Crystal and Molecular Structure of the 2:1 Adduct of Bis(pentafluorophenyl)mercury(II) and Bis(diphenylarsino)methane

By **A. J. Canty** and **B. M. Gatehouse,*** Chemistry Department, Monash University, Clayton, Victoria, Australia 3168

The title compound crystallizes in the monoclinic system with a = 14·07, b = 17·34, c = 19·33 Å, β = 91° 3′, Z = 4, and space-group $C2/c$. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares techniques to R 0·9 for 1218 independent reflections. The compound has a two-fold axis about the methylene carbon atom of the diarsine moiety. Each mercury atom has one arsenic atom within the sum of van der Waals radii from it, and there is a **T**-shaped distribution of two C_6F_5 groups and the arsenic atom about mercury with a Hg · · · As distance of 3·40 ± 0·02 Å and C–Hg–C angle of 173 ± 4°. X-Ray powder diffraction photographs indicate that the compound $[(C_6F_5)_2Hg]_2Ph_2P{\cdot}CH_2{\cdot}PPh_2$ has the same structure.

An effective co-ordination number of three for mercury is rare[1] and where three-co-ordination would be expected additional contacts between mercury and other atoms occur to give a higher co-ordination number.[1,2] In a compound in which three-co-ordination has been confirmed by X-ray diffraction, bis(ethylene oxide)-mercury,[3] it results from an intramolecular interaction with oxygen. Three-co-ordination is believed to occur in 8-quinolinolato-(ethyl)mercury(II) and -(phenyl)mercury-(II)[4] and recently several complexes of bis(pentafluorophenyl)mercury with neutral donor ligands have been prepared[5] for which i.r. spectra and solution stability indicated three-co-ordination.

However, some of the complexes have no properties indicating co-ordination of the ligands,[5] *e.g.*, the present compound completely dissociates in non-polar solvents and its i.r. spectrum is virtually identical to that of the free ligand and original organo-mercury compound. The crystal structure of one of these compounds, of formula $[(C_6F_5)_2Hg]_2(Ph_2As{\cdot}CH_2{\cdot}AsPh_2)$, has been determined to find whether there is evidence of three-co-ordination. A preliminary communication of this work has appeared previously.[6]

EXPERIMENTAL

Crystals were grown from hexane solution. A crystal of optimum diameter, 0·13 mm, and elongated in the [001] direction (0·40 mm) was chosen for data collection.

Crystal Data.—$C_{49}H_{22}As_2F_{20}Hg_2$, M = 1542, Monoclinic, a = 14·07, b = 17·34, c = 19·33 (all ± 0·02) Å, β = 91° 3′ ± 6′, U = 4715·1 Å^3. D_m = 2·15 (by flotation), Z = 4, D_c = 2·17, $F(000)$ = 2888. Space-group Cc or $C2/c$, from systematic absences, shown by the subsequent successful refinement to be the centrosymmetric space-group $C2/c$ (C^6_{2h}). Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 15·05 cm^{-1}.

1218 Independent non-zero reflections were collected with a Nonius equi-inclination Weissenberg goniometer for reciprocal lattice levels $hk0$—12 and measured visually with a calibrated scale. The data were corrected for spot-shape and for Lorentz and polarization effects. A three-dimensional Patterson synthesis gave a solution for the mercury position and a subsequent difference Fourier synthesis led to location of the arsenic atom. These positions led to R 0·33 but the remaining light atoms were present as broad diffuse peaks in a difference Fourier synthesis. Difference Fourier syntheses indicated that the mercury atom was vibrating anisotropically, and satisfactory positions for the light atoms could only be found when anisotropic thermal parameters were used for mercury (R 0·27). The carbon and fluorine atoms were introduced gradually through several cycles of structure-factor calculations and difference Fourier syntheses. With all light atoms included R was 0·18.

Throughout the refinement difficulty was experienced with the light atoms. With the relatively large contribution of the mercury and arsenic atoms, the data seemed to be insensitive to shifts of the light atoms of the order of one-half of their standard deviations from the final model. Two cycles of block-diagonal least-squares refinement varying atom positional parameters led to R 0·16 and three further cycles varying all positional parameters, anisotropic thermal parameters for mercury and arsenic, isotropic for all other atoms, led to R 0·13.

At this stage a bond-lengths and -angles calculation showed that all atoms except C(2), C(3), C(13), and C(14) were in positions which give bond lengths within 3σ of the results obtained on completion of the refinement. The C(2)–C(3) and C(13)–C(14) distances were only 0·9 and 1·0 Å respectively. Slight adjustments were made to the positions of these atoms to give bond lengths of 1·36 Å and refinement proceeded. All atom parameters were held constant while one cycle varying individual scales was carried out (R 0·10).

Two more cycles varying positional and thermal parameters and finally two cycles of full-matrix least-squares refinement varying positional parameters were carried out. The final R was 0·9 for all observed reflections (1218), and 0·11 for all observed and unobserved reflections; the unobserved reflections (201) were given an arbitrary intensity value of one-half of that of the weakest observed reflections. In the last two cycles parameter shifts were less than 0·5σ. A three-dimensional difference Fourier synthesis showed no maxima $>\frac{1}{4}$ or minima $<-\frac{1}{4}$ of the mean electron-density value of the observed carbon atoms in the structure. No correction was made for anomalous dispersion or absorption and in all refinements reflections were assigned unit weight.

The following programs were used: block-diagonal least-squares by Shiono, University of Pittsburgh, 1968; full-matrix least-squares by Busing and Levy, modified by White; and ORTEP: a thermal-ellipsoid plot program for crystal-structure illustrations, Johnson, Oak Ridge National

---

[1] D. Grdenic, *Quart. Rev.*, 1965, 303.

[2] See, *e.g.*, J. G. White, *Acta Cryst.*, 1963, **16**, 397.

[3] D. Grdenic, *Acta Cryst.*, 1952, **5**, 367.

[4] R. Barbiera, G. Faraglia, M. Giustiniani, and L. Roncucci, *J. Inorg. Nuclear Chem.*, 1964, **26**, 203.

[5] A. J. Canty and G. B. Deacon, *Austral. J. Chem.*, 1971, **24**, 489.

[6] A. J. Canty and B. M. Gatehouse, *Chem. Comm.*, 1971, 443.

Laboratory, 1965. The first- and last-named of these were modified by J. E. Davies for the CDC 3200 computer.

Powder photographs were obtained by use of a Philips Debye–Scherrer 114·6 mm powder camera using nickel-filtered Cu-K_{α} radiation, and line intensities were measured with a double-beam recording microdensitometer.

RESULTS AND DISCUSSION

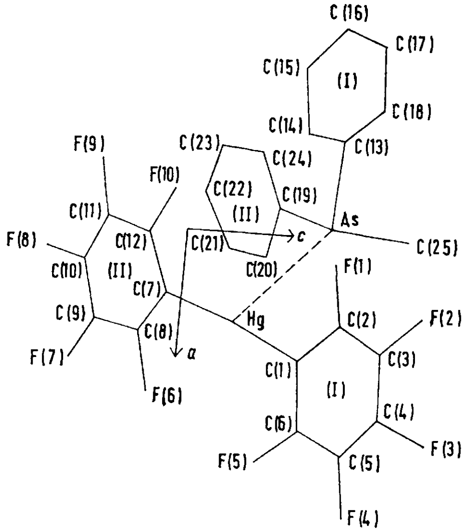

FIGURE 1 A diagram of the asymmetric unit, showing the atom numbering scheme

TABLE 1

Atomic co-ordinates with estimated standard deviations of atoms within the asymmetric unit of one molecule

	x/a	y/b	z/c	$B/\text{Å}^2$
Hg	0·1392(1)	0·0710(1)	0·0579(1)	*
As	−0·0152(3)	0·1623(3)	0·1635(3)	*
C(1)	0·2014(25)	−0·0021(20)	0·1366(20)	3·2
C(2)	0·1401(30)	−0·0484(25)	0·1780(25)	5·1
C(3)	0·1848(34)	−0·0956(27)	0·2187(27)	6·0
C(4)	0·2797(34)	−0·0972(27)	0·2202(27)	6·0
C(5)	0·3368(33)	−0·0576(28)	0·1915(26)	5·8
C(6)	0·3007(35)	−0·0064(29)	0·1415(28)	6·5
C(7)	0·0968(25)	0·1428(21)	−0·0222(20)	3·2
C(8)	0·1603(29)	0·1916(26)	−0·0540(24)	5·0
C(9)	0·1413(31)	0·2424(26)	−0·1051(24)	5·0
C(10)	0·0494(35)	0·2520(30)	−0·1178(27)	6·5
C(11)	−0·0251(29)	0·2067(24)	−0·0957(23)	4·5
C(12)	0·0043(26)	0·1572(22)	−0·0399(22)	3·6
C(13)	−0·1456(27)	0·1189(24)	0·1704(23)	4·2
C(14)	−0·1580(32)	0·0565(28)	0·1283(26)	6·2
C(15)	−0·2521(36)	0·0191(31)	0·1204(27)	7·2
C(16)	−0·3231(30)	0·0541(26)	0·1620(25)	5·7
C(17)	−0·3038(31)	0·1161(27)	0·2112(25)	5·7
C(18)	−0·2126(30)	0·1519(26)	0·2143(25)	5·4
C(19)	−0·0496(25)	0·2545(22)	0·0984(21)	3·5
C(20)	0·0333(28)	0·2980(25)	0·0879(23)	4·8
C(21)	0·0228(34)	0·3628(29)	0·0419(27)	6·6
C(22)	−0·0746(36)	0·3826(31)	0·0145(27)	7·2
C(23)	−0·1502(31)	0·3324(28)	0·0300(26)	5·8
C(24)	−0·1375(31)	0·2693(26)	0·0814(25)	5·5
C(25)	0·0000(0)	0·2261(32)	0·2500(0)	4·1
F(1)	0·0497(14)	−0·0447(11)	0·1691(11)	5·1
F(2)	0·1257(20)	−0·1399(17)	0·2680(16)	6·9
F(3)	0·3166(20)	−0·1432(16)	0·2796(16)	8·9
F(4)	0·4332(19)	−0·0564(16)	0·1945(15)	9·0
F(5)	0·3533(19)	0·0350(16)	0·0983(15)	8·2
F(6)	0·2555(16)	0·1811(14)	−0·0361(13)	5·8
F(7)	0·2081(16)	0·2884(14)	−0·1330(13)	6·1
F(8)	0·0234(20)	0·3103(18)	−0·1672(16)	8·5
F(9)	−0·1135(18)	0·2191(15)	−0·1101(14)	6·9
F(10)	−0·0683(16)	0·1114(14)	−0·0170(13)	5·7

* Anisotropic thermal parameters:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0·0056	0·0043	0·0054	−0·0001	0·0002	0·0002
As	0·0047	0·0041	0·0043	0·0001	0·0005	−0·0001

where the coefficients are from the expression

$$f = f_0 \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

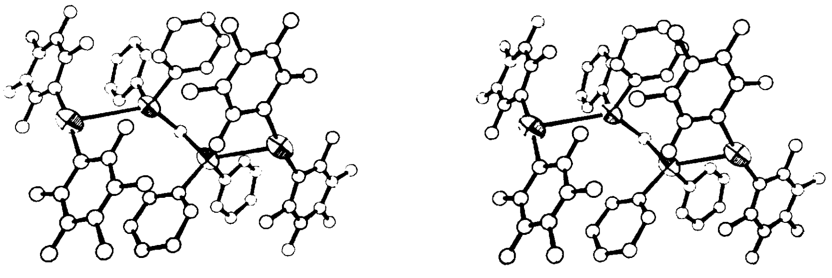

FIGURE 2 Stereoscopic view along the [010] direction to show the two-fold axis

The final atomic co-ordinates are listed in Table 1. Aspects of the molecular geometry are listed in Tables 2 and 3. Observed and calculated structure factors are listed in Supplementary Publication No. 20270 (2 pp., 1 microfiche).* Table 4 gives equations of best least-squares planes. Two different views of the molecule are given in Figures 1 and 2, and Figure 3 shows the contents of one unit cell. The methylene carbon atom of the diarsine lies on the special position $0y,\frac{1}{4}$ imparting a two-fold axis to the compound (Figure 2). Except for one carbon atom from each C_6F_5 group bonded to mercury, the only other atom, which lies within van der Waals distance of it is an arsenic. The two C_6F_5 groups and arsenic atom are distributed in a T-shape about the mercury atom with a mercury–arsenic distance of 3·40 ± 0·02 Å, As · · · Hg–C angles of 90 and 96 ± 3°, and C–Hg–C angles of 173 ± 4°. The arsenic and carbon atoms are within their standard deviations from the mean plane defined by them and the mercury atom, but the mercury atom is 0·057 ± 0·006 Å from it. The C(1)–Hg–C(7) angle is, within experimental error, the same as in the free organo-mercury compound [7] (176·2 ±

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[7] N. R. Kunchur and M. Mathew, *Chem. Comm.*, 1966, 71.

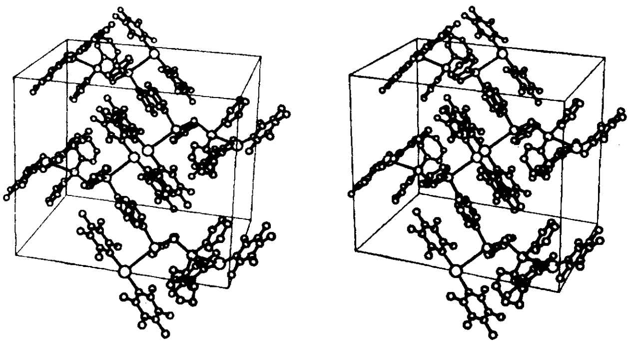

FIGURE 3 Stereoscopic illustration of the contents of one unit cell viewed almost normal to the (100) plane

TABLE 2

Interatomic distances (Å) with estimated standard deviations in parentheses

(*a*) Mercury environment

Hg · · · As	3·40(5)	Hg–C(7)	2·07(4)
Hg–C(1)	2·15(4)		

(*b*) Pentafluorophenyl group, I

C(1)–C(2)	1·43(6)	C(2)–F(1)	1·28(5)
C(2)–C(3)	1·30(7)	C(3)–F(2)	1·49(6)
C(3)–C(4)	1·34(7)	C(4)–F(3)	1·48(6)
C(4)–C(5)	1·20(7)	C(5)–F(4)	1·36(6)
C(5)–C(6)	1·40(7)	C(6)–F(5)	1·33(6)
C(1)–C(6)	1·40(6)		

(*c*) Pentafluorophenyl group, II

C(7)–C(8)	1·38(6)	C(8)–F(6)	1·39(5)
C(8)–C(9)	1·35(6)	C(9)–F(7)	1·35(5)
C(9)–C(10)	1·32(7)	C(10)–F(8)	1·43(6)
C(10)–C(11)	1·38(7)	C(11)–F(9)	1·29(5)
C(11)–C(12)	1·43(6)	C(12)–F(10)	1·37(5)
C(7)–C(12)	1·36(5)		

(*d*) Phenyl group, I

C(13)–C(14)	1·36(6)	C(16)–C(17)	1·46(6)
C(14)–C(15)	1·48(7)	C(17)–C(18)	1·42(6)
C(15)–C(16)	1·43(7)	C(13)–C(18)	1·40(6)

(*e*) Phenyl group, II

C(19)–C(20)	1·41(6)	C(22)–C(23)	1·41(7)
C(20)–C(21)	1·44(7)	C(23)–C(24)	1·49(7)
C(21)–C(22)	1·50(7)	C(19)–C(24)	1·30(6)

(*f*) Arsenic environment

As · · · Hg	3·40(5)	As–C(19)	2·09(4)
As–C(13)	1·99(4)	As–C(25)	2·01(5)

TABLE 3

Angles (°) with estimated standard deviations in parentheses

(*a*) About mercury

As · · · Hg–C(1)	96(1)	C(1)–Hg–C(7)	173(1·4)
As · · · Hg–C(7)	90(1)		

(*b*) Pentafluorophenyl group, I

C(6)–C(1)–C(2)	123(4)	C(1)–C(2)–F(1)	120(4)
C(1)–C(2)–C(3)	114(4)	C(3)–C(2)–F(1)	126(4)
C(2)–C(3)–C(4)	120(5)	C(2)–C(3)–F(2)	116(4)
C(3)–C(4)–C(5)	131(5)	C(4)–C(3)–F(2)	123(4)
C(4)–C(5)–C(6)	116(5)	C(3)–C(4)–F(3)	111(4)
C(5)–C(6)–C(1)	115(4)	C(5)–C(4)–F(3)	116(4)
Hg–C(1)–C(2)	119(3)	C(4)–C(5)–F(4)	132(5)
Hg–C(1)–C(6)	118(3)	C(6)–C(5)–F(4)	112(4)
		C(5)–C(6)–F(5)	125(4)
		C(1)–C(6)–F(5)	120(4)

TABLE 3 (*Continued*)

(*c*) Pentafluorophenyl group, II

C(12)–C(7)–C(8)	114(4)	C(7)–C(8)–F(6)	116(4)
C(7)–C(8)–C(9)	127(4)	C(9)–C(8)–F(6)	116(4)
C(8)–C(9)–C(10)	113(4)	C(8)–C(9)–F(7)	123(4)
C(9)–C(10)–C(11)	128(5)	C(10)–C(9)–F(7)	122(4)
C(10)–C(11)–C(12)	111(4)	C(9)–C(10)–F(8)	117(4)
C(11)–C(12)–C(7)	124(4)	C(11)–C(10)–F(8)	115(4)
Hg–C(7)–C(8)	121(3)	C(10)–C(11)–F(9)	125(4)
Hg–C(7)–C(12)	124(3)	C(12)–C(11)–F(9)	122(4)
		C(11)–C(12)–F(10)	113(3)
		C(7)–C(12)–F(10)	122(3)

(*d*) Phenyl group, I

C(18)–C(13)–C(14)	127(4)	C(16)–C(17)–C(18)	120(4)
C(13)–C(14)–C(15)	121(4)	C(17)–C(18)–C(13)	114(4)
C(14)–C(15)–C(16)	113(4)	As–C(13)–C(14)	112(3)
C(15)–C(16)–C(17)	124(4)	As–C(13)–C(18)	121(3)

(*e*) Phenyl group, II

C(24)–C(19)–C(20)	130(4)	C(22)–C(23)–C(24)	121(4)
C(19)–C(20)–C(21)	116(4)	C(23)–C(24)–C(19)	115(4)
C(20)–C(21)–C(22)	119(4)	As–C(19)–C(20)	108(3)
C(21)–C(22)–C(23)	118(4)	As–C(19)–C(24)	121(3)

(*f*) About arsenic

Hg · · · As–C(13)	118(1)	C(13)–As–C(19)	97(2)
Hg · · · As–C(19)	98(1)	C(13)–As–C(25)	104(2)
Hg · · · As–C(25)	134(2)	C(19)–As–C(25)	96(2)
		As–C(25)–As	113(3)

TABLE 4

(*a*) Equations of best least-squares planes in the form $Ax + By + Cz + D = 0$, referred to crystal axes

	A	*B*	*C*	*D*
Plane (1): Hg, As, C(1), C(7)	−0·6879	−0·6840	−0·2427	2·5042
Plane (2): C(1)—(6)	0·0284	−0·7394	−0·6727	1·6148
Plane (3): C(7)—(12)	0·1139	−0·6785	−0·7257	1·2083
Plane (4): C(13)—(18)	−0·2428	0·6365	−0·7321	0·6146
Plane (5): C(19)—(24)	0·1823	−0·5845	−0·7906	4·267

(*b*) Distances of relevant atoms from the planes

Plane (1): Hg 0·057, As −0·002(5), C(1) −0·027(36), C(7) −0·028(35).

Plane (2): C(1) −0·055, C(2) −0·024(5), C(3) 0·068(50), C(4) 0·109(50), C(5) −0·003(50), C(6) −0·028(52), F(1) 0·008(20), F(2) −0·028(30), F(3) −0·061(30), F(4) −0·019(29), F(5) 0·029(29), Hg 0·006(2)

Plane (3): C(7) −0·005(37), C(8) −0·029(45), C(9) 0·060(46), C(10) −0·021(52), C(11) 0·082(43), C(12) −0·073(40), F(6) −0·004(25), F(7) 0·020(25), F(8) −0·053(31), F(9) −0·002(27), F(10) 0·027(24), Hg −0·219(2)

Plane (4): C(13) 0·028(42), C(14) −0·027(49), C(15) −0·006(53), C(16) 0·037(46), C(17) −0·036(48), C(18) 0·004(46), As 0·158(5)

Plane (5): C(19) 0·050(39), C(20) −0·017(44), C(21) 0·005(52), C(22) −0·025(53), C(23) 0·051(49), C(24) −0·065(47), As 0·073(05)

Planes (2) and (3) are inclined at 7° to each other and at 62 and 60° to Plane (1).

1·2°) but the angle of 7° between the mean planes of the C_6F_5 groups is appreciably different (59·4 ± 1·2°).

The mercury–arsenic distance of 3·40 ± 0·02 Å is 0·10 Å less than the sum of the van der Waals radii (2·0 Å for arsenic,[8] 1·5 Å for mercury [1]), although according to Grdenic an upper limit of 1·73 Å for the radius of mercury can be used as a criterion to indicate some form

---

[8] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell, University Press, Ithaca, New York.

of bonding.[1] Each arsenic atom adjacent to a mercury atom is further away from it than either of the two arsenic atoms considered to be involved in a co-ordinate bond to mercury in tris-[(*o*-diphenylarsinophenyl)-arsine]mercury(II) bromide.[9] This compound has two arsenic atoms at 2·60 and 2·82 Å from mercury, and two others at 3·60 and 5·22 Å, considered to be outside the mercury co-ordination sphere.[9] A weak mercury–sulphur interaction has been confirmed from visible spectra for bis(phenoxathi-in)mercury(II) chloride [10] with mercury–sulphur distances 0·23 Å less than the sum of the van der Waals radii, taking 1·50 Å as the radius for mercury. Thus, any mercury–arsenic interaction in the present compound would be very weak, as suggested from the solution studies mentioned above.

The C–C bond distances within the C_6F_5 rings range from 1·30—1·43 Å, mean 1·36(7) Å, except for one abnormally short value of 1·20 Å in ring I. The two atoms concerned, C(4) and C(5), were found to lie in confused regions of the difference Fourier syntheses. The C–F bond distances range from 1·28—1·49 Å, mean 1·38(0·07) Å. In the parent organo-mercury compound C–C and C–F bond distances are 1·34—1·44 and 1·33—1·47 respectively.[7]

The atoms of the C_6F_5 groups are within two standard deviations of the mean planes of the rings and the mercury atom is within three standard deviations of ring I but is 0·219(2) Å from the mean plane of ring II. Similar results occur for the phenyl rings with the arsenic atom 0·158(5) Å from the mean plane of ring II.

The C–C bond distances in the phenyl rings range from 1·30—1·50 Å, mean 1·42(7) Å. The As–C distances [2·0—2·1(6) Å] and As–C–As angle [113(3)°] are similar to those found in $[Rh(CO)Cl]_2(Ph_2As{\cdot}CH_2{\cdot}AsPh_2)_2$ [11] [1·925—1·943(9) Å and 113·5(4)°].

Throughout the structure phenyl and C_6F_5 groups are packed parallel to each other, the shortest distance between groups being 3·24(7) Å between C(14) and F(10). The shortest intermolecular distance [3·15(7) Å] is from C(3) to F(9) of the molecule transformed by $\bar{x},\bar{y},\bar{z}$. It is possible that this compound should be considered as a crystalline molecular compound of two components with the mercury and arsenic atoms adjacent to one another as the result of advantageous packing of the two molecular species.*

X-Ray powder photographs of the diphosphine compound of formula $[(C_6F_5)_2Hg]_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)$, indicated that this compound probably has the same structure. The powder spectra are virtually identical, and the lines of the diphosphine complex can be indexed with the unit cell of the diarsine complex.

We thank the Australian Research Grants Committee for financial support of this work and the Commonwealth Scientific and Industrial Research Organisation for a studentship (to A. J. C.).

[1/809 *Received*, **20*th May***, **1971**]

---

* Attention was drawn to this aspect by the referees.

[9] G. Dwyer, D. C. Goodall, R. H. B. Mais, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1110.

[10] R. S. McEwen and G. A. Sim, *J. Chem. Soc.* (*A*), **1969**, 1897.

[11] J. T. Mague, *Inorg. Chem.*, **1969**, **8**, 1975.