Journal of Organometallic Chemistry, 69 (1974) 271—278
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CRYSTAL AND MOLECULAR STRUCTURE OF TETRACARBONYLIODO-[*o*-PHENYLENEBIS(DIMETHYLARSINO)]TUNGSTEN(II) TRIIODIDE

MICHAEL G.B. DREW

Department of Chemistry, The University, Whiteknights,
Reading RG6 2AD (Great Britain)

JOHN D. WILKINS

Donnan Laboratories, University of Liverpool, Grove Street,
P.O.Box 147, Liverpool L69 3BX (Great Britain)

(Received August 30th, 1973)

Summary

Crystals of the title compound are monoclinic, spacegroup $P2_1/m$; a = 14.43(1), b = 10.86(1), c = 8.01(1) Å; β = 93.51(8)°; Z = 2. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by least squares to R 0.07 for 1544 independent reflections. The cations have crystallographic m symmetry with the metal and iodine atoms on the mirror plane. The metal atom has a capped trigonal prismatic environment with the iodine atom in the unique capping position [2.842(3) Å], two arsenic atoms [2.636(2) Å] and two carbonyl groups [2.067(24) Å] in the capped quadrilateral face and two carbonyl groups [1.988(25) Å] in the remaining edge. The distortions of the geometry from the ideal are very small despite the variations in ligand type in the quadrilateral face. The triiodide anion is asymmetrical with dimensions [2.895(3), 2.957(4) Å, 178.6(1)°].

Introduction

We have been studying the crystal structures of a number of seven-coordinate complexes in an attempt to understand the various factors which dictate the arrangement of the ligands around the central metal atom. As part of this series we report here the crystal structure of the cation $[W(CO)_4(Diars)I]^+$, Diars = *o*-phenylenebis(dimethylarsine), (I). We wished to compare the structure of (I) with those of other seven-coordinate complexes containing one halogen atom and six smaller atoms in the coordination sphere. In most examples such as $[Mo(CNR)_6I]^+$ [1] (II), $[Mo(Diars)_2(CO)_2Cl]^+$ [2] (III), $[W(Dmpe)_2(CO)_2I]^+$, Dmpe = 1,2-bis(dimethylphosphino)ethane [3] and $W(CO)_3Br \cdot GeBr_3(2,2'\text{-bipyridine})$ [4], the geometry is a capped trigonal prism with the halogen atom occupying the unique capping position. Other geometries have been found; in

$Zr(Acac)_3Cl$ [5], Acac = acetylacetonate, the chlorine atom occupies an axial position in a pentagonal bipyramid and in $NbX(OMe)_2(Dedtc)_2$ [6], X = Cl, Br, Dedtc = diethyldithiocarbamate, the halogen atom occupies an equatorial position of a pentagonal bipyramid.

The structure of (I) is of particular interest as the cation is primarily monodentate, and unlike the situation in the case of all the examples cited above with the single exception of (II), steric effects are not of paramount importance. Indeed as for (II), a configuration in all three ideal geometries for seven-coordination (capped octahedral, CO, C_{3v}, capped trigonal prism, CTP, C_{2v} and pentagonal bipyramid, PB, D_{5h}) seemed reasonable.

Experimental

$W(Diars)(CO)_4I]^+I_3^-$ was prepared by the published method [7] and recrystallised from acetone solution by slow evaporation of the solvent at 0° (for ca. 2 days).

Crystal data: $C_{14}H_{16}As_2I_4WO_4$, mol. wt. 1089.95, monoclinic, $a = 14.43(1)$, $b = 10.86(1)$, $c = 8.01(1)$ Å, $\beta = 93.51(8)°$, $Z = 2$, $U = 1253.7$ Å^3, $d_m = 2.8(1)$, $d_c = 2.87$, $F(000) = 968$, Mo-K_α radiation $\lambda = 0.7107$ Å, $\mu = 126.3$ cm^{-1}. Spacegroup confirmed as $P2_1/m$ by the systematic absences, $0k0$, $k = 2n + 1$ and the successful structure determination.

A crystal with dimension ca. 0.025 × 0.3 × 0.4 mm was mounted with the (011) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium-filtered molybdenum X-radiation was used. The stationary-crystal-stationary-counter method was used to measure 2188 independent reflections with $2\theta < 50°$ and counts were taken for 10 s. Individual backgrounds were taken for those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were measured repeatedly during the course of the experiment but no significant changes in intensity were observed. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0.03I^2)]^{\frac{1}{2}}$, where E is the estimated background of the reflection. 1544 reflections with $I > \sigma(I)$ were used in subsequent calculations. An absorption correction was applied using the program ABSORB (see ref. 8). Transmission factors varied between 0.05 and 0.72. No extinction correction was applied.

Determination of the structure and refinement

The structure was determined from Patterson and Fourier syntheses and refined successfully in spacegroup $P2_1/m$. The cation had crystallographic m symmetry with the tungsten and iodine atoms in special positions 2(e). The remaining atoms in the cation occupied general positions 4(f). All three iodine atoms in the triiodide anion were in special positions 2(e), thus the anion was contained in the mirror plane but had no imposed symmetry. The structure was refined, using the 1516 non-zero reflections with all atoms given anisotropic thermal parameters defined as $\exp(-2\pi^2 \sum_{ij}\sum U_{ij,a_i^*} \cdot h_i \cdot h_j;\ i,j = 1,2,3)$, to R 0.070.

TABLE 1

ATOMIC COORDINATES (× 10^5 FOR W, I, As, × 10^4 FOR C,O) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
W	35724(9)	25000[a]	24293(15)
I(1)	43677(17)	25000[a]	—07294(30)
I(2)	94064(18)	25000[a]	17605(34)
I(3)	79258(17)	25000[a]	41532(28)
I(4)	64420(20)	25000[a]	64266(33)
As(1)	24056(16)	09759(20)	08328(27)
C(1)	3147(15)	1425(26)	4239(28)
O(1)	2918(16)	0802(19)	5335(24)
C(2)	4648(16)	1267(23)	2901(31)
O(2)	5220(16)	0620(22)	3132(27)
C(3)	2949(16)	—0329(24)	—0340(28)
C(4)	1495(18)	0087(24)	2122(33)
C(5)	1659(18)	1852(19)	—0893(22)
C(6)	1126(18)	1216(27)	—2095(31)
C(7)	0616(19)	1846(26)	—3294(32)

[a] Parameters not refined.

Earlier refinement before an absorption correction had been applied gave R 0.11. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 60$ and $\sqrt{w} = 60/F_o$ for $F_o > 60$. Calculations were made on a C.D.C. 7600 computer at the University of London Computer Centre using the programs described in ref. 8. Atomic scattering factors for tungsten, iodine, arsenic, carbon and oxygen were taken from ref. 9 as were the corrections for the real and imaginary part of the anomalous dispersion for the tungsten, iodine and arsenic atoms.

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (× 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	31.6(7)	38.9(7)	30.9(6)	0[a]	0.0(5)	0[a]
I(1)	51.4(15)	73.3(16)	50.2(13)	0[a]	17.5(11)	0[a]
I(2)	55.8(15)	50.0(13)	73.7(16)	0[a]	13.2(12)	0[a]
I(3)	60.4(15)	42.1(11)	49.3(12)	0[a]	—2.2(10)	0[a]
I(4)	62.8(17)	80.7(18)	56.3(14)	0[a]	9.0(12)	0[a]
As(1)	39.1(12)	36.7(12)	38.9(11)	0.7(9)	2.7(9)	0.4(9)
C(1)	30(11)	72(16)	41(12)	03(11)	03(10)	13(13)
O(1)	98(17)	73(13)	57(11)	—01(12)	03(11)	28(10)
C(2)	30(12)	49(14)	65(15)	—02(12)	04(11)	—16(12)
O(2)	65(14)	87(15)	85(15)	28(13)	—08(11)	—01(12)
C(3)	38(13)	57(14)	48(12)	15(11)	—12(10)	17(12)
C(4)	51(16)	53(15)	74(16)	—31(13)	30(14)	—10(13)
C(5)	45(12)	44(11)	20(08)	24(10)	—00(8)	10(8)
C(6)	49(14)	69(17)	49(13)	10(14)	—03(11)	—11(13)
C(7)	67(18)	61(15)	56(15)	—07(14)	—28(13)	02(13)

[a] Parameters not refined.

A difference Fourier map was calculated after the refinement had been concluded but showed no significant peaks. The 644 zero reflections had no large discrepancies. In the final cycle of refinement, no shift was greater than 0.05σ. The final list of coordinates and thermal parameters are given in Tables 1 and 2. Table 3 lists the bond distances and angles in the molecule, except for the angles subtended at the metal atom which are listed in Table 4. The final observed and calculated structure factors can be obtained from the authors on request.

Discussion

The unit cell of $[W(CO)_4(Diars)I]^+I_3^-$ is shown in Fig. 1, the *c* projection, together with the atomic numbering scheme. The geometry of the coordination sphere of the cation (I) is a capped trigonal prism with the iodine atom in the unique capping position [2.842(3) Å], two arsenic atoms of the bidentate Diars ligand [2.636(2) Å] and two carbonyl groups [2.067(24) Å] in the capped quadrilateral face and two further carbonyl groups in the remaining edge [1.988(25) Å]. This idealised geometry is shown in Fig. 2 and angles subtended at the metal atom are compared with those found in two other capped trigonal prisms, namely $[Mo(CNR)_6I]^+$ (II) and $[Mo(Diars)_2(CO)_2Cl]^+$ (III) in Table 4.

The W—I(1) bond length of 2.842(3) Å in (I) is comparable with the Mo—I bond length of 2.862(3) Å in (II). This is not surprising as the iodine atoms both occupy the capping position of the CTP and W^{II} and Mo^{II} radii are very similar. For instance in the two capped octahedral seven-coordinate complexes $WBr_2(CO)_3(Dam)_2$ and $MoBr_2(CO)_2(Dam)_2$ [10], Dam = bis(diphenylarsino)-methane, W—Br bond lengths are 2.64 and 2.67 Å and Mo—Br lengths are 2.65, 2.67 Å. The W—As bonds in (I), 2.636(2) Å, are slightly longer than the Mo—As bond lengths in (III) [2.614(5), 2.617(5) Å], but shorter than the bonds in

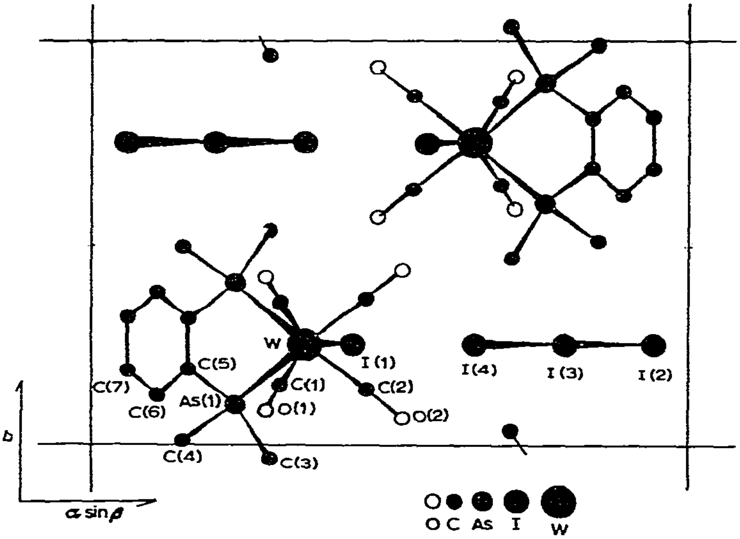

Fig. 1. The unit cell of $[W(CO)_4(Diars)I]^+I_3^-$ in the *c* projection.

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°)[a,b]

I(2)—I(3)	2.957(4)	I(2)—I(3)—I(4)	178.6(1)
I(3)—I(4)	2.895(4)	W—As(1)—C(3)	116.0(7)
W—I(1)	2.842(3)	W—As(1)—C(4)	118.6(8)
W—As(1)	2.636(2)	W—As(1)—C(5)	110.3(6)
W—C(1)	1.988(25)	C(3)—As(1)—C(4)	101.7(11)
W—C(2)	2.067(24)	C(3)—As(1)—C(5)	103.9(9)
As(1)—C(3)	1.897(25)	C(4)—As(1)—C(5)	104.7(10)
As(1)—C(4)	1.972(27)	W—C(1)—O(1)	178.0(20)
As(1)—C(5)	1.949(19)	W—C(2)—O(2)	179.1(23)
C(1)—O(1)	1.17(3)	As(1)—C(5)—C(6)	120.7(20)
C(2)—O(2)	1.09(3)	As(1)—C(5)—C(5$^{\mathrm{I}}$)	119.2(14)
C(5)—C(6)	1.38(3)	C(6)—C(5)—C(5$^{\mathrm{I}}$)	120.1(19)
C(5)—C(5$^{\mathrm{I}}$)	1.41(3)	C(5)—C(6)—C(7)	119.7(25)
C(6)—C(7)	1.36(4)	C(6)—C(7)—C(7$^{\mathrm{I}}$)	120.2(24)
C(7)—C(7$^{\mathrm{I}}$)	1.42(4)		

[a] Angles subtended at the metal atom given in Table 4. [b] The meaning of the superscript I is defined in Table 5.

$WBr_2(CO)_3(Dam)_2$ [2.65, 2.67 Å]. Two factors weaken metal—arsenic bonds; excessive steric crowding (which site in which polyhedron?) and π-bonding effects. For instance, it has been found that in Mo^{II}— and W^{II}—CO structures, M—P and M—As bonds are weakened by the *trans* influence of carbonyl groups to the extent of 0.03 to 0.11 Å [11]. Thus it can be argued that π-bonding effects will increase the W—As bond length in (I) with respect to the Mo—As bonds in (III) while steric effects will have the opposite effect, the net result being an insignificant difference. The variations in the metal—carbon bond

TABLE 4

A COMPARISON OF THE ANGLES (°) IN THE COORDINATION POLYHEDRON OF (I), (II) AND (III)[a]

Number	Angle in	(I)	(II)	(III)
1	I(1)—W—As(1)	81.3(1)		81.2(2), 82.2(2)
	I(1)—W—C(2)	79.8(7)	81.4(5), 81.6(5)	
2	As(1)—W—As(1$^{\mathrm{I}}$)	77.8(7)		75.6(1)
	C(2)—W—C(2$^{\mathrm{I}}$)	80.8(19)	85.5(7)	
3	C(1)—W—As(1)	76.6(7)		76.3(9), 78.1(11)
	C(1)—W—C(2)	75.4(10)	74.6(6), 74.5(6)	
4	C(1)—W—As(1$^{\mathrm{I}}$)	120.4(7)		118.3(7), 116.6(9)
	C(1)—W—C(2$^{\mathrm{I}}$)	120.6(10)	120.5(6), 120.8(6)	
5	I(1)—W—C(1)	144.0(7)	145.2(6), 145.1(6)	145.3(16), 147.0(18)
6	C(1)—W—C(1$^{\mathrm{I}}$)	72.0(10)	69.7(9)	67.7(24)
7	As(1)—W—C(2)*	97.6(7)	88.4(7), 92.2(7)	101.6(2), 102.2(2)
8	As(1)—W—C(2$^{\mathrm{I}}$)*	161.0(7)	163.0(7)	163.4(2)

[a] There are eight unique angles in a CTP with C_{2v} symmetry and the angles in the Table are numbered accordingly (see Fig. 2). Angles subtended at the metal by the same atoms (ignoring differences in metal and halogen type) in the same sites in the three cations are listed on the same line. In addition for the two angles marked * which are unique to (I), angles subtended from the same sites in (II) and (III) are compared even though the sites are occupied by different atoms.

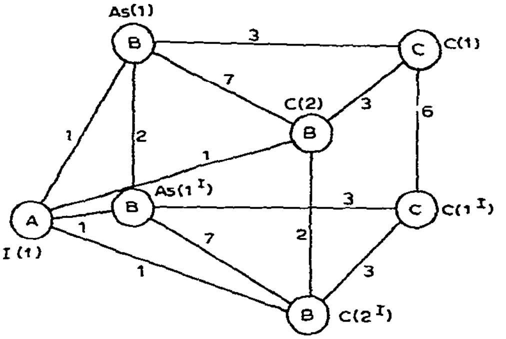

Fig. 2. (I) as an idealised capped trigonal prism, the central tungsten atom omitted. Letters A, B, C inside circles represent the three different sites. Lines are drawn along edges; numbers refer to Table 4. In (II), the A site is occupied by iodine, B and C sites by carbon. In (III), the A site is occupied by chlorine, the B sites by arsenic and the C sites by carbon.

lengths in (I), 1.988(25), 2.067(25) Å are almost certainly not significant, particularly when the metal—oxygen distances are considered as these are equivalent at 3.16 Å. Inaccurate placement of a carbon atom towards a heavy metal along the M···O vector is often found in refinement for carbonyl groups [12].

In the capped trigonal prism of (I), the Diars ligand occupies bite 2 (see Fig. 2) in the capped quadrilateral face rather than bite 7, an arrangement equivalent to that found in (III) [2] and $[W(CO)_2(Dmpe)_2I]^+$ [3]. This is the shorter of the two bites in the monodentate cation (II) [1]. As far as the dimensions in (I) are concerned, the overall impression gained from Table 4 is of similarity with (II) and (III), which have ideal C_{2v} symmetry, despite the asymmetric arrangement of atoms.* Thus, the carbon atoms in the quadrilateral face are shifted only slightly more towards the iodine atom than are the arsenic atoms [I(1)—W—As(1) 81.3(1)°, I(1)—W—C(2) 79.8(7)°]. And in the C(1), C(2), As(1) triangles, the C(1)—W—As(1) and C(1)—W—C(2) angles are equivalent at 76.6(6) and 75.4(10)° respectively. Also worthy of note is that the C(2)—W—C(2^I) angle in the quadrilateral face (bite 2) is 80.8(19)° compared to 85.5(7)° for the equivalent C—Mo—C angle in (II). This is not a steric effect and may be due to the symmetry requirements of the metal *d* electrons as the angle in the other bite 2 subtended by the Diars ligand is 77.8°. The As(1)—W—C(2) is 97.6(7)° in the quadrilateral face, almost the average of the angles at that bite in (II) and (III). This similarity between the dimensions in (I), (II) and (III) establishes that the CTP is a polyhedron with a recognisable set of angles at an energy minimum and in the absence of significant steric effects, that molecules (and ions) attain this ideal geometry even when different atoms occupy equivalent sites.

We listed in the introduction the structures of a number of seven-coordi-

---

* It is of interest that these three cations (I), (II) and (III) as well as $[W(CO)_2(Dmpe)_2I]^+$ have crystallographically imposed *m* symmetry. This suggests that crystal packing energy is low (if not lowest) when symmetry elements in the molecule coincide with those in the unit cell. As the energy differences between the PB, CO and CTP are very low, the attainment of *m* symmetry for these cations (and hence low crystal packing energies) may tip the balance (for at least some of these cations) towards the CTP.

nate complexes which contain one halogen atom and six smaller ligands. In most of these examples (and all of them including iodine), the structure is a CTP with the halogen in the capping position. Of the exceptions, the geometry of Zr(Acac)$_3$Cl is probably determined by the three bidentate ligands while in Nb(OMe)$_2$Cl(Dedtc)$_2$, Nb—O bonds, with orders greater than 1, take precedence over the chlorine atom in occupying the two least crowded sites in a PB. Steric effects are important in (III) and in [W(CO)$_2$(Dmpe)$_2$I]$^+$ and it has been shown [2] that these are minimised by the CTP. However in (I) this is not so. In a geometry in which the iodine atom occupied an axial site in a PB with the Diars ligand in the equatorial plane, steric effects would not noticeably be increased.

Thus, for both (I) and (II) steric effects are probably not decisive in the choice of geometry. It could well be that electronic effects are important in that the CTP is the favoured geometry for metal atoms with d^4 configuration and six π acceptors in the coordination sphere but such a correlation will not be attempted here.

Given the CTP for (I) with the iodine atom in the unique capping position, there are two possible arrangements with the Diars ligand in the quadrilateral face or in the remaining edge. This latter arrangement has the superficial advantage of corresponding to the stoichiometry of the compound and would have C_{2v} symmetry. However it can easily be seen from models that this 1/4/2 structure would involve four close CO...Me contacts as four of the eight (CO)—W—As—Me dihedral angles would be close to zero. We know that such contacts are important by referring to the non-planarity of the W(Diars) grouping in (I), which is bent such that the angle between the W, As(1), As(1^{I}) plane and the As$_2$C$_6$ grouping (which is planar within experimental error) is 15.6° [in (III) the angle is 21.2°]. This bend increases the C(3)—As(1)—W—I(1) dihedral angle to 49.5 and the C(3)...I(1) contact to 3.72 Å and also increases the C(1)—W—As(1)—C(4) dihedral angle to 19.7° and the C(1)...C(4) and O(1)...O(4) distances to 3.19, 3.29 Å; values which are unexceptional.

Of the remaining dimensions in (I) the angles subtended at arsenic follow the usual pattern [2] W—As—Me > W—As—C(5) > C—As—C with mean values

TABLE 5

SELECTED INTRAMOLECULAR CONTACTS, TOGETHER WITH ALL INTERMOLECULAR CONTACTS < 3.80 Å

I(1)...C(3)	3.72	O(2)...C(1^{III})	3.78
I(1)...C(5)	3.97	O(2)...O(1^{III})	3.27
C(1)...C(4)	3.19	O(2)...C(2^{III})	3.78
O(1)...C(4)	3.29	O(2)...O(2^{III})	3.38
I(4)...O(2)	3.70	O(2)...C(3^{IV})	3.58
O(1)...C(3^{II})	3.67		
O(1)...C(5^{II})	3.80		
O(1)...C(6^{II})	3.43		
O(1)...C(7^{II})	3.74		

[a] Roman numerals as superscripts refer to atoms in the following equivalent positions, relative to the reference coordinates x, y, z in Table 1. I $x, \frac{1}{2}-y, z$; II $x, y, 1+z$; III $1-x, -y, 1-z$; IV $1-x, -y, -z$.

117.3, 110.3, 103.4° respectively. The remaining dimensions are well within the expected range of values. The dimensions of the triiodide anion are unsymmetrical [2.895(3), 2.957(4) Å, 178.6(1)°] but these values are well within the (wide) range found for this anion [14]. The packing of the cations and anions in the unit cell show no unusual features. We list the intramolecular contacts and intermolecular contacts of special interest in Table 5.

Acknowledgement

We thank A.W. Johans for his assistance with the crystallographic investigations.

References

1 D.F. Lewis and S.J. Lippard, Inorg. Chem., 11 (1972) 621.
2 M.G.B. Drew and J.D. Wilkins, J.Chem. Soc. Dalton Trans., (1973) accepted for publication.
3 M.G.B. Drew, A.P. Wolters and C.J. Rix, in preparation.
4 E.M. Cradwick and D. Hall, J. Organometal. Chem., 25 (1970) 91.
5 R.B. van Dreele, J.J. Stezowski and R.C. Fay, J. Amer. Chem. Soc., 93 (1971) 2887.
6 J.W. Moncrieff, D.C. Pantaleo and N.E. Smith, Inorg. Nucl. Chem. Lett. 7 (1971) 255.
7 J. Lewis, R.S. Nyholm, C.S. Ponde and M.H.B. Stiddard, J. Chem. Soc., (1963) 3600.
8 'X-ray' system of programs, J.M. Stewart (Ed.), University of Maryland, Technical Report, TR-192, June 1972.
9 'International Tables for X-ray Crystallography', Vol. III, Kynoch Press, Birmingham, 1965.
10 M.G.B. Drew, A.W. Johans, A.P. Wolters and I.B. Tomkins, J. Chem. Soc. D, (1971) 819.
11 M.G.B. Drew, J. Chem. Soc.Dalton Trans., (1971) 1329.
12 A. Mawby and G.E. Pringle, J. Inorg. Nucl. Chem., 34 (1972) 517.
13 T.F. Brennan and I. Bernal, Inorg. Chim. Acta, 7 (1973) 283.
14 J.W. Bats, J.J. Deboer and D. Bright, Inorg. Chim. Acta, 5 (1971) 605.