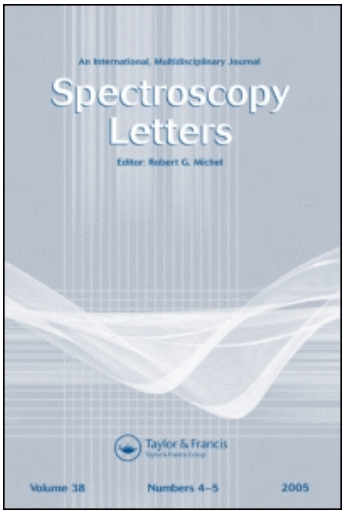

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Infrared Spectra of Metal (II) Complexes of 1, 3, 4-Thiadiazole-2, 5-Dithiol, 5-Amino-L, 2, 4-Dithiazol-3-Thione and Their Acetyl Derivatives

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INFRARED SPECTRA OF METAL (II) COMPLEXES OF 1,3,4-THIADIAZOLE-2,5-DITHIOL, 5-AMINO-1,2,4-DITHIAZOL-3-THIONE AND THEIR ACETYL DERIVATIVES

Key words: 1,3,4-thiadiazole-2,5-dithiol, 5-amino-1,2,4-dithiazol-3-thione, bismuthiol, xanthane, infrared band assignment, tautomerism, complex structure.

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ABSTRACT

An infrared spectral interpretation of the structure of fifteen solid complexes formed by Co(II), Cu(II), Cd(II), Hg(II), Pb(II) and Zn(II) with ligands 1,3,4-thiadiazole-2,5-dithiol (bismuthiol), 5-amino-1,2,4-dithiazolin-3-thione (xanthane) and the 2-acetyl-1,3,4-thiadiazol-5-thione and 5-acetylamide-1,2,4-dithiazol-3-thione derivatives is performed. The coexistence of different tautomers of bismuthiol and xanthane in the solid state is proposed. The bismuthiol-metal complexes display a unique and similar polymeric structure involving one tautomer. The xanthane-

metal complexation stabilizes the 1,1-dithiolate-type polymeric species; complexation with Cd, Co and Hg metal ions also stabilizes polymers involving the perthiocyanic tautomer.

INTRODUCTION

Ligands 1,3,4-thiadiazole-2,5-dithiol (bismuthiol) and 5-amino-1,2,4-dithiazol-3-thione (xanthane) are known to react with heavy metals to form polymers [1-3] which are not soluble in current solvents. This characteristic makes bismuthiol and xanthane good candidates for the treatment of polluted water. However, the physical nature of the polymers makes x-ray structural determination and the interpretation of the ^{13}C- and ^{15}N-NMR spectra very difficult. On the other hand, both bismuthiol and xanthane are normally present in solution in at least three and four tautomeric forms, respectively [4,5]. See Fig. 1. Thus, vibrational spectroscopy is an alternative to infer about the molecular structure. The aim of this paper is to give some insights about the structure of the bismuthiol (B) and xanthane (X) metal (II) complexes, by using infrared data. Bivalent metal ions here considered are Cd, Cu, Co, Hg, Pb and Zn. We have also included in this study the acetyl derivative in position 2 of bismuthiol (AB) and xanthane (AX) (see Fig.2) in order to investigate the effect that this substitution has on the molecular structure of the corresponding metal complexes.

EXPERIMENTAL

Synthesis

Analytical reagent bismuthiol (B) and metal salts were furnished by Aldrich. Xanthane (X) was synthesized following described procedures [3].

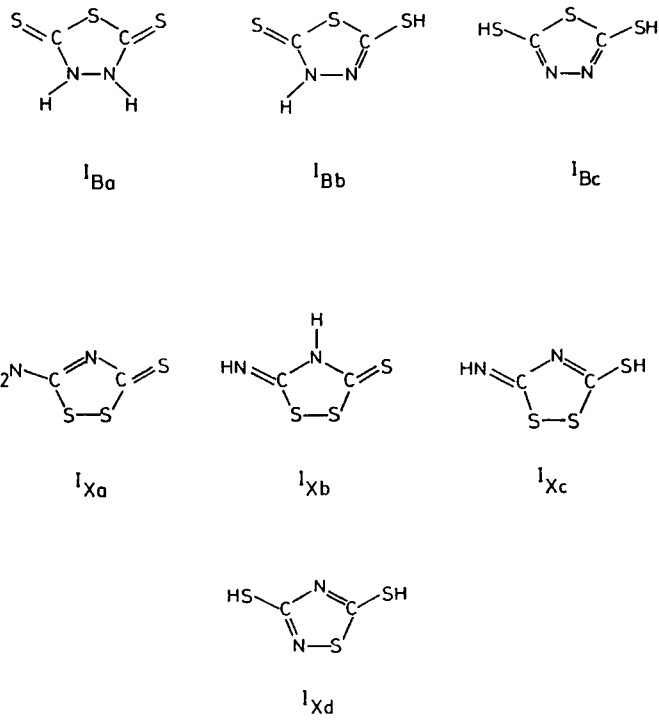


Fig.1. Tautomers of bismuthiol (I_B) and xanthane (I_X).

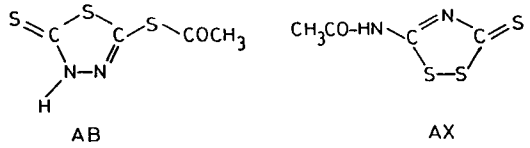


Fig.2. 2-acetyl-1,3,4-thiadiazol-5-thione (AB) and 5-acetylamide-1,2,4-dithiazol-3-thione (AX)

Metal complexation of B and X. Equal volumes of equimolar solutions of metal chlorides and ligands were mixed. Resulting materials are amorphous solids not soluble in common solvents or water.

2-aminoacetyl derivative of bismuthiol (AB). 1.5 g of B (0.01 mol) and 20 ml of diethylether were mixed. Then, 0.79 g (0.01 mol) of freshly destilled acetyl chloride were slowly added; the mixture was stirred and refluxed during 15 minutes and then cooled on ice. A beige material was obtained.

5-acetylamide-1,2,4-dithiazol-3-thione (AX). 1 g of X, 20 ml of acetic anhydride and 20 ml of glacial acetic acid were mixed. The reaction mixture was heated at 60ºC with stirring for two and half hour. Then, 10 ml of both acetic anhydride and acetic acid were added and the reaction was allowed to reflux for 30 minutes. The mixture was added to cold water and the yellow-orange precipitate was collected by filtration, washed with water and dried in a desiccator.

AB and AX metal complexes (ABM and AXM). Equal volumes of equimolar solutions of AB and AX and metal chloride were mixed. Amorphous solids not soluble in common solvents or water were obtained. Sulphur and S species were not detected during the metal complexation.

Before measurements ligands were recrystalized from ethanol; the metal complexes were washed with ethanol at 40 degrees Celsius and then washed with cold water.

Stoichiometry and colours of the BM, ABM and XM complexes is given in Table 1.

Vibrational measurements

FTIR spectra of anhydrous ligands and complexes were registered by using a Bruker IFS66V interferometer. KBr and polyethylene

TABLE 1.
Stoichiometry of the bismuthiol, acetyl-bismuthiol and xanthane metal complexes. L, ligands; M, metal ions.

L/M	Co	Cu	Cd	Hg	Pb	Zn
B	1/1	1/1	1/1	1/1	1/1	-
	Pink	Brown	Yellow	Yellow	Yellow	-
AB	1/1	1/1	1/1	1/1	1/1	-
	Pink	Brown	Yellow	Yellow	Yellow	-
X	-	1/1	1/1	1/1	1/1	1/1
	-	Brown	Green	Yellow	Yellow	White
AX	-	2/1	2/1	2/1	2/1	2/1

disks were used in the middle and far spectral regions, respectively.

Spectra of B, AB, X and AX in the regions 4000-400 cm^{-1} and 400-120 cm^{-1} are displayed in Figs. 3 and 4, respectively. Typical spectra of complexes BM, XM and AXM are shown in Figs. 5 and 6.

For the ligands routine FT-Raman spectra were obtained with a Perkin-Elmer series 2000 apparatus; no different frequencies were observed in comparison with the FT-IR spectra. Due to thermal defects it was not possible to obtain the Raman spectra of complexes.

RESULTS AND DISCUSION

Bands assignment. The spectral assignment of bands belonging to ligands and complexes is proposed on the basis of data reported for related systems [3-15], and in terms of characteristic group frequencies [16]. The molecular vibrations of the present molecules, will probably not be pure, with coupling to other modes of vibration generally being expected. Thus, when describing the vibration with various degrees of purity we mean that in assigning a band to a particular mode, we infer that the

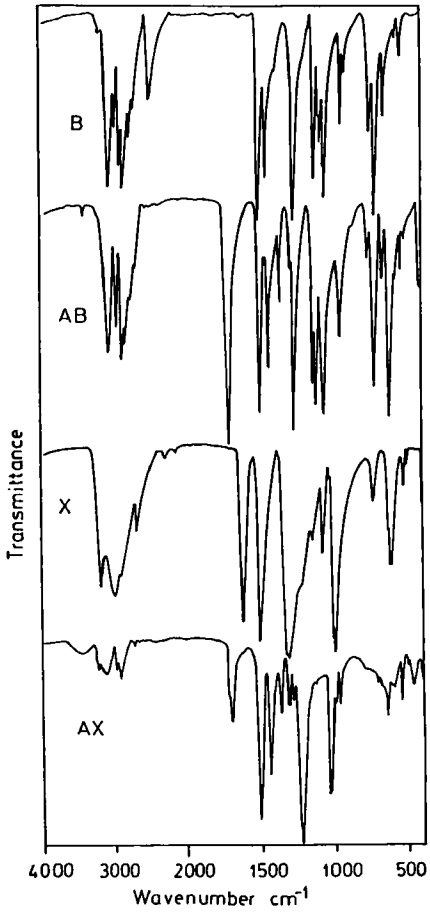


Fig.3. Infrared spectrum of bismuthiol (B), 2-acetyl-1,3,4-thiadiazol-5-thione (AB), xanthane (X) and 5-acetylamide-1,2,4-dithiazol-3-thione (AX) in the region 4000-400 cm^{-1}.

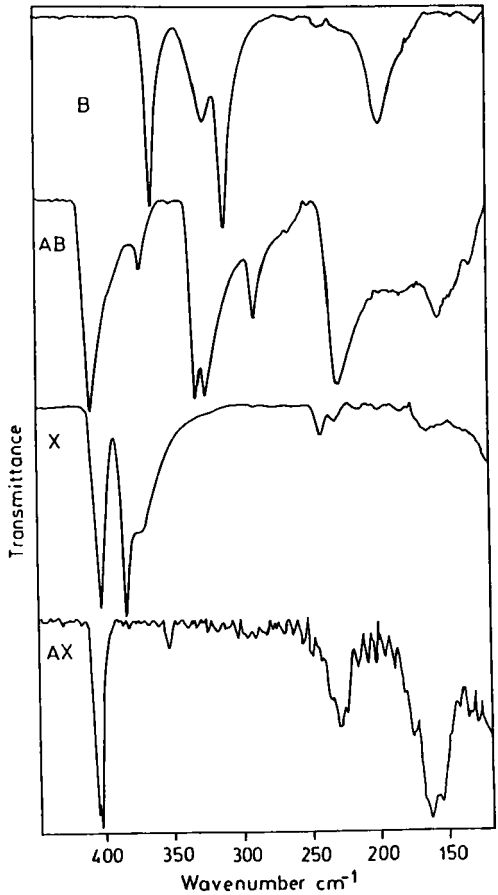


Fig.4. Infrared spectrum of bismuthiol (B), 2-acetyl-1,3,4-thiadiazol-5-thione (AB), xanthane (X) and 5-acetylamide-1,2,4-dithiazol-3-thione (AX) in the region 400-120 cm^{-1}.

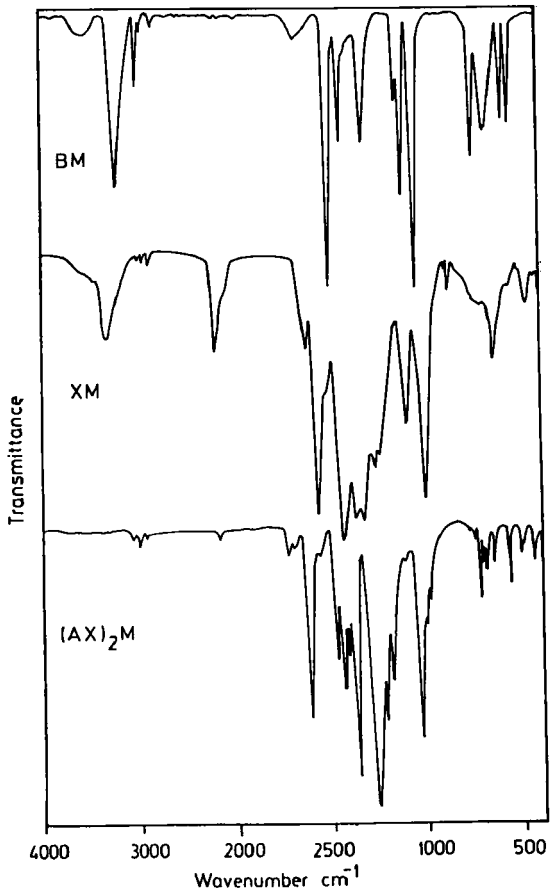


Fig.5. Typical infrared spectrum of metal complexes of bismuthiol BM ($B=I_{Bc}$, M=Zn), xanthane XM ($X=I_{Xd}$, M=Cd) and 5-acetylamide-1,2,4-dithiazol-3-thione $(AX)_2M$ (M=Hg) in the region 4000-400 cm^{-1}.

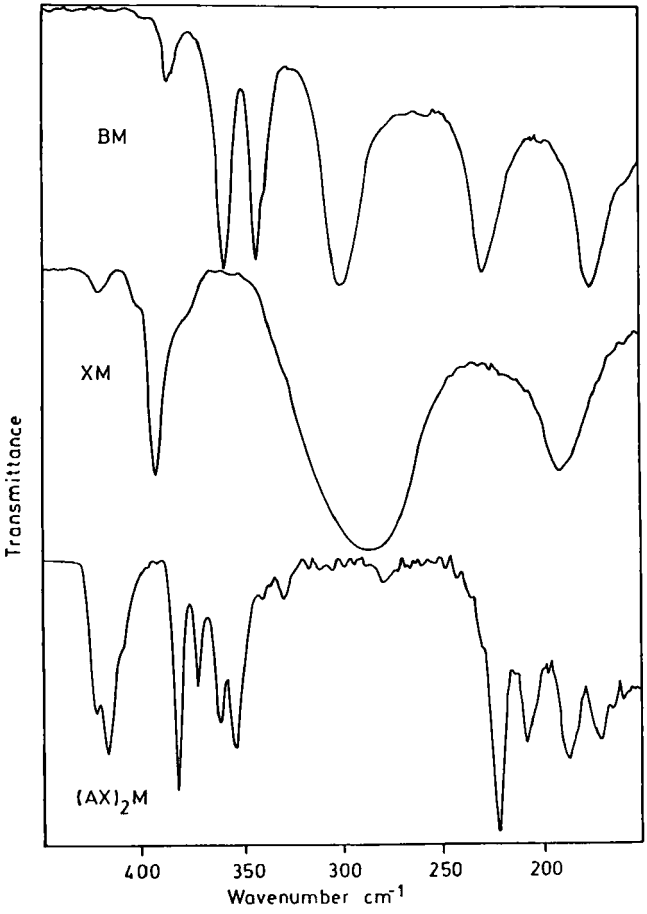


Fig.6. Typical infrared spectrum of metal complexes of bismuthiol BM ($B=I_{Bc}$, M=Zn), xanthane XM ($X=I_{Xd}$, M=Cd) and 5-acetylamide-1,2,4-dithiazol-3-thione $(AX)_2M$ (M=Hg) in the region 400-120 cm^{-1}.

Table 2. Infrared bands assignment of bismuthiol (B), 2-acetyl-1,3,4-thiadiazol-5-thione (AB) and bismuthiol metal complexes.

B	AB	CuB	ZnB	CdB	HgB	PbB	Assignment
		3453 bm	3516 bw	3500 bvw	3474 bw	3470 bw	νOH(H_2O)
2920 msm.		3155 bm	3154 ms	3177 m	3148 mb	3031 m	νNH
	2965 mm.	2918 vw	2836 wm	2930 wm			νNH +νCH
	2850 vw	2882 vw	2855 dvw	2873 m			+ overtones
2478 m							νSH
	1709 s						νCO
		1629 bw	1641 bw	1641 bvw	1630 wb	1630 wb	δOH(H_2O)
1505 s	1499 ms	1510 vw					
		1468 mst.	1480 s	1475 s	1467 ms	1465 ms	νCN
1452 ms	1437 m	1408 md	1412 m	1419 m	1411 dm	1384 ms	
	1353 m						δCH_3
	1289 sh		1301 m	1298 bm	1272 msb	1284 ms	ring
1265 s	1268 s	1259 wm.					δNH
1122 ms	1133 m	1121 dm	1124 ms	1117 m	1105 dms	1113 wm	νCN +νCH_3
1076 md	1106 msd	1105 ms	1099 m				ring
1050 msd	1060 msd	1045 sm.	1038 sd	1041 sd	1038 sd	1050 s	νC=S
941 m	954 bm						νCS exo-
918 w							-ring
751 mb	765 w					762 w	
715 s	720 msb	723 ms	735 m	731 m	718 msm.	721 ms	νCS ring
658 m	658 wm	659 vw	667 mb	638 mb		654 w	
	622 s						δCH_3
575 vw	585 vw	570 vw	582 m	577 w	580 w	587 w	δNCS
534 wd	536 w	536 wmd	544 m	544 wd	545 wd	544 w	δNCS
	500 vw						δCCO
	408 s						pCCO
371 ms	371 w	389 vw	385 w	381 m	385 msd	387 md	ring def.+νM-OH_2
		347 wd	357 s	352 s	353 s	370 m	νMS
336 wb	331 ms		342 msd	333 ms	330 mw	317 ms	ring def.
324 s	324 ms						ring def.
			300 sb	291 sb	267 s		νMS
				260 w	255 vwd	254 sh	ring def.
	289 m						acet. def.
220 m	229 ms		230 msb	206 mb	240 m	237 bms	δCSC
156 vw	156 m	177 vw	175 msb	162 wb	171 m	162 msb	ring def.?

Relative intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; m., multiple; d, double; t., triple; sh, shoulder (irrespective of their strength).

band originates mainly from that mode but understand that the vibrations are likely to contribute to the vibrational energy. The proposed assignment is given in Tables 2-4.

B and AB ligands.

Six bands between 3150 and 2650 cm^{-1} and the asymmetric broad absorption in the spectrum of ligand B at 1265 cm^{-1} are assigned

Table 3. Infrared bands assignment of xanthane (X) and xanthane metal complexes.

X	CuX	CdX	CoX	HgX	PbX	Assignment
3207 ms	3260 bw	3278 mb	3338 sb	3426 msb		νOH (H_2O) + νNH
3021 msb				3242 w		νNH
2697 w	2875 wd		2750 wd	2900 wd		νCH + νNH
	2185 m	2171 m	2250 wm.	2157 m	2156 ms	νCN
1629 s	1614 mb	1610 wm		1614 msb		NH_2 + δOH (H_2O)
	1555 m	1551 s	1554 sbd			
1516 s	1500 w	1500 vw		1502 w	1526 msb	
1450 sh		1421 s	1412 bsd	1414 wb		νCN + δNH
	1384 s	1360 s			1386 s	
1314 vsm.	1350 s	1313 s	1330 m	1343 sd	1341 s	
1230 sh	1238 w	1250 wd		1247 s		
1150 sh	1110 mb		1106 mw		1125 vw	δNH_2
1083 mw		1088 ms				ρNH_2
1016 s			1020 md		1038 m	νCS exo-
1003 s	992 mb	987 s		985 m		-ring +
960 sh					963 w	νCS ring
747 mb		750 wb				
		868 w	885 wd	843 w		νNS +
			679 ms		663 m	νCS ring
640						
627 mt.	617 m	632 m	619 dw	618 wm.	620 vvw	νCS + δNH
619						
534 w	523 sh	534 vw	520 bvw	536 vvw	534 vw	νSS
505 vw		502 vvw		505 vvw	512 vw	νSS
	457 bm	457 bm			457 vw	δCNC +
408 s		419 vw				νSS
390 s	386 wb	387 m	387 vw		388 wb	νMS+νM-OH_2
380 mw						+ ring def.
			325 wb	351 sb	340 wb	νMS
262 w		271 sb				νMS +
250 w			252 sb			τCCN +
			210 vw			ring def.

Relative intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; m., multiple; d, double; t., triple; sh, shoulder (irrespective of their strength).

to different NH stretching (νNH) and deformation (δNH) modes, respectively [15]; see Fig. 3 and Table 2. The asymmetric band at 2478 cm^{-1} is readily assigned to νSH [3,4], while the double band at 1050 cm^{-1} is characteristic of νC=S [14]. The broad and asymmetric absorptions at 1505 and 1452 cm^{-1} are due to νCN modes [3,4]. The double absorption with maxima at 941 and 918 cm^{-1}, and the broad bands at 751, 715 and 658 cm^{-1} are assigned to stretching vibrations of different CS single bonds [7,17-19]; the

Table 4. Infrared bands assignment of 5-acetylamide-1,2,4-dithiazol-3-thione (AX) and 5-acetylamide-1,2,4-dithiazol-3-thione metal complexes.

AX	$Cu(AX)_2$	$Cd(AX)_2$	$Co(AX)_2$	$Hg(AX)_2$	$Pb(AX)_2$	Assignment
3500 mb			3339 mb			νOH(H_2O)cryst.
3213 w						νNH
3111 bw						νNH
2986 w				3000 wt.		νCH
2920 bw	2918 wt.	2919 wt.				νCH
1692 dm						νCO
	1578 w	1597 sd	1552 vsb	1591 s	1597 msb	νCC+ νCN
1509 s	1513 mb				1512 s	νCC+ νCN
				1450 m		
1440 ms	1421 sm.	1440 sd	1421 st.	1412 ms	1420 sb	νCN
				1392 m		
1368 wm	1368 m	1354 s	1331 sh	1354 s	1351 ms	δCH_3
1312 wm						δNH + νCN
1274 w						δCH_3
1235 s	1250 sh	1262 s	1259 sh	1253 s	1250 vsm.	δNH + νCN
1217 s	1230 s		1216 dm	1204 m		δCH_3+δCNC+
	1161 w					+νCO
1022 msd	1031 s	1025 s	1027 s	1014 s	1025 s	νC=S + νCS
961 w			960 vw		965 m	νCS
			884 w			νNS + νCS
					789 wb	νNS + νCS
	705 w	694 m	678 ms	688 m	689 m	
640 wm	666 wd	667 m		658 m	666 m	νCS+ CH_3def+
	627 vvw		617 w	617 m	640 m	+NH def.
	592 vvw					νC-CH_3
					587 wm	νSS
540 wm	541 w	543 mb	539 w	540 wm	539 ms	νSS
457 mb	462 wb	470 wb	458 wb	477 wd	467 wb	δCNC +νSS
	424 m	421 ms				ring def.+
404 sd	404 md	412 ms	405 vw	415 msd	405 md	+νSS
	362 vw	368 ms		376 s		
		356 ms		364 m	361 m	
353 vw				353 m	340 m	νMO + νMN
				345 ms		
				318 vw		
		286 m				
		270 sh				νMN +
		244 mb	250 sb	262 vvw	240 mb	+ring def.
230 vw						τ(acetyl)
	217 m					?
	192 m	200 vw		201 s		chelate ring
164 vw	160 mb	171 m.		159 m	163 mb	?
		155 vw		142 w		?

Relative intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; m., multiple; d, double; t., triple; sh, shoulder (irrespective of their strength).

two highest frequencies evidence certain degree of conjugation. These results suggest the coexistence of tautomers I_{Ba}, I_{Bb} and I_{Bc}; see Fig. 1. Vibrations at 575, 534, 371, 336, and 324 cm^{-1} are attributables to ring deformations [6,10,16].

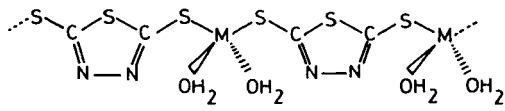
Formation of the acetyl derivative AB is evidenced by the appearence of the strong νCO band at 1709 cm^{-1}. The absorptions

at 1353 and 622 cm^{-1}, are assigned to deformations of CH_3; the $\delta_{asym.}CH_3$ is probably masked by the strong νCN band at 1437 cm^{-1}. Other new bands at about 500 cm^{-1} and those at 408 and 289 cm^{-1} (see Figs. 3 and 4) are attributed to deformation modes of the acetyl fragment [16]. Substitution of the mercapto-hydrogen is evidenced by the disappearence of the νSH mode, near 2478 cm^{-1}. The spectra indicate that the acetyl substitution does not involve the C=S bond. The energy increasing by acetylation (954 cm^{-1}) of the double band at about 930 cm^{-1}, is due to an energy redistribution on the CS bonds.

The rest of the spectrum being quite similar to that of B, suggests that species I_{Rn} coexists with AB. There is no spectral evidences to confirm or discard a double acetylation of tautomer I_{Rc}.

BM and ABM complexes.

Spectra of BM and ABM resulted identical; no bands associated to the acetyl group are now present, which is an evidence that CH_3CO^- is hydrogen substituted during the metal complexation (see Figs.5 and 6 and Table 2 for the BM spectra and assignment). The broad band at about 3500 cm^{-1} is assigned to the νOH mode of coordination water; the δOH vibration could be associated to one of the components of the asymmetric band near 1620 cm^{-1}. A medium strong broad band at about 390 cm^{-1} could contains the metal-water coordination absorption. Metal-ligand bonding is evidenced by both the dissapearence of the νSH and $\nu CS_{ext.}$ modes, and the presence of new bands at 352 and near 265 cm^{-1} ascribed to νM-S stretching vibrations [11,13,16,20,21]. Complexation is also accompained by the spectral shift to lower frequency of the νCN modes (1505 to 1420 cm^{-1}). Bands of ligand B at 941 and 918 cm^{-1} are absent in the spectrum of complexes; this strongly suggests



I

Fig.7. Structure I. Proposed polymeric structure for the I_{Bc} bismuthiol metal complexes BM.

that these absorptions are attributable to the exo-ring νCS modes. B bands at 1122, 1076, 371, 220 and 156 cm^{-1} resulted sensitive to metal-complexation; thus, the spectral shifting is attributable to ring structural modifications. This set of results suggest that the metal complexation could involve both tautomers I_{Bb} and I_{Bc}. Bands in the spectra of complexes, in particular those at about 3150 cm^{-1} (νNH) and 1040 cm^{-1} (νC=S), suggest the presence of the free tautomer I_{Ba} coexisting with the metal complex; this is corroborated by our Job's experiments [21] which indicate that ligands are partially adsorbed on the complex surface when solutions of free ligand are used to obtain complexes. The spectral features and physical-chemical characteristics of the metal complexes (vide supra) allow us to propose a polymeric structure for the BM complexes involving only the I_{Bc} tautomer. See Fig.7.

X and AX ligands.

The IR spectrum of xanthane shows bands characteristics of NH (around 3250 cm^{-1}) and NH_2 (1629, 1314, 1083, 747 and 620 cm^{-1}) [4,13] (see Figs.3 and 4 and Tables 3 and 4); this suggest that tautomers I_{Xa} and I_{Xb} coexist in the solid samples, see Fig.1. The fact that no band was observed about 2480 cm^{-1} (νSH) confirms the absence of tautomers I_{Xc} and I_{Xd}. The strong and broad

band at 1516 cm^{-1} is assigned to a νC=N mode; its shoulder at about 1450 cm^{-1} and the absorption at 1230 cm^{-1} are assigned to coupled νCN vibrations [7]. The C=S bond is inferred at 1003 cm^{-1}; the νC-S modes, strongly coupled to NH deformations, are attributable to some of the bands at about 747 and 620 cm^{-1}. Sharp bands at 536 and 507 cm^{-1} are ascribed to ring vibrations involving the S-S bond [8,15,20,22]. Absorptions at 408, near 390 and 262 cm^{-1} are consistent with ring vibrations [6,10,16] The X-aminoacetylation (AX) should be recognizable by the disappearence of bands assigned to the NH_2 group (see Figs. 3 and 4, and Tables 3 and 4); in fact, the groups of bands around 3000, 1314, 747 and 620 cm^{-1} are simplified, while bands at 1629 cm^{-1} (δNH_2) and 1083 cm^{-1} (ρNH_2) are now absent. The new broad band at 457 cm^{-1} is attributed to an exo-ring CNC deformation [16]. Other bands of the acetyl group are observed at 1692 cm^{-1}(νCO), 2986 and 2920 cm^{-1} (νCH), 1368 cm^{-1} (δCH_3) and near 592 cm^{-1} (νC-CH_3). With the present experimental data we can not explain the disappearence by acetylation of the ring deformation band at about 390 cm^{-1}. Vibrations at about 229 and 164 cm^{-1} are tentatively assigned to acetyl framework torsions [23]. The spectral characteristics of the AX compound suggests that tautomer I_{x_a} is mainly involved in the acetylation. The fact that several bands of X still remain in the AX spectrum allow us to infer that tautomer I_{x_b} coexists with the I_{x_a} aminoacetylated tautomer.

XM complex formation.

The broad band at about 3400 cm^{-1} is ascribed to the νOH mode of coordination water; the asymmetric band at about 1620 cm^{-1} should contain the OH deformation mode. The metal-water coordination

stretching mode could be assigned to one of the bands in the region 390 cm^{-1}. Three different CN bonds can be inferred; the multiple band at 2171 cm^{-1} is assigned to a νC≡N mode [7], and the broad bands at 1551 and 1421 cm^{-1} are ascribed to stretching vibrations of the C=N and C-N bonds, respectively. Absorptions at 868 and near 750 cm^{-1} are characteristics of a νCS mode of an ionic 1,1-dithiolate group [16,24]. The band at 457 cm^{-1} is a δCNC mode while those near 350 and 271 cm^{-1} are certainly M-S stretching vibrations [11,15,19] (see Table 3).

Several bands remain at about the same frequency that in the spectrum of X but, in general, they display a low relative intensity: the group of bands at about 3000 cm^{-1} (νNH) is simplified and the bands near 1610 (δNH_2), 1510 (νC=N), 1330 (νCN), 1083 (ρNH_2), 990 (νC=S), 750 (ωNH_2), 632 (δNH coupled to νCS), 530, 505 cm^{-1} (νSS) and 387 cm^{-1} (ring vibration), still remain. This situation suggests that a small quantity of the unreacted I_{xa} tautomer coexists with the metallic complex. The bands at about 885, 679 and 210 cm^{-1}, observed mainly in the spectrum of the cobalt complex, are ascribed to ring vibrations involving the N-S and C-S ring bonds [10]; this suggests that tautomer I_{xd} (perthiocyanic acid) could also be stabilized in the processus of the xanthane metal complex formation; the corresponding metal-ligand stretching modes could be inferred from the broadness of the bands near 340 and 250 cm^{-1} in the spectrum of CoX, HgX and PbX.

Other very weak bands between 3000 and 2800 cm^{-1} (νCH), near 1368 cm^{-1} (δCH_3) and one shoulder about 2100 cm^{-1} (νC≡N), belong to the residual CH_3CN solvent used in the synthesis of the complexes. Thus, the most probable species involved in the XM formation are tautomer I_{xa} and the 1,1-dithiolate-type and I_{xd} complexes, see Fig. 8.

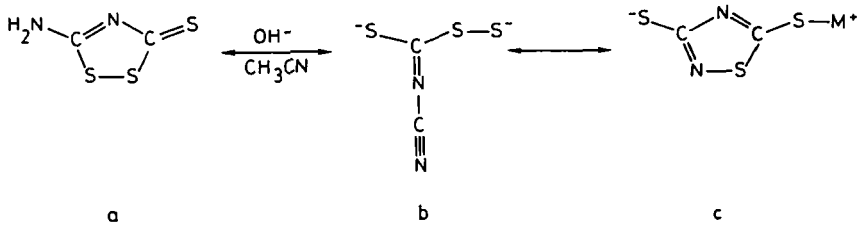
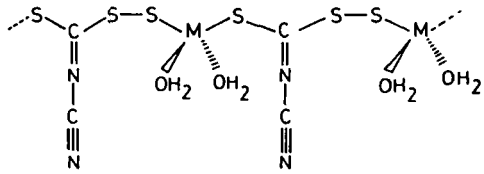
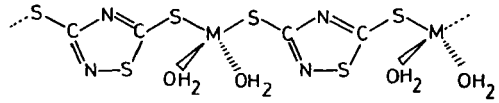


Fig.8. Most probable species in the xanthane-metal complexation. a: tautomer I_{xa}, b: 1,1-dithiolate-type metal complex and c: I_{xd} metal complex.



II



III

Fig.9. Structure II: proposed polymeric structure for the 1,1-dithiolate-type metal complexes. Structure III: proposed polymeric structures for the I_{xd} xanthane metal complexes XM.

The spectral characteristics of the XM complexes and their physical-chemical properties are consistent with a polymeric structure for both metal dithiolate-type and I_{xd} compounds (see Fig.9).

AXM complex formation

The metal complexation involves the CO group of the acetyl anion and the NH_2 group of tautomer I_{xa}. This is supported by the fact

that the νNH and νC=O modes are not observed in the IR spectrum of the AXM complexes; other bands appearing at 1417 cm^{-1} and between 1250 and 1160 cm^{-1} are due to a single CO bond [9] (see Table 4). Moreover, the new bands near 1590 and 477 cm^{-1} are related to the ring [25] and aminoacetyl [16] moieties, respectively ; the bands observed only in the spectrum of complexes near 420, 380 and 270 cm^{-1} are attributable to νM-O [7,11], νM-N [11] and chelate vibrations [11,26,27], respectively. The fact that the C=S stretching mode remains in the whole series at about the same frequency (1025 cm^{-1}) allow us to propose that the metal coordination does not involve the sulfur atom of the C=S bond. The rest of the absorptions are consistent with the structure of tautomer I_{XA}. The present experimental data are insufficient to propose a structure for the AXM complexes; however, the general assignment performed suggests for the $(AX)_2M$ complexes a coordination site involving the N and O atoms. No coordination water vibrations were observed in the spectra of these complexes.

CONCLUSIONS

The IR technique resulted to be appropriated to identify ligand tautomers coexisting in the solid state. The spectral assignment allows us to propose that the bismuthiol-metal complexes display a unique and similar polymeric structure involving the I_{BA} tautomer; small quantities of the I_{BA} tautomer remain adsorbed onto the polymer surface.

The xanthane-metal complexation stabilizes 1,1-dithiolate-type polymeric species; complexation with Cd, Co and Hg metal ions also stabilizes polymers involving the I_{XA} tautomer. These facts seem to be related to kinetic aspects of the metal complexation

processus. Most of the new species involved in the xanthane metal-complexation were independently identified through the spectral analysis.

The identification of water vibrations in the spectra of the BM and XM complexes suggests a coordination number not less than four for the present cations.

The ensemble of results for the BM and XM complexes suggests that the spectral modifications of the CN bonds by complexation are rather due to a ring electronic energy redistribution than to a M-N coordination.

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