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Antimony(III) and Bismuth(III) Complexes of 2,6-Dimethyl- and 2-Amino-5-methyl-1,3,4-thiadiazole

ANTONIO C. FABRETTI, GIAN CARLO FRANCHINI and GIORGIO PEYRONEL
Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy
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The following antimony(III) and bismuth(III) complexes of 2,5-dimethyl-(dtz) and 2-amino-5-methyl-1,3,4-thiadiazole (matz) have been prepared and investigated by conductometric method and i.r. and Raman spectra: $SbCl_3 \cdot 1.5dtz$, $BiI_3 \cdot 1.5dtz$, $MX_3 \cdot dtz$ (M = Sb, X = Br, I; M = Bi, X = Cl, Br), $Bi(ClO_4)_3 \cdot 1.33dtz$, $MX_3 \cdot 1.5matz$ (M = Sb, Bi, X = Cl, Br, I), $Bi(ClO_4)_3 \cdot 5matz$. dtz acts as N,N-bridging ligand in all these complexes; matz is presumably only H_2N-bonded in the perchlorate complex and acts as H_2N- and N_{ring}-bridging ligand in its halide complexes.

Introduction

Among the 1,3,4-thiadiazoles the 2,5-dimethyl-(dtz)* and 2-amino-5-methyl-derivative (matz) have been little studied as metal ligands especially with non-transition elements. Both ligands have 2N and S endocyclic atoms and matz another NH_2 exocyclic group as potential coordination sites. The tin(IV) halide complexes have been previously studied [1]. The antimony(III) and bismuth(III) complexes of dtz and matz are investigated in this study by conductimetric, i.r. and Raman methods.

Experimental

The complexes were prepared as follows.

$SbCl_3 \cdot 1.5dtz$

A filtered saturated solution of $SbCl_3$ in cyclohexane was slowly added to a filtered saturated solu-

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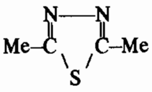
*dtz 

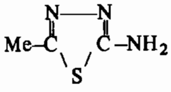
matz 

TABLE I. Analytical Data, Found % (Calcd. %), Colour and Molar Conductivity Λ_M (Ω^{-1} mol^{-1} cm^2) in 10^{-3} *M* Nitromethane (NMT) and DMF Solution.

	Colour	N	C	H	Λ_M NMT
$SbCl_3 \cdot 1.5dtz$	white	10.10(10.52)	18.12(18.04)	2.10(2.27)	39.9
$SbBr_3 \cdot dtz$	light yellow	5.60(5.89)	10.19(10.10)	1.16(1.27)	66.8
$SbI_3 \cdot dtz$	orange	4.46(4.54)	8.09(7.79)	0.96(0.98)	69.1
$BiCl_3 \cdot dtz$	white	6.34(6.52)	11.26(11.19)	1.37(1.41)	60.2
$BiBr_3 \cdot dtz$	canary yellow	4.71(4.98)	8.35(8.54)	1.01(1.07)	72.9
$BiI_3 \cdot 1.5dtz$	light red	5.42(5.52)	9.71(9.47)	1.20(1.19)	42.4
$Bi(ClO_4)_3 \cdot 1.33dtz$	white	5.22(5.66)	9.80(9.71)	1.27(1.22)	90.1
$SbCl_3 \cdot 1.5matz$	white	15.36(15.72)	13.63(13.48)	2.00(1.89)	43.4
$SbBr_3 \cdot 1.5matz$	yellow	11.56(11.80)	10.24(10.12)	1.52(1.42)	67.9
$SbI_3 \cdot 1.5matz$	red	8.91(9.34)	8.04(8.01)	1.10(1.12)	91.1
$BiCl_3 \cdot 1.5matz$	white	13.07(12.91)	11.36(11.07)	1.73(1.55)	29.5
$BiBr_3 \cdot 1.5matz$	yellow	9.94(10.14)	8.75(8.70)	1.30(1.22)	71.3
$BiI_3 \cdot 1.5matz$	dark red	8.08(8.27)	7.17(7.10)	1.03(0.99)	89.1
$Bi(ClO_4)_3 \cdot 5matz$	white	19.18(19.22)	16.59(16.48)	2.42(2.31)	insol[a]

[a] In DMF: 348.

tion of dtz in cyclohexane; the instantaneous precipitate was washed with cyclohexane.

$SbX_3 \cdot dtz$ (X = Br, I), $BiX_3 \cdot dtz$ (X = Cl, Br, I), $MX_3 \cdot 1.5matz$ (M = Sb, Bi; X = Cl, Br, I)

A warm solution of MX_3 (1 mmol) in HAc (5 cm^3) was added to a warm solution of L (1 mmol) and KX (0.1 mmol) in HAc (5 cm^3); by cooling the crystalline compounds precipitated and were washed with HAc and EtOH.

$Bi(ClO_4)_3 \cdot 1.33dtz$ and $Bi(ClO_4)_3 \cdot 5matz$

A solution of Bi_2O_3 (0.5 mmol) in conc. $HClO_4$ (5 cm^3) was added to a solution of L (2 mmol) in HAc (5 cm^3); by adding EtOH to the solution until it became turbid the product crystallized in about 24 hours and was washed with 50/50 HAc/EtOH and then with EtOH.

Microanalyses were performed with C. Erba Mod. 1106 Elemental Analyzer (Table I). Molar conductivities were determined at 25 °C with a WTW conductivity bridge. Infrared spectra were recorded on the solids in KBr disks (4000–250 cm^{-1}) or as nujol mulls on polythene (600–60 cm^{-1}) with a Perkin Elmer 180 spectrophotometer. The ligand matz was deuteriated by refluxing with CH_3OD. Its i.r. spectrum was recorded also in $CHCl_3$ solution in the 4000–1500 cm^{-1} region. The matz·HCl derivative was obtained from EtOH solution by adding gaseous HCl.

The Raman spectra were recorded at room temperature with a Jobin Yvon Ramanor HG2S spectrometer. The spectra were exited by the 514.5 nm line of a Spectra-Physics 165 argon ion laser with incident power of about 60–150 mw. Plasma radiation was removed from the source by means of an interference filter (Tables II and III).

Results and discussion

The antimony and bismuth trihalide dtz complexes have M:L ratios of 1:1.5 for $SbCl_3$ and BiI_3 and 1:1 for the other halides, while all the matz halide-complexes have a 1:1.5 M:L ratio. Some of the halide complexes have in nitromethane a molar conductivity in the range (75–95) given for 1:1 electrolytes [2] but this is very likely due to solvolytic processes in solution, which may occur also for the $Bi(ClO_4)_3 \cdot 1.33$dtz complex which has a low molar conductivity of the order of that of some halide complexes. $Bi(ClO_4)_3 \cdot 5$matz is insoluble in nitromethane and has in anhydrous DMF a molar conductivity (348) lying in the range of values observed for 3:1 electrolytes (340–440) [3].

In the 2-amino-5-methyl-1,3,4-thiadiazole the $\nu(NH_2)_{asym}$ (3492 cm^{-1}) and $\nu(NH_2)_{sym}$ (3393 cm^{-1}; calcd. 3404 cm^{-1}) [4] bands observed in $CHCl_3$ solution are shifted in the solid to lower frequencies (3260 and 3085 cm^{-1}) by strong hydrogen bonds. In all the matz-complexes of this series a ν(NH) frequency decrease of 90–140 cm^{-1} with respect to the ligand in $CHCl_3$ solution indicates a NH_2-coordination of matz to the metal ions. In the solid deuteriated ligand the ν(NH) bands (in brackets the ν_H/ν_D ratio) are shifted to 2460 (1.33) and 2268 (1.36) cm^{-1} while the $\delta(NH_2)$ band at 1639(vs) cm^{-1} is shifted to 1290 (1.27) cm^{-1}. Also the $\delta(NH_2)$ shows in the complexes a frequency decrease of 12–24 cm^{-1} in agreement with a H_2N-coordination.

In the matz·HCl derivative the $\delta(NH_2)$ band is substituted by two very strong bands at 1630 and 1590 cm^{-1} which may be tentatively assigned to $\delta(NH_3^+)_{asym}$ and $\delta(NH_3^+)_{sym}$ modes due to the protonation of the more basic aminic nitrogen atom. Consequently to this NH_2 protonation an electronic shift from the adjacent ring nitrogen atom to the $-\bar{N}\overset{\cdots}{-}C(-\bar{N}H_2)$ bond should occur increasing its double bond character and consequently its ν(C=N) frequency. In agreement with this three ligand bands at 1540, 1527 and 1505 cm^{-1} which remain unaltered in the deuteriated ligand and may be assigned to ring vibration modes containing a high $\nu(C\overset{\cdots}{-}N)$ contribution are substituted in the matz·HCl derivative by a band at a higher frequency (1574 cm^{-1}). The fact that this frequency increase is observed also in the matz-complexes confirms furtherly a H_2N-coordination of the ligand.

In the ν(C–S) region (720–570 cm^{-1}) [4] the ligand bands at 685 and 649 cm^{-1} seem to be shifted at higher frequencies both in the matz·HCl derivative and in the matz-complexes. A ν(CS) frequency increase excludes a sulphur-coordination and is attributable to an electronic shift from the endocyclic sulphur atom toward the S–C bonds as a consequence of the H_2N-coordination.

The 2,5-dimethyl-1,3,4-thiadiazole ligand shows in the ν(C–S) region only one very strong band at 642 cm^{-1} which in the complexes becomes weaker and is accompanied by other bands at higher frequencies in a region in which the ligand does not have other bands. This fact may be attributed to an important ν(CS) contribution of this band, the increased frequency in the complexes being attributable to a coordination of the ligand through its ring nitrogen atoms which causes an electronic shift from the sulphur atom to the ring.

The matz Complexes

The antimony and bismuth halide complexes of matz show new strong bands in the 488–402 cm^{-1} region assignable to aminic nitrogen–metal stretching modes in agreement with the $\nu(Sn–NH_2)$ frequencies (485–470 cm^{-1}) observed for the SnX_4 (X = Cl, Br) complexes of matz [1]. The band at 408–402 cm^{-1}, Raman active in all the complexes

TABLE II. Principal Infrared and Raman Bands (cm^{-1}) of matz and Its Sb and Bi Complexes.

	matz = L		matz·HCl IR	$SbCl_3$·1.5L		$SbBr_3$·1.5L		SbI_3·1.5L IR	$BiCl_3$·1.5L		$BiBr_3$·1.5L		BiI_3·1.5L IR	$Bi(ClO_4)_3$·5L[a]	
	IR	R		IR	R	IR	R		IR	R	IR	R		IR	R
ν(NH_2)	3492w			3370s		3365s		3355sm	3375s		3375s		3370ms	3405s	
														3305s	
	3393w			3280m		3275m		3265m	3275ms		3270ms		3265vm	3280m	
														3220m	
δ(NH_2)	1639vs			1627vs		1615vs		1615vs	1625vvs		1623vvs		1616vs	1630vs	
														1610vs	
ν(CN)	1540ms		1574s	1568sm		1555sm		1555sm	1565s		1562s		1555sm	1555s	
			768ms	772m		770m		768mw	770mw		770ms		770ms	770m	
ν(CS)	685ms		718sm	715m		715m		710m	710m		718wm		714wm	714m	
	649sm		642m	690m		670mb			683ms		665m			692m	
			624m	640w		640w		635m	640w	645ms	640w		640m		
Ligand		527m													
and other		523m	519wm	523wm	526m	522sm	526vw	520ms	522m	525m	521ms	527vw	520ms	515sb	524vs
bands	427s	418vvs	419sm												
			402sm												
	350ms		343sm	349sm	348vw	348sm		344m	348vs	348vw	346ms	335vwb	345ms	349vs	
	304vs	302m	301s	302s	303vvs	292sm		286ms	292vs	292w	288sm		284sm	293vs	300wm
	295vs	292m	290ms												
			222s					222w	220sh	215sh				193s	194w
	165wm	167m	180vsb								167wm	164vvs	165m		
	129w	134w	150s	143s							147sh			145vs	133vvs
	101wm	90vvs	98m		92sm	100vs			107sh	89s	101sh			97vs	93sh
	78w	74w			70vw	83m	82ms			72vs	75sh	76s	80ms	75s	78sm
ν(MN)				484sb		466sb		466sb	488sb		471msb		465sb		466s
					408m		405vw		406wm	405wm		403vw	437sb		457s
				248ms	248vs	252w		252w	251vw	252vvs	251vw		251vw	402s	403s
ν$(MX)_t$				248ms	248vs	201s	203vvs	165wm	188vs	212vs	141vs	146s	114sh		
				219sb	222vs	155vs	150ms	127vs	172vs	172w	122sh		107vs		
ν$(MX)_b$				183vsb		133m	128s	120vs	137vsb	130sh	101sh		(80ms)		
				158vs	156wm	117vs			120sh	122vvs	91vs	91ms			

[a] ClO_4^- bands: 1130vs, 1080vs, 625s.

TABLE III. Principal Infrared and Raman Bands (cm^{-1}) of dtz and its Sb and Bi Complexes.

	dtz = L′		SbCl$_3$·1.5L′		SbBr$_3$·L′		SbI$_3$·L′	BiCl$_3$·L′		BiBr$_3$·L′		BiI$_3$·1.5L′	Bi(ClO$_4$)$_3$·1.33L′ [a]	
	IR	R	IR	R	IR	R	IR	IR	R	IR	R	IR	IR	R
			770sm		779sm		775m	773s		780sm		768s		
					723sb		720mb	700wm		705mb		746ms		
			690w									690m		
			658sm		642m		644wm	650m		645m		655wm	655wm	
	642vs		649sh									640wm	635m,sh	
			605w		599s		596wm	600wm		595sm		600wm	575vsb	
	518m	524vvs		526m		520w					525w		521w	523s
	362s	368vs	368wm		356mw	356vw	356wm	360wm		356m	359vw	360m	373m,sh	375m
		346m				342vw					344vw			
	278s	287wm	273sh	297m	267w		271wm	274vs	290vs	277w	269vw	277s	273ms,sh	280wmb
	197mb		(190vs)		199w		195sh						(185mb)	
	82m	84m												
			480s(b)					414wb(c)						
ν(MN)			408w		340wm		338w	342wm		340m		337wm	328w	351wm
			392w							266mw			263vs	260wmb
			336s	338vvs										
(MN)def									(222s)	225w		224w	228w	
				174w	175m			(173vs)	170vw	(170vvs)	(178vs)	179sm	177m	183vvs
ν(MX)$_t$			320s	322vw	210s	222vvs	165s	254vvs	256s	182s,sh	196vvs	145wm,sh		464sh
			302vs	303vs	190vs	196sm	156vs	244s,sh	242vw	170vvs	178vs	121vvs		458ms
			290vs	291vs	159m,sh	158wm	119wm		222s		163ms	98ms	401sb	426mb
(MX)def			198mb					173vs		133s	135mb			
			169ms	156m	103sm	107wm		140vs	140sh	96s	104m	76s		
			149mw	139wm	94sh			122sh	122s					
			116smb											

[a] ClO_4^- bands: 1140s, 1102vs, 1086vs, 924w, 635m,sh, 624vs, 461wm. [b] and [c] Combination bands: 290 + 198 = 488; 244 + 173 = 417.

while it is only i.r. active in the matz•HCl derivative, is tentatively assigned to a ν(M–NH$_2$) mode. A new weak band at about 250 cm^{-1} observed in all the antimony and bismuth halide complexes may be assigned to ν(M–N$_{\rm ring}$) mode in agreement with the lower frequency value observed for this type of stretching vibration in other 1,3,4-thiadiazole complexes [5]. It may be excluded that the strong band observed at about 300 cm^{-1} in the i.r. and Raman spectrum of the antimony chloride complex corresponds to a ν(SbCl) band as it is present also in the spectra of all the other matz complexes with variable intensity and it is very strong in the i.r. spectrum (293 cm^{-1}) of the bismuth perchlorate complex. This band must be considered as corresponding to the ligand band observed at 304(vs) cm^{-1}. The ν(SbCl) both i.r. and Raman active band at 248 cm^{-1} is likely coupled or superimposed to the ν(Sb-N$_{\rm ring}$) band and this may alter a little its frequency.

The first two bands assignable to (SbX) modes have rather low frequencies with respect to those normally found for Sb–X terminal stretching modes. ν_s(SbCl) and ν_{as}(SbCl) frequencies were reported in the 272–222 and 257–206 cm^{-1} regions, respectively, for square pyramidal L$_2$SbCl$_3$ complexes even if a third ν(SbCl) band, expected to be considerably higher, was not identified with certainty [6]. For the mononuclear SbX$_3$•bipy complexes ν(SbBr)$_t$ at 200–175 cm^{-1} and ν(SbI)$_t$ at 179–153 cm^{-1} have been observed [7].

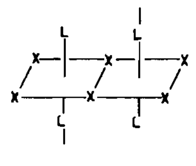
Owing to the fact that matz is strongly H$_2$N-bonded to the metal and that the molar conductivities of the antimony and bismuth halide complexes in nitromethane are very high, increasing from the chloride to the iodide up to the values characteristic for 1:1 electrolytes (75–95) [2], rather low ν(MX)$_t$ frequency values are acceptable for this class of complexes.

Assigning the bands at 248 and 219–222 cm^{-1} to ν(SbCl)$_t$ modes the bands at 183 and 158 cm^{-1} may be assigned to ν(SbCl)$_b$ modes, their frequency ratios 183/248 = 0.74 and 158/219 = 0.72 being in the range (0.60–0.85) given for ν(MX)$_b$/ν(MX)$_t$ ratios [7]; also ν(SbBr)$_b$ modes have been given in the 149–100 cm^{-1} region [8]. The ν(SbX)/ν(SbCl) ratios are almost in the ranges accepted for complexes having similar structures

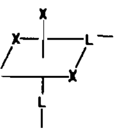
A polymer octahedral structure (A) of the SbX$_3$•1.5matz complexes with two *cis*-terminal and two *cis*-bridging halide ions one H$_2$N-monodentate and one H$_2$N- and N$_{\rm ring}$-bridging ligand molecule in axial position may account for 2ν(SbX)$_t$, 2ν(SbX)$_b$, 2ν(Sb–NH$_2$) (one i.r. and one Raman active) and 1ν(Sb–N$_{\rm ring}$) bands, all observed for the chloride complex.

The BiX$_3$•1.5matz (X = Cl, Br) complexes show two very strong Raman bands at 252 cm^{-1} for the chloride, with the same frequency of the ν(Bi–N$_{\rm ring}$) band, and at 164 cm^{-1} for the bromide, with the same frequency of a ligand band. It is therefore difficult to assign them to ν(BiX) modes even if they lie in the frequency range of ν(BiCl)$_t$ and ν(BiBr)$_t$ bands, respectively. Also the bands observed for the chloride at 188 (i.r.) and 212 (Raman) cm^{-1}, with a difference of 24 cm^{-1}, seem to be different bands. It is therefore doubtful if these bismuth complexes have the same structure of the corresponding antimony complexes.

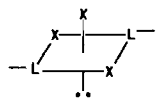
(A)



(B)

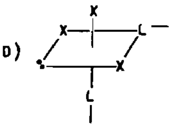


(C)



or

(D)



The bismuth iodide complex shows two i.r. strong ν(Bi–NH$_2$) bands at 465 and 437 cm^{-1}, one ν(Bi–N$_{\rm ring}$) at 251 and two or three bands assignable to ν(BiI) modes. The presence of two ν(Bi–NH$_2$) bands may indicate that in a distorted octahedral structure like that proposed for the SbCl$_3$•1.5matz the H$_2$N–Bi–NH$_2$ subunit is bent or *cis* giving two infrared active bands.

In the Bi(ClO$_4$)$_3$•5matz complex the perchlorate ion is not coordinated. Three strong bands above 400 cm^{-1}, only one of which is i.r. active, may be safely assigned to ν(Bi–NH$_2$) modes. The bands at 349 and 293–300 cm^{-1} are very likely ligand bands. The band at 193–194 cm^{-1} has a rather low frequency for a ν(Bi–NH$_2$)$_t$ band. A C$_{4v}$ octahedral structure in a dimer with two bridging ligand molecules should give 3ν(Bi–NH$_2$) and 1ν(Bi–N$_{\rm ring}$) bands in i.r. spectrum (respectively 4 and 1 in the Raman spectrum). A square C$_{4v}$ pyramidal structure with lone pair in the sixth position should give 3 and 4 ν(Bi–NH$_2$) bands in the i.r. and Raman spectra, respectively; while a trigonal bipyramidal D$_{3h}$ structure should give 2 and 3 ν(Bi–NH$_2$) bands in the i.r. and Raman spectra, respectively. The last two structures seem to be the most likely, their choice depending on the assignment of the band at 193 cm^{-1}.

The dtz complexes

The SbCl$_3$•1.5dtz complex shows three ν(SbN) i.r. active bands between 408 and 336 cm^{-1} the last of which is also Raman active and three ν(SbCl) bands between 320 and 290 cm^{-1} which are all i.r. and Raman active. The multiplicity of the ν(SbN) i.r. bands indicates that all the dtz molecules act as N,N-bridging ligands. Because of the weak character of the first two bands and the very high fluorescence in this spectral region of the Raman spectrum it was not possible to ascertain if these first two bands are also Raman active. Three ν(SbN) and three ν(SbCl) bands, all i.r. and Raman active, should correspond to an octahedral *trans(mer)* C_{2v} coordination (B) which seems to be the most likely structure for this complex.

The band at 350–330 cm^{-1} present with variable intensity also in the i.r. spectra of the other complexes of this series may be assigned to a ν(MN) mode, a ligand band being only Raman active at 346 cm^{-1}. The band at 290–266 cm^{-1}, i.r. and Raman active in several complexes, corresponds to the ligand band appearing at 278 (i.r.) and 287 (R) cm^{-1} but, owing to its variable position and intensity for the different complexes, it may mask a second ν(MN) band.

Three bands may be assigned in the i.r. and/or Raman spectra of the MX_3·dtz (M = Sb, X = Br, I; M = Bi, X = Cl, Br) complexes to $\nu(MX)_t$ modes in agreement with other literature values [7, 9–11]. Their rather low frequencies may be accepted owing to the high molar conductivity of these complexes [6]. Very likely dtz acts also in these complexes as N,N-bridging ligand. A distorted square pyramidal coordination with the stereochemically active lone pair in the sixth position may be proposed for these complexes, a C_s symmetry of the MX_3 subunit giving three ν(MX) bands i.r. and Raman active [11]. Whether the MN_2 subunit has a *trans* or *cis* configuration (C, D) can not be decided because of the uncertainty in the identification of the ν(MN) bands [11].

Also the BiI_3·1.5dtz complex shows three (BiI) bands which may be assigned to $\nu(BiI)_t$ modes in agreement with other literature values and the high molar conductivity of this complex. The number of ν(BiN) bands should be three for an octahedral *trans(mer)* coordination but it seems rather unlikely to consider as $\nu(BiN)_t$ bands those at 277 cm^{-1}, which is a ligand band, and at 224 cm^{-1} which appears also in the bromide and perchlorate complexes as i.r. active.

As shown by the ClO_4^- i.r. bands this anion is coordinated in the $Bi(ClO_4)_3$·1.33dtz. Four ν(BiO) (three Raman and one i.r. active) bands are observed in the 464–401 cm^{-1} region in agreement with other ν(BiO) values [9, 11–13] and at least two ν(BiN) bands are observed in the 351–260 cm^{-1} region. This complex, having a rather unusual stoichiometry, has very likely a polymeric structure probably containing different types of bismuth coordination.

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