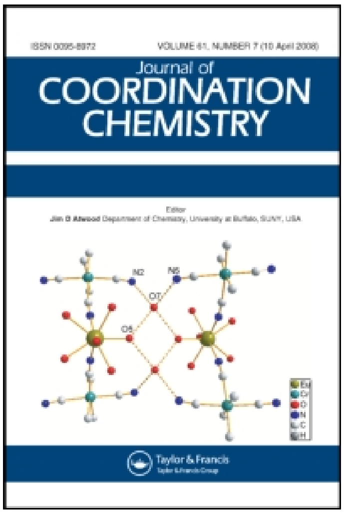

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE SYNTHESES AND PROPERTIES OF COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES WITH SOME 1,4-BENZODIAZEPINES

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To cite this Article Preti, Carlo and Tosi, Giuseppe(1976) 'THE SYNTHESES AND PROPERTIES OF COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES WITH SOME 1,4-BENZODIAZEPINES', Journal of Coordination Chemistry, 6: 2, 81 — 87

To link to this Article: DOI: 10.1080/00958977608079890

URL: http://dx.doi.org/10.1080/00958977608079890

J. Coord. Chem.
1976, vol. 6, pp. 81–87

THE SYNTHESES AND PROPERTIES OF COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES WITH SOME 1,4-BENZODIAZEPINES

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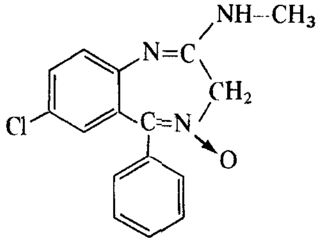
(Received March 17, 1976; in final form June 1, 1976)

The preparation and characterization of some cobalt(II), nickel(II) and copper(II) complexes with 7-chloro-2-methylamino-5-phenyl-3H-1,4-benzodiazepin-4-oxide and 1,3-dihydro-7-nitro-5-phenyl-2H-1,4-benzodiazepin-2-one are reported. The complexes have been studied by means of magnetic susceptibility measurements, infrared and far infrared spectra, electronic spectra and conductivity measurements. Assignments for the metal-ligand and metal-halide bands have also been made. The evidence suggests that the cobalt(II) and nickel(II) complexes have a pseudotetrahedral symmetry, whereas the copper(II) complexes are octahedral.

INTRODUCTION

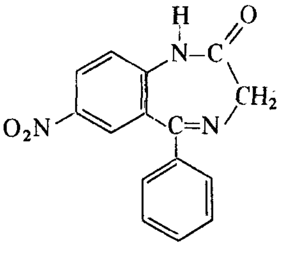
In recent years the complexes of cyclic diamines have been object of particular interest and have been extensively studied[1-8]. These complexes show very often uncommon geometries due to the steric hindrance of the cyclic ligands[9]. Some papers appeared recently dealing with the coordinating behaviour of 1,5-benzodiazepines[10-12]. Although the benzodiazepines have had considerable application in the pharmaceutical industry and in some cases have carcinostatic activity[13-15], relatively little is known of their behaviour towards metal ions in the coordination.

We now report the preparation and characterization of the cobalt(II), nickel(II) and copper(II) complexes with 7-chloro-2-methylamino-5-phenyl-3H-1,4-benzodiazepin-4-oxide



(Lib)

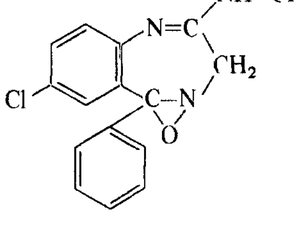
and 1,3-dihydro-7-nitro-5-phenyl-2H-1,4-benzodiazepin-2-one



(Mog)

These two ligands, commercially known as Librium and Mogadon, show strong pharmacological properties and the study of the stereochemistries and the chemical reactivity of their coordination compounds will help to determine what relationship exists between chemical structure and biological activity of these drugs. It is well known that the metal complexes of ligands which have biological activity are more active than the free ligands[16-17].

The ligand Lib on exposure to daylight undergoes a photoisomerization resulting in a rearrangement to a oxaziridine of the type:



which is quantitatively reconverted into nitrone form on heating or on treatment with an excess of 0.1N hydrochloric acid at room temperature. The ultraviolet absorption spectrum of a dilute isopropyl alcohol solution of the nitrone form shows two maxima at 245 and 265 nm, while the oxaziridine shows in its spectrum a single peak of lower intensity at 278 nm[18].

RESULTS AND DISCUSSION

According to the method reported in the experimental section we have obtained complexes of the type $[M_2lig_3X_4]$, M=Co,Ni; lig=Lib,Mog; X=Cl,Br,I and $[Culig_2X_2]$, lig=Lib,Mog; X=Cl,Br. The compounds have been studied by means of magnetic susceptibility measurements, electronic and infrared spectra and conductivity measurements in N,N′-dimethylformamide (DMF).

In Table I the coordination compounds obtained are reported together with analytical results, colours, melting points, and magnetic values. The principal features of the visible absorption spectra of this series of complexes are given in Tables II–IV. The most important infrared data are shown in Tables V and VI. The complexes are microcrystalline, soluble in DMF, methanol, ethanol and acetone, less soluble in non-polar solvents. These derivatives are nonelectrolytes, Λ lying in the range 32.9–53.0 $ohm^{-1}cm^2mole^{-1}$ in DMF; the Λ values, even for 1:1 electrolytes, are 70–90 $ohm^{-1}cm^2mole^{-1}$ in this solvent[19].

It is interesting to point out that all the bands typical of the ligands appear in the i.r. spectra of the complexes and the ligands can be recovered by chemical decomposition.

I.r., u.v. and visible spectroscopic, conductivity and magnetic data led us to believe that stereochemistries other than tetrahedral would be unlikely for the metal complexes when M = Co,Ni; the copper derivatives resulted exacoordinated.

Electronic Spectral and Magnetic Studies

The spectral data and the values chosen for the energies ν_2 and ν_3, from which the values of the parameters Dq, B′ and β have been derived, are presented in Tables II, III and IV. With the cobalt and nickel halides, complexes of essentially pseudotetrahedral geometry are formed; their magnetic moments and solid state electronic spectra are in accord with those expected for this stereochemistry.

The Dq values for the complexes suggest the order Cl > Br > I for the halides in the spectrochemical series and this order is consistent with the generally accepted sequence. The B′ values of the complexes here studied are of the order of 63–67% and 74–84% of the free ions values for the cobalt and nickel derivatives respectively (967 cm^{-1} for Co^{2+} and 1041 cm^{-1} for Ni^{2+}), suggesting that there is a considerable orbital overlap in the metal-ligand σ bond.

In the cobalt derivatives the bands in the range 14800–15400 cm^{-1} may be assigned as the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition, the second at 7300–

TABLE I
Analytical data and other physical properties

Compounds	Colour	Found %				Required %				μ	Dec.
		C	H	N	M	C	H	N	M	B.M.	point °C
$Co_2Lib_3Cl_4$	green	50.0	3.6	11.4	10.0	49.8	3.6	10.9	10.2	4.4	170–175
$Co_2Lib_3Br_4$	green	42.5	3.1	9.3	8.7	43.1	3.2	9.4	8.8	4.5	200–205
$Co_2Lib_3I_4$	dark green	38.6	2.7	8.2	7.7	37.8	2.8	8.3	7.7	4.5	165–170
$Ni_2Lib_3Cl_4$	brown	49.7	3.4	10.5	10.4	49.8	3.6	10.9	10.1	3.2	180–185
$Ni_2Lib_3Br_4$	brown	43.2	3.2	9.5	8.8	43.1	3.2	9.4	8.8	3.4	163–168
$Ni_2Lib_3I_4$	brown	38.0	2.8	8.2	7.8	37.8	2.8	8.3	7.7	3.4	170–175
$CuLib_2Cl_2$	brown	52.9	3.3	10.8	8.6	52.4	3.8	11.4	8.7	0.7	153–158
$CuLib_2Br_2$	brown	46.9	3.1	10.2	7.8	46.7	3.4	10.2	7.7	0.9	158–163
$Co_2Mog_3Cl_4 \cdot 2H_2O$	light green	47.6	3.2	11.3	9.8	47.4	3.3	11.1	10.3	4.3	178–184
$Co_2Mog_3Br_4$	light green	42.1	2.8	9.8	9.2	42.2	2.6	9.8	9.2	4.6	167–172
$Co_2Mog_3I_4$	dark brown	35.0	2.3	8.4	7.9	35.9	2.5	8.4	8.0	4.7	180–185
$Ni_2Mog_3Cl_4 \cdot 4H_2O$	green	46.4	3.6	10.7	10.0	46.0	3.5	10.7	9.9	3.2	218–225
$Ni_2Mog_3Br_4 \cdot 4H_2O$	grey-green	39.0	2.6	9.3	8.8	39.9	3.0	9.3	8.7	3.2	> 350
$Ni_2Mog_3I_4$	brown	37.0	2.1	9.3	8.0	36.8	2.3	8.6	8.0	3.3	180–185
$CuMog_2Cl_2$	brown	51.5	3.2	12.2	9.2	51.7	3.2	12.0	9.1	1.0	172–178
$CuMog_2Br_2$	dark brown	46.1	2.8	10.9	8.1	45.9	2.8	10.7	8.1	0.5	175–180

TABLE II
Solid state electronic spectra (cm^{-1})

Compounds	Absorption maxima
Lib	27030, 8160, 6600, 5700, 5100
$Co_2Lib_3Cl_4$	26670sh, 21275sh, 15950, 15430, 14860, 8235, 7635, 6610, 5820, 4970, 4600, 4290
$Co_2Lib_3Br_4$	21280sh, 15820, 15200, 14490, 8000, 7520, 6895, 5780, 5075, 4705, 4220
$Co_2Lib_3I_4$	22220sh, 15385, 15080, 14530, 8420, 7350, 6910, 5815, 5060, 4670, 4265
$Ni_2Lib_3Cl_4$	21550sh, 15270, 8200, 7920, 6565, 5815, 5180
$Ni_2Lib_3Br_4$	21275sh, 15040, 8600, 7880, 6780, 5950, 5260
$Ni_2Lib_3I_4$	21100sh, 14600, 8300, 7825, 6800, 5795, 5130,
$CuLib_2Cl_2$	21500sh, 15750, 13690sh, 8130, 6620, 5790, 5175
$CuLib_2Br_2$	21050sh, 14285, 11500sh, 8165sh, 6880, 5800, 5130, 4700, 4250
Mog	8060, 6550, 5660, 5050
$Co_2Mog_3Cl_4 \cdot 2H_2O$	21050sh, 16260, 15875, 15150, 7810, 7580, 6400, 5630, 5130, 4730, 4220, 4005
$Co_2Mog_3Br_4$	20920sh, 15975, 15150, 14600, 7750, 7530, 6360, 5585, 5130, 4700, 4165sh, 3985
$Co_2Mog_3I_4$	21050sh, 15315, 14815, 14325, 7710, 7490, 6340, 5495, 5115, 4710, 4145sh, 3960
$Ni_2Mog_3Cl_4 \cdot 4H_2O$	22220sh, 16260, 8510, 7810, 6755, 5770, 5065, 4705
$Ni_2Mog_3Br_4 \cdot 4H_2O$	21600sh, 16075, 8330, 7845, 6790, 5800, 5120, 4690
$Ni_2Mog_3I_4$	23200sh, 15975, 7935, 7700, 6870, 5795, 5075, 4705
$CuMog_2Cl_2$	21970sh, 15625, 13515sh, 7635, 6645, 5760, 5115, 4670, 4190
$CuMog_2Br_2$	21370sh, 15270, 13330sh, 7550, 6690, 5730, 5095, 4695, 4165

7700 cm^{-1} as the ${}^4A_2(F) \rightarrow {}^4T_1(F)$ transition. These bands passing from the chloro- to the iodo-derivative are shifted towards lower energies. The ν_3 transition is split because of the distorted tetrahedral structure of the complexes. We have calculated the ligand field parameters using only the ν_2 transition and the visually estimated frequencies of the centres of gravity of the split bands corresponding to ν_3 using the equations proposed by Underhill and Billing[20]. The assignments of ν_1 are made difficult by the presence of vibrational modes of the ligands in the range where these transitions should be expected. The calculated ν_1 wave numbers are reported in Table III.

A pseudotetrahedral stereochemistry has been assigned to the nickel derivatives on the basis of their electronic spectra[20-23]. The medium strong band in the range 14600–16200 cm^{-1} may be assigned to the ν_3 transition ${}^3T_1(F) \rightarrow {}^3T_1(P)$, while the band present at some 8000 cm^{-1} can be attributed to the ${}^3T_1(F) \rightarrow {}^3A_2(F)$ transition (ν_2). The values of Dq and B′ have been calculated using ν_3 and ν_2 only, the assignment of ν_1 being very often ambiguous because of the presence of vibrations due to the ligands in the region near 4000 cm^{-1}; the calculated ν_1 values are listed in Table IV. Comparison of the electronic spectra of our complexes with those of derivatives involving Ni–O bonds and Ni–N bonds suggests that these derivatives are N-bonded, as the band energies are at higher values than in O-bonded derivatives.

The magnetic susceptibility results, 4.3–4.7 B.M., of the cobalt derivatives confirm the presence of the metal tetrahedrally coordinated in high-spin complexes.

TABLE III
Electronic spectra and ligand field parameters (cm^{-1}) of cobalt(II) derivatives

Compounds	${}^4A_2(F) \rightarrow {}^4T_1(P)$ ν_3	${}^4A_2(F) \rightarrow {}^4T_1(F)$ ν_2	${}^4A_2(F) \rightarrow {}^4T_2(F)$ $\nu_1{}^a$	Dq	B′	β
$Co_2Lib_3Cl_4$	15385	7635	4490	449	637	0.66
$Co_2Lib_3Br_4$	14925	7520	4430	443	610	0.63
$Co_2Lib_3I_4$	14815	7350	4320	432	614	0.63
$Co_2Mog_3Cl_4 \cdot 2H_2O$	15505	7580	4450	445	649	0.67
$Co_2Mog_3Br_4$	15150	7530	4430	443	626	0.66
$Co_2Mog_3I_4$	14925	7490	4410	441	612	0.63

[a]calculated values
B is taken to be 967 cm^{-1} for the Co^{++} free ion.

TABLE IV
Electronic spectra and ligand field parameters (cm^{-1}) of nickel(II) derivatives

Compounds	${}^3T_1(F) \rightarrow {}^3T_1(P)$ ν_3	${}^3T_1(F) \rightarrow {}^3A_2(F)$ ν_2	${}^3T_1(F) \rightarrow {}^3T_2(F)$ $\nu_1{}^a$	Dq	B′	β
$Ni_2Lib_3Cl_4$	15270	7920	3630	429	820	0.78
$Ni_2Lib_3Br_4$	15040	7880	3610	427	768	0.74
$Ni_2Lib_3I_4$	14600	7825	3585	424	778	0.75
$Ni_2Mog_3Cl_4 \cdot 4H_2O$	16260	8510	3900	461	871	0.84
$Ni_2Mog_3Br_4 \cdot 4H_2O$	16075	8330	3830	450	861	0.83
$Ni_2Mog_3I_4$	15975	7935	3635	430	867	0.83

[a]calculated values
B is taken to be 1041 cm^{-1} for the Ni^{++} free ion.

The μ values of the nickel derivatives are as expected for nickel(II) high-spin pseudo-tetrahedral complexes.

On the basis of the solid state electronic spectra, Table II, we can assign an octahedral distorted symmetry to the copper(II) derivatives[24]; the band at 14285–15750 cm^{-1} accompanied by a shoulder at some 13000 cm^{-1} and a second band around 21000 cm^{-1} are in accord with this stereochemistry. The anomalously low effective magnetic moments observed for the copper complexes at room temperature indicate that there is a strong spin-spin interaction between two cupric ions. This could take place either by the formation of a σ or δ bond by the overlap of the two d-orbitals whereby spins of the electrons are paired up or by the formation of molecular orbitals by the extended overlap of copper and one of the two ligand donor orbitals. In quite a large number of copper(II) complexes having anomalous μ values, partial or complete quenching is explained by the superexchange mechanism. It is very difficult to decide without complete X-ray analyses whether spin-spin interaction takes place because of σ or δ bond formation or by superexchange mechanism.

Infrared Spectral Studies

The spectra of the ligands Lib and Mog in the solid state and in chloroform solution show a noticeable difference in the position of ν(NH) stretching frequency, clearly indicating the presence of inter- or intra-molecular hydrogen bonding. The ν(NH) in the complexes is shifted towards lower wave numbers by about 280 cm^{-1} in the Lib-derivatives and by about 210 cm^{-1} in the Mog-derivatives using as reference the value of ν(NH) for the free ligands in chloroform solution. The extensive hydrogen bonding disappears after dissolution in chloroform and after complexation.

According to Singh and Rivest[25] a sharp NH band in the metal derivatives is indicative of absence of hydrogen bonding and a comparison of these values with the ν(NH) solution frequency of the ligand could be used to suggest a coordination through the nitrogen atom. In our complexes sharp bands are present in the range 3220–3160 cm^{-1} and 3210–3150 cm^{-1} for the derivatives of Lib and Mog respectively and a comparison with the ν(NH) value of the free ligands in chloroform solution would indicate a M–N coordination.

The exact assignments of the other peaks are not easy, as the vibrations of the ligands conjugate with each other and they can be separated into group vibrations only with difficulty. However, the band at 1630 cm^{-1} in the free ligand Lib chloroform solution, Table V, attributed to the prevailing contribution of ν(C=N)[26,27] is split towards lower and higher energies in the complexes. The medium strong band at 1285 cm^{-1} can be attributed to the N→O stretching[28,29] and appears unchanged at the same wave number in the spectra of the complexes.

As for the derivatives of Mog, Table VI, the band of the free ligand at 1620 cm^{-1}, due to the ν(C=N), shows in the complexes red shifts, while the vibrational mode due to the ν(C=O) appears at the same value as in the free ligand or shows very small positive shifts.

The spectra of the complexes of Lib show the band characteristic of the grouping Ph–Cl at the same wave number, 1090 cm^{-1}, as in the free ligand; similarly the spectra of the Mog-derivatives show the bands due to the symmetric and antisymmetric stretching modes of the nitro-group unchanged after coordination at 1340–1350 cm^{-1} and at 1530–1540 cm^{-1} [30].

The medium absorption bands present in the range 3440–3470 cm^{-1}, ν(OH) and at 1630–1640 cm^{-1}, δ(HOH) in all the water containing complexes, Table I, clearly confirm the presence of water of crystal-

TABLE V
Infrared absorption bands of Lib derivatives (cm^{-1})

Compounds	ν(NH)	ν(C=N)	ν(N→O)	ν(M–X)	ν(M–L)	Other bands
Lib solid	3210s	1625vs	1285ms	–	–	430vs, 395m, 376m, 352m, 317m, 296m, 258ms, 236s, 211w, 206w
Lib $CHCl_3$ sol.	3480s	1630vs	–	–	–	
$Co_2Lib_3Cl_4$	3160s	1675ms, 1615vs	1280ms	330m, 300m	251ms, 223ms	428ms, 390m, 372m, 346m, 318m, 295m, 260m, 235s, 211w, 207w
$Co_2Lib_3Br_4$	3200s	1680ms, 1620vs	1290ms	265m, 230mw	252m, 221m	436s, 394m, 374m, 346m, 317m, 296m, 260m, 236ms, 211w, 206w
$Co_2Lib_3I_4$	3205s	1660m, 1620vs	1288m	215m	248ms, 222m	435ms, 400m, 377m, 344m, 315m, 293m, 258m, 233s, 212w, 205w
$Ni_2Lib_3Cl_4$	3200s	1660ms, 1610vs	1285m	333m, 312m	250ms, 218m	430ms, 392m, 377mw, 347mw, 318m, 295m, 259ms, 235ms, 212w, 206w
$Ni_2Lib_3Br_4$	3210s	1680vs, 1620vs	1290m	262mw	249ms, 219m	431ms, 393m, 379mw, 345m, 317m, 296m, 258m, 233s, 210w, 204w
$Ni_2Lib_3I_4$	3200s	1675ms, 1620vs	1290m	206s	250ms, 219ms	429ms, 393m, 379mw, 345m, 317m, 295m, 260ms, 235s, 211w, 204w
$CuLib_2Cl_2$	3210m	1660s, 1610vs	1285m	306m, 276m	311m	434ms, 392m, 371m, 357m, 318mw, 293m, 250ms, 234s, 212w, 206w
$CuLib_2Br_2$	3220m	1665vs, 1615vs	1290m	258m	312m	430ms, 391m, 373m, 360m, 318mw, 294m, 250ms, 233s, 211w, 206w

lization; the vibrational modes of the coordinated water, such as wagging, twisting and rocking, have not been found in the expected ranges[31]. Furthermore this water is lost near 95–100°C, while coordinated water is lost near 150–160°C.

Some strong bands are present in the spectra of the metal derivatives in the range 400–200 cm^{-1}, Tables V and VI, that may be attributed to metal-halogen stretching modes, for terminal halides in pseudotetrahedral cobalt(II) and nickel(II) complexes and distorted octahedral copper(II) complexes[32-34]. We have never observed the vibrational modes typical of ν(M–X) for bridging halides nor the wave numbers of the ν(M–X) bands similar to the values observed in the spectra of other halogenometallates[33-37].

New halogen independent bands are present in the ranges expected for ν(Co–N), ν(Ni–N), and ν(Cu–N) respectively, Tables V and VI, in very good agreement with the literature data[33-35]. No bands are present in the range where ν(M–O) usually lies for these metals.

These far i.r. results are in accord with the observed behaviour of the vibrational modes ν(C=N), ν(N→O) and ν(C=O) of the ligands in the 4000–1000 cm^{-1} region.

TABLE VI
Infrared absorption bands of Mog derivatives (cm^{-1})

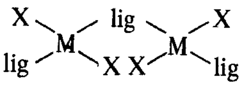
Compounds	ν(NH)	ν(C=O)	ν(C=N)	ν(M–X)	ν(M–L)	Other bands
Mog solid	3190s	1695vs	1615vs	–	–	442ms, 413m, 386s, 318s, 213w, 206w
Mog $CHCl_3$ sol.	3400s	1700vs	1620vs	–	–	
$Co_2Mog_3Cl_4 \cdot 2H_2O$	3200s	1695vs	1610vs	329m, 306ms	267m, 216ms	430m, 414m, 387ms, 315ms, 210w, 204w
$Co_2Mog_3Br_4$	3150s	1700vs	1610vs	249m, 235s	266m, 222s	430m, 412m, 378ms, 318m, 213w, 207w
$Co_2Mog_3I_4$	3200s	1690vs	1615vs	221m	268ms, 218ms	413m, 381m, 310s, 212w, 204w
$Ni_2Mog_3Cl_4 \cdot 4H_2O$	3190s	1695vs	1615vs	301m, 282ms	263s, 219m	440m, 413m, 385s, 316s, 211w, 207w
$Ni_2Mog_3Br_4 \cdot 4H_2O$	3210s	1700vs	1615vs	253m	262s, 219ms	410m, 384m, 316s, 212w, 208w
$Ni_2Mog_3I_4$	3205s	1695vs	1615vs	200m	262s, 218s	416m, 390ms, 318ms, 212w, 209w
$CuMog_2Cl_2$	3170ms	1695vs	1617vs	306s	327ms	438ms, 411m, 385s, 315s, 211w, 205w
$CuMog_2Br_2$	3200ms	1700vs	1615vs	256m	329ms	440ms, 412m, 390ms, 316s, 211w, 204w

CONCLUSIONS

The complexes obtained were always of the type $M_2lig_3X_4$ even working with a metal:ligand ratio over 1:1.5; all these derivatives resulted non conducting in DMF. This fact allows us to exclude the possibility of a mixture of two (or more) types of complexes (e.g. $ColigX_2$ + $Co(lig)_2^{2+}$ + $2X^-$); a mixture of the type $ColigX_2$ + $Colig_2X_2$ must be ruled out because repeated syntheses and repeated elemental analyses gave reproducible results. The presence of binuclear complexes in which the two metal ions would be of necessity in slightly different ligand environments can be excluded because in the solid state electronic spectra bands typical of geometries other than tetrahedral are nor present, Table II. Thus the observed spectrum, for each metal complex, is certainly not two or more superimposed metal complex spectra.

Unfortunately no good results have been obtained neither from vapour phase osmometric molecular weight determinations, nor from the electronic spectra in methanol, ethanol or DMF; these measurements require a time longer than that of conductivity measurements. It is clear that dissociative and solvolytic problems, which could seriously interfere, can not be discounted. Therefore we can propose stereochemistries based upon the reported data only.

The tetrahedral complexes could be dimeric of the type:



M = Co, Ni

while the copper derivatives attain an octahedral geometry in polymeric materials having bridging ligands and terminal halides.

EXPERIMENTAL

The ligands Lib and Mog, kindly supplied by Roche, were in high purity grade and have been used without further purification.

Preparation of the Complexes

The complexes were all prepared by reaction of the appropriate metal(II) salt with a small excess of the molten ligands, preliminary studies having shown that in each case only a single product was formed, regardless of the presence of excess ligand. The compounds have been purified by means of repeated washing with chloroform. We have obtained complexes only in the metal:ligand ratios reported in Table I. Repeated syntheses and elemental analyses gave reproducible results; the recrystallization of the products has not been successful working in methanol, ethanol and N,N′-dimethylformamide.

Infrared Spectra

The i.r spectra have been recorded in the range 4000–200 cm^{-1} with Perkin–Elmer 457 and 225 spectrophotometers as KBr discs or nujol mulls between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing dry nitrogen.

Electronic Spectra

The solid state electronic spectra have been recorded in nujol mulls with a Shimadzu MPS-50L spectrophotometer in the range 3800–35000 cm^{-1}.

Magnetic Susceptibility Measurements

These measurements were carried out by use of Gouy's method. The molecular susceptibilities were corrected for the diamagnetism of the component atoms by use of the Pascal's constants.

Conductivity Measurements

These measurements were carried out with a WTW LBR type conductivity bridge for freshly prepared 10^{-3} M solutions in N,N′-dimethylformamide at 25°C.

ACKNOWLEDGEMENTS

We thank Dr. F. Giusti for his experimental work, Mr. G. Pistoni for elemental analyses, Roche of Milano for the supply of the ligands and the National Research Council (C.N.R.) of Italy for financial support.

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