Journal of Organometallic Chemistry, 59 (1973) 299–307

CRYSTAL AND MOLECULAR STRUCTURE OF THE EIGHT-COORDINATE COMPLEX TETRAMETHYLBIS(*N*-METHYL-*N*-NITROSOHYDROXYLAMINATO)TUNGSTEN(VI)

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(Received January 26th, 1973)

SUMMARY

The crystal structure of the title compound, $W(Me)_4[ON(Me)NO]_2$, has been determined from three-dimensional X-ray data. The crystals are orthorhombic, with unit-cell dimensions $a = 13.033$, $b = 14.825$, $c = 12.954$ Å; space group is *Pbca* and $Z = 8$. Full-matrix least-squares refinement, using 818 independent reflections, has reached *R* 0.073.

The complex is monomeric and the eight-coordinate tungsten atom is bonded to four methyl groups and to the oxygen atoms of two bidentate *N*-methyl-*N*-nitrosohydroxylaminato ligands. The coordination geometry is intermediate between square-antiprismatic and dodecahedral, and the mean W–C and W–O distances are 2.15 and 2.07 Å respectively. The *N*-methyl groups in the two chelate rings adopt a *cis*-configuration so that the molecule has almost perfect *m* symmetry.

Shortland and Wilkinson have recently reported[1] the preparation of hexamethyltungsten and that it reacts quantitatively with nitric oxide. Insertion reactions of nitric oxide with transition-metal-to-carbon bonds are rare and the products have not hitherto been structurally investigated. The best characterised example[2] is the reaction between NO and $(h^5\text{-}C_5H_5)_2ZrMe_2$, giving a compound believed to be $(h^5\text{-}C_5H_5)_2ZrMe[ON(Me)NO]$, in which the *N*-methyl-*N*-nitrosohydroxylaminato ligand was suggested to be monodentate. Uncertainty about the nature of the tungsten compound prompted us to undertake an X-ray single-crystal structure determination. This has shown that the compound is $WMe_4[ON(Me)NO]_2$ and that the $[ON(Me)NO]$ ligands are bidentate, giving the hexavalent tungsten atom an eightfold coordination. A preliminary account of this work has been published[3].

EXPERIMENTAL

Tetramethylbis(*N*-methyl-*N*-nitrosohydroxylaminato)tungsten(VI) crystallises from toluene as air-sensitive yellow prisms, which are elongated along the *a* axis.

A crystal of approximate dimensions 0.55 × 0.12 × 0.06 mm was sealed under nitrogen in a Lindemann tube, and was mounted about its *a* axis on a Siemens auto-

TABLE 1

CRYSTAL DATA

$C_6H_{18}N_4O_4W$: molecular weight 394.1
Orthorhombic, $a = 13.033$, $b = 14.825$, $c = 12.954$ Å
Systematic absences: $hk0$, $h = 2n+1$
$0kl$, $k = 2n+1$
$h0l$, $l = 2n+1$
Space group: *Pbca* (No. 61)
$V = 2502.9$ Å^3, $Z = 8$, $F(000) = 1504$
$D_{calc.} = 2.04$, $D_{obs} = 2.06$ g·cm^{-3}; Cu K_α radiation, $\lambda = 1.5418$ Å, μ(Cu K_α) = 171.4 cm^{-1}

matic off-line four-circle diffractometer. Intensity data were collected using Cu K_α radiation at a take-off angle of 4.5°, a nickel β filter, and a Na(Tl)I scintillation counter. A total of 818 independent reflections were measured using the $\theta - 2\,\theta$ scan technique with a "five-value" measuring procedure (one side of peak, background, full peak, background on other side of peak, other side of peak). Of these 376 reflections were judged to be unobserved as their net count was below 2.58 times the standard deviation (*i.e.* below the 99% confidence level). The net count of the 021 reflections measured as a reference every 25 reflections, decreased to approximately 35% of its original value during the period of data collection (ca. 5 days). The net counts of the four control reflections, measured every 300 reflections to monitor the alignment of the crystal, diminished by a similar amount. The data were scaled using the reference reflection and the Lorentz and polarisation corrections were applied.

Structure analysis and refinement

The structure was solved and refined using the Crystal Structure Calculations System X-Ray '63[4], and its updated version of July 1970[5]. The calculations were carried out on the Imperial College IBM 7094 and the University of London CDC 6600 computers.

A three-dimensional Patterson revealed the position of the tungsten atom, and least-squares refinement gave R 0.263. Two rounds of difference Fourier synthesis and isotropic refinement showed the positions of all fourteen non-hydrogen atoms and reduced R to 0.128. When the tungsten atom was allowed to refine with anisotropic thermal parameters only a small improvement in R (0.121) resulted.

At this stage the data were corrected for absorption according to the method of Busing and Levy[6] using an $8 \times 8 \times 8$ grid, with crystal pathlengths determined by the vector analysis procedure of Coppens *et al.*[7] Refinement as before reduced R to 0.078. Twelve of the hydrogen atoms could be located on a difference Fourier, and the positions of the remaining six were calculated. When the hydrogen atoms were included in subsequent refinement as a fixed-atom contribution with isotropic temperature factors of their parent atoms, R reached its final value of 0.073. In the later stages of refinement a weighting scheme of the type suggested by Hughes[8] was applied, where $w = 1$ for $F_o < F^*$ and $\sqrt{w} = F^*/F_o$ for $F_o \geqslant F^*$, with $F^* = 160$ found to be optimum. Application of the weighting scheme did not change R, but gave lower standard deviations. The only notable features on the final difference Fourier were a few peaks of up to 1 e·Å^{-3} in the immediate vicinity of the tungsten atom.

The identification of the light atoms as carbon, nitrogen and oxygen is consistent[1,3] with the elemental analyses and with the physical measurements carried out on the compound by Shortland and Wilkinson. As a further test a number of refinements were carried out with atomic identities in the bidentate ligands interchanged, and all gave less acceptable thermal parameters and worse *R* factors.

Full-matrix least-squares refinement was used throughout. The atomic scattering factors were those tabulated by Cromer and Waber[9], except those for hydrogen[10]. The real and the imaginary parts of the anomalous dispersion correction for tungsten were those given by Cromer[11]. The fractional coordinates of the non-hydrogen atoms and their estimated standard deviations are listed in Table 2, while Table 3 shows the coefficients in the expression for the anisotropic temperature

TABLE 2

FRACTIONAL COORDINATES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
W	0.19005(16)	0.12098(13)	0.19673(14)
O(1)	0.083(2)	0.220(2)	0.164(2)
O(2)	0.104(2)	0.088(2)	0.064(2)
O(3)	0.113(2)	0.138(2)	0.330(2)
O(4)	0.120(2)	0.001(2)	0.240(2)
N(1)	0.029(3)	0.221(2)	0.077(3)
N(2)	0.051(3)	0.156(2)	0.025(3)
N(3)	0.066(3)	0.070(2)	0.384(3)
N(4)	0.074(3)	−0.001(3)	0.330(3)
C(1)	0.289(4)	0.188(3)	0.079(4)
C(2)	0.306(4)	0.076(3)	0.300(4)
C(3)	0.249(4)	0.236(4)	0.276(5)
C(4)	0.271(4)	0.020(3)	0.114(4)
C(21)	−0.001(4)	0.131(3)	−0.074(4)
C(41)	0.041(3)	−0.090(3)	0.371(3)

TABLE 3

THERMAL PARAMETERS, ANISOTROPIC FOR TUNGSTEN AND ISOTROPIC FOR ALL OTHER ATOMS

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
W	1282(20)	773(13)	888(15)	−32(20)	16(18)	18(16)

Atom	*B*(Å^2)	*Atom*	*B*(Å^2)
O(1)	9.3(8)	N(1)	8.7(1.0)
O(2)	7.0(7)	N(2)	6.8(8)
O(3)	8.0(7)	N(3)	7.6(9)
O(4)	8.7(7)	N(4)	8.3(9)
C(1)	10.7(1.4)	C(3)	13.0(1.8)
C(2)	10.9(1.3)	C(4)	10.6(1.4)
C(21)	10.5(1.3)	C(41)	7.4(1.1)

TABLE 4

FRACTIONAL COORDINATES OF THE HYDROGEN ATOMS[a] (calculated positions in parentheses)

Atom	*x*	*y*	*z*
H(11)	0.230	0.235	0.038
H(12)	0.322	0.138	0.040
[H(13)	0.330	0.243	0.112]
H(21)	0.345	0.130	0.333
H(22)	0.252	0.053	0.368
H(23)	0.331	0.015	0.281
H(31)	0.235	0.225	0.358
H(32)	0.318	0.245	0.260
[H(33)	0.212	0.295	0.241]
H(41)	0.250	0.025	0.035
[H(42)	0.351	0.035	0.142]
[H(43)	0.242	−0.050	0.131]
H(211)	0.039	0.151	−0.144
H(212)	−0.075	0.162	−0.079
[H(213)	−0.012	0.057	−0.078]
H(411)	0.038	−0.135	0.305
H(412)	0.090	−0.113	0.420
[H(413)	−0.037	−0.088	0.395]

[a] The hydrogen atoms are numbered so that the first two digits correspond to the numbering of the carbon atoms to which they are bonded.

factor exp $[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\,\beta_{12}\cdot hk+2\,\beta_{13}\cdot hl+2\,\beta_{23}\cdot kl)]$ for the tungsten atom, and the isotropic temperature factors for O, N and C atoms. The coordinates of the hydrogen atoms are given in Table 4, and the observed and the calculated structure amplitudes can be obtained from the authors on request.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

This X-ray structure analysis has shown the complex to be monomeric, and two views of the molecular structure are given in Fig. 1. The tungsten atom is eight-coordinate, being bonded to four methyl groups and to the four oxygen atoms of two bidentate [ON(Me)NO] ligands. Eight-coordinate tungsten compounds are very unusual and this is the first reported structure analysis for such a complex of tungsten(VI). The compound K_2WF_8 is known[12], but only powder data are available and it is not certain whether WF_8^{2-} ions are present.

The more important bond lengths and bond angles are quoted in Table 5. The differences between the four W–O distances are probably not significant, and the average distance is 2.07 Å. A wide range of W–O bond lengths have been reported, 1.7–2.3 Å, but it is difficult to find ones which are strictly comparable. The mean W^{VI}–O distance in this compound, however, is consistent with the mean Zr^{IV}–O distance of 2.19 Å in the eight-coordinate cupferron complex $Zr(C_6H_5N_2O_2)_4$[13] if one compares a mean octahedral W^{VI}–Cl distance of 2.32 Å in $WSCl_4\cdot WOSCl_2\cdot$DME[14] with octahedral Zr^{IV}–Cl distances of 2.44–2.45 Å in Rb_2ZrCl_6 and Cs_2ZrCl_6[15].

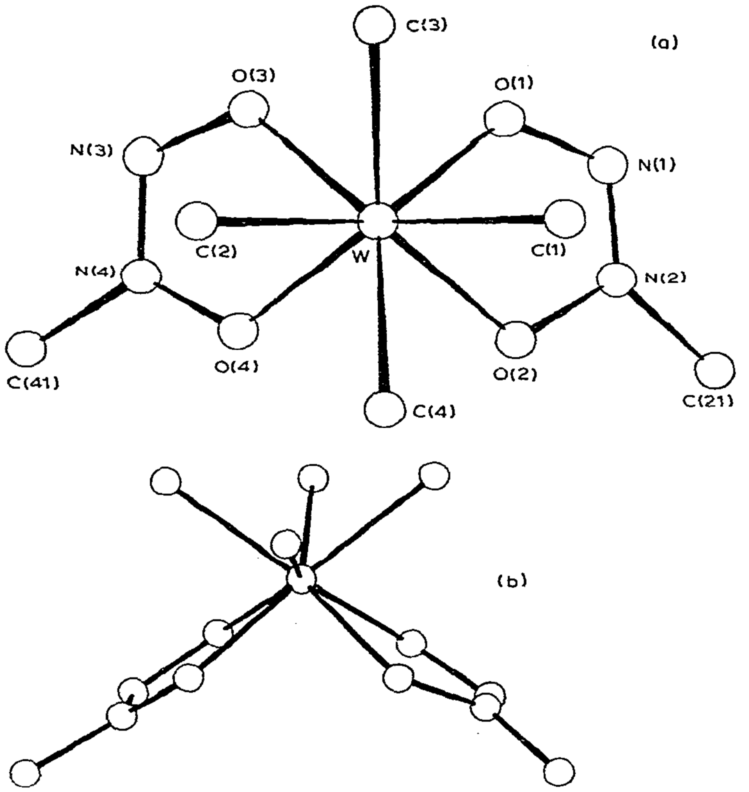

Fig. 1. Two views of the molecular structure of $W(Me)_4[ON(Me)NO]_2$. That in (a) shows the almost perfect *m* symmetry of the molecule.

Shortland and Wilkinson have shown[1,3], on the basis of the splitting of the peak due to WMe_4 protons in the NMR spectrum, that in solution the title compound exhibits non-rigid behaviour. Such behaviour of eight-coordinate species is unusual but three other cases have recently been reported involving molybdenum and tungsten hydrido complexes[16]. Although there are marginal differences in the environments of the two pairs of opposite methyl groups (see Fig. 1) in the crystal structure, the four W–C distances are not significantly different, with a mean distance of 2.15 Å. One must bear in mind, however, that the standard deviations are high and the existence of genuine minor differences cannot be ruled out. [The high standard deviations are a consequence of a number of factors: the presence of a very heavy central atom, the unusually high thermal motion of the molecule giving rise to a high proportion of "unobserved" reflections and enforcing a low θ-cutoff in the data collection, and the instability of the crystals.] The W–C distances may be compared to Mo–C of 2.131 Å in $Mo_2(CH_2SiMe_3)_6$[17] and Cr–C of 2.199 Å in $Li_4[Cr_2Me_8]\cdot 4C_4H_8O$[18]. In the latter case the methyl hydrogen atoms were not allowed for in the refinement and the true distance may therefore be fractionally shorter – for instance, in this refinement the mean W–C distance was 2.20 Å at a comparable stage.

The structure found represents the first case of a chelate *N*-methyl-*N*-nitrosohydroxylamine complex confirmed crystallographically, although cupferron

TABLE 5

BOND LENGTHS (Å) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a). Distances			
W–O(1)	2.07(3)	W–C(1)	2.23(5)
W–O(2)	2.11(2)	W–C(2)	2.12(5)
W–O(3)	2.01(2)	W–C(3)	2.14(6)
W–O(4)	2.07(3)	W–C(4)	2.12(5)
Mean W–O	2.07	Mean W–C	2.15
O(1)–N(1)	1.33(5)	O(3)–N(3)	1.38(4)
O(2)–N(2)	1.32(4)	O(4)–N(4)	1.32(5)
N(1)–N(2)	1.20(5)	N(3)–N(4)	1.26(5)
N(2)–C(21)	1.49(6)	N(4)–C(41)	1.49(5)
(b). Angles			
O(1)–W–O(2)	68.9(1.0)	O(3)–W–O(4)	70.2(1.1)
O(1)–W–O(4)	111.6(1.1)	O(2)–W–O(3)	117.7(1.0)
O(1)–W–O(3)	75.4(1.1)	O(2)–W–O(4)	77.9(1.1)
C(1)–W–C(2)	99.4(1.9)	C(3)–W–C(4)	129.1(1.9)
C(1)–W–C(3)	76.5(2.0)	C(2)–W–C(4)	75.4(1.9)
C(1)–W–C(4)	71.5(1.8)	C(2)–W–C(3)	72.0(2.0)
O(1)–W–C(1)	86.1(1.5)	O(3)–W–C(2)	81.6(1.5)
O(1)–W–C(2)	146.0(1.5)	O(3)–W–C(1)	144.8(1.4)
O(1)–W–C(3)	76.8(1.7)	O(3)–W–C(3)	70.4(1.7)
O(1)–W–C(4)	137.0(1.6)	O(3)–W–C(4)	140.5(1.6)
O(2)–W–C(1)	81.3(1.4)	O(4)–W–C(2)	82.7(1.5)
O(2)–W–C(2)	145.0(1.4)	O(4)–W–C(1)	145.0(1.5)
O(2)–W–C(3)	140.1(1.7)	O(4)–W–C(3)	135.6(1.8)
O(2)–W–C(4)	71.7(1.5)	O(4)–W–C(4)	75.4(1.6)
W–O(1)–N(1)	122.3(2.3)	W–O(3)–N(3)	124.0(2.2)
W–O(2)–N(2)	114.4(2.0)	W–O(4)–N(4)	117.4(2.3)
O(1)–N(1)–N(2)	110.3(3.3)	O(3)–N(3)–N(4)	107.7(3.1)
O(2)–N(2)–N(1)	121.1(3.3)	O(4)–N(4)–N(3)	120.2(3·4)
O(2)–N(2)–C(21)	112.0(3.0)	O(4)–N(4)–C(41)	118.2(3.2)
N(1)–N(2)–C(21)	124.9(3.5)	N(3)–N(4)–C(41)	121.3(3.4)

complexes have been studied[13,19,20]. The arrangement of the bidentate ligands is such that the *N*-methyl groups adopt a *cis* configuration so that the molecule has almost perfect *m* symmetry (see Fig. 1a). It has been shown[1] that during the insertion of NO into WMe_6 the chelate rings are formed successively, and so presumably the configuration of the *N*-methyl groups is a result of steric factors involved in the formation of the second ring. Within the [ON(Me)NO] ligands all like bonds are equal within the accuracy of the experiment, and they are also in reasonable agreement with the corresponding bond lengths in the cupferron (L) complexes ZrL_4[13], FeL_3[19], and CuL_2[20]. As regards the angles within the five-membered rings the mean O–W–O angle of 69.6° compares well with the mean O–Zr–O angle of 67.3° in the eight-coordinate ZrL_4 complex, bearing in mind that the Zr–O distances are somewhat longer. Comparison of the other ring angles with corresponding ones in the three cupferron complexes suggests the following relation between them: $\delta \approx \beta > \alpha > \gamma$. Table 6 gives details of the planarity of various groups of atoms in the structure. The [ON(Me)-

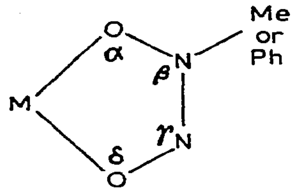

TABLE 6

PLANARITY OF GROUPS OF ATOMS IN THE STRUCTURE[a]

The equations of the planes are expressed as $Px+Qy+Rz=S$

	P	*Q*	*R*	*S*	*Deviation (Å) of atoms from plane*
A	10.20	6.32	−5.87	1.27	O(1) −0.001, O(2) 0.026, N(1) 0.034, N(2) −0.081, C(21) 0.023 Atom not defining plane: W −0.274
B	11.58	−2.67	5.45	2.70	O(3) −0.038, O(4) 0.003, N(3) 0.030, N(4) 0.041, C(41) −0.036 Atom not defining plane: W −0.251
C	12.90	1.92	−0.77	1.42	O(1) 0.050, O(2) −0.048, O(3) −0.051, O(4) 0.048 Atom not defining plane: W −1.114
D	12.97	1.46	−0.19	3.76	C(1) 0.236, C(2) 0.253, C(3) −0.242, C(4) −0.248 Atom not defining plane: W 1.161
E	8.31	8.97	−6.17	1.50	O(1) −0.148, O(2) 0.238, C(2) 0.133, C(4) −0.223 Atom not defining plane: W 0.053
F	10.44	−6.23	5.52	2.41	O(3) 0.271, O(4) −0.161, C(1) 0.134, C(3) −0.243 Atom not defining plane: W 0.094

[a] Groups C and D should be strictly planar for square antiprismatic coordination; similarly groups E and F for dodecahedral coordination.

NO] ligands are essentially planar (A and B), with none of the atoms having a statistically significant deviation from the plane. The metal atom is in each case ca. 0.25 Å out of the plane.

The most common coordination polyhedra for eight-coordination complexes are the square antiprism and the triangular dodecahedron. Lippard and Russ[21] have suggested that the angle between the intersecting trapezoidal planes of the coordinating atoms gives the most reliable identification of the polyhedron. In the idealised case this angle should be 77.4° for a square antiprism and 90° for a dodecahedron. In this compound the trapezoidal planes comprise atoms O(1), O(2), C(2), C(4), and O(3), O(4), C(1), C(3), and the angle between them is 86.9° *i.e.* much closer to the dodecahedral value, however, the "planes" themselves (E and F) are not at all convincing. Other criteria, such as an analysis of the polyhedron-shape parameters[22], have proved similarly inconclusive. Probably the best approximation is to describe the WO_4 half of the molecule as characteristic of square-antiprismatic coordination, and the WMe_4 half as dodecahedral. Thus the four oxygen atoms form quite a good plane (C) and the angles O(1)–W–O(4) and O(2)–W–O(3) are similar, 111.6 and 117.7° respectively, while the four methyl carbon atoms are not planar (D) and the angles C(1)–W–C(2) and C(3)–W–C(4) are quite different, 99.4 and 129.1° respectively.

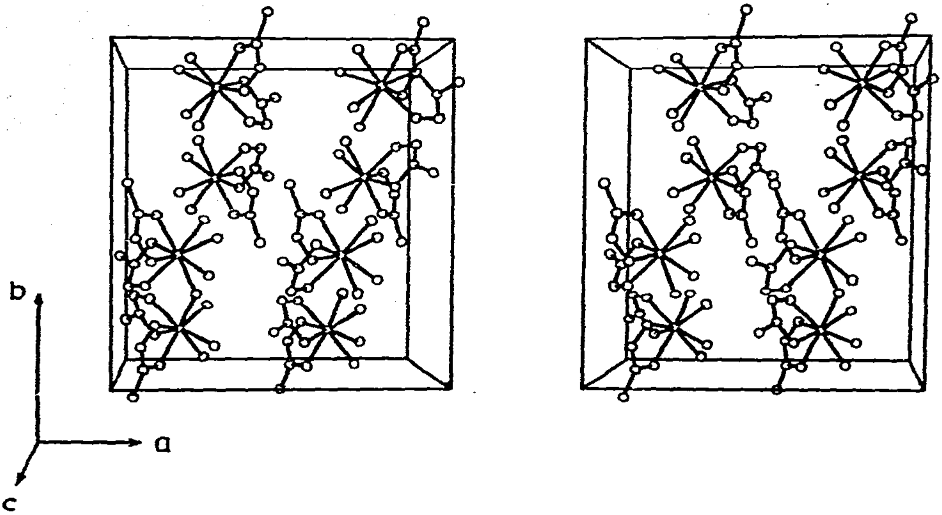

Fig. 2. A stereoscopic view showing the packing of $W(Me)_4[ON(Me)NO]_2$ molecules.

The packing of the complex molecule in the unit cell is shown in Fig. 2 as a stereoscopic pair[23] of drawings. The main outward-facing groups in the molecule are the six methyl groups and the intermolecular cohesive forces are of the Van der Waals type.

ACKNOWLEDGEMENTS

We thank Mr. A. Shortland and Professor G. Wilkinson for providing the crystals and for discussions, Professor D. Rogers for the use of a diffractometer, and the Science Research Council for financial support.

REFERENCES

1 A. Shortland and G. Wilkinson, *J. Chem. Soc., Chem. Commun.,* (1972) 318; *J. Chem. Soc., Dalton Trans.,* (1973) in the press.
2 P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.,* 34 (1972) 155.
3 S. R. Fletcher, A. Shortland, A. C. Skapski and G. Wilkinson, *J. Chem. Soc., Chem. Commun.,* (1972) 922.
4 J. M. Stewart, *"X-Ray-63" system of programs,* University of Maryland Technical Report TR-64-6.
5 J. M. Stewart, F. A. Kundell, and J. C. Baldwin (Eds.), *X-Ray system version of July* 1970.
6 W. R. Busing and H. A. Levy, *Acta Crystallogr.,* 10 (1957) 180.
7 P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.,* 18 (1965) 1035.
8 E. W. Hughes, *J. Amer. Chem. Soc.,* 63 (1941) 1737.
9 D. T. Cromer and J. T. Waber, *Acta Crystallogr.,* 18 (1965) 104.
10 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.,* 42 (1965) 3175.
11 D. T. Cromer, *Acta Crystallogr.,* 18 (1965) 17.
12 G. B. Hargreaves and R. D. Cox, *J. Chem. Soc.,* (1958) 2170.
13 W. Mark, *Acta Chem. Scand.,* 24 (1970) 1398.
14 D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, *J. Chem. Soc., Chem. Commun.,* (1972) 468.
15 G. Engel, *Z. Kristallogr.,* 90 (1936) 341.
16 J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.,* 93 (1971) 5261; B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J. Chem. Soc., Chem. Commun.,* (1972) 32; J. R. Moss and B. L. Shaw, *J. Chem. Soc., Trans.,* (1972) 1910.

17 F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *J. Chem. Soc. D*, (1971) 1079.
18 V. Krausse, G. Marx, and G. Schödl, *J. Organometal. Chem.*, 21 (1970) 159.
19 D. van der Helm, L. L. Merritt, R. Degeilh, and C. H. MacGillavry, *Acta Crystallogr.*, 18 (1965) 355.
20 L. M. Shkolnikova and E. A. Shugan, *Zh. Strukt. Khim.*, 4 (1963) 380.
21 S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 7 (1968) 1686.
22 J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2 (1963) 235.
23 C. K. Johnson, *ORTEP Thermal Ellipsoid Plotting Program*, Oak Ridge National Laboratory Report, ORNL-3794 (1965).