Stereochemistry of Some Organic Derivatives of Group Vb Elements. Part VIII.[1] Crystal and Molecular Structure of μ-Chloro-bis[hydroxytriphenylarsenic](1+) Dichloroiodate(1−)

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Crystals of the title compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 14{\cdot}259(2)$, $b = 14{\cdot}374(2)$, $c = 17{\cdot}653(3)$ Å, $\beta = 90{\cdot}15(1)°$. The structure was solved by the heavy-atom method and refined by least-squares techniques to $R = 0{\cdot}046$ for 2441 observed intensities. The compound is correctly formulated as $[Ph_3As{-}O{-}H \cdots Cl \cdots H{-}O{-}AsPh_3]^+ICl_2^-$. The chloride ion bridges the hydroxy groups *via* strong hydrogen bonds. The stereochemistry of the arsenic atoms is very slightly distorted tetrahedral. Mean dimensions are: As–C(Ph) 1·901(10), As–O 1·727(7) and 1·716(7), I–Cl 2·513(3) and 2·542(4) Å. The hydrogen atoms involved in the bridging have been located, with mean distances O–H 0·89 and $H \cdots Cl^-$ 2·13 Å.

TRIPHENYLARSINE hydroxide chloride and bromide are weak electrolytes in methyl cyanide and *X*-ray investigations of their crystal structures have shown [2,3] that in the solid state they exist as strongly hydrogen-bonded species which may be represented by $Ph_3AsO(H)Cl$. While conductometric titrations of these compounds in methyl cyanide with bromine and iodine chloride indicated that the halogen adducts $Ph_3As(OH)BrBr_3$ and $Ph_3As(OH)Cl,ICl_2$ were strong electrolytes of the form $Ph_3AsOH^+X_3^-$ (X = halogen), attempts [4] to isolate crystals by precipitation from methyl cyanide solution with ether repeatedly gave orange crystals which, on the basis of spectroscopic measurements, were formulated as $(Ph_3\overset{+}{A}sOH)_2Br^-Br_3^-$ and $(Ph_3\overset{+}{A}sOH)_2Cl^-,ICl_2^-$. In view of the unexpected composition and in the light of our previous work with the triphenylarsine hydroxide halides, we undertook three-dimensional *X*-ray analyses of both adducts. The structure of $(Ph_3\overset{+}{A}sOH)_2Br^-Br_3^-$ has been reported [5] and we now report that of $(Ph_3\overset{+}{A}sOH)_2Cl^-,ICl_2^-$.

EXPERIMENTAL

Crystal Data.—$C_{36}H_{32}As_2Cl_3IO_2$, $M = 879{\cdot}8$, Monoclinic, $a = 14{\cdot}259(2)$, $b = 14{\cdot}374(2)$, $c = 17{\cdot}653(3)$ Å, $\beta = 90{\cdot}15(1)°$, $U = 3618$ Å^3, D_m not measured (insufficient material), $Z = 4$, $D_c = 1{\cdot}615$, $F(000) = 1736$. Space group $P2_1/c$ (C_{2h}^5, No. 14). Mo-K_α *X*-radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 30·6 cm^{-1}.

Crystallographic Measurements.—Preliminary precession and Weissenberg photographs indicated that the crystals were isomorphous with the tribromide salt.[5] Accurate cell dimensions were obtained from least-squares refinement of the setting angles of 12 reflexions measured on a Hilger and Watts Y 290 four-circle diffractometer. The crystal chosen for data collection was a square plate 0·04 × 0·09 × 0·07 mm (face perpendicular to the *a* axis) bounded by (0,−1,1) and (0,1,1), with the *b* and *c* axes along the plate diagonals. Intensity data were collected by use of Mo-K_α *X*-radiation to $\theta_{max.}$ of 20° by the θ—2θ scan technique with a symmetric scan of 0·6° and a scan rate of 0·6° min^{-1}. Stationary-crystal–stationary-counter background counts of 15 s were measured at each end of the integrated scan. The intensities of 3 standard reflexions, monitored regularly throughout data collection, showed no significant variation.

Each intensity was corrected for background and the estimated standard duration for each intensity was given by $\sigma(I) = [\text{scan} + 4 \times (\text{sum of backgrounds}) + (p \times \text{intensity})^2]^{1/2}$. A value of 0·05 for p gave an adequate weighting of the data. The forms hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ were collected and equivalent intensities averaged. Of 3370 independent intensities obtained, 2441 having $I > 3\sigma(I)$ were considered observed and used in the subsequent refinement. Data were corrected for Lorentz and polarization factors, but not for absorption or extinction.

Structure Determination.—The co-ordinates of the iodine and arsenic atoms were obtained by comparison of the three-dimensional Patterson function with the known co-ordinates for the isomorphous tribromide.[5] A structure-factor calculation carried out after least-squares refinement of the scale factor, with the heavy atoms assigned isotropic temperature factors (B_{iso} 2·0 Å^2), gave R 0·381. Atomic scattering factors for carbon, oxygen, chlorine, arsenic, and iodine were taken from ref. 6, and for hydrogen from ref. 7. Corrections for anomalous dispersion for arsenic and iodine were included later. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and absolute weights [based on $\sigma(F_o) = 0{\cdot}5\sigma(F_o{}^2)/F_o$] were used throughout. The first difference-Fourier calculation revealed all non-hydrogen atom positions and, when all these were included in isotropic least-squares refinement by the block-diagonal approximation, convergence was achieved at R 0·106. The arsenic, iodine, chlorine, and oxygen atoms were allowed anisotropic vibration and the refinement then converged at R 0·047. On the last cycles the maximum change in any parameter was 0·5σ. A final difference-Fourier synthesis was computed and revealed the positions of 29 of the 30 phenyl hydrogen atoms as small peaks (0·6—1·0 eÅ^{-3}). In addition two poorly resolved peaks were observed slightly above background between the oxygens and Cl(3) (see Figure 1). The theoretical positions of all 30 phenyl hydrogen atoms were computed (taking C–H 1·08 Å) and a further structure-factor calculation, with all hydrogen atoms assigned B_{iso} 6·5 Å^2, gave R 0·046. A final difference synthesis revealed two clearly resolved peaks, each 0·62 eÅ^{-3} and *ca.* 0·9 Å from O(1) and O(2), and lying between these atoms and Cl(3). Although these peak

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[1] Part VII, F. C. March, G. Ferguson, and D. Lloyd, preceding paper.

[2] G. Ferguson and E. W. Macaulay, *Chem. Comm.*, 1968, 1288.

[3] E. W. Macaulay, Ph.D. Thesis, 1968, University of Glasgow.

[4] G. S. Harris and F. Inglis, *J. Chem. Soc.* (*A*), 1967, 497.

[5] M. Calleri and G. Ferguson, *Cryst. Struct. Comm.*, 1972, **7**, 331.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

[7] R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

Table 1

Atomic positional and thermal parameters

Atom	x/a	y/b	z/c	U_{iso}
I	0·59576(6)	0·49462(6)	0·37075(4)	*
As(1)	0·17467(8)	0·28424(7)	0·42261(6)	*
As(2)	−0·19873(8)	0·11739(8)	0·43778(6)	*
Cl(1)	0·6264(3)	0·6682(3)	0·3592(2)	*
Cl(2)	0·5571(4)	0·3242(3)	0·3759(3)	*
Cl(3)	0·0309(2)	0·0629(2)	0·3332(2)	*
O(1)	0·0964(5)	0·2559(5)	0·3515(4)	*
O(2)	−0·1013(5)	0·0535(5)	0·4614(4)	*
C(11)	0·2782(7)	0·2057(7)	0·4192(6)	0·053(3)
C(12)	0·3191(8)	0·1771(8)	0·4869(7)	0·068(3)
C(13)	0·4000(9)	0·1177(9)	0·4846(8)	0·084(4)
C(14)	0·4383(9)	0·0908(9)	0·4154(7)	0·079(4)
C(15)	0·3955(9)	0·1205(9)	0·3473(8)	0·090(4)
C(16)	0·3145(8)	0·1794(8)	0·3487(7)	0·073(4)
C(21)	0·1164(7)	0·2717(7)	0·5184(5)	0·046(3)
C(22)	0·0629(8)	0·1951(8)	0·5318(6)	0·061(3)
C(23)	0·0239(8)	0·1827(8)	0·6050(7)	0·072(3)
C(24)	0·0407(8)	0·2460(9)	0·6623(7)	0·074(4)
C(25)	0·0993(8)	0·3231(9)	0·6481(7)	0·079(4)
C(26)	0·1361(8)	0·3382(8)	0·5755(6)	0·066(3)
C(31)	0·2048(7)	0·4105(7)	0·4015(6)	0·048(3)
C(32)	0·2833(7)	0·4489(8)	0·4316(6)	0·060(3)
C(33)	0·3028(8)	0·5460(9)	0·4166(7)	0·071(3)
C(34)	0·2395(8)	0·5944(8)	0·3742(7)	0·070(3)
C(35)	0·1610(8)	0·5552(8)	0·3421(7)	0·068(3)
C(36)	0·1408(8)	0·4604(8)	0·3563(6)	0·064(3)
C(41)	−0·2671(7)	0·1297(7)	0·5291(6)	0·052(3)
C(42)	−0·3438(8)	0·1874(8)	0·5297(6)	0·064(3)
C(43)	−0·3973(9)	0·1974(9)	0·5966(7)	0·081(4)
C(44)	−0·3652(10)	0·1480(10)	0·6613(8)	0·095(4)
C(45)	−0·2907(9)	0·0906(10)	0·6589(8)	0·094(4)
C(46)	−0·2373(8)	0·0783(8)	0·5924(6)	0·065(3)
C(51)	−0·2667(7)	0·0488(8)	0·3622(6)	0·057(3)
C(52)	−0·3376(8)	0·0924(8)	0·3229(7)	0·073(4)
C(53)	−0·3880(9)	0·0339(9)	0·2689(7)	0·083(4)
C(54)	−0·3685(9)	−0·0577(9)	0·2626(7)	0·078(4)
C(55)	−0·2961(9)	−0·0982(10)	0·3013(8)	0·090(4)
C(56)	−0·2390(8)	−0·0456(9)	0·3534(7)	0·072(4)
C(61)	−0·1626(7)	0·2370(7)	0·4019(6)	0·051(3)
C(62)	−0·1568(8)	0·2534(8)	0·3234(7)	0·070(3)
C(63)	−0·1307(9)	0·3446(9)	0·3013(7)	0·081(4)
C(64)	−0·1100(9)	0·4129(9)	0·3538(7)	0·085(4)
C(65)	−0·1147(9)	0·3963(10)	0·4312(8)	0·090(4)
C(66)	−0·1424(8)	0·3042(8)	0·4571(7)	0·070(3)
H(12)	0·290	0·199	0·540	
H(13)	0·432	0·094	0·537	
H(14)	0·500	0·048	0·414	
H(15)	0·424	0·098	0·249	
H(16)	0·282	0·203	0·297	
H(22)	0·050	0·145	0·488	
H(23)	−0·019	0·123	0·616	
H(24)	0·009	0·237	0·717	
H(25)	0·116	0·371	0·694	
H(26)	0·178	0·399	0·563	
H(32)	0·331	0·408	0·466	
H(33)	0·365	0·579	0·439	
H(34)	0·252	0·668	0·365	
H(35)	0·115	0·596	0·307	
H(36)	0·079	0·427	0·333	
H(42)	−0·363	0·225	0·479	
H(43)	−0·459	0·241	0·598	
H(44)	−0·402	0·157	0·714	
H(45)	−0·271	0·053	0·709	
H(46)	−0·177	0·032	0·590	
H(52)	−0·405	0·123	0·333	
H(53)	0·447	−0·063	−0·239	
H(54)	−0·442	−0·042	0·269	
H(55)	−0·281	−0·071	0·293	
H(56)	−0·180	−0·075	0·383	
H(62)	−0·171	0·199	0·283	
H(63)	−0·127	0·361	0·242	
H(64)	−0·089	0·481	0·334	
H(65)	−0·099	0·451	0·471	
H(66)	−0·147	0·288	0·517	
H(1)	0·090	0·201	0·342	
H(2)	−0·044	0·044	0·434	

* Anisotropic thermal parameters: see Supplementary Publication.

heights are not large (estimated σ in electron density [8] 0·3 Å^3) the fact that they are both at the same height and are in similar and chemically sensible positions with respect to the nearest oxygen atoms suggests that they correspond to the hydroxy-hydrogen atoms.

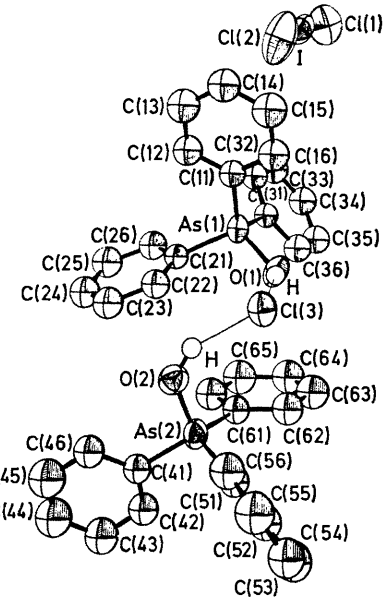

Figure 1 A formula unit showing the atomic numbering scheme

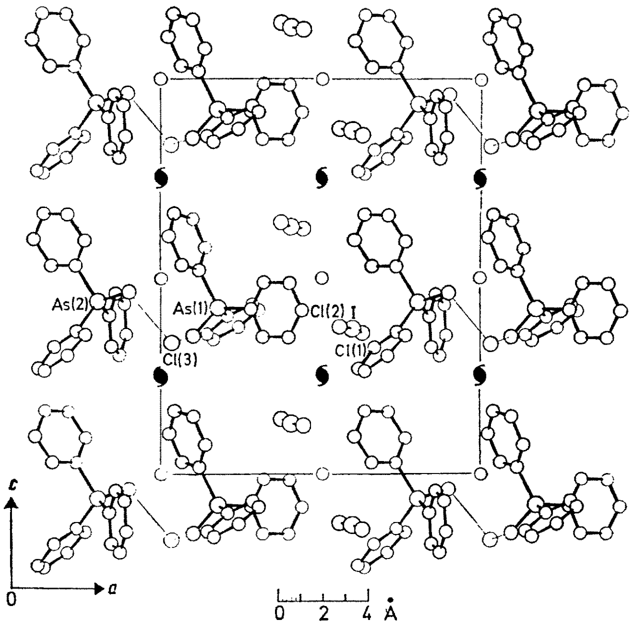

Figure 2 The crystal packing one molecule deep, viewed down the crystallographic b axis

The final error in an observation of unit weight, calculated over all observed data, was 1·98 and ranged from 1·6 to 2·1

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[8] G. H. Stout and L. H. Jenson, 'X-Ray Structure Determination,' Macmillan, Toronto, 1968, p. 403.

over 10 ranges of intensity, indicating that the relative weighting of the data was adequate. Final structure amplitudes, thermal parameters, and details of planes are listed in Supplementary Publication No. SUP 21315 (10 pp, 1 microfiche).† Final values of the agreement factors for all data are R 0·063, R' $\{=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$ 0·062.

TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Distances			
I–Cl(1)	2·542(4) [2·572(4)] *		
I–Cl(2)	2·513(5) [2·560(5)]		
As(1)–O(1)	1·727(7) [1·745(7)]		
As(2)–O(2)	1·716(7) [1·727(7)]		
As(1)–C(11)	1·859(10)		
As(1)–C(21)	1·894(10)		
As(1)–C(31)	1·902(10)		
As(2)–C(41)	1·894(10)		
As(2)–C(51)	1·903(11)		
As(2)–C(61)	1·919(11)		
Mean C–C (all bonds)	1·402(5)		
O(1)–H(1)	0·81	Cl(3) ··· O(2)	2·953(8)
O(2)–H(2)	0·97	Cl(3) ··· H(1)	2·17
Cl(3) ··· O(1)	2·946(8)	Cl(3) ··· H(2)	2·08
(*b*) Angles			
Cl(1)–I–Cl(2)	176·3(2)	C(41)–As(2)–C(61)	109·8(4)
O(1)–As(1)–C(11)	110·2(4)	C(51)–As(2)–C(61)	111·7(4)
O(1)–As(1)–C(21)	110·1(4)	As(1)–O(1)–H(1)	117
O(1)–As(1)–C(31)	103·2(4)	As(2)–O(2)–H(2)	130
O(2)–As(2)–C(41)	105·2(4)	O(1) ··· Cl(3) ··· O(2)	99·3(2)
O(2)–As(2)–C(51)	107·5(4)	As(1)–O(1) ··· Cl(3)	120·4(3)
O(2)–As(2)–C(61)	110·1(4)	As(2)–O(2) ··· Cl(3)	107·9(3)
C(11)–As(1)–C(21)	108·7(4)	Cl(3) ··· H(1)–O(1)	162
C(11)–As(1)–C(31)	113·2(4)	Cl(3) ··· H(2)–O(2)	148
C(21)–As(1)–C(31)	111·4(4)	H(1) ··· Cl(3) ··· H(2)	105
C(41)–As(2)–C(51)	112·3(4)		
(*c*) Intraionic distances			
O(1) ··· C(11)	2·94(1)	O(1) ··· C(31)	2·85(1)
O(1) ··· C(21)	2·97(1)	O(1) ··· C(36)	3·01(1)
O(2) ··· C(41)	2·87(1)	O(2) ··· C(61)	2·97(1)
O(2) ··· C(51)	2·94(1)	O(2) ··· C(46)	3·04(1)
(*d*) Interionic distances			
I ··· C(53$^{\rm I}$)	3·89	I ··· C(32$^{\rm II}$)	3·97
Cl(1) ··· C(26$^{\rm II}$)	3·58	Cl(1) ··· C(55$^{\rm III}$)	3·68
Cl(1) ··· C(12$^{\rm II}$)	3·59		
Cl(2) ··· C(42$^{\rm IV}$)	3·76	Cl(2) ··· C(15)	3·76
C(12) ··· C(56$^{\rm V}$)	3·58	C(22) ··· C(66)	3·57
C(14) ··· C(52$^{\rm IV}$)	3·60	C(33) ··· C(53$^{\rm I}$)	3·50
C(14) ··· C(45$^{\rm V}$)	3·60	C(34) ··· C(53$^{\rm I}$)	3·41
C(15) ··· C(45$^{\rm V}$)	3·38	C(34) ··· C(66$^{\rm VI}$)	3·59
C(15) ··· C(53$^{\rm IV}$)	3·61	C(45) ··· C(63$^{\rm VII}$)	3·52

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $-x, \frac{1}{2}+y, \frac{1}{2}-z$
II $1-x, 1-y, 1-z$
III $1+x, 1+y, z$
IV $1+x, y, z$
V $-x, -y, 1-z$
VI $-x, 1-y, 1-z$
VII $x, \frac{1}{2}-y, \frac{1}{2}+z$

* Distances corrected for thermal motion, based on the riding model approximation, are in square brackets.

Final atomic co-ordinates are listed in Table 1, and important interatomic distances and angles in Table 2. Figure 1 shows a formula unit together with the atomic numbering scheme used in the analysis, and Figure 2 the crystal packing one molecule deep, projected on the xy plane.

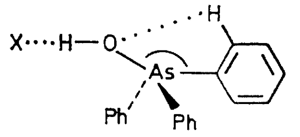
DISCUSSION

The system $[(\mathrm{Ph_3\overset{+}{A}sOH})_2\mathrm{Cl^-ICl_2^-}]$ is more correctly formulated $[\mathrm{Ph_3As{-}O{-}H\cdots Cl\cdots H{-}O{-}AsPh_3}]^+\mathrm{ICl_2}^-$ with two tetrahedral triphenylarsine hydroxide groups linked by strong $\mathrm{O{-}H\cdots Cl^-}$ hydrogen bonds to a single chlorine ion, and with independent, discrete $\mathrm{ICl_2}^-$ ions. The structure closely resembles that of the isomorphous bromide derivative [5] but is of greater accuracy because of the considerably better data set obtained.

The $\mathrm{OH\cdots Cl^-}$ distances [2·946 and 2·953(8) Å] are intermediate between the very short distances found [2] in triphenylarsine hydroxide chloride [2·854 and 2·817(17) Å] and the mean [3·08(1) Å] reported in ref. 9. Mean O–H and $\mathrm{H\cdots Cl^-}$ distances are 0·89 and 2·13 Å, with angles $\mathrm{O{-}H\cdots Cl^-}$ 162 and 148°, and $\mathrm{As{-}O\cdots Cl^-}$ 107·9 and 120·4(3)°. The angles at the chlorine atom which takes part in the bifurcated hydrogen bond are: H(1) ··· Cl(3) ··· H(2) 105 and O(1) ··· Cl(3) ··· O(2) 99·3(2)°.

The $\overset{+}{\mathrm{A}}$s–O distances [1·727(7) and 1·716(7) Å] are as expected.[2,9] The mean $\overset{+}{\mathrm{A}}$s–C distance [1·901(10) Å] is also close to those found in similar molecules.[2,9-11] Bonding about arsenic is close to regular tetrahedral except for angles O(1)–As(1)–C(31) [103·2(4)°] and O(2)–As(2)–C(41) [105·2(4)°]. These angles are similar to those found for a number of other cases where a phenyl group is oriented similarly to that in (I).[5,11] In each case the phenyl group in question lies close to the plane formed by As, O, and the halogen atoms. In the present structure (Figure 1) this results in fairly short C ··· O distances [C(36) ··· O(1) 3·01(1) and C(46) ··· O(2) 3·04(1) Å] and would imply that an *ortho*-C–H group is pointing between the lobes of the non-bonded electron pairs of the oxygen atom. Evidently a type of hydrogen-bonded attraction occurs resulting in closure of the O–As–C(Ph) angle. A somewhat similar situation has been discussed by Mathieson [12] who made a survey of several structures containing ester groups in the equatorial position of six-membered rings. In all these structures the ester group was oriented so that it was coplanar with the axial hydrogen atom of the ring carbon atom and the preference for this was ascribed to an interaction between the hydrogen atom and the double-bonded oxygen atom of the ester group.

(I)



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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[9] G. Ferguson and E. W. Macaulay, *J. Chem. Soc.* (*A*), 1969, 7.

[10] G. C. Pimental and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960.

[11] G. S. Harris, F. Inglis, J. McKechnie, K. K. Cheung, and G. Ferguson, *Chem. Comm.*, 1967, 142, and unpublished results.

[12] A. M. Mathieson, *Tetrahedron Letters*, 1965, **46**, 4137.

The ICl_2^- group is almost linear [Cl–I–Cl 176·3(2)°] and slightly asymmetric with Cl(1)–I 2·513(5) Å and Cl(2)–I 2·542(4) Å, values in accord with those found previously.[13-15] The slight asymmetry indicates that the charge in the group is not symmetrically distributed, with slightly greater negative charge on Cl(2) than on Cl(1).[15] A similar situation is found with the tribromide ion for the analogous structure. In each case this is evidently due to crystal-packing effects.

Interion distances [Table 2(*d*)] correspond to normal van der Waals interactions; the shortest contacts correspond to normal Ph · · · Ph interactions.

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[4/2216 *Received*, 28*th October*, 1974]

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[13] G. F. Visser and A. Vos, *Acta Cryst.*, 1964, **17**, 1336.

[14] N. C. Baenziger, R. E. Buckles, and T. D. Simpson, *J. Amer. Chem. Soc.*, 1967, **89**, 3405.

[15] S. Gran and C. Rømming, *Acta Chem. Scand.*, 1968, **22**, 1686.

[16] J. M. Stewart, Technical Report TR 192, 1972, University of Maryland.

[17] C. K. Johnson, ORTEP, 1965, Oak Ridge Thermal Ellipsoid Program, Oak Ridge, Tennessee.