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Cobalt(II), Nickel(II) and Copper(II) Complexes of N-Amino-Rhodanine

ANTONIO C. FABRETTI, GIAN CARLO FRANCHINI and GIORGIO PEYRONEL

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

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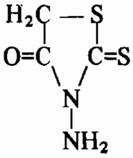
In the cobalt(II), nickel(II) and copper(II) complexes of N-amino-rhodanine (L): $CuLX_2$ *(X = Cl, Br),* ML_2X_2 *(M = Co, X = Cl, I; M = Ni, X = Cl, Br),* $ML_{2.5}X_2$ *(M = Co, X = Br(H₂O); M = Ni, X = I),* $ML_3(ClO_4)_2$ *(M = Co, Cu),* $NiL_4(ClO_4)_2$ *the ligand is bonded through the amine nitrogen atom and through the thiocarbonyl sulphur atom. Spectroscopic evidence suggests the cobalt(II) complexes have a distorted octahedral and the nickel(II) and copper(II) complexes a tetragonal coordination.*

Introduction

N-amino-rhodanine  ($H_2N{\cdot}Rd$, L) has two endocyclic (N,S) and three exocyclic (N,O,S) potentially coordinating atoms. Its cobalt(II), nickel(II) and copper(II) complexes have been investigated in order to establish which of the five sites of the molecule are involved in the coordination.

Experimental

N-amino-rhodanine of chemical grade (Aldrich) was used.

The complexes were prepared by adding a warm solution of the metal salt (0.5 mmol) to a warm solution of the ligand (2 mmol) dissolved: M in HX (2 cm^3) + HAc (2 cm^3) and L in HAc (10 cm^3) for the nickel halides, M in HX (1 cm^3) and L in EtOH (9 cm^3) for the cobalt halides, M in HX (1 cm^3) and L in HAc (10 cm^3) for the copper halides, M in $HClO_4$ (2 cm^3) and L in EtOH (10 cm^3) for the nickel, M in $HClO_4$ (1 cm^3) + HAc (1 cm^3) and L in HAc (1 cm^3) + $HClO_4$ (1 cm^3) for the cobalt, M in $HClO_4$ (1 cm^3) + HAc (2 cm^3) and L in HAc (10 cm^3) for the copper perchlorate. The cobalt chloride and bromide solutions turned from blue to green-brown giving a precipitate overnight. The cobalt iodide solution turned from yellow to green and then to red-brown; by concentration to half volume and cooling the compound crystallized.

The addition of the acids to the solutions was necessary in order to obtain the precipitation of the complexes in a pure and crystalline form. An ethanol-

TABLE I. Analytical Data, Found % (Calcd. %), Colour and Molar Conductivity Λ_M (Ω^{-1} mol^{-1} cm^2) in 10^{-3} *M* DMF Solution of the $H_2N{\cdot}Rd$ (L) Complexes.

	Colour	M	N	C	H	Λ_M
CoL_2Cl_2	pink	13.3(13.8)	13.1(13.1)	17.1(16.9)	2.0(1.9)	26.8
$CoL_{2.5}Br_2{\cdot}H_2O$	brown	9.65(9.7)	11.3(11.5)	15.1(14.8)	1.85(2.0)	112.9
CoL_2I_2	brick	9.4(9.7)	9.25(9.2)	12.2(11.8)	1.35(1.3)	134.8
$CoL_3(ClO_4)_2$	coral	8.2(8.4)	11.9(12.0)	15.3(15.4)	1.8(1.7)	129.6
NiL_2Cl_2	light green	13.7(13.8)	13.2(13.15)	17.35(16.9)	2.0(1.9)	63.5
NiL_2Br_2	light green	11.1(11.4)	10.7(10.9)	14.6(14.0)	1.55(1.6)	119.4
$NiL_{2.5}I_2$	brown	8.5(8.6)	9.9(10.25)	13.3(13.2)	1.5(1.5)	150.9
$NiL_4(ClO_4)_2$	light green	6.6(6.9)	13.1(13.2)	17.6(16.95)	2.1(1.9)	128.4
$CuLCl_2$	light green	21.95(22.5)	9.9(9.9)	13.5(12.75)	1.55(1.4)	25.5
$CuLBr_2$	brown	17.3(17.1)	7.55(7.5)	10.4(9.7)	1.2(1.1)	52.3
$CuL_3(ClO_4)_2$	dark green	8.95(9.0)	11.5(11.9)	15.2(15.3)	1.75(1.7)	156.1

TABLE II. Electronic Spectra and Parameters (cm^{-1}) and Magnetic Moments (B.M.) of the $H_2N{\cdot}Rd$ (L) Complexes.

	ν_1	ν_2	ν_3			L or C.T.	Av. Dq.	Av. B	β	μ_{eff} (B.M.)
L						25640				
CoL_2Cl_2	8510, 8890	17540	18620, 19080, 20200			25320				4.87
Av.	8700	17540	19030				957	778	0.80	
$CoL_{2.5}Br_2$	8330, 9300	17300	18180, 18690, 20000			24390				5.10
Av.	8720	17300	18650				948	756	0.78	
CoL_2I_2	8300, 9090	16000	16860, 17860			21880, 27030				4.72
Av.	8620	16000	17360				910	686	0.71	
$CoL_3(ClO_4)_2$	8510, 9800	17760	18690, 20200, 21050			26600				4.47
Av.	9290	17760	20360				996	850	0.88	
[2.22]	$^3B_{1g} \rightarrow {}^3E_g{}^a$	$\rightarrow {}^3B_{2g}$	$\rightarrow {}^3A_{2g}$	$\rightarrow {}^3E_g{}^b$	$\rightarrow {}^3T_{1g}(P)$	L or C.T.				
NiL_2Cl_2	8400	10740	15800	16950	22730	25320				2.96
NiL_2Br_2	8370	11560	15700	17390	21500	24390				2.96
$NiL_{2.5}I_2$	8300	11300	15620		19800	22220				2.95
$NiL_4(ClO_4)_2$	9760	10810	16830	18180	23260	25970				3.10
		d–d		L or C.T.						
$CuLCl_2$	13070	14080	16950	24390						1.74
$CuLBr_2$	12500	14490	17540	25350						1.73
$CuL_3(ClO_4)_2$		14490	17060	25190						1.71

TABLE III. Far IR Spectra (cm^{-1}) of $H_2N{\cdot}Rd$(L) and its Complexes.[a]

	CoL_2 Cl_2	$CoL_{2.5}$ $Br_2{\cdot}H_2O$	CoL_2 I_2	CoL_3 $2ClO_4$	NiL_2 Cl_2	NiL_2 Br_2	$NiL_{2.5}$ I_2	NiL_4 $2ClO_4$	CuL Cl_2	CuL Br_2	CuL_3 $2ClO_4$
ν(MN) ?	493mw	501mb	494mw	511wm	504ms	506ms	500m	504sm	512sm	512ms	502w
ν(MN)	404wm	429mw	431mw	439wm	440ms	441ms	442mw		456wm	444mw	460w
				406ms							
ν(MS)	298sm	296sm	299sm	303s	300vs	300vs	301vs	305vs	302vs	319vs	329vs
				264sh			262s				262m
ν(MX)	267vs	198mw	168mw		277vs	239s	181sm		335s	245s	
									330s	235s	
Ligand					480vw	471m	468mw	482ms	480wb	477wb	478s
and	418wm	416mw	417wm	421sm	419m	416ms	417mw	419sm	416mw	412m	419ms
other	257sh	250sm	259ms	255sm		250vs	253w	260mb	262s	264s	252vs
bands	235m				234vs	239s	238vs			235s	
	217sm	228s	227sm	226sm	220vs			226wm			
	192wm	183m	188wm	180s	211sh	183m	181sm	185sh	188m		
	171m	168s	168mw		173m	172s	173sh	175ms	174m	170m	174s
	151w	152wm	157mw	147wm	157sm	162s			154w	152sh	
		141mw	136sh	139ms	145s		146vs			146vs	
	131mw	132mw	130ms	133mw	134sh		133w		134ms		131m
	123mw	121mw	122sh	124w	123sm		121sm	122w	122m		
	113sh	112wm	118ms			115wm				113sm	119ms
		101ms			107m	104sm	102w			104ms	107sh
L	481vs, 421sh, 416ms, 363m, 346w, 284mb, 254ms, 245m, 177sm, 153w, 134ms, 122w										

[a] vs = very strong; m = medium; b = broad; w = weak; sh = shoulder.

ic solution saturated with the ligand and with gaseous anhydrous HCl did not give any precipitate; by adding ethyl ether only the free ligand was obtained.

The compounds were analysed by standard methods (Table I). The complexes are soluble only in dimethylformamide (DMF); their molar conductivities were measured with a WTW conductivity bridge at 25 °C. Magnetic susceptibilities were determined by the Gouy method and corrected with the Pascal constants (Table II).

The electronic spectra (Table II) were recorded on the solids in nujol mulls on filter paper with a Shimadzu MPS-50L spectrophotometer. Infrared spectra (Table III) were recorded on the solids in KBr disks (4000–250 cm^{-1}), in nujol mulls on polythene (500–60 cm^{-1}) and in chloroform solution (4000–1200 cm^{-1}) with a Perkin Elmer 180 spectrophotometer. The room-temperature e.p.r. spectra were recorded on a Jeol-PE-3X spectrometer. Quartz sample tubes were employed for polycrystalline samples by using diphenyl-picrylhydrazyl (DPPH, g = 2.0036) [1] as a field marker. Raman spectra were recorded at room temperature on the solids with a Jobin Yvon Ramanor HG2S spectrometer. As most of the solids undergo decomposition under the laser beam these spectra did not give reliable information.

Results and Discussion

In all the complexes the ν(NH) bands of the ligand at 3320(vs) and 3245(m) cm^{-1} in $CHCl_3$ solution (3325(m), 3295(m), 3225(m), 3145(m) cm^{-1} in the solid state) undergo a frequency decrease to 3220–3245 and 3150–3200 cm^{-1} indicating a H_2N-coordination of the ligand, while the very strong ν(CO) band at 1725 cm^{-1} shifts to higher frequencies (1750–1770 cm^{-1}) showing that the CO group is never involved in the coordination. The ligand band at 1050(mw) cm^{-1} shifts to 1030–1040 cm^{-1} while those at 972(sm) and 952(vs) cm^{-1} disappear in the complexes being substituted by a new medium-strong band at 890–930 cm^{-1}. These bands may contain an important ν(CS) contribution as the bands at 1082, 820, 785 cm^{-1} of the CS-coordinated rhodanine in its Co(II), Ni(II) [2] and Pd(II), Pt(II) complexes [3] in which a similar ν(CS) decrease was observed. $H_2N{\cdot}Rd$ may therefore be considered as principally bonded through the H_2N and CS groups in its complexes.

The cobalt halide complexes have, at room temperature, high spin magnetic moments characteristic for an octahedral coordination (4.7–5.2 B.M.) [4], the lower magnetic moment of the perchlorate complex being attributable to a more distorted six-coordination. The nickel complexes have magnetic moments characteristic for an octahedral coordination (2.9–3.4 B.M.) [4] and those of the copper complexes, very close to the spin-only value (1.73 B.M.), exclude a tetrahedral coordination.

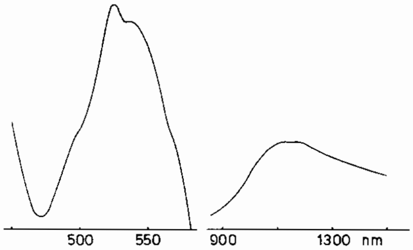


Fig. 1. Electronic spectrum of the CoL_2Cl_2 complex.

The electronic spectra of the solid cobalt complexes show a splitting of the ν_1 and ν_3 bands due to the presence of low symmetry fields [5]. The splitting causes a band envelope due to considerable overlap. The 'average' wavenumbers of the ν_1 and ν_3 bands were obtained by taking into account the relative intensities of the bands of the polyhumped maxima. The 'average' ν_3 value is very close to that of the central more intense band. The ν_2 band is, as expected, weak but well enough localized with an almost normal ν_2/ν_1 (1.86–2.02) ratio [5].

The Dq and B parameters are given as the average of the values calculated from the ν_3/ν_1 and ν_3/ν_2 ratios [6]. In agreement with the rule of the average environment the Dq value of the perchlorate CoS_3N_3 complex, in which the ClO_4^- anion is not coordinated, is intermediate between the values given for the CoS_6 (770–860 cm^{-1}) and CoN_6 (higher than 1000) chromophores [7]. The Dq values of the cobalt halide complexes decreasing in the order Cl > Br > I indicate that the halide ions are coordinated. All the Dq values are in agreement with the spectrochemical series N > S > Cl > Br > I [5]. The high Dq values for the cobalt halide complexes with respect to those of the CoS_6, $CoCl_6$ (764 cm^{-1}) and $CoBr_6$ (649 cm^{-1}) chromophores [5] seem to indicate a predominant influence of the coordinated nitrogen atom over those of the sulphur and halide atoms, these last being weakly coordinated.

The splitting of the ν_1 band into two components indicates for the nickel complexes a tetragonal coordination. On the basis of the NSH theory [8–11] the DT/DQ ratios indicate a tetragonal distortion which is smaller for the perchlorate (DT/DQ = 0.06) than for the halide complexes (DT/DQ = 0.14–0.19).

The cobalt and nickel halide complexes have in DMF a rather high molar conductivity, corresponding for the bromide and iodide complexes to 1:2 electrolyte behaviour (Λ_M = 130–170) [12]. The electronic spectra of these complexes in DMF solution are completely different from those of the solids indicating a strong solvolytic effect of the coordinating solvent. The electronic and infrared spectra indicate that the halide ions are coordinated in the solid state: their weak coordination being overwhelmed by the coordinating and mass actions of the solvent.

The electronic spectra of the copper halide complexes show three bands similar to those of complexes having an elongated tetragonal coordination with $d_{x^2-y^2}$ ground state [13] while the perchlorate shows only two d–d bands but with frequencies very close to the corresponding bands of the halides.

The room temperature e.p.r. spectra of the powdered complexes do not exhibit any hyperfine structure. They show an isotropic spectrum with $\langle g \rangle = 2.10$ for the chloride characterized by one broad signal, an unresolved signal for the bromide and a look-alike axial type spectrum for the perchlorate complex with $g_{\parallel} = 2.112$ and $g_{\perp} = 2.06$ close to the values reported for some CuN_2S_2 chromophores ($g_{\parallel} = 2.160$–2.129 and $g_{\perp} = 2.020$–2.060) [14].

In the far IR spectra the new bands observed at 512–404 cm^{-1} may contain an important contribution or be tentatively assigned to ν(MN) modes. ν(MN) bands are reported for the hydrazine complexes of divalent ions of the transition series in the 473–339 cm^{-1} region [15] and for ligands involving azomethine nitrogen in the complexation at 495–430 cm^{-1} [9–11]. Also in the $H_2N{\cdot}Rd$ complexes of Zn(II), Cd(II) and Hg(II) ν(MN) bands were observed in the same region [16].

In agreement with the ν(MS) frequencies observed for the $H_2N{\cdot}Rd$ complexes of Zn(II), Cd(II), Hg(II) (356–304 cm^{-1}) [16] a ν(MS) mode for the Co(II), Ni(II) and Cu(II) complexes may tentatively be assigned to the mostly strong band at 329–296 cm^{-1}. For three complexes a second ν(MS) mode may be assigned to the band at 264–262 cm^{-1} which is distinct from the ligand band at 254 cm^{-1} observed in these complexes at 252–255 cm^{-1}.

A single ν(MX) band indicates a *trans* coordination for the cobalt and nickel halide complexes and two ν(MX) bands a *cis* coordination for the copper halide complexes. The ν_{Br}/ν_{Cl} ratios (0.74 for Co, 0.86 for Ni, 0.73 and 0.71 for Cu complexes) and ν_I/ν_{Cl} ratios (0.63 for Co and 0.65 for Ni complexes) have or are very close to the values accepted for complexes with similar coordination environments [17]. The ν(MX) frequencies for the cobalt and nickel complexes are as expected lower than those reported for tetrahedral complexes [15, 18] but higher than the $\nu(MX)_b$ frequencies in an octahedral environment [15, 19, 20]. Their rather low value is consistent with a weak character of the M–X bond. The higher ν(CuX) values are in agreement with the low molar conductivity of the copper halide complexes.

No rocking or wagging modes of coordinated water are observed for the $CoL_{2.5}Br_2H_2O$ complex [21].

For the perchlorate complexes the undistinct splitting of the ν_3, the very low intensity of the ν_1 and the absence of the ν_2 band of the ClO_4^- group allows to exclude a coordination of the ion in these complexes.

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References

1 C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem., 17,* 3470 (1978).
2 A. C. Fabretti and G. Peyronel, *Transition Met. Chem., 2,* 207 (1977).
3 A. C. Fabretti, G. C. Franchini and G. Peyronel, *Transition Met. Chem., 3,* 355 (1978).
4 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Interscience Publ., New York, 1972.
5 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam, 1968.
6 A. B. P. Lever, *J. Chem. Education, 45,* 711 (1968).
7 C. Preti and G. Tosi, *Aust. J. Chem., 32,* 989 (1979) and refs. cited therein.
8 J. C. Donini, B. R. Hollebone, G. London, A. B. P. Lever and J. C. Hempel, *Inorg. Chem., 14,* 455 (1975).
9 V. B. Rana, D. P. Singh, P. Singh and M. P. Teotia, *Transition Met. Chem., 6,* 36 (1981).
10 M. P. Teotia, I. Singh and V. B. Rana, *Transition Met. Chem., 6,* 60 (1981).
11 M. P. Teotia, J. N. Gurtu and V. B. Rana, *J. Inorg. Nucl. Chem., 42,* 821 (1980).
12 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).
13 B. J. Hathaway and A. A. Tomlinson, *Coord. Chem. Rev., 5,* 23 (1970).
14 Sungh-Nak Choi and J. R. Wasson, *Inorg. Chem., 14,* 1964 (1975).
15 J. R. Ferraro, 'Low-Frequency Vibrations of Inorganic and Coordination Compounds', Plenum Press, New York 1971.
16 A. C. Fabretti, G. C. Franchini and G. Peyronel, *J. Inorg. Nucl. Chem.,* in press.
17 A. M. Brodie and C. J. Wilkins, *Inorg. Chim. Acta, 8,* 13 (1974).
18 J. R. Allan, D. H. Brown and M. Lappin, *J. Inorg. Nucl. Chem., 32,* 2287 (1970).
19 E. J. Duff, M. N. Hughes and K. J. Rutt, *J. Chem. Soc. (A),* 2101 (1969).
20 J. R. Ferraro and K. C. Davies, *Inorg. Chim. Acta, 3,* 685 (1969).
21 K. Nakamoto, 'Infrared of Inorganic and Coordination Compounds', Wiley, New York, 1970.
22 B. Singh, Lakshmi and U. Agarwala, *Inorg. Chem., 8,* 2341 (1969).