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The Crystal and Molecular Structure of Tetramethylammonium 3,3′-Commo-bis[1,2-dicarba-3-nickela-closo-dodecaborate](1-)

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The crystal and molecular structure of tetramethyl-ammonium 3,3′-commo-bis[undecahydro-1,2-dicarba-3-nickela-closo-dodecaborate] (1−), $(CH_3)_4NNi^{III}(B_9C_2H_{11})_2$, has been determined from three-dimensional single crystal X-ray data. The orthorhombic cell (space group *Ccmm*) with $a = 10.328$ Å, $b = 9.841$ Å, $c = 21.86$ Å contains four formula units. The structure was initially solved by Patterson and Fourier methods from a three-dimensional set of visually estimated intensities, but to solve space group ambiguities a set of diffractometer data had to be collected. Positional and anisotropic thermal parameters for Ni, N, C, and B and positional parameters for H were refined from 716 observed reflections by the method of least squares. The final R-value is 0.054.

The structure of the $Ni(C_2B_9H_{11})_2$ anion is of a symmetrical π-sandwich type (point group 2/m) with the two dicarbollyl icosahedra joined at the Ni apex. The carbon atoms in the dicarbollyl cage are adjacent to each other in the two CCBBB pentagons coordinated to nickel, and they are ordered in the structure.

Several transition metal compounds containing the dicarbollyl ion $C_2B_9H_{11}^{2-}$ have been subject to structural studies. It has been shown [1] that in $(\phi_3PCH_3)Cu(III)(C_2B_9H_{11})_2$ (d^8 configuration), isomorphous with $[\phi_3PCH_3][Au(III)(C_2B_9H_{11})_2]$ (d^8), and in $(Et_4N)_2Cu(II)(C_2B_9H_{11})_2$ (d^9), isomorphous with $(Et_4N)_2$ $Ni(II)(C_2B_9H_{11})_2$ (d^8), the $M(C_2B_9H_{11})_2$-entity (M=transition metal) suffers a distortion from the symmetrical π-sandwich structure found in corresponding compounds with six or less d-electrons. The distortion takes place by an antiparallel slippage of the two cages, making metal-carbon distances longer than the metal-boron distances.

In view of this the d^7-configuration found in the $Ni(III)(C_2B_9H_{11})_2^-$ ion has considerable interest, for which reason we undertook this study of $(CH_3)_4NNi(C_2B_9H_{11})_2$.

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EXPERIMENTAL

The dark red crystals of $(CH_3)_4NNi(C_2B_9H_{11})_2$ were kindly supplied by L. F. Warren and F. Hawthorne. Weissenberg and precession exposures taken with Mo$K\alpha$ radiation showed the crystal system to be orthorhombic with systematic absences: hkl, $h+k=2n+1$; $0kl$, $l=2n+1$. These are consistent with the space groups: $Ccmm$ (centric), $Cc2m$ (acentric), and $Ccm2_1$ (acentric): the first one was shown to be correct in the final refinements of the structure. The unit cell dimensions as determined with Mo$K\alpha_1$ radiation ($\lambda=.70926$ Å) by the method of least squares from angular settings of fourteen non-axial high order reflections on a four circle Picker diffractometer are: $a=10.328\pm.003$ Å, $b=9.841\pm.003$ Å, $c=21.862\pm.006$ Å (measured at room temperature). No density was measured. Assuming $Z=4$, later confirmed by structure analysis, a density of 1.20 g/cm³ is calculated, close to that of 1.304 g/cm³ found by us for Ni(IV) $(C_2B_9H_{11})_2$.

Two sets of data were collected for the solution of the structure. The structure was roughly solved with a visually measured data set. However, space group ambiguities could not be solved from this set of data, so when a four circle diffractometer became available, a new set of intensities was measured and the structure refined with these.

The diffractometer data were collected with a manual four circle Picker diffractometer using Mo$K\alpha$ radiation in connection with a scintillation counter mounted 21 cm from the crystal. The take off angle was 0.8°. A crystal showing very good extinctions in a polarizing microscope and approximately in the form of a box with dimensions $0.35\times0.35\times0.19$ mm³ was mounted with the b-axis parallel to the ϕ-axis of the instrument. One independent set of reflections, totalling approximately 1570 were measured using the $\theta-2\theta$ scan technique with a scan rate of 2° min^{-1}. Data were collected out to $2\theta=60°$ for l even and to 2θ max $=45°$ for l odd, the latter because of a pronounced weakness of these intensities. The scan range was from 0.8° below to 1.2° degrees above the Mo$K\alpha_1$ peak for $2\theta<45°$ and from 0.8° below to 1.53° above for $2\theta>45°$.

Stationary background counts for 10 sec were recorded at the beginning and end of each scan. The diffracted beam was filtered through a 0.0005 inch Zr-foil. The 24 strongest reflections were attenuated with a 0.05 mm Ni foil (attenuation factor 8.1) assuring the intensity to be within the linear response range of the detector. The attenuation factor was only approximately known and accordingly introduced as a parameter in the refinements. Standard reflections were recorded before every layer line but indicated no decomposition.

The intensities were reduced to relative structure factors with the program ACAC.[3] No correction for extinction, anomalous dispersion or absorption was made, the relative absorption effect being not more than about 3 % ($\mu_{MoK\alpha}=8.6$ cm^{-1}). Intensities for which $I<3\sigma(I)$ were taken as unobserved, leaving 721 reflections for refinement of the structure. Of these, five were later discarded as improperly measured, three of them very strong low angle reflections in which incompletely attenuated β-peaks had been measured in the first background.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved roughly from the visual data set. Patterson and successive Fourier syntheses revealed the approximate positions of all atoms except hydrogen. The symmetry restrictions to be imposed on the molecule in each of the possible space groups are:

1. $Ccm2_1$ (acentric):

Ni $(C_2B_9H_{11})_2^-$ and $(CH_3)_4N^+$ have m-symmetry, the mirror-plane in $Ni(C_2B_9H_{11})_2^-$ going through the nickel atom and the two apical (B7 and B7′) boron atoms.

2. $Cc2m$ (acentric):

$(CH_3)_4N^+$ has m-symmetry. $Ni(C_{12}B_9H_{11})_2^-$ has 2-fold symmetry, the 2-fold axis lying parallel to the faces of the coordinating pentagons of the two cages.

3. *Ccmm* (centric):

$(CH_3)_4N^+$ has *mm*-symmetry. $Ni(C_2B_9H_{11})_2^-$ has $2/m$ symmetry, the symmetry being a combination of that in the two other space groups.

In the acentric space groups the Ni atoms have a centre of symmetry, making it impossible to distinguish the centric from the acentric space groups from a breakdown of Friedel's law.

With all cage atoms put in as boron, isotropic and anisotropic refinement (Ni and $(CH_3)_4N^+$ anisotropic) was carried out in all three space groups choosing the origin in the acentric space groups at the Ni atom. However, the results were inconclusive with respect to which space group was the correct one. In trying to locate the carbon atoms in the cage, we used the distances found by Zalkin *et. al.*[3] in $CsC_2B_9H_{11}Re(CO)_3$: C–C = 1.61 Å, C–B = 1.72 Å, B–B = 1.78 Å. The distances showed the carbon atoms probably to be placed in the pentagons coordinated to nickel. However, no models, including some with disorder of the carbon atoms in the pentagons or presence of dicarbollyl isomers, could be set up, accounting for the distances found in the cages. Therefore, refinement with these data was given up and diffractometer data collected.

In the space groups *Ccmm* and *Cc2m* the Ni atoms give no contribution to reflections with $l=2n+1$. Of a total of 721 significant observations only 135 have l odd and these have an average intensity much lower than that for reflections with l even.

To distinguish between the possible space groups a statistical test was run with the 135 reflections to which the Ni atoms do not contribute. This favoured strongly an acentric space group and refinement was initiated in *Cc2m*. Starting with coordinates determined from the visual data set, three cycles of full matrix least squares refinement with the program ORFLS,[4] refining Ni and the tetramethylammonium ion anisotropically and all cage atoms isotropically, lowered the conventional R-value to $R_1 = \sum||F_o| - |F_c||/\sum F_o = 0.083$, $R_2 = (\sum W(F_o - F_c)^2/\sum WF_o^2)^{\frac{1}{2}} = 0.099$.

A difference synthesis was computed and revealed as the 11 highest peaks all hydrogen atoms in the cage. Two atoms adjacent to each other in the pentagons coordinated to Ni had temperature factors of 2.11 and 2.20 Å^2, the other ones ranging from 2.80 to 2.85 Å^2. Furthermore, the distance 1.60 Å between these was the lowest found in the cage, the others being 1.63 – 1.89 Å. Accordingly, these two atoms were taken to be carbon atoms (later proved to be correct), and anisotropic thermal vibrations of the cage atoms were introduced in the refinement. Because of the large number of variables involved, the two pentagons in the cage were refined independent of each other in successive cycles. Two cycles lowered the R-values to $R_1 = 0.074$, $R_2 = 0.085$, but temperature factors of two adjacent cage atoms became non-positive definite and many distances unsatisfactory (ranging from 1.54 Å to 1.99 Å). At this stage a version of ORFLS modified in this department for the IBM 360/75 computer by G. Sproul became available. This version is able to refine 300 variables among 500 parameters. One final cycle was run in the space group *Cc2m* with this program to take into account the correlation between atoms in different pentagons but no improvement in distances was found.

Finally, refinement was carried out in the space group *Ccmm* with the IBM 369/75 version of ORFLS. Starting again with all cage atoms put in as

boron, two cycles gave $R_1 = 7.7$ %. The distances now became chemically very acceptable for an ordered structure with the two carbon atoms in the cage adjacent to each other in the pentagon coordinated to Ni. A difference synthesis was computed and now revealed all the hydrogen atoms in the tetramethylammonium ion except one, supposedly in the mirror plane.

No indication of disorder of this ion was found. Four more cycles gave the final R-values $R_1 = 0.058$, $R_2 = 0.077$ with all hydrogen atoms included.

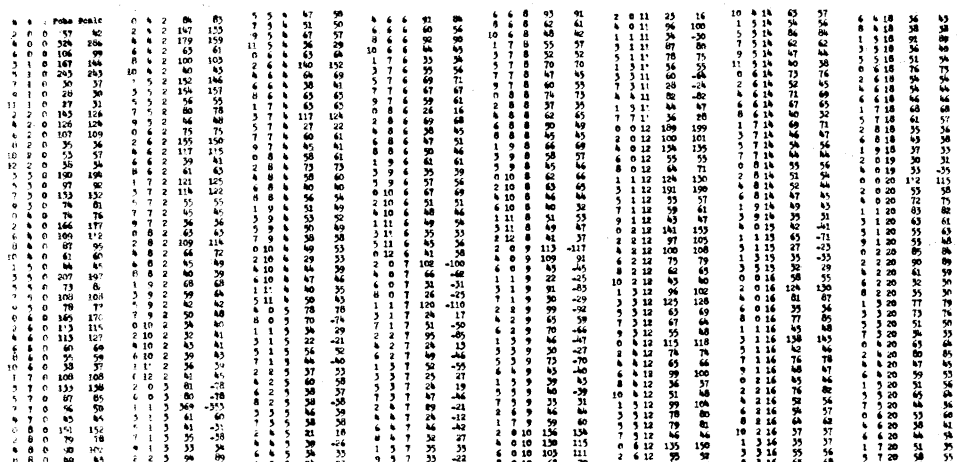
Table 1. Final atomic coordinates in fractions. Standard deviations $\times 10^4$ in parentheses. For hydrogen atoms isotropic B-values with standard deviations are included.

	x	y	z	B(Å²)
Ni	0.0000 (0)	0.0000 (0)	0.0000 (0)	
C2	0.1809 (5)	0.0807 (5)	0.0317 (3)	
B3	0.0458 (6)	0.1426 (7)	0.0686 (3)	
B5	−0.0395 (8)	0.0000 (0)	0.0970 (4)	
B7	0.2927 (10)	0.0000 (0)	0.0797 (5)	
B8	0.2036 (7)	0.1453 (8)	0.1029 (3)	
B9	0.0673 (6)	0.0894 (8)	0.1463 (3)	
B12	0.2150 (10)	0.0000 (0)	0.1516 (5)	
N	0.1624 (10)	0.5000 (0)	0.2500 (0)	
C1N	0.0813 (11)	0.5000 (0)	0.1927 (6)	
C2N	0.2464 (8)	0.3751 (10)	0.2500 (0)	
H1	0.2156 (47)	0.1271 (50)	−0.0039 (23)	1.12 (0.92)
H2	0.0272 (42)	0.2436 (55)	0.0527 (22)	0.80 (0.99)
H3	−0.1446 (59)	0.0000 (0)	0.1040 (30)	−0.15 (1.25)
H4	0.4029 (106)	0.0000 (0)	0.0672 (56)	6.26 (3.09)
H5	0.2584 (74)	0.2226 (77)	0.1185 (45)	6.58 (2.22)
H6	0.0388 (48)	0.1638 (55)	0.1834 (26)	1.63 (1.12)
H7	0.2751 (99)	0.0000 (0)	0.1925 (46)	2.82 (2.39)
H8	0.3182 (68)	0.3748 (80)	0.2095 (31)	4.70 (1.88)
H9	0.0168 (62)	0.5735 (76)	0.2003 (33)	5.09 (1.94)
H10	0.1321 (112)	0.5000 (0)	0.1570 (68)	7.13 (3.78)
H11	0.1743 (81)	0.2957 (87)	0.2500 (0)	−2.28 (1.93)

Table 2. Mean square vibration amplitudes, u_{ij}, in Å² $\times 10^{-4}$, with standard deviations.

	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
Ni	344	5	308	5	287	5	0	0	38	4	0	0
C2	451	28	449	28	414	26	−50	24	86	22	−19	22
B3	485	29	426	31	390	28	20	30	60	28	−35	26
B5	405	43	500	49	406	44	0	0	51	44	0	0
B7	476	51	922	82	422	53	0	0	3	43	0	0
B8	510	36	717	45	444	34	−124	35	71	29	−207	34
B9	448	34	674	43	393	30	−59	31	85	26	−81	32
B12	464	54	1005	88	442	51	0	0	−37	46	0	0
N	401	51	592	60	610	63	0	0	0	0	0	0
C1N	677	71	1096	95	1021	88	0	0	−504	66	0	0
C2N	525	47	634	55	634	53	224	45	0	0	0	0

Table 3. Observed and calculated structure factors on 1.97 × absolute scale.



The weights used in the first cycles were $W = 1/\sigma^2(F)$ with

$$\sigma(|F|) = \frac{|F|}{2I}[\mathrm{CN} + (\mathrm{TC}/\mathrm{TB})^2\ (\mathrm{B}_1 + \mathrm{B}_2) + (k \times I)^2]^{1/2}\ \text{(Ref. 5)}$$

CN is the intensity integrated in a scantime of TC, B_1 and B_2 are the backgrounds counted in a time TB. The systematic "error" factor k was taken to 0.03.

In the final cycles these weights seemed not to account for all errors and a weighting scheme $W = 1/(\mu F)^2$ with

$$\mu F = (\sigma(F_o^2) + (k + 1)\ F_o^2)^{1/2} - F_o$$

was used. The factor k was systematically varied to give a $W\Delta^2$ nearly independent of the size of F_o. All scattering factors were taken from *International*

Tables for X-Ray Crystallography, Vol. III, pp. 202 – 207. In the final cycle the shift/standard deviation was less than one, except for H3, H6, and H7 (up to 3.2).

DISCUSSION

The details of the chemistry of bis[π-(3)-1,2-dicarbollyl]metalates of nickel and palladium have been discussed previously.[5] Singly crystal studies of Ni(II) [1,6] and Ni(IV) [7,8] bis[π-dicarbollyl] metalates have also been reported. The structure of tetramethylammonium 3,3′-commo-bis[1,2-dicarba-3-nickela-closo-dodecaborate](1 –) is of particular interest in that it completes the series of Ni(II) (d^6), Ni(III) (d^7), and Ni(IV) (d^8) dicarbollides which have been studied by single crystal X-ray analysis. The "slipped sandwich" structure observed for the Cu(III), Au(III), Cu(II), and Ni(II) dicarbollides results in the metal-carbon distances being longer than the metal-boron distances. This geometry was originally suggested to be the result of electronic factors;[1] however, the nearly symmetrical π sandwich configuration obtained with the bis-(3)-1,7-dicarbollylnickelate(II) dianion,[6] the distortions observed in the molecular structure of the racemic (3,4′)[$(CH_3)_2B_9C_2H_9$]$_2$Ni(IV),[8] and in the [$Co(B_9C_2H_8Br_3)_2^-$] anion [9] have led to the more recent conclusion that ligand symmetry and inter-cage non-bonded repulsions are probably responsible for observed differences in the geometries of the bis[π-dicarbollyl] metalates.[6]

In particular, in the structure of (3,4′)[$(CH_3)_2B_9C_2H_9$]$_2$Ni(IV),[8] the average Ni – C distance is 2.194 Å (± 0.031) and the average Ni – B distance is 2.109 Å (± 0.050). The structure of this compound strongly implies that inter-cage non-bonded repulsions are important. It is significant that the non-planarity of the two facial pentagonal planes apparently occurs at the expense of the metal-ring carbon bonds.

The nickel-cage interatomic distances given in Table 4 are slightly larger than those obtained for the corresponding Ni(IV) complex, $Ni(B_9C_2H_{11})_2$. In the nickel(IV) compound the average Ni – C distance is 2.071 Å within a range of ± 0.006 Å, while the average Ni – B distance is 2.103 Å within a range of ± 0.018 Å. The corresponding values for the nickel(III) compound are 2.146 Å and 2.134 (± 0.026) Å. The details of the Ni(II) 1,2-dicarbollide must be inferred from the structure of the isomorphous Cu(II) compound.[2] However, the corresponding values for the 1,7-dicarbollylnickelate(II) dianion are 2.25 (± 0.14) Å and 2.14 (± 0.04) Å.

In fact, however, a comparison of the metal-ring atom distances is complicated by the three different configurations observed for the bis(3)-1,2-dicarbollides of nickel. The Ni(II) derivative has the "slipped" sandwich structure with the nickel atom 0.6 Å from the centre of the five face atoms of the cage.[1] The Ni(IV) compound has the carbon atoms in opposite cages nearly *cis* to each other, with staggered five membered rings. In the present structure, the carbon atoms in the two facial five membered rings which form the sandwich are *trans* to each other, and the nickel atom is only 0.05 Å from the (unweighted) centre of the ring (Fig. 1). If inter-cage proton-proton repulsion forces are alone responsible for the differences in these structures,

Table 4. Bond lengths and selected angles. Standard deviations in terms of the last digit.

Bond	Å	Bond	Å
Ni – C2	2.146 (5)	B9 – B9′	1.759 (14)
Ni – B3	2.108 (6)	B9 – B12	1.764 (11)
Ni – B5	2.160 (9)	C2 – H1	0.97 (5)
C2 – C2′	1.589 (10)	B3 – H2	1.07 (5)
C2 – B3	1.724 (8)	B5 – H3	1.10 (6)
C2 – B7	1.750 (10)	B7 – H4	1.17 (11)
C2 – B8	1.698 (9)	B8 – H5	1.01 (8)
B3 – B5	1.769 (8)	B9 – H6	1.13 (6)
B3 – B8	1.795 (9)	B12 – H7	1.09 (10)
B3 – B9	1.791 (9)	N – C1N	1.506 (14)
B5 – B9	1.775 (10)	N – C2N	1.505 (11)
B7 – B8	1.775 (10)	C1N – H9	1.00 (7)
B7 – B12	1.767 (15)	C1N – H10	0.94 (14)
B8 – B9	1.784 (10)	C2N – H8	1.16 (7)
B8 – B12	1.787 (10)	C2N – H11	1.08 (9)

Angle	Degrees	In cage:	Degrees
C1N – N – C1N′	112.4 (9)	C2 – Ni – C2′	43.5 (2)
C1N – N – C2N	108.7 (3)	C2 – Ni – B3	47.8 (2)
C2N – N – C2N′	109.6 (8)	B3 – Ni – B5	49.0 (2)
		C2 – Ni – B3	79.7 (2)
		C2 – Ni – B5	81.2 (3)
		B3 – Ni – B3′	83.5 (2)

Between cages:	Degrees
C2 – Ni – B3	100.3 (2)
C2 – Ni – B5	98.8 (3)
B3 – Ni – B3″	96.6 (2)

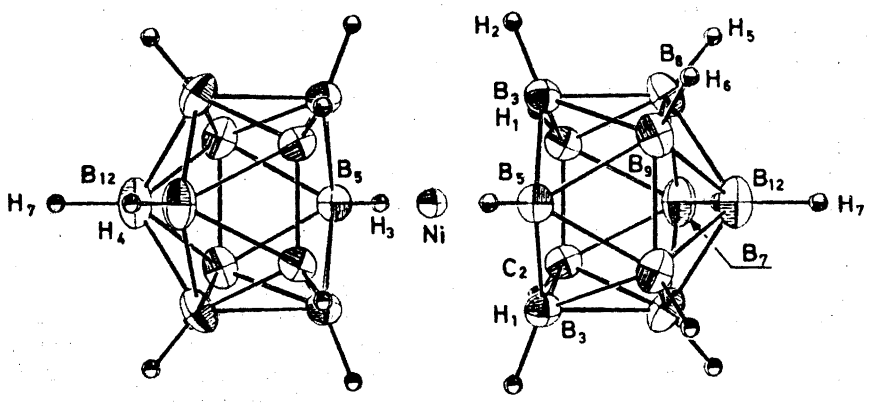


Fig. 1. Perspective drawing of the complex anion showing 50 % probability ellipsoids for the heavier atoms, and small, arbitrary size spheres for hydrogen atoms, made by means of program ORTEP2.[10]

it is difficult to understand why the *trans* structure is possible for the smaller d^7 (Ni(III)) but not for the larger d^8 (Ni(II)).

One is struck by the result that in all of the nickel dicarbollide structures, the average nickel-boron atom distances are within ± 0.04 Å of each other while the average nickel-carbon distances vary from 2.07 to 2.25 Å. In the three unsubstituted compounds, the average nickel-carbon bond lengths are 0.03 Å shorter, 0.01 Å longer and 0.11 Å longer than the nickel-boron bond lengths for Ni(IV), Ni(III), and Ni(II), respectively. Although the last figure must be taken with some reservation since the two nickel carbon distances to the 2,7-dicarbollide anion differ greatly and the distances for the Ni(II) 1,2 dicarbollide are not precisely known, it would appear that the different gross geometries in the unsubstituted nickel series may be the result of relatively constant nickel-boron bond properties but different nickel-carbon bond requirements for Ni(II), Ni(III), and Ni(IV). The observed electron deficiency of the carbon atoms [5] in the Ni(IV) compound would be expected to result in their readily accepting charge in the Ni(II) and Ni(III) complexes, with accordingly larger values for the electron-electron repulsion integrals associated with the metal-carbon interaction. The importance of the inter-cage nonbonded interactions is not lessened by this interpretation, and undoubtedly also must be considered in dicarbollide stereochemistry.

Table 5. Distances from best planes. Plane I through C2, B3, B5, B3′, C2′. Plane II through B7, B8, B9, B9′, B8′.

Atom	Distance from I (Å)	Distance from II (Å)
C2	−0.012	1.468
B3	0.031	1.539
B5	−0.037	1.490
B7	−1.510	−0.037
B8	−1.462	0.030
B9	−1.532	−0.011
B12	−2.430	−0.931
Ni	1.557	3.058

The angle between I and II: 1.0°.

Table 6. Distances between atoms in adjacent cages.

	Å		Å		Å
C2 – B3	3.266	B3 – H1	3.052	H1 – H2	2.956
C2 – B5	3.269	B3 – H2	2.931	H1 – H3	2.625
B3 – B3	3.146	B5 – H1	3.003	H2 – H2	2.370
		C2 – H3	3.094		

The relative planarities of the rings C2′ – C2 – B3 – B5 – B3′, and B7 – B8 – B9 – B9′ – B8′ and the dihedral angle between the above planes are given in Table 5. Selected nonbonded distances are given in Table 6.

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REFERENCES

1. Wing, R. M. *J. Am. Chem. Soc.* **90** (1968) 4828.
2. Guggenberger, L. J. and Prewitt, C. Program ACAC, E. I. duPont de Nemours and Co., Wilmington, Del. 1966.
3. Zalkin, A., Hopkins, T. E. and Templeton, D. H. *Inorg. Chem.* **5** (1966) 1189.
4. Busing, W. R., Martin, K. O. and Levy, H. A. *ORFLS.* Oak Ridge National Laboratory, Oak Ridge, Tenn. 1962.
5. Warren, Jr., L. F. and Hawthorne, M. F. *J. Am. Chem. Soc.* **92** (1970) 1157.
6. Wing, R. M. *J. Am. Chem. Soc.* **92** (1970) 1187.
7. St. Clair, D., Zalkin, A. and Templeton, D. H. *J. Am. Chem. Soc.* **92** (1970) 1173.
8. Churchill, M. R. and Gold, K. *J. Am. Chem. Soc.* **92** (1970) 1180.
9. DeBoer, B. G., Zalkin, A. and Templeton, D. H. *Inorg. Chem.* **7** (1968) 2289.
10. Johnson, C. K. *ORTEP2.* Oak Ridge National Laboratory, Oak Ridge, Tenn. 1971.

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