Inorganica Chimica Acta, 35 (1979) 49–56
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Cobalt(II), Nickel(II) and Copper(II) Complexes of 2-Amino-5-methyl-1,3,4-thiadiazole

A. C. FABRETTI, G. PEYRONEL and G. C. FRANCHINI

Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy

Received October 24, 1978

The following complexes of 2-amino-5-methyl-1,3,4-thiadiazole (L) have been prepared and studied: CoL_2X_2 (X = Cl, Br, I, OAc), pseudotetrahedral with C_{2v} symmetry; $ML_4(NO_3)_2$ (M = Co, Ni), octahedral with uncoordinated NO_3^- ionic groups; $NiLCl_2$, $NiL_{1.5}Br_2 \cdot 0.25EtOH$, $NiL_2I_2 \cdot 0.75EtOH$, with octahedral polymeric structures; $Cu_4L_5Cl_8$, $Cu_3L_4Br_6$, CuL_4Br_2 and $Cu_2L_3(OAc)_4$; The ligand is coordinated to the metal atom through the aminic nitrogen atom in the CoL_2X_2 and CuL_4Br_2 complexes and through the aminic nitrogen together with one or two cyclic nitrogen atoms in the other complexes. Electronic spectra, with their crystal field parameters for cobalt and nickel, infrared and far infrared spectra, magnetic moments and some molar conductivities are reported and discussed.

Introduction

Mono and disubstituted 1,3,4-thiadiazoles have pharmacological properties [1] and are potential coordinating agents. Among them the 2-amino-5-methyl-1,3,4-thiadiazole (Matz or L) has four potential coordination sites: one S and two N cyclic atoms and one exocyclic NH_2 group. As the ligand properties of this substance have never been studied, we have prepared and investigated some of its cobalt(II), nickel(II) and copper(II) complexes. A comparison of their i.r. spectra with those of the deuterium- and HCl-derivatives of the ligand has been made.

Experimental

The ligand (Fluka) and the other reagents were of the best chemical grade. The deuteriated ligand was obtained by repeated isotopic exchange with D_2O and evaporation *in vacuo*. The HCl-derivative was prepared by dissolving the ligand in warm concentrated HCl and evaporating the solution *in vacuo* on NaOH. *Anal.*: found % (calcd.% for $C_3H_5N_3S \cdot HCl \cdot H_2O$) C 21.27(21.24), H 4.80(4.75), N 24.05(24.77). The complexes were prepared as follows.

Co(Matz)$_2$X$_2$ (X = Cl, Br, I)

A filtered solution of the cobalt halide (0.1 mmol) in EtOH (1 cm^3) was added to a warm solution of L (0.2 mmol) in EtOH (3 cm^3). The chloride immediately precipitated from the warm solution, the bromide by cooling the solution, and the iodide after one week. The compounds were also obtained by using a 1:1 ratio of the reagents. They were washed with cold EtOH.

Co(Matz)$_4$(NO$_3$)$_2$

A solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mmol) and L (0.4 mmol) in n-ButOH (1 cm^3) concentrated *in vacuo* to about 2/3 of the volume gave an abundant precipitate which was washed with EtOH.

Co(Matz)$_2$(OAc)$_2$

A warm solution of L (0.2 mmol) in n-ButOH (2 cm^3) was added to a warm solution of cobalt acetate (0.2 mmol) in n-ButOH (2 cm^3); a white precipitate initially formed was transformed in 4 days into a crystalline violet product which was washed with n-ButOH and EtOH.

Ni(Matz)Cl$_2$

A warm solution of L (0.2 mmol) in EtOH (2 cm^3) was added to a solution of $NiX_2 \cdot 6H_2O$ (0.2 mmol) in warm EtOH (1 cm^3). The compound immediately precipitated and was washed with EtOH.

Ni(Matz)$_{1.5}$Br$_2$·0.25 EtOH, Ni(Matz)$_2$I$_2$·0.75 EtOH

A warm solution of $NiX_2 \cdot 6H_2O$ (0.1 mmol) in 1:1 EtOH + Acetone (10 and 3 cm^3 for bromide and iodide, respectively) was added to a solution of L (0.2 mmol) in acetone (12 and 5 cm^3, respectively); the products precipitated immediately and were washed with acetone.

Ni(Matz)$_4$(NO$_3$)$_2$

A warm solution of $Ni(NO_3) \cdot 6H_2O$ (0.2 mmol) and L (0.4 mmol) in EtOH (5 cm^3) was concentrated to small volume; after some hours a blue microcrystalline product was formed and washed with EtOH.

TABLE I. Analytical Data, Found % (Calcd.%), Colour, Magnetic Moment μ_{eff}(B.M.) and Molar Conductivity Λ_M(Ω^{-1} mol^{-1} cm^2) in 10^{-3} *M* Solution.

	Colour	N	C	H	μ_{eff} (B.M.)	Λ_M	Solvent
CoL_2Cl_2	blue	23.45(23.33)	20.54(20.01)	2.78(2.80)	4.59	29	DMF
CoL_2Br_2	blue	18.92(18.71)	16.12(16.05)	2.28(2.24)	4.60	23	MCS
CoL_2I_2	deep green	15.38(15.48)	13.13(13.27)	1.85(1.86)	4.62	10	Acetone
$CoL_2(OAc)_2$	violet	21.13(20.63)	29.61(29.49)	3.98(3.96)	4.55	3	DMF
$CoL_4(NO_3)_2$ [a]	pink	29.73(30.47)	22.86(22.39)	3.29(3.13)	4.61	150	DMF
$NiLCl_2$	light green	16.94(17.17)	14.96(14.72)	2.20(2.06)	3.11		
$NiL_{1.5}Br_2 \cdot 0.25EtOH$	light green	15.55(15.65)	14.98(14.90)	2.57(2.25)	2.96		
$NiL_2I_2 \cdot 0.75EtOH$	light green	14.47(14.56)	15.72(15.60)	2.69(2.53)	3.27		
$NiL_4(NO_3)_2$	light blue	30.81(30.48)	22.80(22.40)	3.12(3.13)	3.20		
$Cu_4L_5Cl_8$ [b]	light green	18.35(18.87)	16.06(16.18)	2.43(2.26)	1.96		
$Cu_3L_4Br_6$ [c]	brown	14.39(14.87)	13.01(12.75)	2.01(1.78)	1.73	52	DMF
CuL_4Br_2	dark green	24.36(24.57)	21.34(21.07)	2.98(2.95)	1.80	57	DMF
$Cu_2L_3(OAc)_4$	blue green	16.85(17.79)	29.05(28.81)	3.82(3.84)	1.62	1	DMF

[a] Co: 9.05(9.16). [b] Cu: 22.73(22.82). [c] Cu: 16.62(16.86).

$Cu_4(Matz)_5Cl_8$ and $Cu_3(Matz)_4Br_6$

From a solution of $CuCl_2 \cdot 2H_2O$ (1 mmol) and L (1 mmol) in n-ButOH (25 cm^3) the chloride precipitated almost instantaneously; from a solution of $CuBr_2 \cdot 2H_2O$ (1 mmol) and L (1 mmol) in 1:1 EtOH + n-ButOH (30 cm^3) the bromide precipitated in about 7 days.

$Cu(Matz)_4Br_2$

By mixing the solutions of $CuBr_2 \cdot 2H_2O$ (1 mmol) in EtOH (15 cm^3) and L (8 mmol) in n-ButOH (120 cm^3) the crystalline compound precipitated in about 10 days and was washed with n-ButOH.

$Cu(Matz)_{1.5}(OAc)_2$

A filtered warm solution of $Cu(OAc)_2 \cdot 2H_2O$ (1 mmol) in 1:1 EtOH + HOAc (10 cm^3) was added to a warm solution of L (2 mmol) in EtOH (10 cm^3). The compound precipitated in about 10 days and was washed with EtOH and Et_2O.

The compounds were analysed by standard methods (Table I). Molar conductivities were determined at 25 °C with a WTW conductivity bridge in the solvent in which the complexes were soluble without decomposition. Magnetic susceptibilities were measured by the Gouy method and corrected for Pascal constants. Electronic spectra were recorded on the solids as nujol mulls on filter paper with a Shimadzu MPS-50L spectrophotometer. Infrared spectra were recorded on the solids in KBr disks (4000–250 cm^{-1}) and as nujol mulls on polythene (600–60 cm^{-1}) with a Perkin Elmer 180 spectrophotometer. The ν(NH) bands of the ligand were recorded on a $CHCl_3$ solution in the 4000–2500 cm^{-1} region and the NO_3^- bands on the solid nitrates as nujol mulls on KBr disks in the 1700–500 cm^{-1} region in order to avoid the presence of ionic NO_3^- bands due to the formation of KNO_3 in the KBr disks.

Results and Discussion

The CoL_2X_2 (X = Cl, Br, I, OAc) complexes behave in solution as non-electrolytes (Λ_M for 1:1 electrolytes: DMF 65–90, acetone 100–140, MCS 32–35) [2, 3]. Their electronic spectra (Table II and Fig. 1) in the solid state show two polyhumped bands corresponding by their positions to the ν_2 and ν_3 bands of a pseudo-tetrahedral coordination, their splitting into three distinct bands being typical for a C_{2v} symmetry [4, 5]. The crystal field parameters were calculated from the averaged values of the ν_2 and ν_3 bands, taking the centre of gravity of the total intensity [6] by using the method of Underhill and Billing [7] and the ν_1 values were obtained from the ν_3/ν_2 ratios [8]. The values of the crystal field para-

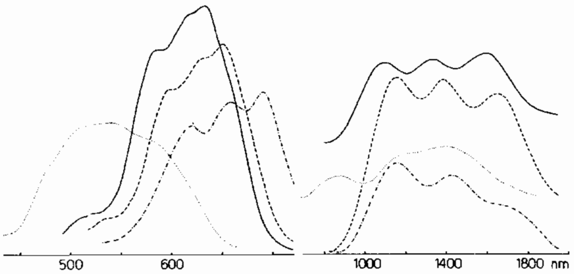


Fig. 1. Electronic spectra (absorbance in ordinate) of the complexes: —— CoL_2Cl_2, – – – CoL_2Br_2, –·–·– CoL_2I_2, ... $CoL_2(OAc)_2$.

TABLE II. Electronic Spectra and Crystal Field Parameters (cm^{-1}) of the Matz Complexes.

	ν_1	ν_2	ν_3	Dq	B	β	$\nu_3 - \nu_2$
Pseudotetrahedral							
CoL_2Cl_2	4250(calcd.)	6250s, 7460s, 9090s 7330 (av.)	15770vs, 16130s, 17090s 16230 (av.)	426	719	0.74	8900
CoL_2Br_2	4150(calcd.)	6050s, 7210s, 8660s 7150 (av.)	15350vs, 15850s, 16720s 15850 (av.)	416	702	0.72	8700
CoL_2I_2	4070(calcd.)	5890m, 7000s, 8650s 7020 (av.)	14470vs, 15160s, 16110s 15220 (av.)	409	663	0.68	8200
$CoL_2(OAc)_2$	4670(calcd.)	7250m, 8440m, 11430w 8100 (av.)	17240sh, 18520s, 19610sh 18450 (av.)	469	831	0.86	10350
Octahedral							
$CoL_4(NO_3)_2$	9090m	19100sh (calcd. 19270)	20620sb	1028	850	0.88	

	ν_1		ν_2		ν_3 $\rightarrow {}^3T_{1g}(P)$	Dq	B	β
	${}^3A_{1g} \rightarrow {}^3T_{2g}$	$\rightarrow {}^1E_g$	$\rightarrow {}^3T_{1g}$	$\rightarrow {}^1T_{1g}$				
Octahedral								
$NiLCl_2$	8330m	(15150sh)	14140ms	(19800sh)	23640s	833	852	0.82
$NiL_{1.5}Br_2 \cdot 0.25EtOH$	8510m	(15150sh)	14180ms	(18870sh)	22940s	851	772	0.74
$NiL_2I_2 \cdot 0.75EtOH$	8700m	(16000m)	14710sh		22470sh	870	739	0.71
$NiL_4(NO_3)_2$	9760m	(14930sh)	15900s		25850vs	976	832	0.80
$Cu_4L_5Cl_8$	13590s, 23530sh							
CuL_4Br_2	15920s, 25250vs							
$Cu_3L_4Br_6$	14290m, 19690sh, 27400s							
$CuL_{1.5}(OAc)_2$	13510s, 26320sh							

TABLE III. Principal Infrared Bands (cm^{-1}) of the Ligand, Its Deuterium- and HCl-Derivatives and Complexes.

	L[a]	$L\cdot HCl\cdot H_2O$	CoL_2Cl_2	CoL_2Br_2	CoL_2I_2	CoL_2Ac_2[b]	$CoL_4(NO_3)_2$
ν(NH)	[3492s]	3382vs	3380vs	3360vs	3420m		3405vs
	3260vs	3278w	3290sh	3280sh	3320sh	3282vs	3292vs
	[3393s]	3200s	3260vs	3248vs	3285ms	3140s	3190sh
	3085vs	3072vs					3120vsb
δ(NH_2)	1639s	1630vs	1620m, sh	1618ms	1604s	1630vs	1628vs
						1615ms	
ν(CN) and		1590vs	1598vs	1599vs	1592s	1598s	
ring vibr.	1540ms	1574wm	1545ms	1548ms	1540mw	1540s	1535s
	1527vs	1537vw	1505m, sh	1505ms			
	1505vs	1460m	1495vs	1495vs	1493vs	1502vs	1498vvs
ν(CS)	685m	768s	712ms	712ms	714mw	718wm	710ms
(CS)	649m	718s	660wm	660wm	655wm	650w	657w
		624s	643wm	643wm			
(MN) vibr.			490sb	473sb	470mb	481s	469s, sh
			460sb	460sb	450sb	439s	460sb
							262mb
							190msb
ν(MX) vibr.			316vs	254vs	230vs	314vs	
			301vs	243s	215s	280wm	
			174ms	138mw	121wm	187ms	
			153ms	119mw			
			121s	93ms			
Ligand bands		452mb					
	427s	419s	415m, sh	416m, sh	419s	431s	431s
		402s	408s	410s	410sh		415sh
	374vw	372mw	367wm	364wm	387m, sh		
	350ms	343s	354w		358mb	361w	366w
	304s	301s	(301vs)	300vs	310m, sh	(314vs)	305vs
	295s	290s	291sh	281sh	297vs	(280wm)	
	245w	268w			267vw		
		222s	235wm	236m		236mw	229wm
		190m, sh	203mb	202wm	202vw	198m	210w
		180vsb	174ms	173wm	177wm		178sh
	165m			167wm	157w	167wm	166w
		150s	153ms	150w	150mw	150w	153wm
	129w		129m, sh	131w, sh	131w	132w	132w
	101m	98m	102sh	99sh	100w	99w	99wm

[a] In brackets [] the values obtained from the $CHCl_3$ solution. [b] $\nu(CO_2)_{as}$ = 1570s, $\nu(CO_2)_{sym}$ = 1408m, $\delta(CO_2)$ = 676s, separa-

meters Dq and B are in the spectrochemical order O-donors > Cl^- > Br^- > I^- characteristic of tetrahedral cobalt(II) complexes [9]. As for other pseudotetrahedral CoL_2X_2 (X = Cl, Br, I) complexes [10, 11] the graph ($\nu_3 - \nu_2$) *vs.* B (Fig. 2) is perfectly linear. The fact that the point of the graph corresponding to the $Co(Matz)_2(OAc)_2$ complex lies on the straight line of the halides may further support a similar pseudotetrahedral structure for the acetate complex.

The $CoL_4(NO_3)_2$ complex has an electronic spectrum typical for cobalt(II) octahedral complexes, its band frequencies and crystal field parameters

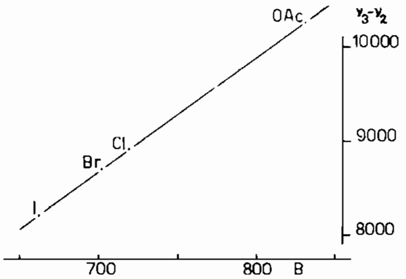


Fig. 2. Plot of $\nu_3 - \nu_2$ *vs.* B of the complexes CoL_2X_2 (X = Cl, Br, I, OAc).

$NiLCl_2$	$NiL_{1.5}Br_2$	NiL_2I_2	$NiL_4(NO_3)_2$	$Cu_4L_5Cl_8$	$Cu_3L_4Br_6$	CuL_4Br_2	$CuL_{1.5}Ac_2$ [c]	L (D)
3390vs	3360vs, sh	3370s, sh	3400vs	3390vs	3360vs	3300vs	3360vs	2460vs
3300vs	3260vs	3250vs	3290vs	3293vs	3266vs	3242vs	3280vs	2360w
3193m	3165s	3160s	3195m	3198m	3175ms	3162s	3182s	2268vs
1608vs	1610vs	1605vs	1630m	1615vvs	1615s	1608vs	1625s	
							1614vs	
			1622s		1602vs		1577s	
1542s	1538s	1537s	1540ms	1538s	1540ms	1545ms	1537w	1540ms
						1510vs		1527vs
1510vs	1506vs	1507vs	1505vs	1509vs	1505vs	1500s	1506vs	1503vs
714mw	705mw	705wm	714m	775ms	718wm	704ms	718w	680w
					705wm			
680w	678w	680w	656m	685wm	688w	687ms	(682s)	642s
					645w		648mw	
460sb	466mb	462mb	461mb	416vs	415vs	465vsb		
323sb	321sb	318sb	320sb	398vs	398vs	423vs	422vs	
			234s	(344vs)	359vs	359mw	341s	
			192s	(327vs)	321s			
263vsb	243ms	229mwb		344vs	260s	251s	325s	
247vsb	233sb			327vs	217vs	200msb	255s	
193sb	121mw			176s		130mw		
				163s	121sm			
430sb	428sb	431sb	431sb		431m, sh			
415vw		415vw	415vw	(398vs)	(398vs)		398vw	
			367mw	366w	371w	371vw		
366vw	366vw		355w					
305w	306s, sh	305s, sh	307vs	302m	304s	302vs	305vs	
278w, sh	279w	279w	277ms	283s	279vw	280w, sh	282wm	
	252w, sh	251w	250mw	244mw	246wm	246sh	244w, sh	
		229mwb		218mw		228w	230w, sh	
	202w	202w	200m	193s		200msb	193wm	
	178wb	178wb	173sh				170mb	
				(163s)	165m	159ms	155ms	
151w	150w	151w	153w	151w, sh	151w	152sh		
	132vw			132w	131w	130mw	132vw	
			99w	103m, sh	98w	100m	99wm	

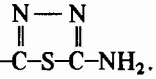
tion = 162 cm^{-1}. [c] $\nu(CO_2)_{as}$ = 1560s, $\nu(CO_2)_{sym}$ = 1408s, sh, $\delta(CO_2)$ = 682s, separation = 152 cm^{-1}.

being very close to the values of the $Co(NH_3)_6^{++}$ complex ion (ν_1 = 9000, ν_3 = 21100, Dq = 1020, B = 885 cm^{-1}; β = 0.91) [9].

The magnetic moments and the electronic spectra of the nickel(II) complexes are typical for an octahedral coordination. The Racah interelectronic parameter B was calculated from the expression $(\nu_2 + \nu_3 - 3\nu_1)/15 = B$ [12]. For the halide complexes the β values decrease in agreement with the nephelauxetic order Cl > Br > I, while their Dq values, assumed equal to $\nu_1/10$, do not follow the spectrochemical order of the halides; the Dq values of the four complexes increase almost linearly with the number of ligand molecules per nickel atom. The Dq value of the $NiL_4(NO_3)_2$ complex is in the range of those given for NiN_6 chromophores [9]. As the i.r. spectra of the complexes exclude a coordination of the ligand through its ring sulphur atom, only the nitrogen atoms of the ligand are involved in the coordination. The increase of the Dq values in the series may therefore indicate a prevailing effect of the increasing number of nitrogen atoms in the coordination sphere of the metal overcoming the spectrochemical effect of the halide ions.

The principal i.r. bands of the ligand, its deuterium- and HCl-derivatives and its complexes are reported in Table III. The ν(NH) bands of the ligand recorded in $CHCl_3$ solution and reported in square brackets in the table have much higher frequencies than those recorded in KBr disks, indicating strong hydrogen bonds in the solid ligand. No significant differences were observed between the ν(NH) bands recorded on the solids in KBr disks and those recorded in nujol mulls on KBr disks. A significant frequency decrease of the ν(NH) bands in all the complexes with respect to those of the ligand in $CHCl_3$ solution indicates that the ligand is bonded to the metal atom through its aminic nitrogen atom. Also the $\delta(NH_2)$ frequency significantly decreases in all the complexes.

The bands appearing in the region 1600–1500 cm^{-1} do not contain significant NH_2 contributions as shown by their values which are almost identical in the deuteriated ligand. They may be assigned to ring vibrations [13] containing important contributions of ν(CN) vibrations, particularly the bands at 1540 and 1527 cm^{-1}; their frequency increase in the ligand derivatives may be related to an electronic shift from the ring nitrogen atom adjacent to the aminic group toward this group involved in the coordination of the proton in the LHCl and the metal atom in the complexes.

The bands at 685 and 649 cm^{-1} lying in the frequency range of the ν(C–S) modes (720–570 cm^{-1}) [13] may be attributed principally to ν(CS) vibrations like the band at 642 cm^{-1} of the similar but symmetrical ligand 2,5-dimethyl-1,3,4-thiadiazole (DTZ) [14]. The presence of two ν(CS) bands in Matz instead of the one in DTZ is attributable to the disymmetry of Matz  $H_3C{-}\overset{\overset{\displaystyle N}{\|}}{C}{-}S{-}\overset{\overset{\displaystyle N}{\|}}{C}{-}NH_2$. The frequency increase of these bands in the LHCl compound and in the complexes indicates that the ring sulphur atom is not involved in the coordination, an electronic shift occurring from sulphur atom to the ring.

Some new bands of the complexes in the 490–320 cm^{-1} region may be or contain ν(MN) vibrations. A similar assignment was given to the bands occurring in the 450–350 cm^{-1} region for the complexes of 1,3,4-thiadiazole-2-thiol-5-amino [15]. In both these ligands the NH_2 donor capacity may be increased by the electronic shifts occurring from the adjacent nitrogen and sulphur atoms of the ring toward the NH_2 group, as is shown by the increased double bond character of the CN and CS bonds of the ring indicated by the frequency increase of their ν(CN) and ν(CS) bands in the Matz complexes. A coupling of the ν(MN) with ring vibrations may also occur for the bands at the highest frequencies. Even for the $M(NH_3)_2X_2$ complexes, both hexa- and tetracoordinated, the ν(MN) vibrations range from 486 to 415 cm^{-1} [16].

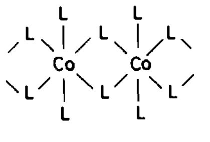
For the acetate complexes the $\nu(CO_2)$ frequencies, their separation and the $\delta(CO_2)$ frequencies (Table III) correspond in part to the values of the unidentate, in part to those of the asymmetric bidentate acetate anion [17]. As these i.r. values depend on the interatomic distances and may be influenced by strong hydrogen bonds between the NH_2 and COO groups coordinated to the same metal atom, they cannot give a definite answer on the type of coordination of the carboxylic group. The C_{2v} pseudo-tetrahedral symmetry of $Co(Matz)_2(OAc)_2$ is consistent with a monodentate coordination of the acetate ion. A weak coordination of the metal ion with a second oxygen atom in a very distorted six coordination as in the ethylenethiourea complex $Co(Etu)_2$-$(OAc)_2$ [18] may be excluded because it would give a quite different electronic spectrum.

The i.r. spectra of the nitrate complexes in KBr disks and in nujol mulls on KBr disks (Table IV) are identical in the 1600–600 cm^{-1} region. Among the bands attributable to the NO_3^- group (Table IV) those at 1355–1364, 1027 and 828–830 cm^{-1} correspond to the values given for the nitrate ion in KNO_3 and NH_4NO_3 [19] while those at 1268–1285, 800 and 743–750 cm^{-1} are close to the values given for the monodentate nitrate ion [16]. Also in this case strong hydrogen bonds between the NO_3^- ion and the NH_2 groups may be responsible for a symmetry lowering of the anion. In both the cobalt acetate and nitrate complexes the strong ν(NH) band at 3140 and 3120 cm^{-1}, respectively, may indicate a strong hydrogen bond formed by some of the NH_2 groups with the oxoanions.

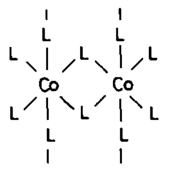
TABLE IV. I.r. Bands of the NO_3^- Group in the Nitrate Complexes of Matz (L).

$CoL_4(NO_3)_2$	1355sb	1275ms	1027m	828w	800ms	743w	[710ms]
$NiL_4(NO_3)_2$	1364m	1285mw 1268s	1027m	830w	800ms	750w	[714m]
Ionic KNO_3 (19)			1049–1028	828–817	974–969	716–705	
Ionic NH_4NO_3 (19)	1350		1050	830		715	
Monodentate NO_3^- (16)		1290	1000		800	740	715
Bidentate NO_3^- (16)		1250	985		785	750	700

The high molar conductivity (Λ_M = 150) of the $Co(Matz)_2(NO_3)_2$ complex in anhydrous DMF is in the range (130–170) characteristic for 1:2 electrolytes [2]. An ionic state of the NO_3 group also in the solid complex may be admitted on the basis of the three i.r. bands corresponding to the ionic nitrate anion. The bands at 262 and 190 cm^{-1} may be therefore assigned to CoN vibrations involving the ring nitrogen atoms of the ligand in order to complete the six coordination of the metal ion in a polymeric structure like



or



with two (NH_2)-monodentate and two (NH_2, N)-bridging ligand molecules. Rather low ν(MN) frequencies (220–270 cm^{-1}) were observed in the $Co(DTZ)_2X_2$ (X = Cl, Br, I, NO_3) complexes in which the coordinating site of the DTZ molecule is the ring nitrogen atom [20].

The CoL_2X_2 (X = Cl, Br, I) halogen mass sensitive bands attributable to MX vibrations mode have frequency ratios:

Cl Br I

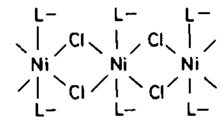
316 : 254 : 230 = 1 : 0.80 : 0.73
301 : 243 : 215 = 1 : 0.81 : 0.71
174 : 138 : 121 = 1 : 0.79 : 0.70
153 : 119 = 1 : 0.78
121 : 93 = 1 : 0.77

a little higher than the values generally accepted for complexes having similar structures [21]. This fact may be due to some coupling of the MCl with the MN modes which tends to reduce the difference between the MX frequencies. The $CoL_2(OAc)_2$ bands in the 314–187 cm^{-1} region, very close to those of the chloride may be assigned to CoO vibration modes. Close values of the MCl and MO vibration frequencies have been observed in other complexes like $Co(DTZ)_2X_2$ (X = Cl, NO_3) of 2,5-dimethyl-1,3,4-thiadiazole [20] and $Cu(HRd)_2X$ (X = Cl, OH) of rhodanine [22].

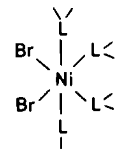
The nickel complexes have very different stoichiometries. The almost linear proportionality between the Dq values and the number of ligand molecules per nickel atom indicates that the number of nitrogen atoms regularly increases from the chloride to the nitrate. The lower ν(NiN) value (about 320 cm^{-1}) may indicate that besides the NH_2 group some ring nitrogen atoms also, giving a lower ν(MN) frequency, participate in the coordination. The ν(NiCl) frequencies (263, 247 cm^{-1}) are in the range of other literature values (270–245 cm^{-1}) for nickel complexes with bridging chloride ions [23, 24]. The ν(NiBr) (243, 233 cm^{-1}) and ν(NiI) (229 cm^{-1}) frequencies correspond to those of terminal Ni–X bonds [25–28].

The following structures may be proposed in agreement with stoichiometry, magnetic, electronic and i.r. data:

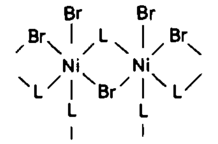
$NiLCl_2$



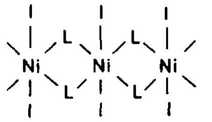
$NiL_{1.5}Br_2$



or



NiL_2I_2



For the bromide it is necessary to admit either that some ligand molecules coordinate three nickel atoms through the NH_2 and the two ring nitrogen atoms or that some bromide ions bridge two nickel atoms. In this latter case the ν(NiBr) bridging bands should be weak and superimposed on ligand bands. The first hypothesis seems to be more likely, taking into account that the similar ligand DTZ is able to coordinate as bidentate ligand through both its ring nitrogen atoms [29].

The $Ni(Matz)_4(NO_3)_2$ complex has an i.r. spectrum very similar to those of the halide complexes, particularly the same ν(NiN) bands at 461 and 320 cm^{-1}, and has also the same NO_3^- bands as those of the ionic cobalt nitrate complex. The bands at 234 and 192 cm^{-1} are very close to those of the cobalt nitrate complex (262 and 190 cm^{-1}) and may be assigned to Ni–N(ring) vibration modes. It is therefore very likely that in this complex also the NO_3^- group is not coordinated, and that it has the same structure as the cobalt nitrate complex.

The halide-mass sensitive bands of the copper complexes assignable to copper–halide ion vibrations have frequency ratios acceptable for similar complexes [21]:

Cl Br

344 : 260(251) = 1 : 0.76(0.73)
327 : 217(200) = 1 : 0.66(0.61)
176 : (130) = 1 : (0.74)
163 : 121 = 1 : 0.74

The ν(CuCl) (344, 327 cm^{-1}) and ν(CuBr) (260–251, 217–200 cm^{-1}) frequencies agree with other literature values for terminal copper–halide bonds [23, 30]. As the $Cu_3L_4Br_6$ complex shows two bands at 359 and 321 cm^{-1} attributable only to $\nu(CuN)$ modes it may be that the corresponding bands in the $Cu_4L_5Cl_8$ complex are superimposed or coupled with the $\nu(CuCl)$ bands appearing in the same spectral region. These lower $\nu(CuN)$ frequencies may be attributed, as for the nickel complexes, to copper–nitrogen(ring) stretching modes arising from NH_2–N-(ring)–bridging ligand molecules in polymeric structures, while in the CuL_4Br_2 complex the ligand acts only as monodentate in an octahedral or tetragonal structure.

For the $CuL_{1.5}(OAc)_2$ complex the bands at 325 and 255 cm^{-1}, similarly to those of the $CoL_2(OAc)_2$ complex at 314 and 280 cm^{-1}, may be assigned to $\nu(CuO)$ modes. As the $\nu(CO_2)_{as}$ (1560 cm^{-1}) and the $\nu(CO_2)$ separation (152 cm^{-1}) are lower than those of the cobalt acetate complex, some of the COO groups may act as asymmetric bridging ligands.

Acknowledgments

This work has been supported by a financial aid of the Consiglio Nazionale delle Ricerche of Italy.

References

1 G. Maffii, E. Testa and R. Ettorre, *Il Farmaco, Ed. Scientifica, 13,* 187 (1958).
2 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).
3 G. C. Pellacani, G. Peyronel, L. Menabue and G. Marcotrigiano, *J. Inorg. Nucl. Chem., 37,* 1551 (1975).
4 A. Flamini, L. Sestilli and C. Furlani, *Inorg. Chim. Acta, 5,* 241 (1971).
5 E. R. Menzel, W. R. Vincent, D. K. Johnson, G. L. Scebach and J. R. Wasson, *Inorg. Chem., 13,* 2465 (1974).
6 F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc., 83,* 4690 (1961).
7 A. E. Underhill and D. E. Billing, *Nature, 210,* 834 (1966).
8 A. B. P. Lever, *J. Chem. Educ., 45,* 711 (1968).
9 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam (1968) pp. 325, 324, 336.
10 K. K. Chatterjee, *Indian J. Chem., 11,* 678 (1973).
11 G. Peyronel and A. Pignedoli, *Transition Met. Chem., 3,* 63 (1978).
12 L. Sacconi, 'Transition Metal Chemistry', ed. by R. L. Carlin, M. Dekker, New York, Vol. 4, p. 212 (1968).
13 C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy', Academic Press, New York (1963) pp. 324, 297.
14 A. C. Fabretti, G. Peyronel and G. C. Franchini, *Tansition Met. Chem.,* in press.
15 M. R. Gajendragad and U. Agarwala, *J. Inorg. Nucl. Chem., 37,* 2429 (1975).
16 J. R. Ferraro, ' Low-frequency Vibrations of Inorganic and Coordination Compounds', Plenum Press, New York (1971) pp. 194–197, 79.
17 N. F. Curtis, *J. Chem. Soc. A,* 1579 (1968).
18 E. M. Holt, S. L. Holt and K. J. Watson, *J. Am. Chem. Soc., 92,* 2721 (1970).
19 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York (1970) p. 98.
20 A. C. Fabretti, G. Peyronel and G. C. Franchini, *J. Coord. Chem.,* in press.
21 A. Brodie and C. J. Wilkins, *Inorg. Chim. Acta, 8,* 13 (1974).
22 A. C. Fabretti, G. Peyronel and G. C. Franchini, *Transition Met. Chem.,* in press.
23 E. J. Duff, M. N. Hughes and K. J. Rutt, *J. Chem. Soc. A,* 2101 (1969).
24 E. J. Duff and M. N. Hughes, *J. Chem. Soc. A,* 2144 (1968).
25 D. M. L. Goodgame, M. Goodgame and G. W. Rayner-Canham, *Inorg. Chim. Acta, 6,* 245 (1972).
26 D. M. L. Goodgame, M. Goodgame and G. W. Rayner-Canham, *Inorg. Chim. Acta, 3,* 406 (1969).
27 A. E. Underhill, *J. Chem. Soc. A,* 128 (1968).
28 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965).
29 A. C. Fabretti, G. Peyronel and G. C. Franchini, *Spectrochim. Acta, 35A,* 229 (1979).
30 D. M. L. Goodgame, *J. Chem. Soc. A,* 305 (1976).