

The Crystal Structure of Bis(trimethylphosphite)tetraphenylboronrhodium(I)

BY M. J. NOLTE AND G. GAFNER

Chemical Physics Group, National Physical Research Laboratory, CSIR, Pretoria, South Africa

(Received 16 November 1973; accepted 19 November 1973)

Bis(trimethylphosphite)tetraphenylboronrhodium(I) is monoclinic with $a=15.59$ (1), $b=11.51$ (1), $c=19.74$ (1) Å, $\beta=120.72$ (7)°, $Z=4$, space group $P2_1/c$. Least-squares refinement with counter data decreased R to 0.051. One carbon ring of the tetraphenylboron group is π -bonded to the rhodium atom which is situated symmetrically with respect to the ring.

Introduction

The crystal structure of bis(trimethylphosphite)tetraphenylboronrhodium(I) was determined for Dr W. Robb and Mrs L. Haines of the National Chemical Research Laboratory. Their interest in the bridge structure of the rhodium-chlorine compounds led to the preparation of the present compound. An ionic complex, characterized as the five-coordinated $\text{Rh}[\text{P}(\text{OCH}_3)_3]_2\text{B}(\text{C}_6\text{H}_5)_4$, was formed on addition of $\text{NaB}(\text{C}_6\text{H}_5)_4$ and an excess of $\text{P}(\text{OCH}_3)_3$ in methanol to $[\text{C}_8\text{H}_{12}\text{RhCl}]_2$. This complex decomposed in air with subsequent formation of $\text{Rh}[\text{P}(\text{OCH}_3)_3]_2\text{B}(\text{C}_6\text{H}_5)_4$. The question to be settled was the manner in which the tetraphenylboron anion was attached to the rhodium atom.

Experimental

Preliminary photographs of the deep-yellow, prismatic crystals indicated the space group $P2_1/c$ (systematic absences for $h0l$, l odd and $0k0$, k odd). Cell dimensions are: $a=15.59$ (1), $b=11.51$ (1), $c=19.74$ (1) Å, $\beta=120.72$ (7)°. The experimental density of 1.39 g cm⁻³ compared well with the calculated value of 1.40 g cm⁻³ for a cell containing four monomer molecules of molecular weight 668.3.

Intensities were measured between 3 and 20° 2θ with graphite-monochromated Mo $K\alpha$ radiation on a Philips PW 1100 diffractometer and a crystal of $0.02 \times 0.02 \times 0.035$ cm dimensions. Each reflexion was scanned over 1.2° in 60 s and the same time was taken to accumulate the background count. The 200, $\bar{1}\bar{3}0$ and $42\bar{4}$ reflexions were chosen as standards and remeasured every hour. Background and L_p corrections were applied. Absorption corrections were obviated by the small change in transmission factor (0.86 to 0.88). Extinction was also negligible. Of the 3112 intensities measured, 2540 were classified as observed with $I > 2\sigma$ above background.

Refinement

All calculations were performed on an IBM 360/65 computer with the X-RAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickenson &

Hall, 1972). A Patterson map revealed the position of the rhodium atom and the remaining atoms were located by Fourier syntheses. Refinement of the positional parameters, isotropic temperature factors and an overall scale factor, with the full-matrix least-squares program *CRYLSQ* and unit weights, decreased R to 0.071 [$R = (\sum ||F_o| - |F_c||) / \sum |F_o|$]. Further refinement, varying the temperature factors of the atoms anisotropically, resulted in $R=0.051$. The scattering factors used were those of Cromer & Mann (1968). The final positional and thermal parameters are listed in Table 1. Tables 2 and 3 contain the interatomic distances and angles calculated by the program *BONDLA*. Table 4 lists the deviations of the phenyl ring atoms from their best planes. The observed and calculated structure factors are available.*

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30283 (15 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

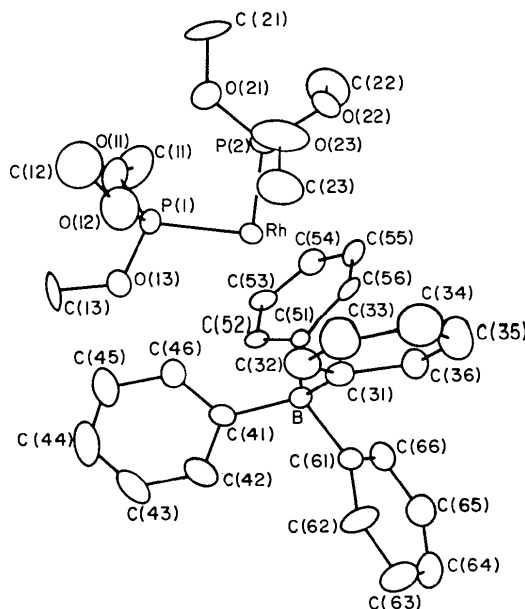


Fig. 1. Molecular geometry of $\text{Rh}[\text{P}(\text{OCH}_3)_3]_2\text{B}(\text{C}_6\text{H}_5)_4$ with atomic numbering.

Discussion

The molecular geometry and atomic numbering are shown in Fig. 1. The main point of interest is the

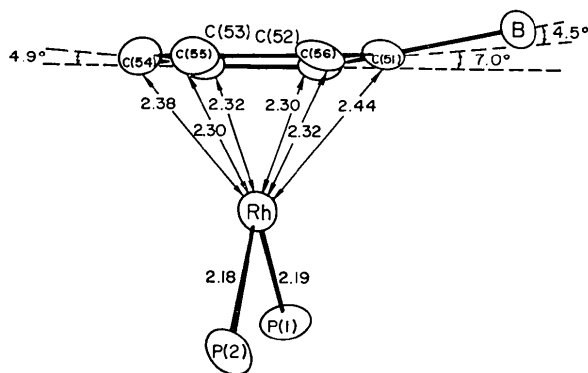


Fig. 2. Bond distances (Å) and angles (°) between the rhodium atom and its nearest neighbours.

bonding of the tetraphenylboron anion to the rhodium atom through a slightly buckled arene ring. After the preliminary results had been reported (Nolte, Gafner & Haines, 1969), publication of the structural details was delayed to allow reconsideration of whether deviations from planarity of the bonding ring were significant. Dr E. Singleton kindly prepared the compound anew and the structure was redetermined. The previous results were reproduced satisfactorily and the present paper reports this redetermination. The rhodium atom is situated symmetrically with respect to one of the phenyl rings of the $B(C_6H_5)_4$ group, 1.87 Å from the mean plane of the ring. Comparison with the value 1.72 Å in $(C_6H_6)Cr(CO)_3$ (Bailey & Dahl, 1965) leads to the conclusion that the rhodium atom is π -bonded to the phenyl ring. The non-bonded phenyl rings are planar with r.m.s. deviations of 0.01–0.02 Å, whereas the bonded phenyl ring displays distortions consistent with a boat configuration, having an r.m.s. deviation of 0.04 Å (Fig. 2). The dihedral angles between the best plane through C(52)C(53)C(55)C(56) and the

Table 1. Final atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\text{Å}^2 \times 10^4$) with their standard deviations in parentheses

Thermal parameters are in the form $T = \exp[-2\pi^2(a^*h^2U_{11} + b^*k^2U_{22} + c^*l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Rh	7968 (1)	2210 (1)	428 (1)	276 (4)	240 (4)	290 (4)	-6 (3)	160 (4)	-20 (3)
P(1)	6854 (2)	1799 (2)	751 (2)	245 (15)	446 (18)	427 (17)	-81 (13)	205 (13)	-98 (14)
P(2)	7079 (2)	1315 (2)	-693 (1)	378 (15)	233 (14)	311 (15)	-27 (12)	188 (13)	-42 (12)
O(11)	6664 (7)	531 (7)	911 (6)	996 (66)	527 (54)	1194 (75)	-273 (51)	895 (63)	-144 (53)
O(12)	5710 (6)	2233 (9)	122 (5)	540 (56)	1232 (81)	824 (63)	-102 (55)	332 (52)	-200 (60)
O(13)	7104 (4)	2496 (6)	1518 (3)	326 (35)	493 (43)	309 (37)	-86 (32)	206 (32)	-97 (33)
O(21)	6391 (5)	299 (7)	-697 (4)	671 (50)	635 (52)	586 (49)	-323 (43)	397 (43)	-201 (42)
O(22)	7661 (5)	728 (6)	-1078 (4)	568 (45)	498 (46)	440 (43)	-69 (38)	340 (38)	-148 (37)
O(23)	6343 (6)	2044 (7)	-1449 (4)	882 (60)	508 (54)	335 (44)	168 (45)	-24 (42)	-73 (39)
C(11)	7522 (11)	-237 (12)	1350 (8)	1100 (111)	627 (93)	958 (108)	-42 (88)	568 (93)	366 (85)
C(12)	4821 (9)	1730 (15)	-244 (8)	307 (76)	1468 (143)	750 (100)	20 (84)	37 (72)	-147 (98)
C(13)	6474 (7)	2433 (11)	1871 (6)	483 (65)	827 (88)	594 (73)	-25 (63)	470 (62)	-36 (66)
C(21)	5734 (10)	-385 (12)	-1418 (8)	891 (97)	866 (102)	698 (90)	-660 (86)	298 (80)	-555 (83)
C(22)	8351 (9)	-234 (11)	-660 (8)	779 (90)	571 (84)	1026 (105)	375 (74)	500 (84)	8 (78)
C(23)	6113 (8)	3229 (9)	-1448 (6)	658 (78)	421 (76)	508 (74)	216 (61)	192 (64)	98 (59)
B	8228 (7)	5536 (8)	543 (6)	238 (59)	178 (58)	321 (63)	10 (47)	162 (52)	-7 (50)
C(31)	7604 (7)	5874 (7)	-415 (5)	394 (62)	152 (50)	348 (57)	28 (44)	202 (53)	36 (44)
C(32)	6568 (7)	6134 (8)	-850 (6)	377 (63)	334 (59)	305 (63)	58 (48)	117 (51)	33 (48)
C(33)	6090 (7)	6392 (9)	-1647 (6)	459 (66)	492 (70)	457 (76)	49 (56)	193 (62)	45 (58)
C(34)	6604 (9)	6406 (9)	-2057 (6)	712 (86)	422 (70)	496 (71)	84 (61)	280 (70)	111 (58)
C(35)	7661 (8)	6186 (9)	-1613 (6)	661 (82)	379 (66)	512 (77)	85 (57)	360 (66)	109 (57)
C(36)	8131 (7)	5932 (8)	-817 (5)	470 (61)	299 (57)	328 (63)	-8 (48)	262 (54)	71 (48)
C(41)	7576 (6)	5673 (7)	978 (5)	310 (57)	158 (48)	262 (55)	53 (44)	146 (45)	30 (44)
C(42)	7948 (7)	6270 (8)	1690 (6)	521 (65)	315 (61)	478 (69)	102 (51)	307 (59)	22 (55)
C(43)	7410 (9)	6299 (10)	2099 (6)	774 (89)	529 (76)	500 (72)	188 (68)	409 (70)	-13 (60)
C(44)	6471 (9)	5762 (11)	1766 (8)	567 (81)	655 (84)	859 (100)	198 (68)	557 (77)	197 (76)
C(45)	6100 (7)	5170 (10)	1065 (6)	415 (63)	555 (73)	491 (71)	115 (55)	296 (59)	83 (61)
C(46)	6653 (7)	5115 (8)	689 (5)	347 (60)	271 (56)	410 (60)	43 (48)	232 (52)	85 (48)
C(51)	8636 (6)	4184 (7)	683 (5)	184 (48)	196 (51)	261 (55)	-55 (40)	112 (43)	-35 (45)
C(52)	8859 (6)	3583 (7)	1376 (5)	180 (48)	235 (55)	234 (54)	-88 (43)	54 (42)	-75 (46)
C(53)	9422 (6)	2511 (8)	1629 (5)	174 (48)	244 (57)	338 (56)	-37 (44)	52 (45)	-40 (47)
C(54)	9733 (6)	1992 (8)	1147 (6)	243 (54)	309 (58)	524 (70)	-11 (45)	216 (53)	-38 (55)
C(55)	9412 (6)	2500 (8)	399 (6)	244 (51)	305 (61)	476 (67)	-61 (48)	232 (50)	-28 (51)
C(56)	8877 (6)	3567 (7)	178 (5)	250 (52)	202 (55)	455 (61)	-98 (45)	232 (49)	-58 (49)
C(61)	9213 (6)	6376 (7)	952 (5)	341 (61)	220 (59)	235 (52)	-42 (45)	155 (47)	-11 (43)
C(62)	9067 (7)	7584 (8)	919 (6)	449 (63)	249 (65)	632 (73)	-114 (54)	261 (57)	-39 (55)
C(63)	9874 (9)	8367 (9)	1279 (7)	647 (84)	352 (66)	584 (75)	-159 (65)	307 (67)	12 (59)
C(64)	10839 (8)	7948 (11)	1645 (6)	545 (79)	656 (90)	339 (63)	-213 (66)	262 (60)	-30 (60)
C(65)	11004 (7)	6757 (10)	1664 (6)	433 (68)	540 (81)	407 (65)	-126 (60)	208 (56)	-84 (58)
C(66)	10185 (7)	5993 (9)	1320 (5)	248 (58)	472 (64)	269 (55)	-68 (52)	113 (47)	-100 (49)

Table 2. Bond distances (Å) and standard deviations

Rh—P(1)	2.19 (1) Å	C(31)—C(32)	1.42 (1) Å
Rh—P(2)	2.18 (1)	C(32)—C(33)	1.39 (1)
P(1)—O(11)	1.55 (1)	C(33)—C(34)	1.40 (2)
P(1)—O(12)	1.65 (1)	C(34)—C(35)	1.44 (2)
P(1)—O(13)	1.58 (1)	C(35)—C(36)	1.38 (1)
P(2)—O(21)	1.58 (1)	C(36)—C(31)	1.41 (2)
P(2)—O(22)	1.60 (1)	C(41)—C(42)	1.40 (1)
P(2)—O(23)	1.58 (1)	C(42)—C(43)	1.43 (2)
O(11)—C(11)	1.46 (2)	C(43)—C(44)	1.40 (2)
O(12)—C(12)	1.32 (2)	C(44)—C(45)	1.38 (2)
O(13)—C(13)	1.47 (2)	C(45)—C(46)	1.40 (2)
O(21)—C(21)	1.49 (1)	C(46)—C(41)	1.40 (1)
O(22)—C(22)	1.47 (1)	C(51)—C(52)	1.41 (1)
O(23)—C(23)	1.41 (1)	C(52)—C(53)	1.45 (1)
Rh—C(51)	2.44 (1)	C(53)—C(54)	1.41 (2)
Rh—C(52)	2.30 (1)	C(54)—C(55)	1.42 (1)
Rh—C(53)	2.32 (1)	C(55)—C(56)	1.42 (1)
Rh—C(54)	2.38 (1)	C(56)—C(51)	1.42 (2)
Rh—C(55)	2.30 (1)	C(61)—C(62)	1.40 (1)
Rh—C(56)	2.32 (1)	C(62)—C(23)	1.41 (1)
B—C(31)	1.67 (1)	C(63)—C(64)	1.38 (2)
B—C(41)	1.64 (2)	C(64)—C(65)	1.39 (2)
B—C(51)	1.65 (1)	C(65)—C(66)	1.41 (1)
B—C(61)	1.64 (1)	C(66)—C(61)	1.38 (1)

C(51)C(52)C(56) and C(53)C(54)C(55) planes are 5 and 7° respectively. The dihedral angles vary between 0.5 and 2° for the non-bonded rings. The four distances Rh—C(52), Rh—C(53), Rh—C(55) and Rh—C(56) average 2.31 Å, while the other two, Rh—C(51) (2.44 Å) and Rh—C(54) (2.38 Å), are significantly longer. This distortion of the bonded phenyl ring might be a consequence of packing forces, but is probably the result of a slight

localization of the bonding M.O.'s of the ring on the carbon atoms 2, 3, 5 and 6.

Considering the deviations from planarity of the bonding ring 5, it appears unsatisfactory to describe the π -bonding to the rhodium atom in terms of undistorted sixfold symmetry as was the case with $(C_6H_6)Cr(CO)_3$. The structures described by Ibers & Snyder (1962) and Coetzer & Gafner (1970), where the rhodium atom is in an approximately square-planar configuration, being bonded to two chlorine atoms and

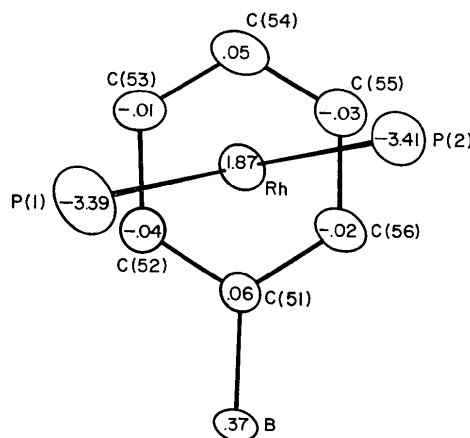


Fig. 3. Configuration around the rhodium atom including deviations (Å) from the mean plane of the bonded phenyl ring atoms.

Table 3. Bond angles (°) and standard deviations

P(1)—Rh—P(2)	90.4 (1)°	Rh—P(1)—O(11)	121.6 (5)°
P(1)—Rh—C(523)*	101.5 (3)	Rh—P(1)—O(12)	115.4 (4)
P(1)—Rh—C(556)	164.9 (3)	Rh—P(1)—O(13)	109.1 (3)
P(2)—Rh—C(523)	167.3 (3)	Rh—P(2)—O(21)	115.6 (3)
P(2)—Rh—C(556)	102.4 (3)	Rh—P(2)—O(22)	117.5 (2)
C(523)—Rh—C(556)	66.6 (4)	Rh—P(2)—O(23)	119.1 (3)
C(31)—B—C(41)	114.4 (7)	O(11)—P(1)—O(12)	101.1 (5)
C(31)—B—C(51)	111.1 (8)	O(11)—P(1)—O(13)	105.2 (5)
C(31)—B—C(61)	106.0 (8)	O(12)—P(1)—O(13)	102.3 (5)
C(41)—B—C(51)	107.0 (8)	O(21)—P(2)—O(22)	103.5 (4)
C(41)—B—C(61)	111.2 (8)	O(21)—P(2)—O(23)	102.9 (4)
C(51)—B—C(61)	106.8 (7)	O(22)—P(2)—O(23)	95.1 (5)
B—C(31)—C(32)	123.9 (11)	B—C(51)—C(52)	120.4 (9)
B—C(31)—C(36)	118.7 (8)	B—C(51)—C(56)	124.9 (9)
C(31)—C(32)—C(33)	121.2 (12)	C(51)—C(52)—C(53)	123.9 (10)
C(32)—C(33)—C(34)	121.6 (10)	C(52)—C(53)—C(54)	119.2 (9)
C(33)—C(34)—C(35)	117.4 (10)	C(53)—C(54)—C(55)	118.0 (8)
C(34)—C(35)—C(36)	120.5 (13)	C(54)—C(55)—C(56)	121.0 (11)
C(35)—C(36)—C(31)	121.8 (9)	C(55)—C(56)—C(51)	122.6 (9)
C(36)—C(31)—C(32)	117.4 (9)	C(56)—C(51)—C(52)	114.5 (8)
B—C(41)—C(42)	121.7 (8)	B—C(61)—C(62)	118.2 (8)
B—C(41)—C(46)	121.6 (8)	B—C(61)—C(66)	125.1 (8)
C(41)—C(42)—C(43)	121.2 (9)	C(61)—C(62)—C(63)	121.9 (9)
C(42)—C(43)—C(44)	119.7 (11)	C(62)—C(63)—C(64)	119.6 (10)
C(43)—C(44)—C(45)	119.4 (15)	C(63)—C(64)—C(65)	119.7 (10)
C(44)—C(45)—C(46)	120.0 (10)	C(64)—C(65)—C(66)	119.5 (9)
C(45)—C(46)—C(41)	123.1 (9)	C(65)—C(66)—C(61)	122.5 (9)
C(46)—C(41)—C(42)	116.5 (11)	C(66)—C(61)—C(62)	116.7 (8)
P(1)—O(11)—C(11)	118.5 (9)	P(2)—O(21)—C(21)	121.9 (9)
P(1)—O(12)—C(12)	135.1 (10)	P(2)—O(22)—C(22)	118.7 (9)
P(1)—O(13)—C(13)	122.2 (6)	P(2)—O(23)—C(23)	125.1 (6)

* C(523) and C(556) represent the midpoints of the bonds C(52)—C(53) and C(55)—C(56), respectively.

Table 4. Equations of mean planes $PX + QY + RZ = S$, atomic displacements, standard deviations (σ) and χ^2 for the planar arrangements

(X , Y and Z coordinates in orthogonal Å space with X measured parallel to \mathbf{a} , Y perpendicular to \mathbf{a} in the plane of \mathbf{a} and \mathbf{c} and Z perpendicular to the plane of \mathbf{a} and \mathbf{c}).

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
C(31)	-0.017 Å	C(41) 0.008 Å	C(51) 0.056 Å	C(61) 0.011 Å	Rh -0.025 Å
C(32)	0.008	C(42) 0.009	C(52) -0.039	C(62) -0.018	P(1) 0.122
C(33)	0.009	C(43) -0.018	C(53) -0.013	C(63) 0.010	P(2) -0.107
C(34)	-0.016	C(44) 0.011	C(54) 0.046	C(64) 0.004	C(523)* -0.143
C(35)	0.007	C(45) 0.007	C(55) -0.028	C(65) -0.009	C(556) 0.153
C(36)	0.009	C(46) -0.016	C(56) -0.024	C(66) 0.002	
σ	0.013	0.013	0.041	0.011	0.133
χ^2	6.19	6.18	80.94	4.31	1353.04
P	0.08949	-0.23248	0.74186	-0.50166	-0.36529
Q	0.97218	0.83441	0.50660	-0.05655	0.85418
R	0.21645	-0.49971	0.43931	0.86321	-0.37006
S	7.53306	2.09219	12.36660	-5.75416	-2.45130

* C(523) and C(556) represent the midpoints of the bonds C(52)-C(53) and C(55)-C(56), respectively.

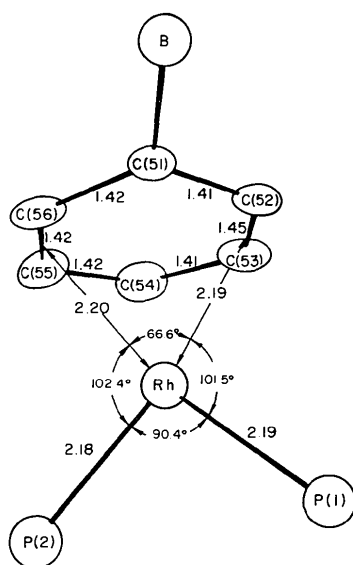


Fig. 4. Distances (Å) and angles (°) involved in a square-planar interpretation.

two double-bond centres of a cyclo-octadiene ring, show similarities with the present structure. The plane defined by the atoms Rh, P(1), and P(2) makes an angle of 91° with the mean plane of the bonded phenyl ring and intersects it in an asymmetric manner, as depicted in Fig. 3. The equation of the best plane through Rh, P(1), P(2) and bond centres of C(52)-C(53) and C(55)-

C(56) is given in Table 4. Deviations from this plane do not exceed 0.16 Å. The angles and distances involved in this grouping are shown in Fig. 4. Bearing in mind that the p orbitals are situated above and below the ring plane, the true configuration may approach a square-planar condition more nearly than appears at present.

Intramolecular distances are as expected. The mean Rh-P, P-O, O-C and benzene C-C bond lengths are respectively 2.18 (1), 1.59 (1), 1.44 (1) and 1.41 (2) Å (Coetzer & Gafner, 1970). The closest intermolecular approach distance is 3.28 Å between C(12) and O(11), the parent molecules of which are related by an inversion centre. The shortest distance between two ring members is 3.67 Å for C(34) and C(43) (glide plane). The rhodium atoms related through an inversion centre are 8.93 Å apart.

References

- BAILEY, M. F. & DAHL, L. F. (1965). *Inorg. Chem.* **4**, 1314-1319.
 COETZER, J. & GAFNER, G. (1970). *Acta Cryst.* **B26**, 985-991.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
 IBERS, J. A. & SNYDER, R. G. (1962). *Acta Cryst.* **15**, 923-930.
 NOLTE, M. J., GAFNER, G. & HAINES, L. M. (1969). *Chem. Commun.* pp. 1406-1407.
 STEWART, J. M., KRUGER, G. J., AMMON, H., DICKINSON, C. H. & HALL, S. R. (1972). Univ. of Maryland. Comput. Sci. Tech. Rep. TR-192.