2$ ($CpTiAlH_4 \cdot 1/2TMEDA \cdot 1/2C_6H_6$), $d_{dif} = 1.21$ g/cm^3. Crystal data were determined on a Syntex P3 diffractometer (Mo-K_α, graphite monochromator, $\theta/2\theta$-scan, $2\theta \leqslant 38°$, 1224 reflections from monocrystal ($0.2 \times 0.3 \times 0.5$ mm^3) placed in a glass capillary).

The structure was resolved by direct methods. The hydride hydrogens were localized by difference Fourier synthesis, and the hydrogens of the organic fragments were partly found from the difference series and partly from geometric calculations. The structure was refined by the full-matrix least-squares method. The non-hydrogen atoms were refined to an anisotropic approximation. Two cycles of coordinate refinement were conducted, and B_{iso} was determined for the hydrogen atoms. The final R-factor (0.056) was found from 834 reflections. Table 1 gives the coordinates of symmetrically-independent atoms, and Tables 2 and 3 the main bond lengths and valence angles.

References

1 T.J. Marks and J.R. Kolb, Chem. Rev., (1977) 263.
2 G. Henrici-Olive and S. Olive, J. Organomet. Chem., 23 (1970) 155.
3 P.C. Wailes and H. Weigold, J. Organomet. Chem., 24 (1970) 405.
4 V.M. Ischenko, G.L. Soloveichik and B.M. Bulychev, Zh. Neorg. Khim., 29 (1984) 119.
5 V.K. Bel'skii, A.B. Erofeev, B.M. Bulychev and G.L. Soloveichik, J. Organomet. Chem., 265 (1984) 123.
6 R. Stern and L. Sajus, Tetrahedron Lett., (1968) 6313.
7 E.V. Evdokimova, G.L. Soloveichik and B.M. Bulychev, Kinet. Katal., 23 (1982) 1109.
8 G.L. Soloveichik, Dissertation, MGU, 1976.
9 L.J. Guggenberger and F.N. Tebbe, J. Am. Chem. Soc., 95 (1973) 7870.
10 F.N. Tebbe and L.J. Guggenberger, J. Chem. Soc., Chem. Commun., (1973) 227.
11 A.I. Sizov and B.M. Bulychev, Zh. Neorg. Khim., 26 (1981) 2652.
12 G.J. Palenik, Acta Crystallogr., 17 (1964) 1573.
13 K.M. Melmed, D. Coucouvanis and S.J. Lippard, Inorg. Chem., 12 (1973) 232.
14 N.M. Alpatova, V.V. Gavrilenko, Yu.M. Kessler, O.P. Osipov and D.N. Maslin, The Complexes of Organometallic, hydride and halogen compounds of aluminium, Nauka, Moscow, 1970.
15 B.M. Bulychev, A.L. Kostenko, N.A. Yakovleva and G.L. Soloveichik, Trans. Met. Chem., 6 (1981) 32.
16 A.I. Sizov, G.L. Soloveichik and B.M. Bulychev, Koord. Khim., in press.
17 W.C. Hamilton, Acta Crystallogr., 12 (1959) 609.