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Infrared and Raman Spectral Studies of γ-Butyrolactam Complexes of Antimony(III), Bismuth(III), and Mercury(II) Halides

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Complexes $SbCl_3(BuL)_2$, $SbBr_3(BuL)_2$, $BiCl_2(BuL)_{2.5}$, and $HgCl_2(BuL)$ (BuL = γ-butyrolactam) have been prepared and investigated spectroscopically. Infrared and Raman assignments for the solids are discussed, with special emphasis on metal-ligand vibrations. All BuL molecules are shown to be coordinated through oxygen, as indicated by the internal ligand frequency shifts. Structure considerations are presented for the solid-state species.

Introduction

The ability of γ-butyrolactam (BuL) to form stable complexes with transition and nontransition metals has been investigated extensively by Madan *et al.*[1(a-h)]

As a continuation of our work with amides, $SbCl_3(BuL)_2$, $SbBr_3(BuL)_2$, $BiCl_3(BuL)_{2.5}$, and $HgCl_2(BuL)$ have been prepared, and their infrared and Raman spectra are reported. The infrared data show that coordination is through oxygen in all cases. Furthermore these new complexes offer an excellent opportunity to (1) distinguish between metal-BuL and metal-halide vibrational frequencies, and (2) draw some structural conclusions from spectral evidence.

Experimental Section

Materials. The BuL was reagent grade and was obtained from Aldrich Chemical Company. All other materials were at least reagent grade.

Analytical. All carbon, hydrogen, and nitrogen analyses were done by Strauss Microanalytical Laboratory, Oxford, England.

Preparation of Complexes. The complexes were prepared and subsequently handled in a dry-nitrogen atmosphere. In general, the complexes were crystallized from a methanolic solution of the appropriate metal halide, to which BuL had been added in the following mole ratios (BuL: metal): Sb^{III} complexes, 5:1; $BiCl_3(BuL)_{2.5}$, 7:1; $HgCl_2(BuL)$, 2:1. In all cases, the crystals were washed with ether and dried *in vacuo* at room temperature. The BuL complexes were obtained in approximately 75 percent yield and were non-hygroscopic.

Physical Measurements. A Perkin-Elmer Model-521 recording spectrophotometer was used to measure infrared spectra (5000-250 cm^{-1}) with Nujol mulls between CrBr windows. The intrumen was purged with dry nitrogen and calibrated with polystyrene. Frequencies were considered accurate to ± 2.0 cm^{-1}. Raman spectra (<1700 cm^{-1}) of all solid samples were recorded using a Jarrell-Ash 25-300 argon laser Raman spectrometer with a 4880 Å excitation line. The conductance measurements were performed with an Industrial Instruments Model RC-18 bridge, using a conventional cell calibrated with an aqueous KCl solution. All measurements were conducted at 25.0° in nitrobenzene. The cell constant, K, was found to be 0.3150 cm^{-1}. X-ray diffraction patterns were obtained by the use of a General Electric XRD-5 unit and a direct recording diffractometer. The K_α X-ray line from a nickel-filtered copper target (1.54 Å) was employed. The compounds were ground in a mortar and packed into a sample holder. The relative intensities were estimated according to relative peak height. Molecular weight measurements were obtained with a Hewlett-Packard Model 301A vapor pressure osmometer, with a nonaqueous probe at 37.0° in nitrobenzene. The instrument was calibrated with standard benzil solutions in nitrobenzene.

Results

The analytical data, melting points and molar conductances are summarized in Table I. The infrared frequency shift for BuL after coordination are listed in Table II, and the infrared and Raman data of BuL complexes are shown in Table III. The low-frequency infrared and Raman spectra are shown in Figures 1 and 2.

The X-ray powder diffraction studies indicate that crystals of all four samples are not isomoprhous.

Among the four complexes, only $SbCl_3(BuL)_2$ and

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Table I. Analytical data, melting points and molar conductance.

Compound	Calculated %C	Calculated %H	Calculated %N	Found %C	Found %H	Found %N	Melting Point (°C)	Molar conductance* λ_M (Ω^{-1} cm^2 mole^{-1})
SbCl$_3$(BuL)$_2$	24.10	3.51	7.02	24.15	3.69	7.02	145-147°	3.8
SbBr$_3$(BuL)$_2$	18.00	2.63	5.26	18.95	2.75	5.77	69-70°	0.7
BiCl$_3$(BuL)$_{2.5}$	22.71	3.31	6.62	22.84	3.24	6.76	119-120.5°	6.5
HgCl(BuL)	13.46	1.96	3.92	13.67	2.24	3.80	128.5-129.5°	0.1

* Concentration in nitrobenzene at 25.0° ~2×10^{-3} *M*. Under similar conditions, 1:1 electrolytes normally exhibit λ_M ~20-30 Ω^{-1} cm^2 mole^{-1}.

Table II. Infrared Data for BuL Complexes.

Compound	ν_{CO}	$\Delta\nu_{CO}$	ν_{CN}	$\Delta\nu_{CN}$	δ_{CO}	γ_{CO}	$\Delta\gamma_{CO}$
BuL	1688	—	1280	—	806	472	—
SbCl$_3$(BuL)$_2$	1630	—58	1290	+10	—*	450	—22
SbBr$_3$(BuL)$_2$	1630	—58	1285	+5	—*	440	—28
BiCl$_3$(BuL)$_{2.5}$	1634	—54	1290	+10	—*	451	—21
HgCl$_2$(BuL)	1655	—33	1285	+5	—*	470	—2

* These bands may be masked by N-H (γ) out-of-plane bending vibrations.

Table III. Vibration frequencies (cm^{-1}) for BuL and its complexes [a]

BuL		SbCl$_3$(BuL)$_2$		SbBr$_3$(BuL)$_2$		BiCl$_3$(BuL)$_{3.5}$		HgCl$_2$(BuL)		
IR	Raman	IR	Raman	IR	Raman	IR	Raman		Raman	Band Assignments [b]
1690 vs	1660 w	1630 vs	1625 mw	1630 vs	1630 mw	1634 vs	1630 vw	1655 vs	1645 w	ν(C=O)
1490 mw		1490 mw	1494 mw	1480 sh	1470 sh	1480 mw		1460 ms	1462 mw	CH$_2$ rocking
1460 mw		1460 mw	1465 ms	1455 s	1450 s	1455 mw	1448 w			
			1445 s							
1369 mw	1370 vw									ν(N-H)
1280 s		1290 s	1300 mw	1275 s	1275 w	1290 s		1285 s	1272 vw	ν(C-N)
1225 w	1230 mb	1230 sh,w	1230 mw		1230 ms			1215 w	1223 mw	CH$_2$ rocking
1164 w	1190 vw	1163 w		1165 vw	1170 vw			1160 w		
1064 s	1070 vw	1065 mw	1060 mw	1070 mw	1080 mw	1065 mw	1060 w	1063 mw	1065 vw	Ring mode
					1060 mw					
992 s	993 wb	1000 mw	1000 ms	1000 vw	990 ms	994 mw		990 mw	998 ms	CH$_2$ rocking
917 w	920 mw	885 mw	894 mw	885 mw	895 s	887 mw	895 w	885 w	894 s	Ring mode
885 w	895 vs									
806 mw	810 wb									δ(C=O)
740 m		765 ms		760 mw		765 ms		750 s		γ(N—H)
684 mw	688 w	695 mw	693 w	684 w	690 mw	693 mw	680 vw	690 s	695 s	Ring mode
625 w	630 w	629 mw	632 w	630 w	629 mb	630 mw	622 mw	625 ms	630 vw	
534 w										
		492 s	492 w	487 s	685 vw	495 sh	490 vw		490 mw	ν sym (M—O)
		480 mw	485 mw	480 mw	482 vw	490 s	483 vw	497 s		ν asym (M—O)
472 s	478 w		420 vw	450 m	432 vw	450 m	450 mb	470 m		γ(C—O)
		330 mw	324 vs		284 ms	285 ms	285 s	350 s		ν sym (M—X)
		309 mw	300 mw		205 vs					ν asym (M—X)
		290 s	293 vs		155 s		210 vs	300 w	298 vs	
							196 sh			
			228 w		124 mw		80 mw		170 w	deformation + lattice modes
			164 w		100 ms				78 s	
			130 w							
			95 w							
			91 w							
			70 s							

[a] Infrared spectra for solids as Nujol mulls, Raman spectra for crystalline powders. s, strong; w, weak; v, very; sh, shoulder; b, broad; m, medium. [b] ν, stretching vibration; δ, in-plane bending vibrations; γ, out-of-plane bending vibration.

HgCl$_2$(BuL) are sufficiently soluble in nitrobenzene for the molecular weight to be measured cryscopically. (334 found vs 398 calc. for monomeric SbCl$_3$(BuL)$_2$; 344 found vs 356 for monomeric HgCl$_2$(BuL).

Discussion

The conductances and molecular weight data, together with spectral evidence show that all BuL molecules are coordinated to the metal, and the oxygen atom in BuL is the donor. Since in nitrobenzene solution, there is dissociation of complexes, structural spectroscopic studies should be most meaningful if carried out using the solid complexes.

Infrared and Raman spectra were examined for the solid Nujol mulls and crystalline powders, respectively, for each compound. The absence of infrared absorption over the range 3000-4000 cm^{-1} served to rule out the absence of a water or hydroxyl group.

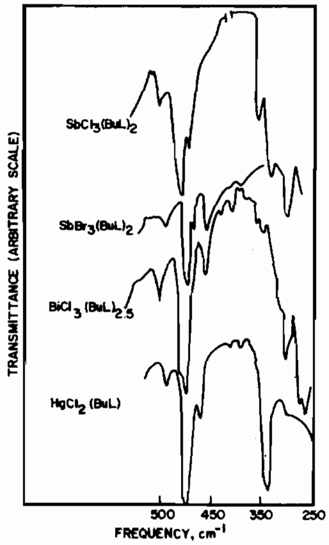

Figure 1. .Low-frequency Infrared Spectra of Solid Complexes $SbCl_3(BuL)_2$, $SbBr_3(BuL)_2$, $BiCl_3(BuL)_{2.5}$, and $HgCl_2$-(BuL) in Nujol mulls.

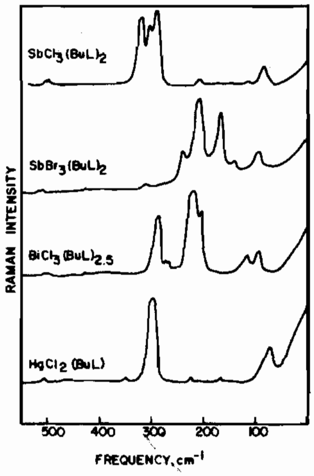

Figure 2. Low-frequency Raman Spectra of Solid Complexes $SbCl_3(BuL)_2$, $SbBr_3(BuL)_2$, $BiCl_3(BuL)_{2.5}$, and $HgCl_2(BuL)$ as crystalline powders.

Internal Ligand Frequencies

In the infrared and Raman spectra of uncoordinated BuL, the band at 1688 cm^{-1} represents the C–O stretching vibration. The direction of frequency shift of this band upon complexation can be used to distinguish between oxygen-bound and nitrogen-bound BuL; a decrease in frequency accompanies oxygen coordination, whereas nitrogen bonding should lead to a frequency increase. The intensity and frequency of the C–O out-of-plane and in-plane bending vibration should also decrease after coordination, if this occurs through oxygen. The band at 806 cm^{-1} was assigned to C–O in-plane bending vibration[2,3,4] for the uncoordinated BuL. After coordination, this band shifts to a lower frequency and the intensity also decreases as expected. The band at 472 cm^{-1} was assigned to C–O out-of-plane bending vibrations[3,4] in the free ligand. After cordoination, this band is also shifted to a lower frequency, as shown in Table II, and its intensity decreases. This has been reported for other systems.[1d,5,6]

The band at 1280 cm^{-1} represents the C–N stretching vibration in the uncoordinated BuL. After coordination, this band does show a slight shift to higher frequency, as shown in Table II.

The γ(N–H) out-of-plane bending vibration (740 cm^{-1}) was also shifted to frequency higher than that of the free ligand. So, judging from the internal frequency for the ligand (BuL), we conclude that the carbonyl oxygen is the donor atom.

Metal-Ligand Frequencies and Solid-State Structures

Low-frequency infrared (250-600 cm^{-1}) and Raman (less than 500 cm^{-1}) spectra of the complexes are shown in Figures 1 and 2. The bands near 480 cm^{-1} are described to vibrational modes involving predominately M–O stretching. Similar assignments have been made for some related species.[7]

Intense Raman bands located within the range 160-320 cm^{-1} can be assigned to M–X stretching vibrations. Lower-frequency Raman bands may be due to deformation and lattice vibrations. The assignment of M–X stretching vibrations and some conclusions as to the likely structure for each compound will now be discussed in some detail.

$SbCl_3(BuL)_2$. The intense Raman peak of $SbCl_3$-BuL)$_2$ at 324 cm^{-1}, which is assigned to the symmetric Sb–Cl stretching mode, is somewhat higher in frequency than the strong 290 cm^{-1} and 301 cm^{-1} bands, which are similarly assigned for five-coordinated $SbCl_5^{2-}$ [8] and $SbCl_3(DMSO)_2$, respectively.[7] All these bands fall between the symmetric Sb–Cl stretching frequencies of the supposedly three-coordinated $SbCl_3$ (345 cm^{-1})[9] and of the six-coordinated $SbCl_6^{3-}$ (267 cm^{-1}).[10] The two bands at 300 and 293 cm^{-1} are assigned to the antisymmetric Sb–Cl stretching mode. It should be noted that for this compound the symmetric and antisymmetric Sb–Cl sretching vibrations are both infrared and Raman active.

Judging from the X-ray structures of $SbCl_3 . 2(C_6H_5)_3AsO$[11] and $SbCl_5^{2-}$,[8] it appears that five-coordinated species containing Sb^{III} and chloride most often have a distorted square pyramidal configuration with

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a stereochemically active electron pair occupying a sixth position.

In the arsine oxide adduct, the oxygen atoms are in *cis* positions at the base of the pyramid and the Sb—Cl bond opposite the electron pair is shorter than the two Sb—Cl bonds in the base. A recent article[7] also suggests this kind of structure for $SbCl_3(DMSO)_2$ complex on the basis of spectral evidence. The vibrational spectra described herein are consistent with a similar structure for $SbCl_3(BuL)_2$. Finally it should be noted that the symmetric and antisymmetric Sb—O stretching modes are both infrared and Raman active, as expected for a bent $Sb–O_2$ sub-unit.

$SbBr_3(BuL)_2$. For this complex, the Raman band at 234 cm^{-1}, which is assigned to the symmetric Sb—Br stretching mode, occurs at a frequency lower than the analogous band in $SbBr_3$ (at 243 cm^{-1}), as expected. The two bands at 205 and 155 cm^{-1} can be thought to result from the removal of the degeneracy of the antisymmetric stretching vibration in pyramidal $SbBr_3$, owing to complexation. For this complex, the possibility of trigonal bipyramidal structure is ruled out, because (1) three M–X vibrations appear in the Raman spectra, and (2) both the symmetric and the antisymmetric M—O vibration are IR active. So it seems that $SbBr_3(BuL)_2$ also has an octahedral structure with *cis* BuL groups because the symmetric and antisymmetric M—O vibrations are both IR active, whereas for *trans* configuration the symmetric M—O vibration should be only IR active. The sixth position would then be occupied by a non-bonding electron pair, just as in the $SbCl_3(BuL)_2$ system. Since X-ray diffraction shows that these two complexes are not is imorphous, it is reasonable to assume that $SbBr_3(BuL)_2$ has a more distorted octahedral structure due to the larger bromide ligand.

$BiCl_3(BuL)_{2.5}$. Since it is established that six-coordinated halide complexes of Bi^{III} are octahedral, it is logical to assume that the compound $BiCl_3(BuL)_{2.5}$ will possess a pseudo-octahedral symmetry. In solid state, $BiCl_3(BuL)_{2.5}$ must exist as a dimer with one BuL acting as a bridging group connecting two $BiCl_3(BuL)_{2.5}$ units.

The arrangement of the chloride ligands in the octahedral unit may be either *cis* or *trans*. Selection rules for the stretching modes are as follows: for *cis* chloride configuration, 2 Bi–O and 2 Bi–X,[7] all infrared and Raman active; for *trans* chloride configuration, 3 Bi–O and 3 Bi–X, all infrared and Raman active.

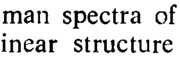
The Raman band at 285 cm^{-1} for $BiCl_3(BuL)_{2.5}$ is assigned to the symmetric Bi—Cl stretching vibration. This frequency agrees quite closely with that for the $BiCl_3(DMSO)_2$ system (273 cm^{-1}), but is a little lower than that for $BiCl_3$ (288 cm^{-1}), and considerably higher than that for $BiCl_6^{3-}$ (258 cm^{-1}),[10,13,14] as expected.

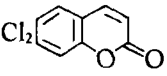
The bands at 210 and 196 cm^{-1} for the bismuth complex can be considered to arise from the removal of the degeneracy of the antisymmetric stretching mode of pyramidal $BiCl_3$ (242 cm^{-1}).[15]

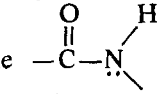
While the Raman spectrum of $BiCl_3$ reveals three Bi-X stretching bands, as mentioned above, the 250 cm^{-1} infrared spectrophotometer cutoff allows observation of only the highest Bi-Cl band for $BiCl_3(BuL)_{2.5}$. Largely because of the Raman evidence, it may be assumed that the *trans* symmetry is the more likely. The Bi-O-Bi bending mode has been assigned in the literature. In the Raman and infrared spectra for this complex, however, there are two bands ($\sim$250 cm^{-1}), which are absent in all other three systems in this study. Therefore, these bands may be due to Bi—O—Bi bending modes.

$HgCl_2(BuL)$. In the $HgCl_2(BuL)$ system, the intense infrared band at 350 cm^{-1}, which is assigned to the asymmetric Hg—Cl stretching mode, is about 18 cm^{-1} lower than in $HgCl_2$ (368 cm^{-1}), as expected.

The intense Raman band at 298 cm^{-1} as assigned to the symmetric Hg—Cl stretching mode. Selection rules for the stretching mode in a linear MX_2 molecules are as follows: (1) antisymmetric M–X stretching is only infrared active, and (2) symmetric M–X stretching is only Raman active.

The crystal structure of $HgCl_2$  has been determined.[11] The geometry of the linear molecule is unchanged and the Hg–Cl bond length is 2.33 Å. The donor oxygen atom of the C=O bond is added perpendicular to the linear $HgCl_2$ molecule. Three chlorine atoms in neighboring $HgCl_2$ molecules complete the distorted octahedron around the mercury atom, at a distance much greater than 2.33 Å.

So from the infrared and Raman spectra of $HgCl_2(BuL)$, we conclude that the linear structure of the $HgCl_2$ moiety in the $HgCl_2(BuL)$ complex is unchanged. It is not unreasonable to assume that the $HgCl_2(BuL)$ complex will have the same geometric arrangement as does the $HgCl_2$  system.

Another point of interest is that usually $HgCl_2$ forms more stable compounds with a N or S donor[16] than with oxygen, but in $HgCl_2(BuL)$, the coordination is through the carbonyl oxygen, and not through the available nitrogen of the >NH group. This may be due to steric factors because the  $-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\cdot\cdot}{N}\genfrac{}{}{0pt}{}{/^{H}}{\backslash}$ group in the BuL molecule is in a plane and has a *cis* configuration.[3]

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