Vibrational Spectroscopic Studies of Tetra-n-butylammonium Trihalogenomercurates; Crystal Structures of $[NBu^n{}_4](HgCl_3)$ and $[NBu^n{}_4](HgI_3)$ †

By **Peter L. Goggin, Paul King, David M. McEwan, Graham E. Taylor,** and **Peter Woodward,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS
Magnus Sandström, Department of Inorganic Chemistry, Royal Institute of Technology, 100 44 Stockholm, Sweden

The crystal structures of the title compounds have been determined. Crystals of $[NBu^n{}_4](HgCl_3)$ are triclinic, space group $P\bar{1}$ (no. 2) with $a = 11.011(3)$, $b = 11.267(3)$, $c = 19.341(5)$ Å, $\alpha = 87.33(2)$, $\beta = 102.70(2)$, $\gamma = 96.45(2)°$, and $Z = 4$. The final R value was 0.034 for 2 167 observations. The structure is the first example established where $(HgCl_3)^-$ is solely in the form of dimeric $[Hg_2Cl_6]^{2-}$ doubly chloride-bridged anions with distorted tetrahedral geometry about the mercury atoms; these anions are not centrosymmetric and although the terminal Hg–Cl bond lengths are not significantly different from one another (2.38 ± 0.01 Å) the bridge is asymmetric with bond lengths $2.66_5 \pm 0.01$ and 2.57 ± 0.02 Å. Crystals of $[NBu^n{}_4](HgI_3)$ are tetragonal, space group $I\bar{4}2d$ (no. 122) with $a = 13.790(5)$, $c = 26.537(5)$ Å, and $Z = 8$. The final R value was 0.059 for 1 189 independent intensities measured at 200 K. The structure consists of discrete $[NBu^n{}_4]^+$ cations and $[HgI_3]^-$ anions. One Hg–I bond lies on a crystallographic two-fold axis and is of length 2.683(2) Å; the other two bonds are not significantly different [2.688(2) Å] but make an interbond angle of 115° giving the anion C_{2v} and not D_{3h} symmetry. The closest approach between atoms of different anions is *ca.* 7.4 Å precluding any significant polymeric interaction and making this the first example containing a truly monomeric trihalogenomercurate(II) anion. The $[NBu^n{}_4]^+$ groups show the expected regular tetrahedral arrangement of bonds around the N atom, but each of the n-butyl chains has the C atoms approximately co-planar, and the ion as a whole is crystallographically constrained to C_2 symmetry. Vibrational spectra are rationalised in the light of the crystal structures and indicate that the anion of $[NBu^n{}_4](HgBr_3)$ is dimeric $[Hg_2Br_6]^{2-}$. The spectral detail is greatly enhanced in measurements at low temperature (*ca.* 100 K), especially for the dimeric anions. The structural variety shown by trihalogenomercurates is discussed.

CRYSTAL structures of several trihalogenomercurate(II) salts have been reported, and show a wide variety of stereochemical arrangements. If mercury halide contacts within the sum of van der Waals radii are regarded as bonds, no case described so far contains three-coordinate mercury.

Trichloromercurates ‡ with relatively small cations, $[C_5H_5NH](HgCl_3)\cdot 1.5H_2O$,[1] $[NH_4](HgCl_3)$,[2,3] $Na(HgCl_3)\cdot 2H_2O$,[4] and $Cs(HgCl_3)$,[4,5] all have the mercury atom in some form of distorted octahedral environment whilst those with somewhat larger cations, $[S_4N_3](HgCl_3)$,[6] $[SMe_3](HgCl_3)$,[7] and α-$[NEt_4](HgCl_3)$,[8] have the metal in distorted trigonal-bipyramidal sites. A trigonal-bipyramidal arrangement also occurs for $[SMe_3](HgI_3)$ [9] but structures of all tribromomercurates and all other tri-iodomercurates reported have four halides around the metal in a distorted tetrahedral fashion: $K(HgBr_3)H_2O$,[10] $[NMe_4](HgBr_3)$,[11] $K(HgI_3)H_2O$,[12] $[NMe_4](HgI_3)$,[13] $[(Ph_3AsO)_2H](HgBr_3)$,[14] $[(Cu_2Au)(S_2CNBu_2)_6](HgBr_3)_2$,[15] $[Cu_3(S_2CNBu_2)_6](HgBr_3)_2$,[16] and $[S_3C_2N_2Et_4](HgI_3)_2$.[17] In the last four of these, the anions are discrete doubly halide-bridged dimers $[Hg_2X_6]^{2-}$, a structural form which had not been observed crystallographically for a trichloromercurate salt.

Since the completion of this work two significant structures of trihalogenomercurates have been reported. In $[NPr^n{}_4](HgI_3)$ discrete dimeric $[Hg_2I_6]^{2-}$ anions are present.[18] The salt $[C_6H_4S_4](HgCl_3)$§ is a unique case where the anion is present in two different forms,[19] one polymeric $(HgCl_3)_n{}^{n-}$ and the other dimeric $[Hg_2Cl_6]^{2-}$. Vibrational spectra of $[NBu^n{}_4](HgX_3)$ salts suggested that there might be a close structural similarity between anion structures in the case of the chloride and bromide systems and could best be rationalised in terms of dimeric $[Hg_2X_6]^{2-}$ anions. The spectra of $[NBu^n{}_4](HgI_3)$ are of quite a different type indicative of a structural change with change of halide. Accordingly we have undertaken single-crystal *X*-ray studies on $[NBu^n{}_4](HgCl_3)$ and $[NBu^n{}_4](HgI_3)$ which we report together with vibrational spectra for these and for $[NBu^n{}_4](HgBr_3)$.

EXPERIMENTAL

Preparation of the Salts.—Equimolar quantities of HgX_2 and $[NBu^n{}_4]X$ were stirred with acetone (typically 0.01 mol, 100 cm³) until a clear solution was obtained. Diethyl ether was added until the onset of turbidity. The solutions were then cooled to −20 °C to yield white (Cl or Br) or lemon-yellow (I) crystals. For $[NBu^n{}_4](HgCl_3)$, m.p. 92 °C (Found: C, 34.95; H, 6.8; N, 2.75. $C_{16}H_{36}Cl_3HgN$ requires C, 34.95; H, 6.55; N, 2.55%). For $[NBu^n{}_4](HgBr_3)$, m.p. 100—102 °C (Found: C, 28.0; H, 5.5; N, 2.1. $C_{16}H_{36}Br_3HgN$ requires C, 28.15; H, 5.3; N, 2.05%). For $[NBu^n{}_4](HgI_3)$, m.p. 101 °C (Found: C, 23.2; H, 4.6; N, 1.7. $C_{16}H_{36}HgI_3N$ requires C, 23.35; H, 4.4; N, 1.7%).

For the preparation of $[NPr^n{}_4](HgI_3)$, equimolar amounts of $[NPr^n{}_4]I$ and HgI_2 were stirred together with hot acetone, using only sufficient solvent to cause complete dissolution. On cooling lemon-yellow crystals were deposited; m.p. 179

---

† Bis(tetra-n-butylammonium) di-μ-chloro-bis[dichloromercurate(II)] and tetra-n-butylammonium tri-iodomercurate(II) respectively.

‡ The anionic stoicheiometry is denoted in round brackets throughout this paper where a specific anionic structure is not being implied.

§ $[C_6H_4S_4]^+$ = 2-(1,3-dithiol-2-ylidene)-1,3-dithiole cation.

°C (Found: C, 19.0; H, 3.8; N, 1.8. $C_{12}H_{28}HgI_3N$ requires C, 18.75; H, 3.7; N, 1.8%).

Vibrational Spectra.—Far-i.r. spectra were measured with a Nicolet 7199A F.t. i.r. spectrometer using a 6.25-μm (500—100 cm^{-1}) Mylar beamsplitter and Glowbar source. Ground samples were dispersed in polyethylene powder (Specac Ltd.) and compressed to translucent discs. Measurements at low temperature (*ca.* 100 K) were made using a Specac cryostat cooled with liquid nitrogen.

Raman spectra of the powdered solids were excited with a Coherent Radiation Laboratories model 52 argon-ion laser using the 514.5-nm line. Spectra were recorded with a Coderg T800 triple monochromator using d.c. amplification. For measurement at *ca.* 100 K, a Coderg Cryocirc cryostat cooled with liquid nitrogen was used.

Crystal-structure Determination.—A parallelepipedic crystal of $[NBu^n_4](HgCl_3)$ with dimensions $0.16 \times 0.15 \times 0.08$ mm was chosen for the intensity measurements. Measurements were made at room temperature with a Syntex $P2_1$ four-circle diffractometer in conjunction with a Nova computer in the range $3 < 2\theta < 37°$. Four reflections, 0 1 0, $\bar{2}$ 0 3, $\bar{1}$ 3 0, and 0 4 0, were remeasured every 68 reflections. Their intensities decreased linearly with nearly the same relative rate during the 400 h of crystal exposure time, to a total extent of 34%. A linear correction was therefore applied on all intensities and sigma values. Of the 3 435 independent intensities measured 2 515 had $I > 2.0\sigma(I)$ of which 2 187 with $|F|_{obs.} > 20$ were used in the solution and refinement of the structure. The semi-empirical ψ scan method for correction of *X*-ray absorption was applied. The range of the normalised transmission factors was from 0.43 to 1.

The crystals of $[NBu^n_4](HgI_3)$ grow as multifaceted yellow subspheres and a crystal of approximate 'diameter' 0.15 mm was used for intensity measurements at 200 K in the range $2.9 < 2\theta < 55°$, using a Nicolet four-circle diffractometer. Check reflections 2 6 0 and 3 1 10 were remeasured every 50 reflections but showed no significant decay during the 2 d of exposure to *X*-rays. Of the 1 547 independent intensities measured, 1 189 had $I > 2.0\ \sigma(I)$ and only these were used in the solution and refinement of the structure. The intensities were corrected for Lorentz, polarisation, and *X*-ray absorption effects.[20]

Crystal data. $C_{16}H_{36}Cl_3HgN$, $M = 549.42$, Triclinic, $a = 11.011(3)$, $b = 11.267(3)$, $c = 19.341(5)$ Å, $\alpha = 87.33(2)$, $\beta = 102.70(2)$, $\gamma = 96.45(2)°$, at 298 K, $U = 2\ 326(1)$ Å^3, $D_m = 1.573(3)$, $Z = 4$, $D_c = 1.569$ g cm^{-3}, $F(000) = 1\ 080$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, and μ(Mo-K_α) = 70.9 cm^{-1}.

$C_{16}H_{36}HgI_3N$, $M = 823.8$, Tetragonal, $a = 13.790(5)$, $c = 26.537(5)$ Å, at 200 K, $U = 5\ 046.5$ Å^3, $D_m = ca.\ 2$, $Z = 8$, $D_c = 2.17$ g cm^{-3}, $F(000) = 3\ 024$, space group $I\bar{4}2d$ (no. 122), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, and μ(Mo-K_α) = 99.3 cm^{-1}.

Solution and refinement of the structures. The structures were solved by the heavy-atom method. For $[NBu^n_4](HgCl_3)$ a Patterson map revealed centrosymmetrically related positions for mercury atoms and, therefore, the centrosymmetrical space group $P\bar{1}$ was assumed. Least-squares refinements and difference-Fourier syntheses in turn revealed the positions of all non-hydrogen atoms. With anisotropic thermal parameters for the Hg and Cl atoms and isotropic thermal parameters for C and N atoms an *R* value of 0.045 (*R'* 0.056) was obtained. When anisotropic thermal coefficients were introduced for the C and N atoms, *R* decreased to 0.037 (*R'* 0.048). Finally, all 48 non-methyl hydrogen atoms were placed in calculated tetrahedral positions with a fixed isotropic thermal parameter of $U_H = 0.09$ Å^2 which gave *R* 0.034 (*R'* 0.045). A standard C–H distance of 0.96 Å was used, in accordance with the usual underestimate (by about 0.13 Å) for C–H bond distances determined by *X*-ray methods.[21]

Weights were applied according to the scheme $w = 1/[\sigma^2(F) + 0.03|F|^2]$ which gave a satisfactory weight analysis. In a final electron-density difference synthesis all remaining peaks were less than 0.5 e Å^{-3}. Using the scattering factors from ref. 22 for H and ref. 23 for all other atoms, computations were carried out with the Nova 32K computer with a disc memory unit using Syntex (XTL version 2) programs.[24]

Systematically absent reflections for $[NBu^n_4](HgI_3)$ indicated either symmetry $I4_1md$ or $I\bar{4}2d$. Patterson synthesis showed two vectors of length *ca.* 2.7 Å, a typical Hg–I bond length. These could only be interpreted, in conjunction with the other vectors, as comprising planar HgI_3 units aligned with one Hg–I bond on a crystallographic two-fold axis in space group $I\bar{4}2d$, such that the centre of the four-fold rotational inversion relates different ions to one another.

TABLE 1

Fractional atomic co-ordinates for non-hydrogen atoms of $[NBu^n_4]_2[Hg_2Cl_6]$ with estimated standard deviations in parentheses *

Atom	*x*	*y*	*z*
Hg(1)	0.040 04(7)	0.273 96(7)	0.187 93(4)
Hg(2)	0.203 12(7)	0.493 57(7)	0.328 10(4)
Cl(1)	0.006 8(4)	0.487 4(4)	0.218 6(3)
Cl(2)	0.222 5(5)	0.275 8(4)	0.303 9(3)
Cl(3)	−0.139 4(5)	0.142 2(4)	0.201 5(3)
Cl(4)	0.144 2(5)	0.252 4(5)	0.094 0(3)
Cl(5)	0.125 1(5)	0.531 5(6)	0.428 9(3)
Cl(6)	0.374 0(4)	0.616 3(4)	0.296 4(3)
N(1)	0.314 0(13)	0.608 0(12)	0.654 7(7)
C(1)	0.420 5(16)	0.617 0(14)	0.720 4(11)
C(2)	0.384 8(20)	0.610 7(20)	0.791 6(12)
C(3)	0.500 7(27)	0.606 4(27)	0.849 2(15)
C(4)	0.507 5(40)	0.573 0(43)	0.910 0(21)
C(5)	0.241 2(18)	0.713 6(18)	0.649 8(10)
C(6)	0.137 8(16)	0.725 3(19)	0.585 0(9)
C(7)	0.067 8(23)	0.835 1(21)	0.586 3(10)
C(8)	−0.046 1(18)	0.831 7(21)	0.524 4(11)
C(9)	0.373 4(16)	0.601 8(17)	0.591 4(10)
C(10)	0.448 1(17)	0.714 7(17)	0.573 2(10)
C(11)	0.516 0(20)	0.691 4(26)	0.505 8(11)
C(12)	0.589 2(22)	0.806 3(20)	0.489 5(12)
C(13)	0.224 0(16)	0.494 3(18)	0.658 9(9)
C(14)	0.279 3(20)	0.378 9(23)	0.668 7(11)
C(15)	0.193 4(21)	0.271 5(27)	0.678 2(13)
C(16)	0.253 0(27)	0.151 7(21)	0.694 8(15)
N(2)	0.148 9(17)	0.856 1(15)	0.150 8(10)
C(17)	0.148 6(17)	0.835 6(19)	0.230 4(14)
C(18)	0.126 5(24)	0.942 8(22)	0.268 4(18)
C(19)	0.151 2(34)	0.914 4(26)	0.350 6(17)
C(20)	0.278 0(29)	0.907 2(30)	0.390 3(16)
C(21)	0.168 9(18)	0.735 0(18)	0.122 7(14)
C(22)	0.172 8(23)	0.730 5(27)	0.045 2(15)
C(23)	0.196 4(32)	0.594 6(34)	0.037 0(20)
C(24)	0.186 4(35)	0.568 7(34)	−0.039 5(18)
C(25)	0.033 7(23)	0.897 1(17)	0.112 7(10)
C(26)	−0.096 7(22)	0.806 3(18)	0.120 0(13)
C(27)	−0.215 7(29)	0.853 8(26)	0.077 3(12)
C(28)	−0.334 2(29)	0.763 8(29)	0.076 3(18)
C(29)	0.248 9(28)	0.952 5(18)	0.139 6(12)
C(30)	0.379 1(29)	0.917 4(26)	0.174 7(16)
C(31)	0.480 9(32)	1.054 2(34)	0.178 2(24)
C(32)	0.496 4(41)	1.052 0(34)	0.102 6(25)

* The numbering schemes for anion and cation atoms are illustrated in Figures 1 and 2 respectively.

Subsequent electron-density difference maps revealed the positions of all the light atoms except the H atoms of the methyl groups, and the space-group assignment was confirmed by the successful refinement of the structure. Anisotropic thermal parameters were allowed for all non-hydrogen atoms. The hydrogen atoms were constrained to tetrahedral positions with C–H bond lengths of 0.96 Å and with fixed isotropic thermal parameters $U_H = 0.052$ Å^2 for methyl H atoms and $U_H = 0.036$ Å^2 for methylene H atoms.

Weights were applied according to the scheme $w = 1/[\sigma^2(F) + 0.003|F|^2]$, and this gave a satisfactory weight analysis. Refinement converged at $R = 0.059$ ($R' = 0.069$), and a final electron-density difference synthesis showed residues *ca.* ± 2 e Å^{-3} in the neighbourhood of the Hg and I atoms but a much lower general background level. Using scattering factors from ref. 22 for H and from ref. 23 for the other atoms, computations were carried out on the laboratory's own Eclipse (Data General) minicomputer with the SHELXTL system of programs.[20]

TABLE 2

Fractional atomic co-ordinates for non-hydrogen atoms of $[NBu^n_4][HgI_3]$ with estimated standard deviations in parentheses *

Atom	*x*	*y*	*z*
Hg	0.000 00 †	0.000 00 †	0.245 76(5)
I(1)	0.000 00 †	0.000 00 †	0.145 00(8)
I(2)	0.137 66(16)	0.089 36(17)	0.300 42(7)
N	0.268 8(18)	0.2500 †	0.1250 †
C(1)	0.314 3(34)	0.578 0(25)	0.051 9(14)
C(2)	0.360 4(22)	0.494 8(23)	0.070 3(11)
C(3)	0.287 4(19)	0.422 7(18)	0.089 4(9)
C(4)	0.334 6(20)	0.328 9(20)	0.106 7(8)
C(5)	0.201 2(17)	0.213 6(20)	0.082 7(10)
C(6)	0.250 4(18)	0.165 5(25)	0.038 1(8)
C(7)	0.179 5(20)	0.124 9(22)	0.002 0(12)
C(8)	0.229 5(28)	0.085 5(32)	−0.045 1(9)

* The atoms are numbered according to the scheme illustrated in Figure 4. † Parameter fixed by symmetry.

Final positional parameters for non-hydrogen atoms for the chloride and iodide are given in Tables 1 and 2 respectively. Observed and calculated structure factors, anisotropic thermal parameters, and methylene H-atom positions are deposited as Supplementary Publication No. SUP 23236 (35 pp.).*

RESULTS AND DISCUSSION

The structure of the trichloromercurate consists of discrete bi-tetrahedral $[Hg_2Cl_6]^{2-}$ anions and $[NBu^n_4]^+$ cations. Selected bond distances and angles of the anion are given in Table 3, according to the numbering scheme of Figure 1. A projection of the unit cell down the *b* axis, showing only one of its two formula units, is given in Figure 2. Individual $[Hg_2Cl_6]^{2-}$ anions are not crystallographically required to be centrosymmetric, unlike the $[Hg_2Cl_6]^{2-}$ ion in the $[C_6H_4S_4]^+$ salt and the known $[Hg_2Br_6]^{2-}$ (refs. 14 and 15) and $[Hg_2I_6]^{2-}$ (refs. 16 and 17) examples; the bridge is slightly bent, Hg(2) being 0.22(1) Å away from the plane containing Hg(1), Cl(1), and Cl(2).

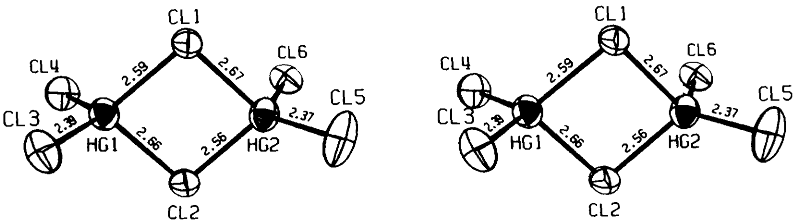

FIGURE 1 Stereoscopic view of the bi-tetrahedral $[Hg_2Cl_6]^{2-}$ anion (bond lengths in Å). The atoms are represented by 30% equiprobability ellipsoids

The terminal Hg–Cl bond lengths are not significantly different from each other but are marginally longer (average 2.38 Å) than the short, diagonally related bonds in most of the extended $(HgCl_3)^-$ salt structures where the metal is in a distorted octahedral environment {*e.g.* 2.33 Å in $[NH_4](HgCl_3)$,[2] 2.29 Å in $Cs(HgCl_3)$ [5]}, but are similar to the shortest bond in the polymeric anion fragment in the $[C_6H_4S_4]^+$ salt (2.37 Å). The bridging bonds (average 2.62 Å) whilst being longer than the terminal bonds are nevertheless shorter than the long contacts in the structures of effective co-ordination number five or six. However, it should be noted that of one the two Hg–Cl (bridging) bonds is *ca.* 0.1 Å shorter than the other; this might be visualised as being related to what would happen

TABLE 3

Interatomic distances and angles within the anions $[Hg_2Cl_6]^{2-}$, with estimated standard deviations in parentheses

(*a*) Distances (Å)

Hg(1)–Cl(1)	2.587(4)
Hg(1)–Cl(2)	2.662(5)
Hg(1)–Cl(3)	2.390(5)
Hg(1)–Cl(4)	2.387(6)
Hg(2)–Cl(1)	2.670(5)
Hg(2)–Cl(2)	2.560(5)
Hg(2)–Cl(5)	2.370(6)
Hg(2)–Cl(6)	2.381(5)
Hg(1)–Hg(2)	3.766(1)

(*b*) Angles (°)

Cl(1)–Hg(1)–Cl(2)	87.7(2)
Cl(1)–Hg(1)–Cl(3)	108.4(2)
Cl(1)–Hg(1)–Cl(4)	118.1(2)
Cl(2)–Hg(1)–Cl(3)	111.9(2)
Cl(2)–Hg(1)–Cl(4)	103.8(2)
Cl(3)–Hg(1)–Cl(4)	121.5(2)
Hg(1)–Cl(1)–Hg(2)	91.5(2)
Hg(1)–Cl(2)–Hg(2)	92.3(2)
Cl(1)–Hg(2)–Cl(2)	88.1(2)
Cl(1)–Hg(2)–Cl(5)	105.8(2)
Cl(1)–Hg(2)–Cl(6)	109.0(2)
Cl(2)–Hg(2)–Cl(5)	117.5(2)
Cl(2)–Hg(2)–Cl(6)	108.7(2)
Cl(5)–Hg(2)–Cl(6)	121.9(2)

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

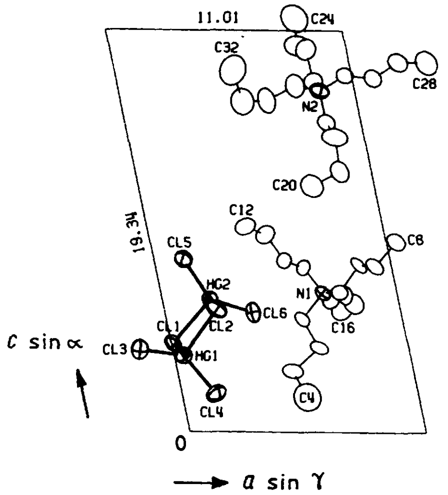

FIGURE 2 Projection along the b axis of the unit cell of $[NBu^n_4]_2[Hg_2Cl_6]$ showing only one of the formula units. The C atoms of Table 1 are numbered sequentially along the chains with the numbers of the terminal atoms shown here

on rupturing the extended chain of $HgCl_3^-$ units of α-$[NEt_4](HgCl_3)$ into dimeric units in the course of rearranging to $[Hg_2Cl_6]^{2-}$ anions of D_{2h} symmetry, an extreme which is not quite reached. Indeed the sum of the Cl–Hg–Cl angles between the three shortest bonds is 348°, closer to the 360° of a trigonal-planar unit than to the 328.4° sum of three angles of an ideal bi-tetrahedral case. The $[Hg_2Br_6]^{2-}$ and $[Hg_2I_6]^{2-}$ anions similarly showed slightly unsymmetrical bridges.[16,17]

Comparison with the other example of an $[Hg_2Cl_6]^{2-}$ anion (ref. 19) reveals a number of points of interest. The sum of the angles between its three shortest bonds about Hg is 349°, virtually the same as found in the $[NBu^n_4]^+$ salt but the angle between the two terminal bonds is 10° larger at 132.2°. Although the differences in bond lengths in the $[NBu^n_4]^+$ and $[C_6H_4S_4]^+$ salts are barely significant they are all in the direction expected if the HgCl terminal bonds of the former are slightly weaker than the latter and the bridging bonds slightly stronger, and are in keeping with the trend in terminal Cl–Hg–Cl bond angles.

The comparison between the dimeric and polymeric anions in $[C_6H_4S_4](HgCl_3)$, illustrated in ref. 19, shows clearly the manner in which dimers associate into polymers, with the polymer being a zigzag chain in terms of the mercury atoms. Only a minor redistribution of bond lengths is required to convert the structure shown by the polymer in the $[C_6H_4S_4]^+$ salt into that found in α-$[NEt_4](HgCl_3)$ where the three short Hg–Cl bonds are of nearly equal length.

The atoms of the $[NBu^n_4]^+$ cation are generally remote from the anion although a few of the calculated H-atom positions are 2.7—2.8 Å from Cl with Cl · · · H–C angles 160—170°. The cations do not show any sign of disorder, although the thermal parameters of the atoms are high (Figure 2).

The tetragonal crystals of the tri-iodomercurate comprise an array of discrete $[NBu^n_4]^+$ and $[HgI_3]^-$ species in equal numbers. Atomic positional parameters are shown in Table 2; selected bond distances and angles in Table 4. The $[HgI_3]^-$ moiety is planar but does not have exact three-fold symmetry; one Hg–I bond lies on a crystallographic axis of two-fold symmetry and although the Hg–I bond lengths do not differ significantly the I–Hg–I bond angles do. The relationships between cations and anions are shown viewed parallel and perpendicular to the plane of the anion (Figure 3). The packing of the ions in the tetragonal unit cell is shown in projection down a in Figure 4. There is no interaction between different anions, the closest approach between an iodine of one anion to a heavy atom in another anion being *ca.* 7.4 Å.

TABLE 4

Interatomic distances and angles for $[NBu^n_4][HgI_3]$ (excluding hydrogen atoms) with estimated standard deviations in parentheses

(*a*) Distances (Å)			
Hg–I(1)	2.683(2)	Hg–I(2)	2.688(2)
C(1)–C(2)	1.52(5)	C(8)–C(7)	1.53(4)
C(2)–C(3)	1.50(4)	C(7)–C(6)	1.48(4)
C(3)–C(4)	1.52(4)	C(6)–C(5)	1.52(4)
C(4)–N	1.50(3)	C(5)–N	1.54(3)
(*b*) Angles (°)			
I(1)–Hg–I(2)	122.7(1)	I(2)–Hg–I(2′)	114.7(1)
C(1)–C(2)–C(3)	113(3)	C(8)–C(7)–C(6)	111(2)
C(2)–C(3)–C(4)	112(2)	C(7)–C(6)–C(5)	112(2)
C(3)–C(4)–N	117(1)	C(6)–C(5)–N	116(2)
C(4)–N–C(4′)	105(3)	C(5)–N–C(5′)	106(2)
C(4)–N–C(5)	105(3)	C(4)–N–C(5′)	111(1)

Primes are used to indicate atoms related by an axis of two-fold rotation parallel to c (through Hg or N).

The Hg–I bond lengths in $[NBu^n_4][HgI_3]$ are virtually the same as those of the terminal Hg–I bonds of $[S_3C_2N_2Et_4][Hg_2I_6]$ [17] and $[NPr^n_4]_2[Hg_2I_6]$ [18] and are not significantly shorter than the mean bond length in $[SMe_3](HgI_3)$ where there is weak axial bonding to neighbouring HgI_3 units.[9]

The nitrogen atom of a tetra-n-butylammonium ion is surrounded tetrahedrally by the four C atoms which initiate the n-butyl chains. For each of the chains the four component C atoms are nearly co-planar. The closest cation–anion contacts are between H atoms and both I and Hg atoms at *ca.* 3.3 Å, close to the sum of their van der Waals radii.

Vibrational spectra of $[NBu^n_4]_2[Hg_2Cl_6]$ and the stoicheiometrically analogous bromide show relatively broad bands at room temperature (Figure 5) but there is a striking resemblance between the i.r. spectra which suggests that the anion structures are similar. As we have noted in other studies of mercury complexes,[25] marked enhancement of detail is obtained if the spectra are measured at low temperature and we base our discussion on those obtained at *ca.* 100 K (Figure 6). There have been several previous reports of the vibrational spectra of trihalogenomercurate salts, the most comprehensive being those of Barr and Goldstein [26,27] whose

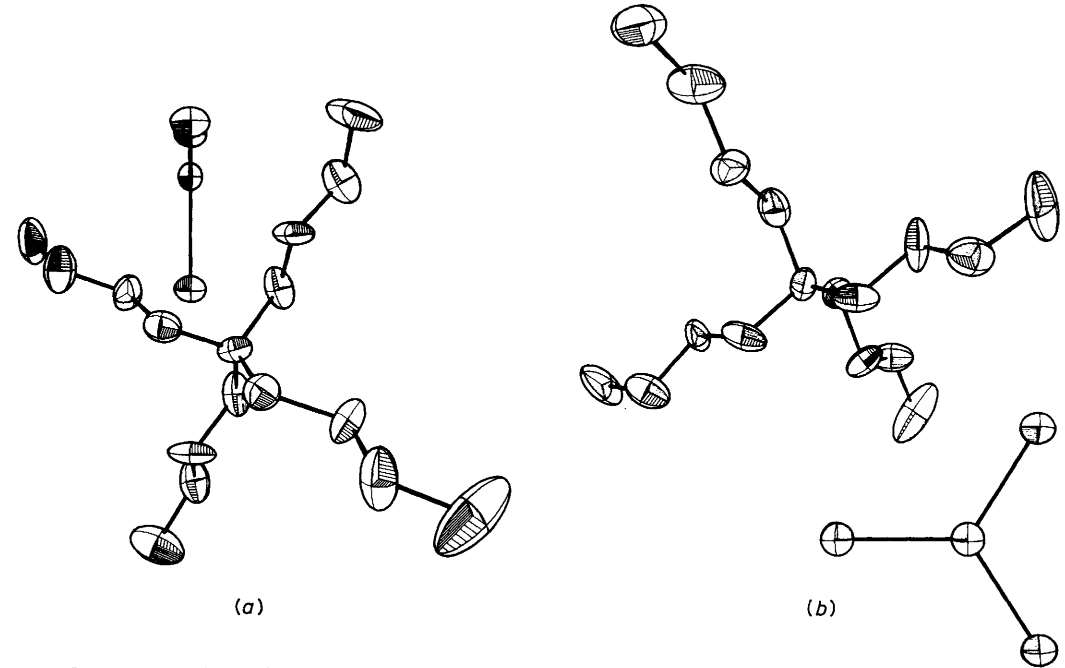

FIGURE 3 Views of $[NBu^n_4][HgI_3]$, (a) parallel and (b) perpendicular to the plane of the anion

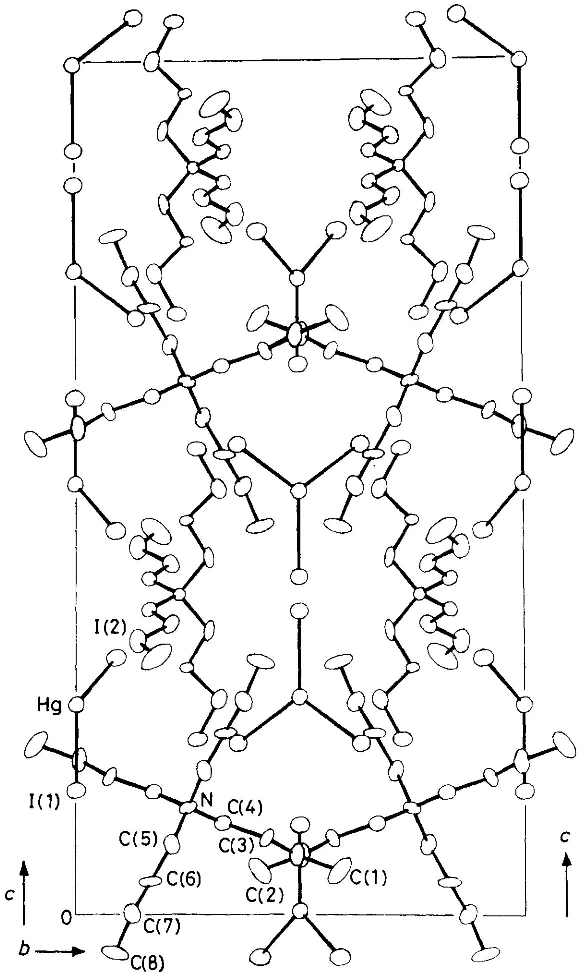

FIGURE 4 Projection along the a axis of the unit cell of $[NBu^n_4][HgI_3]$

work included a number of tetra-alkylammonium salts. Following the criteria of these workers[27] the bands of $[NBu^n_4]_2[Hg_2Cl_6]$ around 280 cm^{-1} are considered as arising from terminal stretching vibrations and those between 230 and 150 cm^{-1} from stretching vibrations in the bridges. An isolated $[Hg_2Cl_6]^{2-}$ anion lacking a centre of symmetry should show four terminal and four bridging modes, all i.r. and Raman active. Consideration of the unit cell on the basis of the C_i factor group permits the same number of active modes but does not require coincidence between i.r. and Raman frequencies. The i.r. spectrum shows three clear terminal stretching features (292, 284, and 275 cm^{-1}) and in the bridging stretch region two strong bands (198 and 161 cm^{-1}) carry shoulders at *ca.* 217 and 151 cm^{-1}. The Raman spectrum also shows three terminal stretches (294, 283, and 276 cm^{-1}); the additional weak band at 267 cm^{-1} relates to the cation. The spectrum is much less rich in the bridging region than is the i.r. spectrum, showing only one prominent band at 233 cm^{-1} although there may also be a weak band at *ca.* 160 cm^{-1}. It is likely that the band at 223 cm^{-1} arises from the symmetric breathing mode of the Hg_2Cl_2 ring.

The spectra Barr and Goldstein[27] report for the high-temperature β form of $[NEt_4](HgCl_3)$ and for $[NPr^n_4]$-$(HgCl_3)$ resemble those of our $[NBu^n_4]^+$ salt, and it is probable that all three contain the $[Hg_2Cl_6]^{2-}$ anion. The wavenumbers and separation of i.r. bands due to HgCl bridge vibrations differ considerably between the three salts and this suggests that bond lengths and asymmetries in the bridges vary substantially with crystal packing.

Considering $[NBu^n_4](HgBr_3)$ in the same way as the chloride, terminal Hg–Br stretches give rise to bands at 201, 194, and 181 in the i.r. and 196 and 185 cm^{-1} in the Raman spectrum; bridging modes contribute bands at

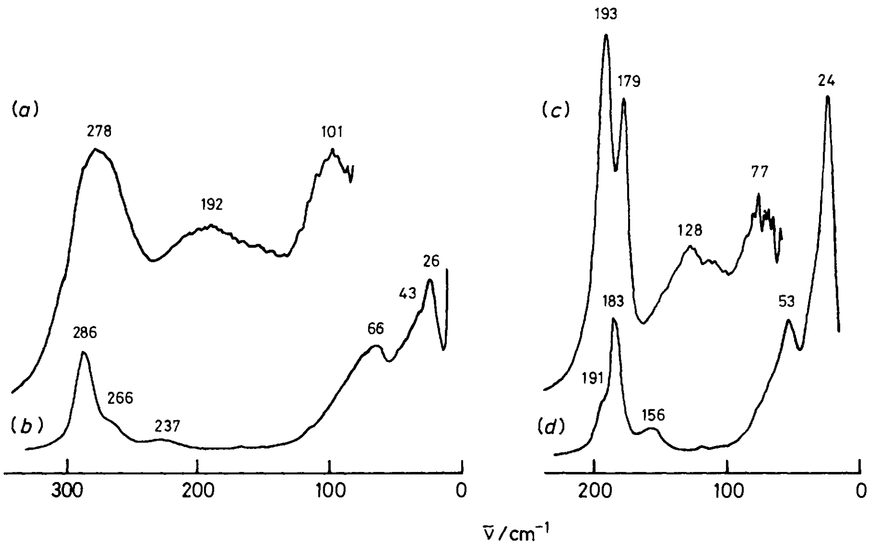

Figure 5 Vibrational spectra of [NBu$^n_4$]$_2$[Hg$_2$Cl$_6$] [(*a*) i.r. absorbance, (*b*) Raman] and [NBu$^n_4$]$_2$[Hg$_2$Br$_6$] [(*c*) i.r. absorbance, (*d*) Raman] at room temperature

154, 135, and 111 to the i.r. spectrum but the Raman spectrum shows only one prominent band (150 cm^{-1}). There is a fair similarity between these spectra and those of [NEt$_4$](HgBr$_3$) for which Barr and Goldstein [27] cited an unpublished crystallographic observation of a centrosymmetric [Hg$_2$Br$_6$]$^{2-}$ anion.

The spectra reported by Contreras *et al.*[18] for [NPr$^n_4$]$_2$[Hg$_2$I$_6$] are a logical extension of those given here for the dimeric chloride and bromide complexes. We were somewhat surprised by the relative intensities quoted (often a rather subjective matter especially where spectra are recorded as transmission plots) and so we have remeasured the spectra (Figure 7). The wavenumber separation between what may be termed terminal and bridging modes becomes proportionately less as the atomic weight of the halide is increased; at the same time the intensity of the most intense Raman band in the bridging region increases relative to those of the terminal stretches.

Apart from a slight sharpening of bands there was very little difference between spectra of [NBu$^n_4$][HgI$_3$] at room temperature and at *ca.* 100 K; the latter are shown in Figure 8. The predicted vibrations and activity for a D_{3h} structure are HgI$_3$ stretches A_1' (Raman only) and E' (i.r. and Raman), in-plane bend E' (i.r. and Raman), and out-of-plane bend A_2'' (i.r. only). Although degrad-

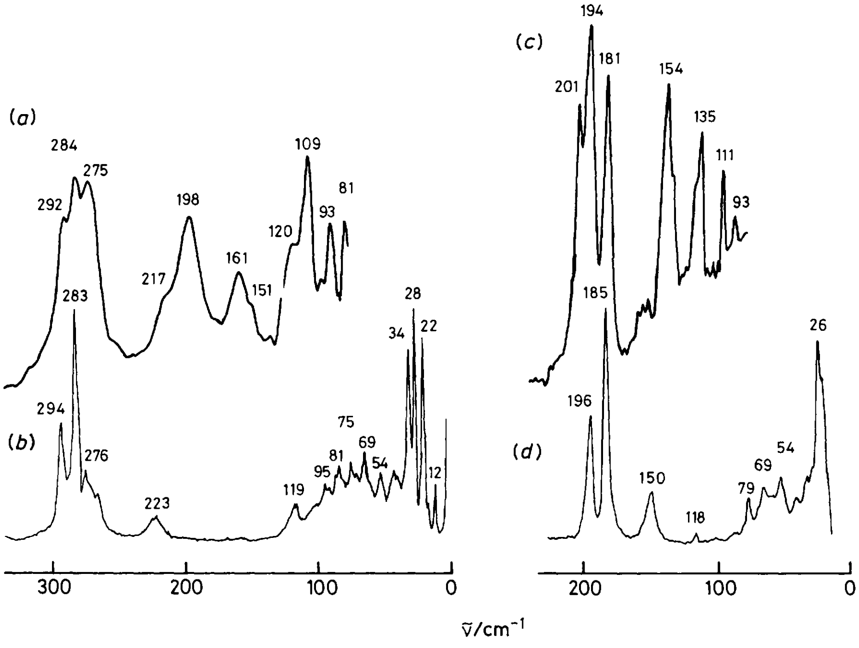

Figure 6 Vibrational spectra of [NBu$^n_4$]$_2$[Hg$_2$Cl$_6$] [(*a*) i.r. absorbance, (*b*) Raman] and [NBu$^n_4$]$_2$[Hg$_2$Br$_6$] [(*c*) i.r. absorbance, (*d*) Raman] at *ca.* 100 K

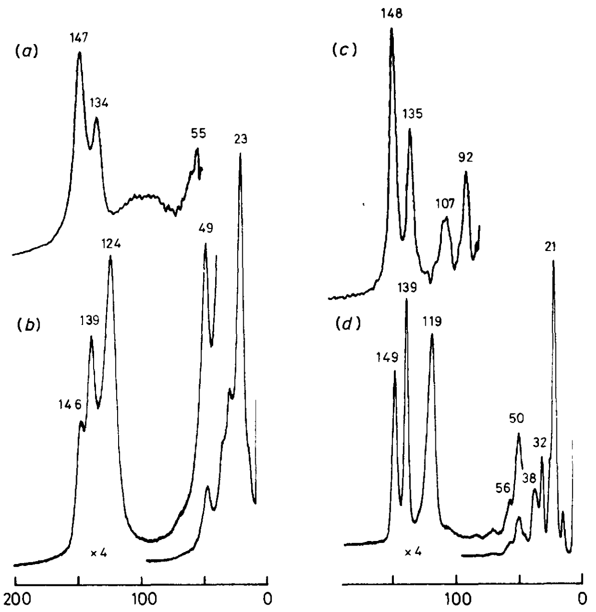

FIGURE 7 Vibrational spectra of $[NPr^n_4]_2[Hg_2I_6]$ at room temperature [(*a*) i.r. absorbance, (*b*) Raman] and at *ca.* 100 K [(*c*) i.r. absorbance, (*d*) Raman]

ation of symmetry to C_{2v} in principle renders all modes active and removes degeneracy, it is the effect of the latter in replacing *E'* modes by two distinguishable components which is expected to have the most marked influence on the appearance of the spectra. This gives rise to the doublets at 160, 154 cm^{-1} (seen in both i.r. and Raman spectra) and at 54, 46 cm^{-1} (only covered in the Raman); the lowered symmetry is insufficient to impart enough i.r. intensity to the symmetric HgI_3 stretching mode (134 cm^{-1} in the Raman spectrum) for it to be distinguished above noise level. The simplicity of the spectra indicates that there are no significant correlation forces between different anions.

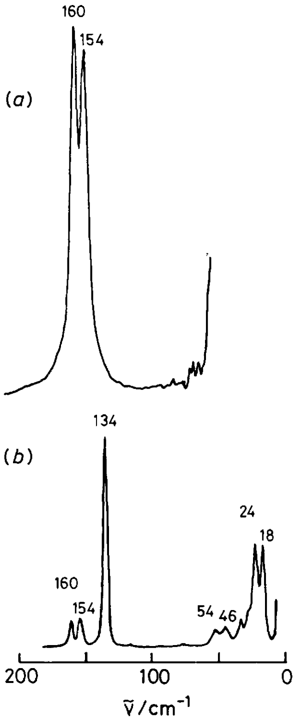

FIGURE 8 I.r. absorbance (*a*) and Raman (*b*) spectra of $[NBu^n_4][HgI_3]$ at *ca.* 100 K

Our spectra differ markedly from those reported by Barr and Goldstein, who report a strong i.r. band at *ca.* 133 cm^{-1} in the spectra at both ambient and liquid-nitrogen temperatures. They also report a strong band at 93 cm^{-1} from the low-temperature measurements which was absent at room temperature and infer that the complex anion contains Hg–I–Hg bridging. The only difference in mode of preparation was that they crystallised their product from a concentrated acetone solution whereas we used diethyl ether to effect crystallisation from a more dilute solution in acetone. We have attempted to obtain an alternative crystalline form using their method or by slow evaporation of a dichloromethane solution but no spectral differences between any of the products were observed. The spectra of this compound are also reported by Contreras *et al.*[18] and are essentially in agreement with ours; we cannot understand why they concluded that this salt was isostructural with $[NPr^n_4]_2[Hg_2I_6]$.

Berg [28] inferred from vibrational spectra that $[Ni(en)_2](HgI_3)_2$ (en = 1,2-diaminoethane) contains the nearly planar, isolated $[HgI_3]^-$ anion. His spectra do not resemble those we have reported here; their complexity more closely parallels those of $[Hg_2I_6]^{2-}$ but neither the frequencies nor the relative intensities correspond well. Thus a monomeric structure cannot be deduced justifiably from the evidence. Far-i.r. spectra of salts $[B_2H](HgI_3)$ (B = pyridine or aniline) very recently reported by Perlepes *et al.*[29] appear to resemble those of $[NPr^n_4]_2[Hg_2I_6]$.

From the variety of co-ordination structures adopted by trihalogenomercurates it must be presumed that the energy differences between different effective co-ordination number arrangements about mercury are very slight. Ionic forces between the cations and halide of the complex anions may be the important feature dictating the structures with the smallest cations (*e.g.* the alkali metals). With cations of large diameter the optimum packing arrangements may well preclude structures with continuous chain-polymer anions and the extra space required by $[NBu^n_4]^+$ over $[NEt_4]^+$ may dictate rupture of the polymer into smaller fragments.

It had occurred to us that the distinction between HgI_3^- being dimeric in the case of $[S_3C_2N_2Et_4]^{2+}$ but monomeric with $[NBu^n_4]^+$ might be accounted for either in terms of the elongated nature of the former cation or its doubly charged nature. However, the dimeric structure in the case of the $[NPr^n_4]^+$ salt precludes such a simple rationalisation.

We wish to thank the S.R.C. for grants towards equipment and for a Research Assistantship (to G. E. T.) and the

Swedish Natural Science Research Council for financial support.

[1/1544 *Received*, 6*th October*, 1981]

REFERENCES

[1] M. Authier-Martin and A. L. Beauchamp, *Can. J. Chem.*, 1975, **53**, 2345; 1977, **55**, 1213.

[2] K. Sagisawa, K. Kitahama, and R. Kiriyama, *Acta Crystallogr., Sect B.*, 1974, **30**, 1603, and refs. therein.

[3] E. J. Harmsen, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1938, **100**, 208.

[4] Z. V. Zvonkova, V. V. Samodurova, and L. G. Vorontsova, *Dokl. Akad. Nauk SSSR*, 1955, **102**, 1115.

[5] D. E. Scaife, *Aust. J. Chem.*, 1971, **24**, 1753.

[6] K. Weidenhammer and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, 1977, **434**, 152.

[7] P. Biscarini, L. Fusina, G. Nivellini, and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1977, 664.

[8] M. Sandström and D. H. Liem, *Acta Chem. Scand., Ser. A*, 1978, **32**, 509.

[9] R. H. Fenn, *Acta Crystallogr., Sect. B.*, 1966, **20**, 20, 24.

[10] V. M. Padmanabhan and V. S. Yadava, *Acta Crystallogr., Sect. B.*, 1969, **25**, 647.

[11] J. G. White, *Acta Crystallogr.*, 1963, **16**, 397.

[12] L. Nyquist and G. Johansson, *Acta Chem. Scand.*, 1971, **25**, 1615.

[13] B. I. Pakhomov, P. M. Fedorov, I. M. Alymov, I. N. Ivanova-Korfini, and G. K. Semin, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1975, **39**, 2519, and refs. therein.

[14] G. S. Harris, F. Inglis, and J. McKechnie, *Chem. Commun.*, 1967, 442.

[15] A. W. Gal, G. Beurskens, J. A. Cras, P. T. Beurskens, and J. Willemse, *Recl. Trav. Chim. Pays-Bas.*, 1976, **95**, 157.

[16] A. L. Spek, *Cryst. Struct. Commun.*, 1979, **8**, 577.

[17] P. T. Beurskens, W. P. J. H. Bosman, and J. A. Cras, *J. Cryst. Mol. Struct.*, 1972, **2**, 183.

[18] J. G. Contreras, G. V. Seguel, and W. Hönle, *J. Mol. Struct.*, 1980, **68**, 1.

[19] T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. Van Duyne, and A. R. Siedle, *Inorg. Chem.*, 1980, **19**, 3604.

[20] G. M. Sheldrick, ' SHELXTL ' programs for use with the Nicolet R 3/M *X*-ray system.

[21] I. Olovsson and P. G. Jönsson in ' The Hydrogen Bond,' eds. P. Schuster, G. Zundel, and C. Sandorfy, North Holland Publishing Co., Amsterdam, 1975, vol. 2, ch. 8.

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

[23] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[24] Syntex (XTL version 2) programs, Syntex Analytical Instruments Inc., 10040 Bubb Rd., Cupertino, California 95014, U.S.A.

[25] N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, K. Kessler, T. Jones, I. W. Nowell, and D. M. McEwan, *J. Chem. Res.*, 1981, (*S*) 2, (*M*) 201.

[26] R. M. Barr and M. Goldstein, *J. Chem. Soc., Dalton Trans.*, 1974, 1180.

[27] R. M. Barr and M. Goldstein, *J. Chem. Soc., Dalton Trans.*, 1976, 1593.

[28] R. W. Berg, *Spectrosc. Lett.*, 1976, **9**, 715.

[29] S. P. Perlepes, Th. F. Zafiropoulos, J. K. Kouinis, and A. G. Galinos, *Z. Naturforsch., Teil B*, 1980, **35**, 1244.