DALTON

Reactions of (diethyldithiocarbamato)halogenotellurium(II); crystal structures of R[Te{S_2CNEt_2}X_2] [R = NEt_4, X = I; R = $H(phen)_2$ (phen = 1,10-phenanthroline), X = I or Br]

Ramanathan Krishnakumar,[a] Gopalaswamiengar Aravamudan,*[,a] M. Ramakrishna Udupa,[a] Maha Seshasayee[b] and Thomas A. Hamor *[,c]

[a] *Department of Chemistry, Indian Institute of Technology, Madras 600 036, India*
[b] *Department of Physics, Indian Institute of Technology, Madras 600 036, India*
[c] *School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

The reactions of (diethyldithiocarbamato)halogenotellurium(II) with thiourea, benzimidazole-2-thiol, halides (Cl^-, Br^-, I^-) and 1,10-phenanthroline (phen) have been studied. The products were principally characterized by elemental analyses, IR and ^1H NMR spectroscopies. Novel anionic (diethyldithiocarbamato)dihalogenotellurate(II) complexes resulted from the reactions of $Te(S_2CNEt_2)X$ (X = Br or I) with NEt_4X (X = Br or I) and phen. The crystal structures of the complexes $[NEt_4][Te(S_2CNEt_2)I_2]$, $[H(phen)_2][Te(S_2CNEt_2)I_2]$ and $[H(phen)_2][Te(S_2CNEt_2)Br_2]$ have been determined. In the anions tellurium is co-ordinated to two sulfur atoms of the dithiocarbamate in an almost isobidentate manner and to two halides in an overall planar trapezoidal geometry. In $[NEt_4][Te(S_2CNEt_2)I_2]$ the two iodides are almost equidistant to tellurium with distances of 3.079(1) and 3.072(1) Å, whereas in $[H(phen)_2][Te(S_2CNEt_2)I_2]$ the two Te–I distances are 3.151(1) and 3.038(1) Å and in $[H(phen)_2][Te(S_2CNEt_2)Br_2]$ the two Te–Br distances are 2.911(1) and 2.986(1) Å. In $[H(phen)_2]^+$ the proton is bound to one of the nitrogen atoms of a phenanthroline group and the two phen groups are held together by three hydrogen bonds, of which two are of the interesting type C–H ··· N.

Extensive studies have been carried out on the preparation of mono- and di-halogeno-substituted tellurium(IV) dithiocarbamate complexes.[1–5] However nothing was known about the mixed halide–dithiocarbamate complexes of Te^{II} until we reported the synthesis and structural studies of $Te(S_2CNR_2)I$ (R = Et[6] or Pr^i[7]). The complexes $Te(S_2CNEt_2)X$ (X = I,[6] Br[8] or Cl[8]) have halide-bridged helical polymeric structures. Tellurium is bound to two sulfur atoms of the dithiocarbamate and to two iodides in a planar trapezoidal fashion. However, in dichloromethane solution $Te(S_2CNEt_2)I$ exists as a monomer, and $Te(S_2CNEt_2)X$ (X = Br or Cl) as dimers according to vapour-pressure osmometry. As a part of our systematic investigation on the mixed halide–dithiocarbamate complexes of Te^{II}, the co-ordination effect of ligands such as thiourea, benzimidazole-2-thiol, chloride, bromide, iodide and 1,10-phenanthroline on $Te(S_2CNEt_2)X$ has now been studied.

Experimental

Starting materials and methods

Thiourea, benzimidazole-2-thiol, NEt_4X (X = I or Br), 1,10-phenanthroline monohydrate and dichloromethane were used as obtained commercially. Methanol and acetone were distilled and stored over molecular sieves before use.

The complex $Te(S_2CNEt_2)I$ was prepared as described previously[6] by stirring a suspension of a dichloromethane solution (50 cm^3) of $Te(S_2CNEt_2)_2I_2$ (0.34 g, 0.5 mmol) and elemental tellurium (0.095 g, 0.75 mmol) for 12 h at room temperature. Both $Te(S_2CNEt_2)X$ (X = Br or Cl) were obtained by stirring a suspension of $Te(S_2CNEt_2)I$ (0.201 g, 0.5 mmol) and AgX (X = Br or Cl) (1.0 mmol) for 4 h in dichloromethane at room temperature. The unreacted AgX and AgI formed were filtered off. Brown long needle-like crystals of $Te(S_2CNEt_2)X$ were obtained from dichloromethane–ethyl acetate (10 : 1 v/v).

The C, H and N analyses of the complexes were performed using a Heraeus CHN-O-RAPID analyser. The halides were estimated by Volhard's method, sulfur by gravimetric determination as barium sulfate and tellurium by dichromate titration. The infrared spectra were recorded in the region 4000–400 cm^{-1} on a Shimadzu IR-470 spectrophotometer using KBr pellets, NMR spectra on a JEOL GSX-400 spectrometer in appropriate deuteriated solvents, either $CDCl_3$ or $(CD_3)_2CO$, using $SiMe_4$ as the internal standard.

Reactions of $Te(S_2CNEt_2)X$ (X = I, Br or Cl) with thiourea (tu) and benzimidazole-2-thiol ($C_7H_5N_2SH$)

To a dichloromethane solution (15 cm^3) of $Te(S_2CNEt_2)X$ (0.25 mmol) was added a methanol solution containing thiourea (0.076 g, 1 mmol) or $C_7H_5N_2SH$ (0.150 g, 1 mmol). The solvent was evaporated at room temperature and the residue washed with carbon tetrachloride in which only $Te(S_2CNEt_2)_2$ is soluble. The carbon tetrachloride extract was recrystallized from a dichloromethane–ethyl acetate mixture to obtain $Te(S_2CNEt_2)_2$ crystals.[9] The yellow carbon tetrachloride-insoluble residue was found to be $Te(tu)_4X_2$[10] or $Te(C_7H_5N_2SH)_4X_2$[11] by analysis.

Preparation of $[NEt_4][Te(S_2CNEt_2)I_2]$ 1 and $[NEt_4][Te(S_2CNEt_2)Br_2]$ 2

To $Te(S_2CNEt_2)I$ (0.201 g, 0.5 mmol) dissolved in dichloromethane (30 cm^3) in a beaker (100 cm^3) was added a methanol solution containing tetraethylammonium iodide (0.257 g, 1.0 mmol). The beaker was covered with a watch-glass and the solvent allowed to evaporate. The brown residue obtained was treated with acetone, in which only the complex is highly soluble; the solubility of NEt_4I is very low and most of the unreacted reagent was thus removed. Hexane (5 cm^3) was added to the acetone solution of the complex which was allowed to crystallize. Brown rectangular crystals of $[NEt_4][Te(S_2CNEt_2)I_2]$ were obtained. Yield 75% (Found: C, 23.7; H, 4.5; I, 38.3; N, 4.2; S, 9.7; Te, 19.6. Calc. for $C_{13}H_{30}I_2N_2S_2Te$: C, 23.65; H, 4.6; I, 38.5; N, 4.2; S, 9.7; Te, 19.3%); $\tilde{\nu}_{max}$/cm^{-1} (CN) 1510s; ^{1}H NMR data in Table 1.

Complex **2** was obtained similarly from the reaction of $Te(S_2CNEt_2)Br$ (0.178 g, 0.5 mmol) and tetraethylammonium bromide (0.210 g, 1.0 mmol) in 30 cm^3 of a 1:1 dichloromethane–methanol mixture. The unreacted NEt_4Br was removed by dissolving the complex in acetone, and crystallization of the solution gave brown rectangular crystals of $[NEt_4][Te(S_2CNEt_2)Br_2]$. Yield 60% (Found: C, 27.7; H, 5.8; Br, 28.5; N, 4.8; Te, 22.4. Calc. for $C_{13}H_{30}Br_2N_2S_2Te$: C, 27.6; H, 5.3; Br, 28.2; N, 4.95; Te, 22.55%).

Reaction of $Te(S_2CNEt_2)I$ with 1,10-phenanthroline (phen)

To $Te(S_2CNEt_2)I$ (0.201 g, 0.5 mmol) dissolved in dichloromethane (30 cm^3) in a beaker (100 cm^3) was added 1,10-phenanthroline monohydrate (0.099 g, 0.5 mmol) dissolved in dichloromethane (10 cm^3) with continuous stirring. The solution became turbid immediately due to the formation of a grey precipitate, which was found to be a mixture of elemental tellurium and tellurium dioxide. The precipitate was separated by centrifugation. The solution was kept aside for solvent evaporation, during which brown crystals of the complex separated along with a red residue of $Te(S_2CNEt_2)_2$, unreacted phenanthroline and TeI_2(phen). Of these, $Te(S_2CNEt_2)_2$ and phenanthroline were removed by washing with benzene. The anion $[Te(S_2CNEt_2)I_2]^-$ was separated from TeI_2(phen) by dissolving in dichloromethane, as the latter is insoluble, and slow evaporation of the solvent resulted in the formation of brown crystals of $[H(phen)_2][Te(S_2CNEt_2)I_2]$ **3**. Yield 80% (Found: C, 39.6; H, 3.0; I, 28.1; N, 7.9; Te, 14.2. Calc. for $C_{29}H_{27}I_2N_5S_2Te$: C, 39.1; H, 3.05; I, 28.5; N, 7.9; Te, 14.3%); $\tilde{\nu}_{max}$/cm^{-1} (CN) 1497s. TeI_2(phen) **4**: yield 80% (Found: C, 25.7; H, 1.9; N, 5.5. Calc. for $C_{12}H_8I_2N_2Te$: C, 25.7; H, 1.4; N, 5.0%).

Reaction of $Te(S_2CNEt_2)Br$ with 1,10-phenanthroline

The complex $Te(S_2CNEt_2)Br$ (0.178 g, 0.5 mmol) was dissolved in dichloromethane (25 cm^3) and a dichloromethane solution containing 1,10-phenanthroline monohydrate (0.099 g, 0.5 mmol) was added with continuous stirring. A mixture of elemental tellurium and TeO_2 separated as a grey precipitate, and was removed by centrifugation. The brown solution was allowed to evaporate slowly at room temperature, when brown needle-like crystals of $[H(phen)_2][Te(S_2CNEt_2)Br_2]$ deposited in addition to a red residue containing $Te(S_2CNEt_2)_2$ and the unreacted excess of phenanthroline. The last two were separated from the brown crystals by leaching with a limited amount of benzene. A rapid wash of the crystals with dichloromethane (3 cm^3) yielded the complex $[H(phen)_2][Te(S_2CNEt_2)Br_2]$ **5** in high purity. Yield 77.5% (Found: C, 43.5; H, 3.5; Br, 20.4; N, 8.2; Te, 15.8. Calc. for $C_{29}H_{27}Br_2N_5S_2Te$: C, 43.7; H, 3.4; Br, 20.05; N, 8.8; Te, 16.0%).

Reaction of $Te(S_2CNEt_2)Cl$ with 1,10-phenanthroline

To a dichloromethane (20 cm^3) solution of $Te(S_2CNEt_2)Cl$ (0.156 g, 0.5 mmol) was added 1,10-phenanthroline monohydrate (0.198 g, 1.0 mmol) with continuous stirring for a few minutes. The grey precipitate of a mixture of Te and TeO_2 formed was removed immediately. White needle-like crystals of phenanthrolinium chloride formed from the dichloromethane solution. The red residue of $Te(S_2CNEt_2)_2$ and free phenanthroline were removed by dissolving in benzene.

X-ray crystallography

Brown rectangular crystals of complex **1** and needle-shaped crystals of **3** and **5** were mounted on an Enraf-Nonius CAD4 diffractometer, fitted with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å). Cell constants and the orientation matrix for data collection, obtained from a least-squares refinement using 25 carefully chosen reflections in the range θ 10–15°, corresponded to monoclinic cells of dimensions given in Table 3. On the basis of the systematic absences of the reflections and the successful solution and refinement of the structure, the space group was determined to be *C*2/*c* for **1** and *P*2$_1$/*n* for **3** and **5**. The intensity data were collected at room temperature (25 °C) using the ω–2θ scan technique to a maximum 2θ value of 50°.* Of the 3861 (**1**), 6246 (**3**) and 5938 (**5**) reflections measured, 3721, 3278 and 3400 were found to be 'observed', with $I > 3\sigma(I)$ (R_{int} = 0.058, 0.019 and 0.022 respectively). Two standard reflections measured after every hour showed no significant variation in intensity indicating crystal and electronic stability. An empirical absorption correction, based on ψ scans of several reflections, was applied, resulting in transmission factors ranging from 39.56 to 99.91 (for **1**), 85.08 to 99.96 (**3**) and 51.63 to 99.94% (**5**). The data were corrected for Lorentz-polarization effects.

The positions of the tellurium and iodine atoms (bromines for **5**) were obtained from Patterson maps, and successive Fourier maps based on these positions gave the locations of all non-hydrogen atoms. The positions of the hydrogen atoms were also obtained from the Fourier-difference maps. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The refinement was carried out by the full-matrix least-squares method using SHELX76[12] for **1** and **3** (refinement on *F*) and SHELXL 93[13] for **5** (refinement on F^2). The refinement was terminated when the maximum shift per estimated standard deviation (e.s.d.) was less than 0.15 (for **1**), 0.23 (**3**) and 0.181 (**5**). The maximum electron density in the final difference map was 0.99 e Å^{-3} for **1** (ripples near the heavy atoms) and 0.32 and 0.84 e Å^{-3} for **3** and **5** respectively. The final unweighted and weighted residuals were R = 0.050 (for **1**), 0.025 (**3**) and 0.031 (**5**), R' = 0.053, 0.025 and wR_2 = 0.080. The weighting schemes employed were $w = 1.4214/(\sigma^2|F_o| + 0.001\,179|F_o|^2)$, $1.79/(\sigma^2|F_o| + 0.000\,413|F_o|^2)$ and $1/[\sigma^2|F_o|^2 + (0.0488P)^2 + 4.74P]$, where $P = [\max(F_o^2, 0) + 2|F_c|^2]/3$ for **1**, **3** and **5** respectively.

Atomic scattering factors for the non-hydrogen atoms were taken from Cromer and Mann[14] and anomalous dispersion correction factors from Cromer and Liberman.[15] The molecular plots and packing diagrams were drawn using the program ORTEP.[16]

The fractional atomic coordinates for non-hydrogen atoms are given in Tables 4–6 and selected bond distances and angles in Table 2.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Monodentate sulfur compounds such as thiourea and benzimidazole-2-thiol do not react with $Te(S_2CNEt_2)_2$ due to the greater chelating ability of the dithiocarbamate. In the case of $Te(S_2CNEt_2)X$ the halides are weakly bound to tellurium compared to the dithiocarbamate and hence they could be easily substituted. However, in the reaction of $Te(S_2CNEt_2)X$,

---

* For complex **1** the intensity data showed that the *h*0*l* reflections with *l* odd were generally absent or quite weak indicating the presence of a '*c*' glide, but there were also some relatively high-intensity reflections. However, with another crystal when these reflections were remeasured, those which were strong in the first crystal had quite low intensities. Strangely, this second crystal also produced some high-intensity *h*0*l* reflections with *l* odd, which were, however, quite weak in the original crystal. Thus, these reflections were considered as systematically absent and the apparently strong reflections to be due to background streaks from other genuine strong reflections. The space group was hence assigned as *C*2/*c*.

dissolved in dichloromethane, with thiourea in methanol, instead of a simple substitution reaction, a metathetical reaction occurs resulting in the formation of $Te(S_2CNEt_2)_2$ and $Te(tu)_4X_2$. A similar reaction is observed with benzimidazole-2-thiol ($C_7H_5N_2SH$), in accordance with the general equation (1)

$$2\,Te(S_2CNEt_2)X + 4\,L \longrightarrow Te(S_2CNEt_2)_2 + TeL_4X_2 \quad (1)$$

(L = thiourea or benzimidazole-2-thiol). Thiourea or $C_7H_5N_2SH$ displaces the halide from the co-ordination sphere initially and the $Te(S_2CNEt_2)L(X)$ formed is probably unstable and transformed to $Te(S_2CNEt_2)_2$ and TeL_4X_2. The $Te(S_2CNEt_2)_2$ is removed from the residue by dissolving in carbon tetrachloride.

The reaction of NEt_4I with $Te(S_2CNEt_2)I$ resulted in the formation of a novel anionic (diethyldithiocarbamato)diiodo tellurate(II) species by addition of iodide to Te^{II}. This is the first example of a tellurium(II) dithiocarbamate complex having a halide to dithiocarbamate ratio of 2 : 1. The driving force for the reaction is the formation of a favoured four-co-ordinate tellurium(II) complex and stabilization of the compound by the bulky tetraethylammonium cation. Similarly, the reaction of NEt_4Br with $Te(S_2CNEt_2)Br$ resulted in tetraethylammonium dibromo(diethyldithiocarbamato)tellurate(II), $[NEt_4][Te(S_2CNEt_2)Br_2]$, equation (2) (X = I or Br). In contrast to

$$Te(S_2CNEt_2)X + NEt_4X \longrightarrow [NEt_4][Te(S_2CNEt_2)X_2] \quad (2)$$

$Te(S_2CNEt_2)X$ (X = I or Br) which undergo gradual aerial oxidation to TeO_2 in the presence of hydrophilic solvents, both $[NEt_4][Te(S_2CNEt_2)X_2]$ (X = I or Br) are stable in solution even in the presence of acetone and methanol.

Brown rectangular crystals of the complexes were obtained from acetone solution with a small amount of hexane. The characteristic ν(CN) frequency in the IR spectrum of complex **1** was observed at 1510 cm^{-1}. For the unsubstituted $Te(S_2CNEt_2)_2$ it is observed at 1478 cm^{-1} and for $Te(S_2CNEt_2)I$ it appears at 1520 cm^{-1}, which indicates that the dithiocarbamate is bound to Te^{II} more strongly than in $Te(S_2CNEt_2)_2$ but less so than in $Te(S_2CNEt_2)I$. The ν(CS) band in the spectrum of **1** occurs at 988s cm^{-1}, which is similar to that of $Te(S_2CNEt_2)I$. The assignments for the ^1H NMR resonances for the complexes **1**–**3** and **5** are presented in Table 1.

However, the reaction between $Te(S_2CNEt_2)Cl$ and NEt_4Cl does not seem to occur, under the conditions adopted for the iodo and bromo complexes, probably due to the unstable nature of $[Te(S_2CNEt_2)Cl_2]^-$.

When $Te(S_2CNEt_2)I$ was treated with 1,10-phenanthroline monohydrate in dichloromethane, an interesting but quite unexpected reaction was observed. The analysis of the products shows that the reaction is brought about by the water of hydration in phenanthroline which is present in the commercial sample. Phenanthroline, in addition to acting as a chelating ligand to tellurium, is also partially protonated to give the bis(1,10-phenanthroline)hydrogen(I) cation as shown in equation (3). The stoichiometry suggests that the major products are

$$12\,Te(S_2CNEt_2)I + 10\,phen + 2\,H_2O \longrightarrow 4\,[H(phen)_2][Te(S_2CNEt_2)I_2] + 4\,Te(S_2CNEt_2)_2 + 2\,TeI_2(phen) + Te + TeO_2 \quad (3)$$

$[Te(S_2CNEt_2)I_2]^-$ and $Te(S_2CNEt_2)_2$ with small amounts of the dichloromethane-insoluble complex, $TeI_2(phen)$, elemental Te and TeO_2. To a small extent disproportionation of $Te(S_2CNEt_2)I$ takes place to yield Te and TeO_2 which are formed immediately on addition of phenanthroline to $Te(S_2CNEt_2)I$ and were separated by centrifugation. Slow evaporation of the resultant solution gave brown crystals of $[H(phen)_2][Te(S_2CNEt_2)I_2]$ **3**, the formation of which, with four-co-ordination around tellurium, is probably the driving force for the reaction. The counter cation, bis(1,10-phenanthroline)hydrogen(I), is formed by protonation of the nitrogen of phenanthroline. Though mono- or di-protonated phenanthrolinium ions are common,[17–19] only the nitrate, perchlorate, naphthalene-2-sulfonate and iodide salts of $[H(phen)_2]^+$ are known.[20–24] In addition to $[Te(S_2CNEt_2)I_2]^-$, dichloromethane-insoluble $TeI_2(phen)$ **4**, is obtained. The former was characterized by elemental analyses, IR and ^1H NMR data, the latter by elemental analyses.

In the IR spectrum of complex **3** the ν(CN) frequency was observed at 1497 cm^{-1}, less than the 1510 cm^{-1} observed for **1**. The ^1H NMR spectrum recorded in $CDCl_3$ at −60 °C shows the resonance of the acidic proton at δ 10.5. This value is in agreement with those reported[24,25] for $[H(phen)_2]I$ and a monoprotonated bis(2,9-diphenyl-1,10-phenanthroline)-containing catenand.

In the reaction of phenanthroline monohydrate with bromo(diethyldithiocarbamato)tellurium(II) the major product obtained is bis(1,10-phenanthroline)hydrogen(I) dibromo-(diethyldithiocarbamato)tellurate(II) **5** according to reaction (4). As in the reaction of $Te(S_2CNEt_2)I$, the tellurium complex

$$8\,Te(S_2CNEt_2)Br + 8\,phen + 2\,H_2O \longrightarrow 4\,[H(phen)_2][Te(S_2CNEt_2)Br_2] + 2\,Te(S_2CNEt_2)_2 + Te + TeO_2 \quad (4)$$

is partly hydrolysed followed by disproportionation to elemental Te and TeO_2. However, no $TeBr_2(phen)$ could be isolated in contrast to the iodide analogue. Both the IR and ^1H NMR spectra of **5** are identical to those of **3**.

In the reaction with $Te(S_2CNEt_2)Cl$, phenanthroline again becomes protonated to give ionic phenanthrolinium chloride, $[H(phen)]^+Cl^-$, but neither $[Te(S_2CNEt_2)Cl_2]^-$ nor $TeCl_2(phen)$ is formed [equation (5)]. The fact that $[Te(S_2CNEt_2)Cl_2]^-$ is unstable and is not formed in this reaction is supported by the unsuccessful addition reaction of $Te(S_2CNEt_2)Cl$ and NEt_4Cl to isolate $[NEt_4][Te(S_2CNEt_2)Cl_2]$. Thus, in these three reactions involving phenanthroline and $Te(S_2CNEt_2)X$, $Te(S_2CNEt_2)_2$ is a common product. Owing to hydrolysis, phenanthroline becomes protonated to give $[H(phen)_2]^+$ which stabilizes $[Te(S_2CNEt_2)X_2]^-$ (X = I or Br) but not when X = Cl.

$$4\,Te(S_2CNEt_2)Cl + 4\,phen + 2\,H_2O \longrightarrow 4\,[Hphen]Cl + Te + TeO_2 + 2\,Te(S_2CNEt_2)_2 \quad (5)$$

Molecular structure of $[NEt_4][Te(S_2CNEt_2)I_2]$ 1

The compound is composed of anionic $[Te(S_2CNEt_2)I_2]^-$ and tetraethylammonium cationic species. The Te^{II} is bonded to two sulfur atoms of the dithiocarbamate group forming a chelate ring as shown in the ORTEP diagram in Fig. 1. The bond lengths of 2.564(2) and 2.551(2) Å for Te–S(1) and Te–S(2) respectively are comparable to Te–S bond distances in $Te(S_2CNEt_2)X$ complexes, but much greater than the sum of the covalent radii of Te and S (2.41 Å).[26] The co-ordination around Te is completed by two iodides at distances of 3.079(1) and 3.072(1) Å, much greater than the sum of the covalent radii of Te and I (2.70 Å). The mean Te–I distance of 3.076 Å in this complex is longer than that observed[27] in $[TeI_4]^{2-}$ (2.985 Å). In the dithiocarbamate ligand C(1)–S(1) and C(1)–S(2) are 1.702(8) and 1.724(7) Å respectively. The lengthening of the Te–I bond in the complex compared to the covalent distance is attributed to the *trans* influence of the sulfur atoms of the dithiocarbamate. The two sulfur atoms have a similar influence as the two Te–I bond lengths are the same. Further, the near equality of the two Te–S and C–S distances shows that the

Table 1 Proton NMR chemical shifts (δ) for the complexes **1**–**3** and **5**[a]

	$S_2CNEt_2^-$		NEt_4^+		$H(phen)_2^{+}$[b]				
Compd.	CH_3	CH_2	CH_3	CH_2	2,9	3,8	4,7	5,6	NH
1	1.35 (6 H, t)	3.78 (4 H, q)	1.45 (12 H, tt)	3.49 (8 H, q)	—	—	—	—	—
2	1.31 (6 H, t)	3.74 (4 H, q)	1.39 (12 H, tt)	3.49 (8 H, q)	—	—	—	—	—
3	1.32 (6 H, t)	3.76 (4 H, q)	—		9.25 (4 H, d)	7.71 (4 H, q)	8.33 (4 H, d)	7.85 (4 H, s)	10.5 (1 H, s)
5	0.95 (6 H, t)	3.3 (4 H, q)	—	—	8.97 (4 H, d)	7.58 (4 H, q)	8.28 (4 H, d)	7.71 (4 H, s)	10.1 (1 H, s)

[a] The spectra were recorded in $(CD_3)_2CO$ for complexes **1** and **2** and $CDCl_3$ for **3** and **5** and reported in ppm from $SiMe_4$. Number of protons and multiplicities are in parentheses (s = singlet, d = doublet, t = triplet, q = quartet). [b] For the bis(1,10-phenanthroline)hydrogen(I) cation the chemical shift for the hydrogens at various positions of the phenanthroline ring are given. The NH proton appears as a weak broad signal.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**, **3** and **5**

	1	**3**	**5**
Te–X(1)	3.079(1)	3.038(1)	2.911(1)
Te–X(2)	3.072(1)	3.151(1)	2.986(1)
Te–S(1)	2.564(2)	2.512(2)	2.503(2)
Te–S(2)	2.551(2)	2.567(2)	2.545(2)
S(1)–C(1)	1.702(8)	1.723(5)	1.735(6)
S(2)–C(1)	1.724(7)	1.719(6)	1.730(7)
X(1)–Te–X(2)	124.4(1)	124.3(1)	129.07(3)
X(1)–Te–S(1)	84.1(1)	82.4(1)	80.27(4)
X(2)–Te–S(2)	82.0(1)	83.5(1)	80.43(4)
S(1)–Te–S(2)	69.5(1)	69.9(1)	70.25(6)
C(1)–S(1)–Te	86.9(3)	88.2(3)	88.5(2)
C(1)–S(2)–Te	86.9(3)	86.5(3)	87.3(2)
S(2)–C(1)–S(1)	116.7(4)	115.4(3)	113.9(4)

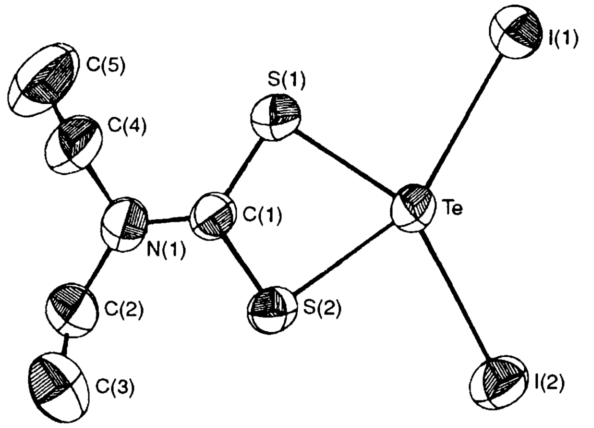

Fig. 1 An ORTEP plot of the anion of $[NEt_4][Te(S_2CNEt_2)I_2]$ **1**. The atoms are drawn with 50% probability ellipsoids, and hydrogen atoms are omitted for clarity

dithiocarbamate is bonded in an isobidentate manner. It has been observed[8] during our detailed study on the mixed halide–dithiocarbamate complexes of Te^{IV} and Te^{II} that by substituting dithiocarbamate by iodide in $Te(S_2CNEt_2)_4$, the extent of deviation from symmetrical bonding decreases in the order $TeL_3I > TeL_2I_2 > TeLI_3$ ($L = S_2CNEt_2$). The tellurium(II) complexes exhibit a similar trend, $TeL_2 > TeL(I) > [TeLI_2]^-$.

The angle subtended at Te between the two iodine atoms is 124.4(1)° whereas that between the two sulfurs is 69.5(1)°. The sum of the four angles at tellurium is approximately 360° indicating that the atoms Te, S(1), S(2), I(1) and I(2) are almost in a plane. Hence the geometry around tellurium is better described as planar trapezoidal, with root-mean-square (r.m.s.) deviation from the mean plane of 0.038 Å.

The eight tetraethylammonium cations in the unit cell occupy two sets of four-fold special positions; four on the two-fold axis $(0, y, \frac{1}{4})$ [Fig. 2(*a*)] and four, in a disordered manner, on the inversion centre $(0, \frac{1}{2}, \frac{1}{2})$ [Fig. 2(*b*)]. The geometry around N(3) is tetrahedral due to the disorder. This highly interesting type of disorder has been previously observed[28] in the trimethylammonium cation of $[NHMe_3]_2[TeI_7]$.

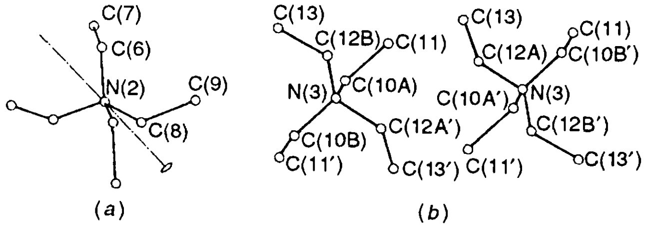

Fig. 2 (*a*) Projection of the tetrahedral arrangement around N(2) with the two-fold axis passing through it. (*b*) Tetrahedral arrangements around N(3) formed by the disordered methylene carbon atoms of $[NEt_4]^+$ cation in complex **1**

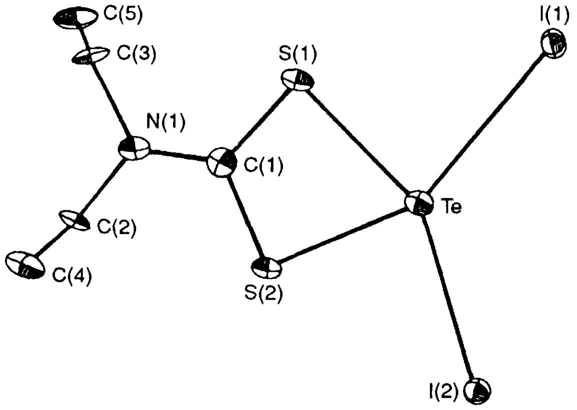

Fig. 3 An ORTEP plot of the anionic species of $[H(phen)_2][Te(S_2CNEt_2)I_2]$ **3**. Details as in Fig. 1

The position of all the hydrogen atoms, except of those of the disordered cation could be located. The C–H bond distances are all of acceptable order.

Molecular structures of $[H(phen)_2][Te(S_2CNEt_2)I_2]$ 3 and $[H(phen)_2][Te(S_2CNEt_2)Br_2]$ 5

The complexes are isomorphous and are composed of bis(1,10-phenanthroline)hydrogen(I) cations and anionic $[Te(S_2CNEt_2)X_2]^-$ (X = I or Br) species. In **3** (ORTEP diagram in Fig. 3) the two sulfur atoms S(1) and S(2) of the dithiocarbamate are bound to tellurium with distances of 2.512(2) and 2.567(2) Å respectively, forming a chelate ring. The two iodines I(1) and I(2) are bound to tellurium with distances of 3.038(1) and 3.151(1) Å respectively, longer than the sum of the covalent radii of Te and I and that observed in $[TeI_4]^{2-}$. The angle at Te between the two iodines is 124.3(1)° and that between the two sulfur atoms is 69.9(1)°. The dithiocarbamate is bound in a more or less isobidentate fashion as reflected in the two Te–S and C–S distances.

Considering the structure of polymeric $Te(S_2CNEt_2)I$ and of $[Te(S_2CNEt_2)I_2]^-$, the geometry around Te in all cases is the same, namely planar trapezoidal. The average Te–S distance in the complexes varies in the order $TeL(I) < [H(phen)_2]$-

Table 3 Crystallographic data

	$[NEt_4][Te(S_2CNEt_2)I_2]$	$[H(phen)_2][Te(S_2CNEt_2)I_2]$	$[H(phen)_2][Te(S_2CNEt_2)Br_2]$
Formula	$C_{13}H_{30}I_2N_2S_2Te$	$C_{29}H_{27}I_2N_5S_2Te$	$C_{29}H_{27}Br_2N_5S_2Te$
M	659.89	891.02	797.01
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	18.299(2)	19.753(5)	18.958(4)
b/Å	8.202(2)	8.338(5)	8.324(2)
c/Å	30.723(6)	19.831(4)	19.672(4)
β/°	93.17(1)	100.8(2)	100.92(2)
U/Å^3	4603.91	3208.45	3048.26
Z	8	4	4
D_c/Mg m^{-3}	1.90	1.84	1.74
D_m/Mg m^{-3}	1.93	1.85	1.76
μ/mm^{-1}	3.873	2.796	3.76
$F(000)$	2496	1704	1560
Crystal size/mm	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.1
No. reflections collected	3861	6246	5938
No. reflections observed [$I > 3\sigma(I)$]	3721	3278	3400
hkl Ranges	−21 to 21, 0–9, 0–36	0–23, 0–9, −23 to 23	0–22, 0–9, −23 to 23
R	0.050	0.025	0.031
R'	0.053[a]	0.025[a]	0.080[b]

[a] $[\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [b] $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}}$.

Table 4 Fractional atomic coordinates of non-hydrogen atoms in $[NEt_4][Te(S_2CNEt_2)I_2]$ **1** with e.s.d.s in parentheses

Atom	x	y	z
Te	0.079 88(2)	0.1070 3(5)	0.625 40(1)
I(1)	0.154 79(3)	−0.006 51(7)	0.543 37(2)
I(2)	0.161 08(3)	0.250 50(7)	0.706 69(2)
S(1)	−0.038 3(1)	0.027 0(2)	0.582 0(1)
S(2)	−0.031 7(1)	0.177 4(2)	0.668 0(1)
C(1)	−0.084 1(4)	0.099 0(8)	0.624 7(2)
N(1)	−0.157 9(3)	0.106 6(9)	0.624 0(2)
C(2)	−0.196 1(5)	0.172 4(14)	0.660 5(3)
C(3)	−0.210 6(6)	0.349 6(14)	0.656 2(4)
C(4)	−0.202 5(5)	0.051 7(15)	0.585 5(3)
C(5)	−0.224 7(7)	−0.123 0(18)	0.591 5(5)
N(2)	0.0	0.288 7(9)	0.25
C(6)	0.061 6(4)	0.176 3(9)	0.238 2(3)
C(7)	0.130 7(6)	0.259 7(13)	0.225 9(6)
C(8)	0.020 8(6)	0.404 0(10)	0.286 1(3)
C(9)	0.051 2(9)	0.311 1(15)	0.329 3(4)
N(3)	0.0	0.50	0.50
C(10A)*	0.035 0(12)	0.432(2)	0.541 3(6)
C(10B)*	−0.019 4(12)	0.362(2)	0.471 5(7)
C(11)	0.060 9(9)	0.575 5(15)	0.574 8(4)
C(12A)*	−0.055 2(13)	0.386(2)	0.525 6(9)
C(12B)*	−0.059 9(17)	0.385(3)	0.509 1(7)
C(13)	−0.125 0(8)	0.493(4)	0.533 4(7)

* Site occupation = 0.5.

$[TeLI_2] < [NEt_4][TeLI_2]$ ($L = S_2CNEt_2$). Likewise, due to the *trans* influence of the sulfur on the iodide, the mean Te–I distance varies in the order TeL(I) > $[H(phen)_2][TeLI_2]$ > $[NEt_4][TeLI_2]$. As the Te–I distance increases the Te–S distance decreases. There seems to be a systematic trend in structures **3** and **5** for a long and a short Te–S bond, with the corresponding *trans*-halide bonds being, respectively, short and long.

In complex **5** (ORTEP diagram in Fig. 4) the sulfur atoms S(1) and S(2) of the dithiocarbamate are bound to tellurium at distances of 2.503(2) and 2.545(2) Å respectively and the bromine atoms Br(1) and Br(2) at 2.911(1) and 2.986(1) Å respectively. The mean Te–Br distance of 2.949 Å is higher than the sum of the covalent radii of Te and Br and also than that observed[27] in $[TeBr_4]^{2-}$ (2.753 Å). As in the iodide analogue the higher distance is attributed to the *trans* influence of the sulfur atoms of the dithiocarbamate. The Br(1)–Te–Br(2) angle is 129.07(3)° and that of S(1)–Te–S(2) is 70.25(6)°. The sum of the four angles around tellurium is approximately 360° and the four atoms are arranged in a planar trapezoidal fashion. The r.m.s. deviation of the atoms from this mean plane is 0.025 Å.

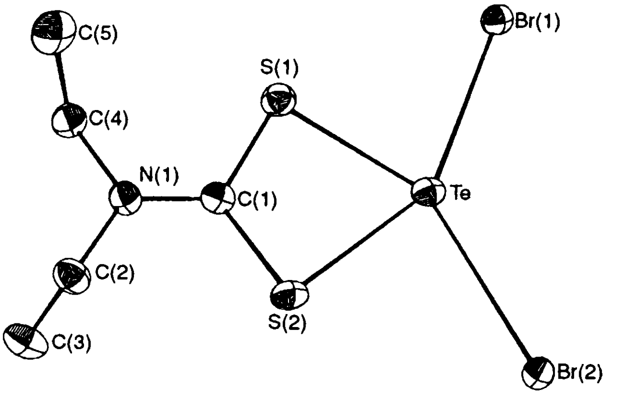

Fig. 4 An ORTEP plot of the anionic species of $[H(phen)_2][Te(S_2CNEt_2)Br_2]$ **5**. Details as in Fig. 1

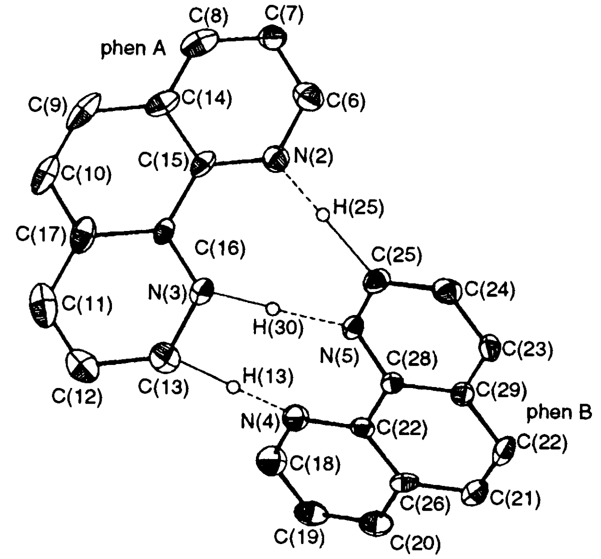

Fig. 5 An ORTEP plot of the bis(1,10-phenanthroline)hydrogen(I) cation of the molecules **3** and **5** with 50% probability ellipsoids. Only the hydrogen atoms involved in the hydrogen bonding are included for the sake of clarity

The bis(1,10-phenanthroline)hydrogen(I) cation in both these complexes consists of two phenanthroline groups A and B, as

Table 5 Fractional atomic coordinates of non-hydrogen atoms with e.s.d.s in parentheses for $[H(phen)_2][Te(S_2CNEt_2)I_2]$ **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Te	0.223 68(2)	0.097 90(4)	0.114 39(2)	C(14)	0.028 8(3)	0.184 5(7)	0.710 1(3)
I(1)	0.075 52(2)	0.161 76(5)	0.045 17(2)	C(15)	0.097 9(3)	0.137 0(7)	0.717 1(3)
I(2)	0.344 16(2)	0.023 24(6)	0.035 08(2)	C(16)	0.128 8(3)	0.058 0(6)	−0.221 4(3)
S(1)	0.174 0(1)	0.129 5(2)	0.221 3(1)	C(17)	0.091 0(3)	0.022 8(7)	0.829 5(3)
S(2)	0.318 9(1)	0.067 9(2)	0.221 1(1)	N(3)	0.196 3(2)	0.009 3(6)	0.789 0(2)
C(1)	0.255 5(3)	0.098 6(7)	0.268 4(3)	N(4)	0.365 9(3)	0.135 8(7)	0.815 9(3)
N(1)	0.267 5(2)	0.100 6(6)	0.335 7(3)	C(18)	0.403 6(4)	0.203 8(10)	0.871 6(4)
C(2)	0.334 6(3)	0.051 7(8)	0.337 6(3)	C(19)	0.472 3(5)	0.251 8(11)	0.875 4(5)
C(3)	0.379 2(4)	0.189 0(9)	0.407 2(5)	C(20)	0.501 0(4)	0.228 3(11)	−0.178 7(6)
C(4)	0.213 7(3)	0.147 0(7)	0.375 3(3)	C(21)	0.496 2(4)	0.121 3(11)	−0.297 1(6)
C(5)	0.171 8(4)	0.007 3(9)	0.391 8(4)	C(22)	−0.038 2(5)	0.450 5(11)	0.149 0(5)
N(2)	0.135 7(3)	0.160 5(7)	0.667 8(3)	C(23)	−0.144 1(5)	0.581 6(11)	0.089 6(4)
C(6)	0.104 6(4)	0.234 2(10)	0.610 8(3)	C(24)	0.290 2(5)	−0.126 3(10)	0.588 7(4)
C(7)	0.037 0(4)	0.285 5(10)	0.599 7(4)	C(25)	−0.240 3(4)	0.587 0(11)	0.144 8(4)
C(8)	−0.001 0(4)	0.261 6(9)	0.648 9(4)	C(26)	0.466 5(3)	0.154 0(8)	0.761 7(4)
C(9)	−0.008 2(3)	0.151 3(9)	0.763 9(4)	C(27)	0.397 2(3)	0.109 3(7)	0.761 1(3)
C(10)	0.021 3(3)	0.071 2(8)	0.819 8(3)	C(28)	0.359 3(3)	0.032 1(7)	0.701 6(3)
C(11)	0.123 3(3)	−0.064 7(7)	0.887 4(3)	C(29)	0.392 5(4)	−0.002 0(8)	0.645 8(4)
C(12)	0.190 6(3)	−0.106 7(8)	0.894 8(3)	N(5)	−0.207 5(3)	0.510 8(7)	0.199 4(3)
C(13)	0.227 4(3)	−0.066 9(8)	0.843 6(3)				

Table 6 Fractional atomic coordinates of non-hydrogen atoms with e.s.d.s in parentheses for $[H(phen)_2][Te(S_2CNEt_2)Br_2]$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Te	0.390 28(2)	0.096 09(5)	0.279 52(2)	C(11)	0.608 1(4)	−0.060 3(9)	0.380 4(4)
Br(1)	0.452 96(4)	0.162 03(9)	0.423 69(3)	C(12)	0.599 8(4)	−0.101 2(10)	0.312 3(4)
Br(2)	0.463 84(4)	0.027 2(1)	0.161 22(3)	C(13)	0.651 8(4)	−0.056 2(9)	0.275 1(4)
S(1)	0.278 0(1)	0.127 0(2)	0.327 77(8)	C(14)	0.792 8(4)	0.193 3(8)	0.474 9(3)
S(2)	0.280 9(1)	0.063 9(2)	0.183 08(8)	C(15)	0.784 7(3)	0.149 8(8)	0.405 1(3)
C(1)	0.228 7(4)	0.096 0(8)	0.245 0(3)	C(16)	0.720 6(3)	0.066 3(7)	0.373 9(3)
N(1)	0.158 2(3)	0.097 2(7)	0.231 7(3)	C(17)	0.668 1(3)	0.026 3(8)	0.412 2(3)
C(2)	0.115 5(4)	0.045 1(10)	0.164 3(4)	C(18)	0.619 0(5)	0.223 7(12)	0.096 6(5)
C(3)	0.086 0(7)	0.185 7(12)	0.118 4(5)	C(19)	0.614 0(9)	0.274 0(17)	0.028 2(7)
C(4)	0.116 6(5)	0.143 9(9)	0.284 3(4)	C(20)	0.671 2(7)	0.240 9(14)	−0.002 9(5)
C(5)	0.099 0(7)	0.003 6(12)	0.327 8(6)	C(21)	0.792 3(8)	0.128 0(14)	0.000 6(5)
N(2)	0.834 9(3)	0.180 3(8)	0.366 0(3)	C(22)	0.849 8(7)	0.050 6(13)	0.035 4(5)
N(3)	0.709 4(3)	0.023 9(8)	0.306 0(3)	C(23)	0.910 8(5)	−0.086 1(12)	0.141 2(6)
N(4)	0.677 8(3)	0.152 1(8)	0.133 3(3)	C(24)	0.912 2(5)	−0.126 9(13)	0.207 1(7)
N(5)	0.798 9(3)	0.003 4(8)	0.205 6(3)	C(25)	0.855 2(5)	−0.078 7(12)	0.238 8(5)
C(6)	0.894 2(5)	0.255 6(11)	0.396 6(5)	C(26)	0.731 6(5)	0.165 7(10)	0.031 6(4)
C(7)	0.905 5(5)	0.305 0(11)	0.465 3(5)	C(27)	0.733 4(4)	0.122 5(8)	0.101 4(3)
C(8)	0.855 1(5)	0.275 7(10)	0.504 5(5)	C(28)	0.795 5(4)	0.041 7(8)	0.139 0(3)
C(9)	0.738 4(5)	0.154 9(10)	0.512 9(4)	C(29)	0.853 1(5)	0.001 4(10)	0.104 1(4)
C(10)	0.679 0(5)	0.073 8(10)	0.483 4(4)				

shown in Fig. 5, with the acidic proton H(30) bound to N(3) of phen A. The hydrogen atom is clearly distinguishable in the Fourier-difference map and is accurately located with N(3)–H(30) 0.76 Å in **3** and 0.74 Å in **5**, almost equal to the N–H bond distance of 0.78 Å observed[25] in a monoprotonated bis(phenanthrolinium) catenand and also similar to those found in other N^+–H groups of similar compounds.[17,18]

Both phenanthrolines A and B are essentially planar. The dihedral angles between these two planes are 55.9 and 57.8° respectively for complexes **3** and **5**. The two phenanthroline rings are held together by three hydrogen-bonding interactions. The stability of the cation is ensured by an efficient hydrogen bond between N(5) of phen B and the acidic proton. The N(3)$\cdots$N(5) distance observed (2.845 Å for **3** and 2.842 Å for **5**) is in close agreement with N$\cdots$N distances (about 3.0 Å) observed[23–25,29,30] in numerous compounds involving N–H$\cdots$N hydrogen bonding. The N(3)–H(30)–N(5) angle is 159 and 162° for **3** and **5** respectively.

Two more weak interactions involving C(H) hydrogen occur in the cation. Though C–H$\cdots$N hydrogen bonding is very uncommon, reports[31] are available on similar interactions. These intramolecular hydrogen-bonding interactions probably contribute to the stability of the cation. The distances between the carbon and nitrogen atoms are C(13)$\cdots$N(4) 3.348 and 3.399 and C(25)$\cdots$N(2) 3.299 and 3.380 Å for **3** and **5** respectively. The corresponding H$\cdots$N distances are 2.71, 2.59, 2.64 and 2.72 Å.

References

1 G. Aravamudan, C. Janakiram and B. G. Sejekan, *Phosphorus Sulfur Relat. Elem.*, 1978, **5**, 185.

2 B. G. Sejekan, C. Janakiram and G. Aravamudan, *J. Inorg. Nucl. Chem.*, 1978, **40**, 211.

3 K. V. Deuten, W. Schnabel and G. Klar, *Phosphorus Sulfur Relat. Elem.*, 1980, **9**, 93.

4 S. P. Chidambaram, G. Aravamudan, M. Seshasayee, M. R. Snow and E. R. T. Tiekink, *Aust. J. Chem.*, 1989, **42**, 969.

5 W. Schnabel, K. V. Deuten and G. Klar, *Phosphorus Sulfur Relat. Elem.*, 1982, **13**, 345.

6 R. Krishna Kumar, G. Aravamudan, M. R. Udupa, M. Seshasayee and T. A. Hamor, *Polyhedron*, 1993, **12**, 2201.

7 V. Kumar, Ph.D. Thesis, Indian Institute of Technology, Madras, 1990.

8 R. Krishna Kumar, Ph.D. Thesis, Indian Institute of Technology, Madras, 1995.

9 C. Fabiani, R. Spagna, A. Vaciago and L. Zambonelli, *Acta Crystallogr., Sect. B*, 1971, **27**, 1499.

10 O. Foss and S. Hauge, *Acta Chem. Scand.*, 1961, **15**, 1616.

11 G. C. Rout, M. Seshasayee, G. Aravamudan and S. Sowrirajan, *Polyhedron*, 1984, **3**, 921.

12 G. M. Sheldrick, SHELX 76, A Program for Crystal Structure Determinations, University of Cambridge, 1976.

13 G. M. Sheldrick, SHELXL 93, A Program for the Refinement of Crystal Structures, University of Göttingen, 1993.

14 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

15 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

16 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

17 G. Thevenet, P. Toffoli, N. Rodier and R. Ceolin, *Acta Crystallogr., Sect. B*, 1977, **33**, 2526.

18 G. Thevenet, P. Toffoli and N. Rodier, *Acta Crystallogr., Sect. B*, 1978, **34**, 2599.

19 G. Thevenet, N. Rodier and P. Khodadad, *Acta Crystallogr., Sect. B*, 1978, 34, 2594.

20 J. V. Rund and P. C. Keller, *J. Chem. Soc. A*, 1970, 2827.

21 M. J. Fahsel and C. V. Banks, *J. Am. Chem. Soc.*, 1966, **88**, 878.

22 M. P. Marzocchi and P. Paoletti, *Chem. Commun.*, 1968, 1063.

23 G. Thevenet and N. Rodier, *Bull. Soc. Chim. Fr.*, 1981, 437.

24 L. Maresca, G. Natile, F. P. Fanizzi and F. Stasi, *J. Am. Chem. Soc.*, 1989, **111**, 1492.

25 M. Cesario, C. O. Dietrich, A. Edel, J. Guilhem, J. P. Kintzinger, C. Pascard and J. P. Sauvage, *J. Am. Chem. Soc.*, 1986, **108**, 6250.

26 L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, NY, 1960.

27 S. Pohl, W. Saak and B. Krebs, *Z. Naturforsch., Teil B*, 1985, **40**, 251.

28 H. Kiriyama, Y. Mizuhashi and J. Ootani, *Bull. Chem. Soc., Jpn.*, 1986, **59**, 581.

29 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, 1984.

30 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, p. 65.

31 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.

Received 11*th October* 1995; *Paper* 5/06741C