cumulated on a particular atom has been suggested as a probable cause of carbonyl scrambling.[14] Then, it could be inferred that the deficiency of electron charge in the basal planes could be mainly responsible for the peculiar fluxional behavior of this cluster. Therefore, the rigidity of the basal ligands could be a consequence of the electron-withdrawing effect of the sulfur atoms, while the mobility of the central ligands is indicative of greater electron density on this section of the cluster. Structural parameters of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$, such as the rhodium–sulfur distances and the rhodium–carbon and carbon–oxygen bond lengths for the terminal carbonyls on the basal and internal planes (Figure 2), also tend to support the ideas above (for basal, Rh–CO = 1.85 Å, C–O = 1.14 Å, Rh–S = 2.33 Å; for central, Rh–CO = 1.81 Å, C–O = 1.19 Å, Rh–S = 2.76 Å). The more closed and crowded basal carbonyl geometry present on the basal squares may be an equally important contribution to the observed barriers. Basal interplanar exchange would seem to require higher energy intermediates than the more open zigzag exchange between the internal planes.[15]

An alternate possibility such as the motion of the skeletal rhodium atoms placed on the internal squares, similar to the one proposed for the internal triangle of $[Pt_9(CO)_{18}]^{2-}$,[16] cannot be completely excluded. The fluxionality suggested for the rhodium skeleton of $[Rh_9P(CO)_{21}]^{2-}$[17] could indicate general scrambling ability of the metal polyhedra of rhodium carbonyl clusters with an encapsulated main-group atom(s). Work is underway to test the occurrence of such behavior.

Registry No. $[C_6H_5CH_2N(C_2H_5)_3]_3[Rh_{17}(S)_2(CO)_{32}]$, 67382-20-1.

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Adducts of Group 5A Trihalides with 1,3-Dimethyl-2(3*H*)-imidazolethione

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A series of complexes with general formula $MX_3(dmit)_n$ were prepared where M = As, Sb, or Bi, X = Cl, Br, or I, and n = 1, 2, or 3. These are in addition to the already reported complexes of $AsCl_3dmit$ and $AsBr_3dmit$. This communication reports the synthesis and physical characterization of these complexes and presents solid-state vibrational data collected for $SbCl_3dmit$ and $SbBr_3dmit$. The solid-state structure of $SbCl_3dmit$ is proposed to be pseudo trigonal bipyramidal with a linear Cl–Sb–Cl group analogous to that reported for the local site symmetry about arsenic in $AsCl_3dmit$. No conclusions were drawn concerning the structure of $SbBr_3dmit$ other than it is apparently different from that of $SbCl_3dmit$.

The recently reported structure of $AsCl_3dmit$[2] (dmit = 1,3-dimethyl-2(3*H*)-imidazolethione) indicated that the HSAB[3] nature of the donor atom can lead to structural differences in complexes with the same acceptor. Such an observation is seen in comparing the structures of $AsCl_3dmit$[2] and $AsCl_3NMe_3$.[4] In the case of $AsCl_3NMe_3$, the structure is a pseudo trigonal bipyramid (tbp) with the amine occupying an apical position trans to a chlorine. The structure of $AsCl_3dmit$ on the other hand is best described as a dimer consisting of two square-pyramidal $AsCl_4dmit$ units sharing a common edge through long bridging chlorine atoms and the sulfur atoms occupying the apices of the two pyramids on opposite sides of the plane formed by the six chlorines. Recently another X-ray structure reported a similar configuration for dibromo(diethyldithiocarbamato)arsenic(III)[5] (see Figure 1). Vibrational data collected for other thiourea type adducts with arsenic trihalides and arylarsenic dihalides were interpreted on the basis of a pseudo-tbp with a linear X–As–X group and the donor in an equatorial position. The crystal structure of $AsCl_3dmit$[6] bore out this prediction but showed that long bridging chlorine bonds connected these tbp units into a loose dimer pair to give the complete bonding picture described above. No evidence of bridging was seen in the solid-state spectra of $AsCl_3dmit$.[2]

This therefore led to the questions of bonding in other complexes of group 5A trihalides and thioureas and the types

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Table I. Physical Properties, Synthesis Summary, and Analytical Data

	% yield[a]	solvent		mp[b]	appearance[c]	% C		% H		% N		% M	
		prep	recryst			calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
AsI_3dmit	20	$CHCl_3$	CH_3CN	170–172	tan pw	10.28	10.47	1.38	1.42	4.80	4.72	12.83	12.75 (As)
$SbCl_3$dmit	100	CH_2Cl_2	CH_3CN	157–158	ye cr	16.84	17.04	2.26	2.36	7.86	8.00	29.86	30.09 (Cl)
$SbBr_3$dmit	100	CH_2Cl_2	CH_3CN	208–209	ye cr	12.26	12.39	1.65	1.71	5.72	5.75	24.86	24.68 (Sb)
SbI_3dmit	98	C_6H_6	CH_3NO_2	211–212	amb cr	9.52	9.51	1.28	1.30	4.44	4.48	19.30	19.11 (Sb)
$BiCl_3(dmit)_2$	75	acetone	CH_3NO_2	249–251	og pw	21.00	21.26	2.82	2.87	9.80	9.24	36.55	36.56 (Bi)
$BiBr_3$dmit	90	acetone	CH_3NO_2	234–235	dk og pw	10.41	10.03	1.40	1.46	4.85	4.66	36.22	35.16 (Bi)
$BiI_3(dmit)_3$	10	methanol	CH_3CN	236–238	rd pw	18.49	18.21	2.48	2.40	8.62	8.53	21.45	20.94 (Bi)

[a] Unrecrystallized product [b] °C uncorrected [c] Key: ye = yellow; og = orange; amb = amber; rd = red; cr = crystals; pw = powder; dk = dark.

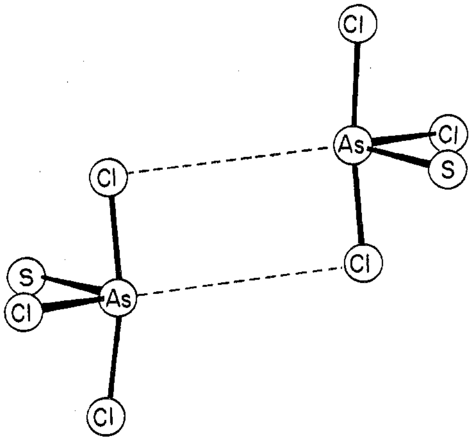

Figure 1. Structure of $AsCl_3$dmit showing two pseudo-tbp units linked into a loose dimer pair.[2]

of structural changes brought on by using soft donors. To further probe this relationship between molecular structure and HSAB character, we prepared a series of adducts of the general form $MX_3(dmit)_n$ where M = As, Sb, or Bi, X = Cl, Br, or I, and n = 1, 2, or 3. These complexes are in addition to the already reported adducts $AsCl_3$dmit and $AsBr_3$dmit. This communication reports the synthesis and physical characterization of these complexes and presents solid-state vibrational data collected for $SbCl_3$dmit and $SbBr_3$dmit for purposes of comparison to the general features of spectra collected for $AsCl_3$dmit and $AsBr_3$dmit.[2]

Experimental Section

Due to the hygroscopic nature of some of the starting materials involved, all preparations were carried out in polyethylene glovebags under a dry nitrogen atmosphere. Recrystallization and general handling of the adducts were done under normal atmospheric conditions.

Spectra. Infrared and Raman spectra were obtained as previously reported.[7]

Chemicals. Antimony trichloride (Mallinckrodt), antimony tribromide (Ventron), bismuth trichloride (MCB), bismuth tribromide (Apache), and bismuth triiodide (Apache) were all used as obtained without further purification. Arsenic triiodide,[8] antimony triiodide,[9] and dmit[10] were prepared as outlined in the literature. Purification of solvents used in preparation and recrystallization was carried out as previously reported.[2]

Analytical Data. Carbon, hydrogen, nitrogen, halogen, and metal analyses were obtained from Galbraith Laboratories, Inc.

Adduct Synthesis. Adducts were prepared by combining solutions of donor and acceptor in 1:1 molar ratios. Table I lists solvents used for synthesis and recrystallization and gives the crude percent yield for each adduct prepared. Below is a typical procedure.

Trichloro[1,3-dimethyl-2(3*H*)-inidazolethione]antimony(III). Antimony trichloride (2.28 g, 10.0 mmol) was dissolved in 25 mL of CH_2Cl_2. To this was added a solution of dmit (1.28 g, 10.0 mmol) in 25 mL of CH_2Cl_2. The resultant precipitate was filtered and dried in vacuo. Recrystallization in CH_3CN yielded yellow crystals melting at 157–158 °C.

A 1:1 adduct of $BiCl_3$ and dmit was never obtained, but a 1:2 adduct was isolated. Likewise, $BiI_3(dmit)_3$ was obtained instead of a 1:1 complex.

Results and Discussion

Table I lists the compounds prepared along with melting points, physical appearance, analytical data, and synthetic information mentioned above. In general, these solids are thermally stable and unlike their arsenic analogues are quite stable to atmospheric moisture. The solids are somewhat soluble in polar solvents like CH_3CN, CH_3NO_2, and *N,N*-dimethylformamide and are insoluble in nonpolar solvents. All of the solids were generally sparingly soluble in a wide range of solvents thus hampering our ability to obtain any solution data.

While attempts to synthesize $BiCl_3$dmit and BiI_3dmit failed, we were able to isolate $BiCl_3(dmit)_2$ and $BiI_3(dmit)_3$ as mentioned earlier. The X-ray structures of both these compounds are presently being undertaken. It will be interesting to compare the structure of $BiCl_3(dmit)_2$ to the recently reported structure of $BiCl_3(etu)_2$ (etu = ethylenethiourea) which is a polymeric zigzag chain of $BiCl_4(etu)_2$ octahedral units sharing cis chlorine vertices.[11] Preliminary information on $BiCl_3(dmit)_2$ indicates that the complex is a discrete dimer.[12] The structure of $BiI_3(dmit)_3$ will be compared to that reported for $BiCl_3(tu)_3$ (tu = thiourea) which contains $[Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]^{3/2-}$ anions and $Bi(tu)_6^{3+}$ cations.[13] To date, we have no preliminary structural information on $BiI_3(dmit)_3$ except for space group and cell dimensions.

We note the synthesis and physical properties of AsI_3dmit, SbI_3dmit and $BiBr_3$dmit in passing since the structures of these complexes were not further investigated. Previous attempts to synthesize AsI_3dmit failed to yield an analytically pure sample of this adduct.[2] The synthetic procedure for AsI_3dmit was altered from the previous attempt which included $CHCl_3$ as the reaction solvent for dmit and CS_2 as the solvent for AsI_3. The two solutions were then mixed and treated as described previously.[2] In the successful synthesis, $CHCl_3$ was used exclusively for both donor and acceptor, and the resultant precipitate was collected at room temperature instead of after cooling to −20 °C as noted in the previous procedure.[2] Presumably this prevents coprecipitation of the sparingly soluble AsI_3 along with AsI_3dmit thus leading to analytically impure samples characterized by C, H, and N results much lower than expected. This also reduces the yield since AsI_3dmit is somewhat soluble in $CHCl_3$.

Solid-State Spectra. Table II lists Raman and infrared (IR) frequencies obtained in the 500–50-cm^{-1} region for $SbCl_3$dmit and $SbBr_3$dmit. These data were considered with regard to the two pseudo-tbp isomeric possibilities described earlier for $AsCl_3NMe_3$ and $AsCl_3$dmit. The distinguishing feature between these two possibilities is the linear X–M–X group which has been shown to display characteristic frequencies and intensities in the solid-state spectra of several main group compounds known to have a linear X–M–X moiety.[2,7,14–17] Generally two bands corresponding to ν_{sym}(X–M–X) and

Table II.[19] Solid-State Vibrational Spectra of $SbCl_3$dmit and $SbBr_3$dmit (cm^{-1})

$SbCl_3$dmit		$SbBr_3$dmit		
Raman[a]	IR	Raman[a]	IR	assignments
117 m				dmit
135 m		135 m		dmit
			172 m, sh	dmit
177 m, br				
		180 m		
		190 m, sh	188 s	ν(Sb–Br)
			202 m, sh	ν(Sb–Br)
		209 ms		
243 s				
				ν(Sb–S)[b]
			245 s	
		249 s		
258 ms				ν_{sym}(Cl–Sb–Cl)[b]
293 w, sh	292 s			ν_{asym}(Cl–Sb–Cl)
306 m, sh	305 m, sh		300 w	dmit[b]
310 s		310 w		ν(Sb–Cl_{eq})[b]
	322 w		320 w	dmit
		342 s		
		347 s		
	350 m			dmit
358 vs				
	400 m		400 m	dmit
	460 s		462 s	dmit
500 m		503 m		dmit
	530 m			

[a] 5145 Å. [b] See text for exact assignments.

ν_{asym}(X–M–X) are observed with ν_{sym} at lower wavenumbers that ν_{asym}. Furthermore, in the case of pseudo-tbp MX_3L (L = ligand) complexes with a linear X–M–X group, a band corresponding to an equatorial M–X stretch should be observed at higher frequencies. On the basis of reported literature examples, the general ranges of ν_{sym} and ν_{asym} should be around 250 to 280 cm^{-1} for Cl–Sb–Cl[14,15] and 170 to 220 cm^{-1} for Br–Sb–Br.[14]

As Table II shows, the Raman and IR spectra for $SbCl_3$(dmit) are interpretable on the basis of a molecular geometry with a linear Cl–Sb–Cl moiety and the remaining chlorine and ligand occupying the equatorial sites of a pseudo-tbp. On the basis of observed frequencies and relative intensities, we assign the Raman peak at 258 cm^{-1} as ν_{sym}(Cl–Sb–Cl) and the IR peak at 292 cm^{-1} as ν_{asym}(Cl–Sb–Cl). The equatorial Sb–Cl stretch is assigned to the strong Raman peak at 310 cm^{-1} since the relative intensity of this peak is clearly out of line with the intensities of dmit peaks noted in the 300–310 cm^{-1} region for $AsCl_3$dmit (308 (w)),[2,19] $AsBr_3$dmit (303 (w)),[2] and $SbBr_3$dmit (310 (w), Table II). Also for this reason, the corresponding dmit peak for $SbCl_3$dmit is assigned to the medium shoulder in the Raman at 306 cm^{-1} (305 cm^{-1} IR).

The remaining strong band in the Raman of $SbCl_3$dmit at 243 cm^{-1} is best assigned to the Sb–S stretch. The corresponding peaks in the IR and Raman of $SbBr_3$(dmit) are seen at 245 and 249 cm^{-1}, respectively. This band, however, is inexplicably absent for the IR of $SbCl_3$dmit. It is interesting to note that the As–S stretches in the AsX_3L and $RAsX_2L$ adducts (L = dmit, tetramethylthiourea) previously reported[2] were generally weak bands. In contrast, Javora et al.[18] reported very strong As–S peaks in the Raman spectra of $[Me_2As(tu)]^+X^-\cdot$tu (tu = thiourea; X = Cl, Br). Thus it appears that the relative intensities of the M–S stretches are quite variable for these complexes.

It should be pointed out that the pseudo-tbp description of $SbCl_3$dmit as evidenced by the solid-state spectra discussed above is only a first approximation of structure. As in the case of $AsCl_3$dmit, it is quite possible that close intermolecular contacts may result in some type of bridged structure. A single-crystal X-ray investigation is presently underway to explore this possibility.

The vibrational data for $SbBr_3$dmit cannot be rationalized by a structure similar to that of $SbCl_3$dmit, nor does the other pseudo-tbp description discussed earlier fit the observed spectra. Peaks which cannot be assigned as dmit modes and furthermore have the characteristic appearance of metal–halide peaks are seen in the Raman region at 190 and 209 cm^{-1}. Corresponding peaks are noted in the IR region at 188 and 202 cm^{-1}. The 188-cm^{-1} peak is clearly an asymmetric mode on the basis of relative intensities while the 209-cm^{-1} Raman peak is suggestive of a symmetric mode. This is obviously not in accord with the expected pattern of $\nu_{asym} > \nu_{sym}$ observed for molecules with a linear X–M–X group. Due to lack of structural information on complexes with soft donors, it is evident that no straightforward prediction of structure for $SbBr_3$dmit can be made based solely on the vibrational data. Further structural investigations will be undertaken for this complex. Thus we simply note those peaks in Table II which are apparently Sb–Br modes.

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Registry No. AsI_3dmit, 70198-08-2; $SbCl_3$dmit, 70198-09-3; $SbBr_3$dmit, 70198-10-6; SbI_3dmit, 70198-11-7; $BiCl_3(dmit)_2$, 70198-12-8; $BiBr_3$dmit, 70198-13-9; $BiI_3(dmit)_3$, 70198-14-0; $SbCl_3$, 10025-91-9; $SbBr_3$, 7789-61-9; $BiCl_3$, 7787-60-2; $BiBr_3$, 7787-58-8; BiI_3, 7787-64-6; AsI_3, 7784-45-4; SbI_3, 7790-44-5.

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