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On the Thiourea Complexes of Mercury(II): $HgTu_2A_2$ and $HgTu_2XA$ (X = Cl, Br, I; A = ClO_4, BF_4, CF_3COO)

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The thiourea complexes of mercury(II) $HgTu_2XA$ (X = Cl, Br, I; A = ClO_4, BF_4, CF_3COO) have been isolated. Their molar conductivities in MetOH (90–100 for A = ClO_4, BF_4; 70–80 for A = CF_3COO) characterize them as 1:1 electrolytes while the corresponding $HgTu_2A_2$ complexes behave as 2:1 electrolytes ($\Lambda_M = \sim 190$ for A = ClO_4, BF_4; 125 for A = CF_3COO). The lower conductivities of the trifluoroacetates seem to indicate an interaction of the trifluoroacetate ion with the complex in solution. The infrared spectra of the solid $HgTu_2A_2$ complexes show that at least one anion is coordinated to the metal. In all the $HgTu_2A_2$ and $HgTu_2XA$ complexes thiourea is S-bonded to the metal with the higher ν(HgS) frequencies tentatively assigned to 300, 290, 280, 250 cm^{-1} for $[HgTu_2Y]A$ (Y = A, Cl, Br, I) complexes respectively. The ν(HgX) (X = Cl, Br, I) frequencies may be tentatively assigned to 210–195, 146–142, 123–94 cm^{-1} for the chlorides, bromides and iodides respectively.

Introduction

In a previous research[1] we prepared the solid mercuric complexes of thiourea (Tu), $HgTu_2A_2$ (A = ClO_4, BF_4, CF_3COO) and we studied by radiochromatographic method their exchange reaction with free ^{35}S-thiourea on paper chromatography elution. We have now prepared the new complexes $HgTu_2XA$ (X = Cl, Br, I) and studied both series of complexes by conductometric method and by infrared spectroscopy.

Experimental

The complexes $HgTu_2XA$ were prepared by dissolving 2.5 m*M* of the complexes $HgTu_2A_2$ in 5 ml H_2O and adding, very slowly and under energic agitation at room temperature, 2,5 m*M* of the corresponding sodium halide dissolved in 1 ml H_2O. The chloride-derivatives precipitate during the addition of the sodium chloride solution. The bromide- and iodide-derivatives crystallize after some hours, preferably on cooling at 5° C. After filtration the crystalline products were washed with water, ethanol and ethyl ether and dried under vacuum.

The complex $HgTu_2IClO_4$ was prepared by adding a solution of 2.5 m*M* KI in 5 ml CH_3OH to a solution of 2.5 m*M* $HgTu_2(ClO_4)_2$ in 5 ml C_2H_5OH and cooling the mixture overnight at 5° C in order to precipitate quantitatively $KClO_4$. After filtration 10 ml of benzene were added to the clear solution and after some hours the compound crystallized in colorless plates; it may be washed with ethanol and ethyl ether. The solubility of these complexes in CH_3OH increases from the chloride- to the iodide-derivatives.

These complexes react in water or methanol solution with thiourea in 1:1 molar ratio according to the scheme:

$$2HgTu_2XA + 2Tu \rightarrow HgTu_2X_2 + HgTu_4A_2$$

(A = ClO_4, BF_4, CF_3COO; X = Cl, Br). The complexes $HgTu_2X_2$ precipitate during the reaction; the complexes $HgTu_4A_2$ can be crystallized from the solution. The complex $HgTu_2I_2$ does not precipitate immediately but on concentration of the solution. These complexes were identified by chemical analysis.

The compounds were analysed by determining: mercury as HgS, sulphur as $BaSO_4$ and nitrogen with the Kjeldhal method (Table I). Conductometric measurements were performed with a WTW conductivity bridge in methanol solution. The infrared spectra were recorded on the solids in KBr pelletts (4000–250 cm^{-1}) or nujol mulls on polythene (500–250 cm^{-1}) with a Perkin–Elmer 521 spectrophotometer and in nujol mulls on polythene (400–60 cm^{-1}) with a Perkin–Elmer FIS3 spectrophotometer.

Results and Discussion

The molar conductivities (Table II) show that in methanolic solution the perchlorato- and fluoborato-complexes $HgTu_2A_2$ behave as 1:2 electrolytes and

TABLE I. Analytical Results, Found % (Calcd. %).

	Hg	S	N
$HgTu_2ClClO_4$	41.37(41.12)	13.07(13.15)	11.18(11.48)
$HgTu_2BrClO_4$	37.82(37.69)	11.96(12.04)	10.30(10.52)
$HgTu_2IClO_4$	34.32(34.63)	10.93(11.07)	10.01(9.67)
$HgTu_2ClBF_4$	42.15(42.21)	13.27(13.49)	11.79(11.78)
$HgTu_2BrBF_4$	38.64(38.60)	12.18(12.34)	10.78(10.77)
$HgTu_2ClCF_3COO$	39.94(40.01)	12.56(12.79)	11.21(11.17)
$HgTu_2BrCF_3COO$	36.61(36.75)	11.65(11.74)	10.25(10.26)
$HgTu_2ICF_3COO$	33.90(33.84)	10.69(10.81)	9.27(9.44)
$HgTu_2Cl_2$	47.07(47.33)	14.91(15.10)	13.18(13.21)
$HgTu_2Br_2$	39.03(39.12)	12.55(12.50)	11.03(10.92)
$HgTu_2I_2$	32.95(33.06)	10.43(10.56)	9.13(9.23)

$HgTu_2XA$ as 1:1 electrolytes. The trifluoroacetato-complexes have a lower conductivity which may be due to the lower mobility of the trifluoroacetato ion but also to a greater coordinating action of this ion,[1] in competition with the solvent.

Following on a sulphur-coordination of thiourea to the metal the infrared spectra of the complexes (Table II) show increased frequencies for the bands mainly due ν(NCN) asymmetric and ν(NCN) symmetric modes,[2] while the band mainly due to a ν(CS) mode[2] is shifted to lower energies. The splitting of these bands in the complexes may indicate that thiourea molecules do not have equivalent coordinations to the metal. The frequency lowering of one of the ν(NCN) symmetric frequencies to ~ 1400 cm^{-1} may be due to the ν(CS) component of this band.

The complexes $HgTu_2A_2$ (A = ClO_4, BF_4) have very similar far infrared spectra (Table II) and therefore similar structures. The very strong band at 299 cm^{-1} may be assigned to ν(HgS) frequency.[3] The very strong and broad band at 182–184 cm^{-1}, containing also the ligand band at 174 cm^{-1}, the very strong bands at 133 and 95 cm^{-1} could be related to some δ(HgSC), π(HgSC), δ(SHgS), π(SHgS) modes, even if an assignment cannot be made without further evidence.[3]

Two infrared bands indicate that in the perchlorato-complex one ClO_4^- ion has changed its T_d into C_{3v} symmetry:[4–7] its band at ~ 1100 cm^{-1} is split giving a very strong band at 1026 cm^{-1} which is absent in the other perchlorato-complexes (Table II) and the band at 923 cm^{-1} is much more intense than in the other complexes. A similar lowering of symmetry ($T_d \rightarrow C_{3v}$) is indicated for the BF_4^- ion[6] by the strong band at 977 cm^{-1} which is not present in the other fluoborato-complexes and by the medium band at 768 cm^{-1} which is stronger than in the other fluoborato complexes.

These complexes may therefore be represented by the structural formulas $[HgTu_2OClO_3]ClO_4$ and $[HgTu_2FBF_3]BF_4$, presumably with a highly deformed trigonal symmetry. The high frequency of the ν(HgS) band may be due to a low energy of the third coordination bond with the anion.

Similarly one trifluoroacetato ion may be considered as coordinated to the metal in the $HgTu_2(CF_3COO)_2$ complex since: (a) this seems to occur even in methanol solution, (b) a strong band appearing at 282 cm^{-1} in the far infrared spectra of the complex $[HgTu_2CF_3COO]CF_3COO$ and of the salt $Hg(CF_3COO)_2$ in which both trifluoroacetato ions are coordinated to the metal, but not in the complexes $[HgTu_2X](CF_3COO)$. The complex $[HgTu_2CF_3COO]CF_3COO$ shows a second very strong band at 270 cm^{-1} which corresponds to the uncoordinated anion and appears also in the spectra of $[HgTu_2X]A$ complexes and in the salt CF_3COOK.

The ν(HgS) frequency may be assigned, in the $[HgTu_2CF_3COO]CF_3COO$ complex, to the band at 307(s) cm^{-1}, which is very close to the bands at 299(vs) cm^{-1} in the other $HgTu_2A_2$ complexes.

The complexes $HgTu_2XA$ (X = Cl, Br, I; A = ClO_4, BF_4, CF_3COO) may be compared with the known complexes $HgTu_2X_2$ (X = Cl, Br, I) which have been studied by diffractometric X-ray analysis. The complex $HgTu_2Cl_2$ has the structure $[HgTu_2Cl]Cl$ with two sulphur atoms and one chlorine atom bonded to mercury in a distorted trigonal plane and the second chloride ion located perpendicular to this plane at 3.22 Å from mercury.[8] $HgTu_2Br_2$[9] has a polymeric pseudo-octahedral structure with four bromine bridging atoms in the plane and two sulphur atoms in a pseudo-*trans*-octahedral deformed position (145°). $HgTu_2I_2$[10] has a deformed tetrahedral structure, the mercury atom being coordinated to both sulphur atoms of the thiourea molecules and to both iodine atoms.

The far infrared spectra of the $HgTu_2X_2$ (X = Cl, Br) complexes[3] show two bands at 251(m), 236(m) and 252(s), 228(m) cm^{-1}, respectively, which were assigned to ν(HgS) frequencies. They are quite independent from the different structures of the two complexes. The higher ν(HgS) bands in the $HgTu_2XA$ complexes can be located only at higher frequencies

TABLE II. More Characteristic Infrared Bands (cm^{-1}) of the Complexes $HgTu_2A_2$, $HgTu_2XA$ (X = Cl, Br, I; A = ClO_4, BF_4, CF_3COO (AF_3)) and Related Compounds. Molar Conductivities Λ_M(Ω^{-1}mol^{-1}cm^2) *in* MetOH (10^{-3} *M*) Solution.

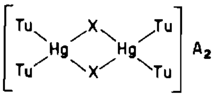
Tu	$HgTu_2$ $(ClO_4)_2$	$HgTu_2$ $Cl\cdot ClO_4$	$HgTu_2$ $Br\cdot ClO_4$	$HgTu_2$ $I\cdot ClO_4$	$HgTu_2$ $(BF_4)_2$	$HgTu_2$ $Cl\cdot BF_4$	$HgTu_2$ $Br\cdot BF_4$	$Hg(AF_3)_2$ $\cdot 2H_2O$	$HgTu_2$ $(AF_3)_2$	$HgTu_2$ $Cl\cdot AF_3$	$HgTu_2$ $Br\cdot AF_3$	$HgTu_2$ $I\cdot AF_3$	KAF_3	
								1655vsb	1660vs	1658vs	1658vs	1665vs	1660vsb	ν(CO) asym
1612vs	1630vs	1628vs	1631vs	1627vs	1629vs	1628vs	1629vs		1628vs	1628vs	1628vs			δ(NH_2) +
	1620sh	1620sh	1618vs	1618vs	1618vs	1620vs	1618vs		1618sh	1616vs	1615vs	1612vs		ν(NCN) asym
								1435s					1442ms	ν(CO) sym
1410vs	1435s	1423s	1438s	1425s	1438s	1430s	1437s		1436s	1437vs	1435vs	1423vs		ν(NCN) sym +
	1399s	1400s	1398s	1390s	1399s	1402s	1398vs		1398s	1399vs	1395vs	1393vs		ν(CS) + ϱ(NH_2)
								1220vs	1192vs	1211vs	1209vs	1210vs	1222vs	
								1176sh	1175sh	1175sh	1180sh	1182vs	1180w	ν(CF_3) asym
								1152vsb	1145vs	1135vs	1135vs	1130vs	1150vs	
1080s	1086vs	1084vsb	1090vsb	1084vs	1085vs	1087sh	1083sh		1080sh	1115sh	1105sh			ν(NCN) asym + ϱ(NH_2)
					1055vs	1060vs	1055vs							
	1026vs				1032vs	1032vs	1032vs							ClO_4
	923s	930vw	942vw	942vw	977s									BF_4
					768m	774vw	772vw							
								836s	838s	840s	838s	840s	840s	ν(C–C)
								804s	805ms	808s	808s	808s	808s	ν(CF_3) sym
									798ms					
								722s	723s	725s	723s	723s	726s	CO_2 def
728vs	714sh	710sh	713s	708ms	713sh	714ms	712s		711s	712s	712s	709s		ν(CS)
	702s	698s	698s	695s	702ms	702s	699ms							
460s	477s	469s		455sh	477vs	480s	478vs		478s	480vs	478vs	472vs		ν(CS) + δ(NCN)
								458sb					440w	
					352sh	346m	347m							BF_4
								281vs	282s					CF_3COO
									270vs	265s	262s	271vs	270s	
	299vs	287s	277s	247s	299vs	287ms	278s	(309w)	307s	288m	284ms	286s		ν(HgS)
		259m	250ms	228s		252m	251s			250sh	244m	246sh		
												236vs	227m	
		210sh	142s	123vsb		210s	144vs			195vsb	146sh	94ms		ν(HgX)
174s	182vsb	177vs	176s	173s	184vs	178vs	176vs	180vs	180 vsb	(195vsb)	180vs	178s	203w	Other bands
					173sh									
	143sh	166sh	(142s)		143sh	150sh	(144vs)	150w	148b	145vsb	146sh	142vs	150w	
	133vsb				134vs									
114ms			120m	(123vsb)			119m				126vsb			
	96vs	103vs			95vs	103s		100vsb	104s	106sh		(94ms)		
	80vs	88sh	78s	77s	84vs		88vs			82w				
	65s				62sh				57ms		66m	67w		
	192	104	99	96	189	99	90		125	79	74	72		Λ_M

as it is indicated in Table II. They show, at least for the perchlorato- and fluoborato-complexes, a decrease in the ν(HgS) frequency going from the chloride to the iodide, perhaps due to a different influence of the coordinated halogen atom(s) on the metal–sulphur bond energy.

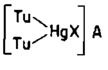
In the far infrared spectra of the $HgTu_2X_2$ (X = Cl, Br) complexes other bands were observed at 215(vs), 193(vs) cm^{-1} for the chloride and at 158(s), 129(msb) cm^{-1} for the bromide[3] but no assignment was made for the ν(HgX) bands. A higher ν(HgCl) frequency should correspond to the terminal Hg–Cl bond ascertained by the X-ray structure determination of the chloride complex.[8]

In the $HgSu_2X_2$ (X = Cl, Br, I)[11] complexes of selenourea (Su) the bands at 204(s), 200(sh) cm^{-1} for the chloride were assigned to ν(HgX) frequencies [ν(HgSe) = 176(s) cm^{-1}] considering that metal–chlorine bond lengths in $HgCl_2$ complexes tend to vary considerably according to the nature of the other ligands in the mercury co-ordination sphere. The 3(νMSe + νMX) bands of the other two complexes: 189m, 172s, 148s cm^{-1} for the bromide and 155s, 126m,sh, 112m? cm^{-1} for the iodide were not distinctly assigned.

For the $HgTu_2XA$ complexes the mostly strong bands at 210–195 cm^{-1} for the chlorides, 146–142 cm^{-1} for the bromides, 123–94(?) cm^{-1} for the iodides may be assigned to ν(HgX) frequencies (Table II). These frequency values are in agreement with the literature values for halide-bridged complexes of mercury(II). This assignment could therefore suggest for this class of complexes a tetrahedral structure in the solid state like



Another interpretation could be that in the case of a trigonal structure like



strong Hg–S bonds, as indicated by their ν(HgS) frequencies, could weaken the Hg–X bonds in such a way as to reduce their stretching frequencies to values very close to those of the halide-bridging bonds.

Owing to the great variety of coordination geometries shown by the mercury(II) ion and considering the above mentioned uncertainties in interpreting the I.R. spectra of simple complexes like $HgTu_2X_2$ and $HgSu_2X_2$, a choice between these two hypotheses or others appears rather difficult.

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References

1 G. Peyronel, G. Marcotrigiano and R. Battistuzzi, *J. Inorg. Nucl. Chem., 35,* 1117 (1973).
2 G.B. Aitken, J.L. Duncan and G.P. McQuillan, *J. Chem. Soc. (A),* 2695 (1971).
3 D.M. Adams and J.B. Cornell, *J. Chem. Soc. (A),* 884 (1967).
4 B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.,* 3091 (1961).
5 A.E. Winckenden and R.A. Krause, *Inorg. Chem., 4,* 404 (1965).
6 I.M. Procter, B.J. Hathaway and P. Nicholls, *J. Chem. Soc. (A),* 1678 (1968).
7 N.M. Karayannis, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski and M.M. Labes, *J. Inorg. Nucl. Chem., 33,* 3185 (1971).
8 P.D. Brotherton, P.C. Healy, C.L. Raston and A.H. White, *J. Chem. Soc., Dalton, 1973,* 334.
9 A. Korczynski, *Zeszyty Naukowe Politechniki Lodzkiej, Chemia, 19,* 85 (1969).
10 A. Korczynski, *Rozniki Chemii, Ann. Soc. Chim. Polon., 42,* 393 (1968).
11 G.B. Aitken, J.L. Duncan and G.P. McQuillan, *J. Chem. Soc., Dalton Trans., 1972,* 2103.