Some Co-ordination Compounds of $TaCl_3S$ and $TaBr_3S$. *X*-Ray Crystal Structure of $[TaCl_3S(PhSCH_2CH_2SPh)]$ *

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The reaction of TaX_5 (X = Br or Cl) with Sb_2S_3 (molar ratio 3:1) led to the formation of TaX_3S. With L these species form complexes of formulation $TaX_3S{\cdot}2L$ (L = dimethyl sulphide, tetrahydrothiophene, or MeCN) and $TaX_3S{\cdot}L$ [L = bpte = 1,2-bis(phenylthio)ethane]. The exact nature of the complexes was ascertained by a single-crystal *X*-ray study on $TaCl_3S{\cdot}$bpte. The crystals are monoclinic, space group $P2_1/c$, $Z = 4$ with $a = 15.538(20)$, $b = 7.352(8)$, $c = 16.619(20)$ Å, and $\beta = 110.88(10)°$. 2 003 Independent reflections with $I > 4\sigma(I)$ were used in the refinement and a R value of 0.062 obtained. The structural study showed that the metal atom was in a distorted octahedral environment with a terminal Ta=S bond [2.204(5) Å], three metal–chlorine interactions [2.322(5), 2.366(5), and 2.241(6) Å], and two bonds to the sulphur atoms of the ligand. The bond *trans* to the terminal sulphur atom is longer [2.836(4) Å] than the bond that is *cis* [2.705(5) Å]. The Ta=S fragment has the expected influence on the three angles it forms at the metal with the three chlorine atoms that are bound *cis* to it, increasing the angles to *ca.* 100°. This is concomitant with a surprisingly small value of 86.5(2)° for the angle S=Ta–S(*cis*).

In contrast to the well characterised niobium chalcogenide halides,[1-11] reports of related tantalum species are very limited. The first niobium compounds to be well characterised were the niobium(IV) ternary species $[Nb_2X_4Y_4]$ (X = Br, Cl, or I; Y = S or Se) [1-3,7] which were prepared by a variety of techniques including reaction of the elements in the appropriate stoicheiometry. However, attempts to extend the work to tantalum led only to the isolation of non-stoicheiometric Ta–Br–S phases.[10]

The synthesis of the tantalum(V) sulphidohalides TaX_3S (X = Br or Cl) from the reaction of the tantalum pentahalides and antimony trisulphide (3 : 1 molar ratio) in carbon disulphide has been reported.[11] Unfortunately all attempts to obtain single crystals of these species failed. Accordingly it was decided to investigate the chemistry of these compounds by synthesising some of their co-ordination compounds and carrying out single-crystal *X*-ray studies on a selected species. The relevance of ascertaining the exact nature of chalcogenide halides is illustrated by the report of crystallographic studies on $NbBr_3Se$, a compound that naively would be expected to contain niobium(V), but in fact contains niobium(IV) with bridging $(Se_2)^{2-}$ groups.[8] A second reason for studying the tantalum compounds was to ascertain if the adducts of the species TaX_3S underwent complex redox-disproportionation reactions as has been observed for NbX_3S (X = Br or Cl) in tetrahydrothiophene (tht) solution which led to the formation of a niobium(IV) species [6] [see equation (1)].

$$NbX_3S{\cdot}2tht \longrightarrow NbX_5{\cdot}n\,tht + (tht)_2X_2Nb(S_2)SNbX_2(tht)_2 \quad (1)$$

Accordingly the isolation and characterisation of some of the adducts of TaX_3S (X = Br or Cl) and the crystal structure of $TaCl_3S{\cdot}$bpte [bpte = 1,2-bis(phenylthio)ethane] is reported.

Experimental

All the compounds that were isolated were extremely air- and moisture-sensitive and so all preparations, filtrations *etc.* were carried out using an all-glass vacuum line. Samples for spectroscopic investigation were prepared in a ' dry box ' fitted with a drying train in which nitrogen was dried, deoxygenated, and recirculated through the box. To ensure that there were no complications from moisture or oxygen on the surface of glassware all reaction ampoules *etc.* were evacuated for periods in excess of 3 h while being maintained at a temperature of approximately 100 °C. Following such treatment the apparatus was allowed to cool and if chemicals were to be added it was filled with dry nitrogen. The pentahalides were prepared by halogenation of tantalum metal at high temperature in a stream of dried halogen. Antimony trisulphide was precipitated by passing H_2S through an acidified solution of antimony trichloride.

Preparation of TaX_3S (X = Br *or* Cl).—The tantalum pentahalide (*ca.* 5 g) was placed in a previously weighed reaction ampoule under a stream of dried nitrogen. The ampoule was quickly evacuated and left to pump for 0.5 h and then refilled with nitrogen and reweighed. Sufficient antimony trisulphide was then weighed so that the pentahalide was slightly in excess of that required for a 3 : 1 molar ratio of the two reactants. The sulphide was pumped at 200 °C overnight. After being allowed to cool it was added to the pentahalide. Dry deoxygenated carbon disulphide (40 cm^3) was distilled into the reaction ampoule which was cooled to liquid-nitrogen temperature. Following the addition of the solvent the ampoule was sealed and allowed to reach room temperature. At this temperature it was stirred using the magnetic follower contained in the ampoule for a period of 3 d. The ampoule was quickly opened under a vigorous stream of dry nitrogen and the contents filtered on the vacuum line. The desired products were insoluble in carbon disulphide while the other product (the antimony trihalide) was soluble in the solvent. The precipitated product was washed with fresh quantities of solvent until all traces of occluded antimony trihalide were removed. Finally the product was pumped for

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* [1,2-Bis(phenylthio)ethane-*SS'*]trichloro(thio)tantalum(V).

Supplementary data available (No. SUP 23866, 20 pp.): structure factors, thermal parameters, H-atom co-ordinates, ligand geometries. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Ta	2 425(1)	2 058(1)	3 351(0)
S(1)	1 448(4)	4 354(7)	3 969(3)
S(2)	3 535(3)	2 295(7)	5 121(3)
S(3)	1 326(4)	2 421(9)	2 084(3)
Cl(1)	1 780(4)	−274(7)	3 892(3)
Cl(2)	3 177(4)	4 893(7)	3 455(3)
Cl(3)	3 499(4)	430(9)	3 061(3)
C(11)	446(13)	3 367(23)	4 030(11)
C(12)	−279(16)	2 965(35)	3 250(13)
C(13)	−1 072(16)	2 298(34)	3 243(15)
C(14)	−1 191(16)	1 847(40)	3 992(17)
C(15)	−477(16)	2 129(39)	4 766(15)
C(16)	330(15)	2 911(38)	4 785(12)
C(10)	2 192(15)	4 770(29)	5 066(11)
C(20)	2 703(13)	3 110(27)	5 554(11)
C(21)	3 825(12)	109(26)	5 649(11)
C(22)	4 139(13)	−1 201(31)	5 240(12)
C(23)	4 406(14)	−2 890(31)	5 658(13)
C(24)	4 395(14)	−3 166(28)	6 461(13)
C(25)	4 075(17)	−1 849(44)	6 840(14)
C(26)	3 818(16)	−172(31)	6 451(13)

Table 2. Selected molecular dimensions: bond lengths (Å), and angles (°)

Ta–S(1)	2.705(5)	Ta–Cl(1)	2.322(5)
Ta–S(2)	2.836(4)	Ta–Cl(2)	2.366(5)
Ta–S(3)	2.204(5)	Ta–Cl(3)	2.241(6)
S(1)–Ta–S(2)	77.54(15)	S(3)–Ta–Cl(2)	99.05(22)
S(1)–Ta–S(3)	86.46(20)	Cl(1)–Ta–Cl(2)	153.16(17)
S(2)–Ta–S(3)	163.99(20)	S(1)–Ta–Cl(3)	167.53(19)
S(1)–Ta–Cl(1)	86.33(18)	S(2)–Ta–Cl(3)	91.83(19)
S(2)–Ta–Cl(1)	80.28(16)	S(3)–Ta–Cl(3)	103.99(22)
S(3)–Ta–Cl(1)	99.48(22)	Cl(1)–Ta–Cl(3)	98.42(22)
S(1)–Ta–Cl(2)	75.62(17)	Cl(2)–Ta–Cl(3)	95.73(21)
S(2)–Ta–Cl(2)	76.58(16)		

24 h to ensure all traces of solvent were removed (Found: Cl, 33.7; Ta, 56.6. $TaCl_3S$ requires Cl, 33.3; Ta, 56.6%. Found: Br, 53.3; Ta, 40.3. $TaBr_3S$ requires Br, 53.0; Ta, 40.0%).

Preparation of the Adducts.—Reactions were carried out in sealed ampoules containing a magnetic follower. In a typical reaction the sulphidohalide (*ca.* 2 g) was weighed under dry nitrogen into the ampoule which was then rapidly evacuated. For the liquid ligands MeCN, tetrahydrothiophene (tht), and dimethyl sulphide (dms) 40 cm^3 of dry deoxygenated ligand were distilled into the ampoule. The ampoules were cooled to liquid-nitrogen temperature and sealed under vacuum.

The reactions with tht were heated to 50 °C for 14 d giving red solutions. Following this period the ampoule was opened, connected to the vacuum line and the excess ligand distilled off under reduced pressure at room temperature to give red and brown-red products for the chloride and bromide, respectively (Found: Cl, 21.8; Ta, 36.1. $TaCl_3S\cdot 2tht$ requires Cl, 21.5; Ta, 36.5%; Found: Br, 38.1; Ta, 28.5. $TaBr_3S\cdot 2tht$ requires Br, 38.1; Ta, 28.8%).

With MeCN the ampoules were kept at 70 °C for 17 d, dark brown solutions being obtained. The excess of ligand was removed as above for tht to give yellow and dark yellow crystalline materials for the chloride and bromide, respectively (Found: Cl, 26.3; Ta, 44.7. $TaCl_3S\cdot 2NCMe$ requires Cl, 26.5; Ta, 45.1%; Found: Br, 45.3; Ta, 33.6. $TaBr_3S\cdot 2NCMe$ requires Br, 44.8; Ta, 33.8%).

With dms red solutions were obtained on stirring the reactants for 7 d. Removal of excess ligand (the same procedure as for tht) gave dark oils. By distilling on to these oils successive quantities of CCl_4 and removing them at the pump dark red solids were obtained (Found: Cl, 24.3; Ta, 41.4. $TaCl_3S\cdot 2dms$ requires Cl, 24.0; Ta, 40.8%; Found: Br, 42.3; Ta, 32.1. $TaBr_3S\cdot 2dms$ requires Br, 41.5; Ta, 31.4%).

Reactions with the solid ligand 1,2-bis(phenylthio)ethane (bpte) were carried out in CS_2 (*ca.* 50 cm^3). Two chalcogenide halide to ligand stoicheiometries were employed, namely 1 : 1 and 1 : 3. The reaction mixtures were heated to 50 °C for 14 d during which time pale green solutions and brown precipitates formed. Isolation of the solids and subsequent analyses indicated that the same products were obtained irrespective of the molar ratio of the reactants. Any excess of ligand was recovered as a white crystalline material on evaporation of the solvent. From the reactions carried out in a 1 : 1 molar ratio pale green filtrates were obtained from which small amounts of compounds with identical analyses to the insoluble products were obtained by evaporation of the solvent (Found: Cl, 19.1; Ta, 32.6. $TaCl_3S\cdot bpte$ requires Cl, 18.8; Ta, 32.0%; Found: Br, 34.5; Ta, 25.8. $TaBr_3S\cdot bpte$ requires Br, 34.3; Ta, 25.9%).

Crystal Structure Determination of $TaCl_3S\cdot bpte$.—Experimental procedures of data collection and data processing were carried out as previously reported.[6] Green crystals in the form of triangular plates were obtained by recrystallisation of $TaCl_3S\cdot bpte$ from CS_2 solution. A crystal was chosen with approximate thickness of 0.2 mm and triangular sides of 0.1 × 0.5 × 0.5 mm. The crystal system was determined as monoclinic with a = 15.538(20), b = 7.352(8), c = 16.619(20) Å and β = 110.88(10)°. Systematically absent reflections were observed for the planes $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) which is characteristic of the space group $P2_1/c$ with $Z = 4$, U = 1 773.80 Å^3, μ = 71.2 cm^{-1}, $F(000)$ = 1 080, D_c = 2.12 g cm^{-3} and D_m = 2.20(5) g cm^{-3}. On the Stoe diffractometer, 3 985 independent reflections were measured with the crystal mounted about axis b, of which 2 003 with $I > 4\sigma(I)$ were used in the final calculations. An absorption correction scheme was made using SHELX 76 [12] with transmission factors ranging from 0.28 to 0.06. The position of the tantalum atom was found from a Patterson function; the positions of all the other non-hydrogen atoms were found by Fourier syntheses and all were refined anisotropically. Hydrogen atoms were placed at the appropriate trigonal or tetrahedral positions around the carbon atoms and refined isotropically. The structure was refined using SHELX 76 at the University of Manchester Computer Centre. The final R was 0.062 (R' = 0.065). The weighting scheme used was $w = [\sigma^2(F) + 0.003F^2]$. The non-hydrogen atomic co-ordinates are given in Table 1; dimensions for the metal co-ordination sphere are given in Table 2.

Results and Discussion

The adducts of TaX_3S whose preparations are reported were of formulation $TaX_3S\cdot 2L$ (L = tht, dms, or MeCN) and $TaX_3S\cdot bpte$. By comparison with the known $NbCl_3O$ complexes [13–15] it would be logical to assume the species to be six-co-ordinate monomeric complexes with two atoms from the ligand(s) in the co-ordination shell of the metal. From low-temperature n.m.r. studies on $NbCl_3O\cdot 2L$ (L = hexamethylphosphoramide) evidence was obtained for the presence of all three isomers in solution.[13]

The present tantalum species were not sufficiently soluble for meaningful molar mass or conductivity measurements to

Table 3. Selected spectroscopic data for the complexes of $TaCl_3S$ and $TaBr_3S$ (CH_2Cl_2 solvent and internal reference, $\delta = 5.30$ p.p.m.; c = complex resonance)

Complex	ν(Ta=S)/cm⁻¹	$\delta(^1H)$/p.p.m. (assignments)	Shift on co-ordination (p.p.m.)
$TaCl_3S{\cdot}2dms$	510m	2.56	+0.47
$TaBr_3S{\cdot}2dms$	506s	2.59	+0.50
$TaCl_3S{\cdot}2tht$	505s	3.11(c)(α-H)	+0.39
		2.06(c)(β-H)	+0.17
$TaBr_3S{\cdot}2tht$	504s	3.13(c)(α-H)	+0.41
		2.06(c)(β-H)	+0.17
$TaCl_3S{\cdot}2NCMe$	510vs	2.02	+0.08
$TaBr_3S{\cdot}2NCMe$	508s	2.08	+0.14
$TaCl_3S{\cdot}bpte$	516vs	7.32(aryl)	+0.20
	510vs	3.52(alkyl)	+0.55
$TaBr_3S{\cdot}bpte$	512vs	7.37(aryl)	+0.25
	508vs	3.60(alkyl)	+0.63

be made, but a slight solubility in CH_2Cl_2 enabled ^1H n.m.r. spectra to be measured, although limitations of apparatus confined measurements to 60 MHz and room temperature. For all the complexes the resonances moved to lower field on co-ordination (see Table 3) as expected. Only one set of ligand resonances was observed for each complex but this is probably due to rapid ligand exchange in solution rather than equivalent ligand bonding. Ligand exchange by dissociation is probable since five-co-ordination of the metal has been observed in the structure of the related niobium complex $NbCl_3S{\cdot}SPPh_3$.[16]

In contrast to the reactions of the niobium compounds NbX_3S with tht and dms,[6] in each reaction of TaX_3S (X = Br or Cl) with tht or dms only single products in high yield were obtained. Thus no evidence was obtained for the occurrence, with tantalum, of complex reactions of the type shown in reaction (1) (see Introduction) that readily occur with niobium. This observation reflects the increase in stability of the group oxidation state on descending Group 5. The most interesting feature of the infrared spectra of the compounds is the appearance of strong bands at *ca.* 505 cm⁻¹ (see Table 3) that are not assignable to any modes of the co-ordinated ligands. These absorptions are thus attributed to the stretching modes of terminally bonded Ta=S fragments. The appearance of these absorptions is interesting, as in the parent chalcogenide halides the highest energy bands are at 463 and 448 cm⁻¹ for the chloride and bromide, respectively. Thus the evidence provided by the i.r. spectra supports the suggestion that there are bridging sulphur atoms in the compounds TaX_3S and that these bridges are broken on adduct formation. This contrasts with the niobium analogues where it is believed terminal Nb=S moieties [Nb=S stretches at 552 cm⁻¹ (Cl) and 542 cm⁻¹ (Br)] are present in NbX_3S. The Nb=S stretch in the compounds NbX_3S lies at *ca.* 530 cm⁻¹ and thus the Ta=S modes are at lower frequency than comparable Nb=S modes, the shift being in accord with the change in reduced mass. No definitive value for a Ta=S stretching mode has been given. A compound that has been shown to contain a Ta=S terminal fragment is $Ta(dtc)_3S$ (dtc = dithiocarbamate), the Ta=S stretch being assigned to a band at 905 cm⁻¹.[17] This assignment is in error, as the band is also observed in the niobium analogue [18] and thus is believed to be a ligand absorption. An unusual feature of the spectra of the bpte adducts is that each contain two bands assignable to Ta=S stretches. Accordingly the structure of the complex $TaCl_3S{\cdot}bpte$ was determined by *X*-ray diffraction. This is the first structure determination of an adduct of a tantalum chalcogenide halide. The structure would show if there were two domains for the Ta=S groups that thus give rise to the two Ta=S stretches. An added reason for studying the complexes is that, unlike niobium, tantalum does not form readily isolable oxo-compounds based on MX_3O and so little structural evidence exists on tantalum compounds containing Ta=Y bonds (Y = O, S, or Se).

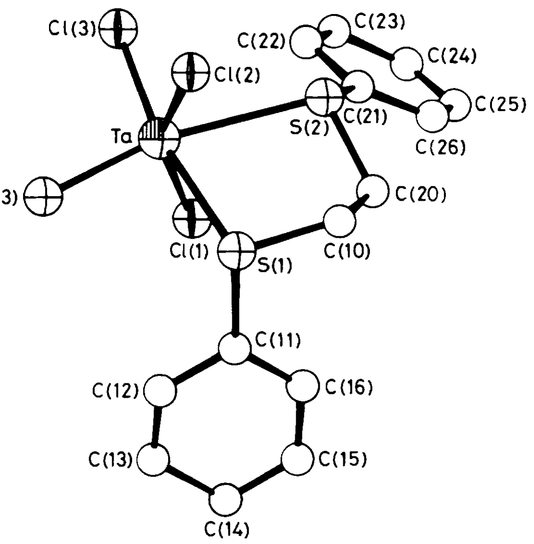

Figure. The structure of $TaCl_3S{\cdot}bpte$

Structure of $TaCl_3S{\cdot}bpte$.—The crystallographic investigation of $TaCl_3S{\cdot}bpte$ revealed that the crystals contained discrete molecules in which the tantalum atoms were six-co-ordinate. The adduct is depicted in the Figure which also shows the atom-numbering scheme. A sulphur atom is terminally bonded to the metal atom [Ta=S(3) 2.204(5) Å] and the bond length is slightly longer than the terminal tantalum–sulphur bond in the seven-co-ordinate compound $Ta(S_2CNEt_2)_3S$ [2.181(1) Å].[17] The length of the Ta–S distance suggests the presence of a double bond and indeed it is of comparable length to the range of known Nb=S bonds.[16] In six-co-ordinate complexes such multiply-bonded fragments have been shown to lead to an increase in the angles such bonds form with the atoms *cis* to them to above 90°. This phenomenon is also observed here with the three chlorine atoms bound to the metal, the S–Ta–Cl angles being 99.48(22) [Cl(1)], 99.05(22) [Cl(2)], and 103.99(22)° [Cl(3)]. These angles are similar to those observed in the tungsten(v) compound $WCl_3S{\cdot}dth$ (dth = 2,5-dithiahexane) [96.4—106.6° (these angles were not given in the publication)].[19]

The Ta–Cl(1) and Ta–Cl(2) bonds [2.322(5) and 2.366(5) Å] lie within the range of Ta–Cl distances found for the tantalum(v) anion $[TaCl_6]^-$ (2.30—2.37 Å)[20] and the terminal Ta–Cl distance found in $[\{TaCl_2(tht)(MeC{=}CCMe_3)\}_2(\mu\text{-}Cl)_2]$ [2.362(3) and 2.365(3) Å].[21] However the Ta–Cl(3) distance is considerably shorter [2.241(6) Å] and the reason for this is not immediately apparent. It was thought possible that there was some disorder between the terminal sulphur atom [S(3)] and Cl(3). Such situations have been observed in a number of crystallographic studies of the chalcogenide halides [6,22] and are usually detected by examining the factors associated with the environment of the two atoms. When such disorder is between, say, chlorine and oxygen or selenium and chlorine, it can easily be detected by examination of the thermal parameters. However disorder between sulphur and chlorine is difficult to establish by this method and there is no evidence either way in the present structure. A refinement was carried out allowing for disorder between the two sites using fixed Ta=S and Ta–Cl distances but this did not lead to satisfactory convergence.

However, a similar disparity in metal–chlorine distances has been observed in the $[WCl_5S]^-$ anion, one distance in particular being quite short.[23] In this case the shortening was attributed to intermolecular contact with another chlorine atom across a centre of symmetry but in the present study there are no short intermolecular contacts. The only reason that can therefore be assigned to causing the short Ta–Cl distance is its unique position in the co-ordination sphere. Unlike the other chlorine atoms, Cl(3) is *trans* to a sulphur atom from the ligand [S(1)] and the poor Lewis basicity of thioethers could permit the short Ta–Cl distance.

The presence of a short Ta–Cl distance cannot be inferred from the i.r. spectrum. Attempts to correlate band positions to particular metal–chlorine distances are contentious for molecules of such low symmetry, particularly as the regions containing the Ta–Cl and Ta–S (ligand) modes overlap.

A similar situation was observed in $WCl_3S{\cdot}dth$ where the W–Cl distance *trans* to a sulphur atom of the ligand was 2.282(7) Å while the two mutually *trans* W–Cl distances were longer at 2.339(6) and 2.345(7) Å.[19]

A further interesting factor to emerge from the study is the size of the S=Ta–S(1) angle which instead of being increased to *ca.* 100° due to the *cis* influence of the Ta=S moiety as are the S=Ta–Cl angles, it is in fact less than 90°, being 86.5(2)°. In $WCl_3S{\cdot}dth$ the disposition of the ligand was found to be similar to that reported here with one of the sulphur atoms being *trans* to the W=S bond the other being *cis*; the S=W–S (*cis*) angle also being just below 90° [89.0(1)°]. The cause of these angles being below 90° could be steric. It is noticeable that both of the chlorine atoms adjacent to S(3), namely Cl(1) and Cl(2), form close contacts with carbon atoms as detected by the size of the torsion angles [Cl(1)–Ta–S(1)–C(11) −27 and Cl(2)–Ta–S(1)–C(10) −25.3°]. These close contacts could push S(1) towards S(3). It is significant that the strongly bonded S(3) is well out of the way of the carbon atoms with torsion angles of 72.8 and −172.7° for S(3)–Ta–S(1)–C(11) and S(3)–Ta–S(1)–C(10), respectively. Thus the S(3)=M–S(1) angle is below 90° and the S(3)–M–S(2) angles are less than 180° (164.0° for $TaCl_3S{\cdot}bpte$, 167° for $WCl_3S{\cdot}dth$ [19]).

The ligand bpte is in the *gauche*, *gauche*, *trans* configuration with torsion angles of 78.2 [C(11)–S(1)–C(10)–C(20)], 67.2 [S(1)–C(10)–C(20)–S(2)], and −167.8° [C(10)–C(20)–S(2)–C(21)]. The 'bite' of the ligand is 3.471(9) Å [S(1) ··· S(2)] and thus the configuration of the ligand is that normally adopted for chelating thioethers. The two aliphatic carbon atoms of the ligand backbone [C(10) and C(20)] lie on opposite sides of the plane of the S(1), S(2), and Ta atoms at +0.21(3) and −0.59(2) Å respectively and these distances are similar to those adopted in a number of complexes involving chelating thioethers. The internal dimensions of the ligand are as expected and in accord with published data.

Conclusions

From the study of TaX_3S (Br or Cl) reported here it has been shown that these compounds are not susceptible to the complex redox-disproportionation reactions observed with NbX_3S that give rise to the niobium(IV) compounds $[Nb_2X_4S_3]$ (X = Cl or Br).[6] These niobium(IV) compounds can also be obtained by the reaction of NbX_5 and Sb_2S_3 in a 2 : 1 molar ratio but similar reactions with TaX_5 (X = Br or Cl) led to the formation of TaX_3S and an excess of Sb_2S.

Finally the formation of the single tantalum(V) compound $TaCl_3S{\cdot}bpte$ from the reaction of $TaCl_3S$ and bpte confirms that $TaCl_3S$ is a tantalum(V) compound and that it does not contain S_2 groups. The observation of two ν(Ta=S) stretches in the i.r. spectrum of $TaCl_3S{\cdot}bpte$ must be due to crystal effects and the failure to observe such a stretch in the spectrum of $TaCl_3S$ is attributable to the presence of Ta–S–Ta bridges.

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References

1 D. A. Rice, *Coord. Chem. Rev.*, 1978, **25**, 199.
2 M. J. Atherton and J. H. Holloway, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 171.
3 J. Fenner, A. Rabenau, and G. Trageser, *Adv. Inorg. Chem. Radiochem.*, 1980, **23**, 330.
4 A. J. Benton, M. G. B. Drew, R. J. Hobson, and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1981, 1304.
5 A. J. Benton, M. G. B. Drew, and D. A. Rice, *J. Chem. Soc., Chem. Commun.*, 1981, 1241.
6 M. G. B. Drew, D. A. Rice, and D. M. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 2251.
7 J. Rijnsdorp, G. J. de Lange, and G. A. Weiger, *J. Solid State Chem.*, 1979, **30**, 365.
8 H. F. Franzen, W. Honle, and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, 1983, **497**, 13.
9 A. Meerschaut, P. Palvadeau, and J. Rouxel, *J. Solid State Chem.*, 1977, **20**, 21.
10 H. Schafer and W. Beckmann, *Z. Anorg. Allg. Chem.*, 1966, **347**, 225.
11 G. W. A. Fowles, R. J. Hobson, D. A. Rice, and K. J. Shanton, *J. Chem. Soc., Chem. Commun.*, 1976, 552.
12 G. M. Sheldrick, SHELX 76, A program for crystal structure determination, University of Cambridge, 1976.
13 L. G. Hubert-Pfalzgraf, R. C. Muller, M. Postel, and J. G. Reiss, *Inorg. Chem.*, 1976, **15**, 40.
14 U. Muller and I. Lorenz, *Z. Anorg. Allg. Chem.*, 1980, **463**, 110.
15 C. Chavant, J. C. Daran, Y. Jeanin, G. Constant, and R. Marancho, *Acta Crystallogr., Sect. B*, 1975, **31**, 1828.
16 M. G. B. Drew, G. W. A. Fowles, R. J. Hobson, and D. A. Rice, *Inorg. Chim. Acta*, 1976, **20**, L35.
17 E. J. Peterson, R. B. von Dreele, and T. M. Brown, *Inorg. Chem.*, 1978, **17**, 1410.
18 D. M. Williams, Ph.D. Thesis, University of Reading, 1982.
19 M. G. B. Drew, G. F. Griffin, and D. A. Rice, *Inorg. Chim. Acta*, 1979, **34**, L192.
20 H. Preiss, *Z. Anorg. Allg. Chem.*, 1971, **380**, 56.
21 F. A. Cotton and W. Hall, *Inorg. Chem.*, 1981, **20**, 1285.
22 Ibrahim bin Baba, Ph.D. Thesis, University of Reading, 1977.
23 M. G. B. Drew, G. W. A. Fowles, E. M. Page, and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1981, 2409.

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