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Cobalt(II), Nickel(II) and Copper(II) Complexes of 1.5-Benzodiazepines: Synthesis, Spectral and Magnetochemical Studies

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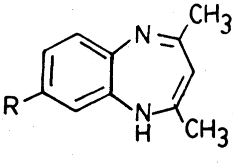
Complexes of benzodiazepines of the 1 : 2 stoichiometry of the type ML_2Cl_2 [where M = Co(II), Ni(II) or Cu(II) and L = 7-substituted-2, 4-dimethyl-6,7-benz-1,5-diazepines (I–IV)] have been synthesised and characterised by molar conductance, magnetic moments, infrared, electronic and X-ray studies. The infrared spectral data support the involvement of both nitrogen atoms in the complex formation. All the observations favour tetrahedral configuration for cobalt(II), nickel(II) and square planar configuration for copper(II).

INTRODUCTION

Cyclic diamines are known to possess a wide spectrum of pharmacological activity[1]. Amongst them diazepines have attracted much attention because of their invaluable therapeutic applications[2]. 1,4-Benzodiazepines appear to have anticonvulsant, muscle relaxant, hypnotic activities below toxic levels[3]. Though there are reports[4–8] on 1,4-benzodiazepines and their metal complexes both in solid and in solution phase, there appears to be very little information on 1,5-benzodiazepines and their interaction with metal ions.

Continuing our probe[9,10] on 1,5-benzodiazepines and their metal complexes, we now report cobalt(II), nickel(II) and copper(II) complexes of 2,4-dimethyl-6,7-benz-1,5-diazepines(I–IV).



I H, II CH_3, III Cl, IV NO_2

EXPERIMENTAL

Substituted *o*-phenylenediamines required for the synthesis were BDH reagents; acetylacetone was a laboratory grade reagent and was used as such without further purification. Cobalt(II), nickel(II) and copper(II) chlorides were AR grade BDH reagents. Absolute ethanol required for the synthesis was purified according to the standard procedure[11]. The

2,4-dimethyl-6,7-benz-1,5-diazepines were synthesised as per the method reported in the literature.[12]

General Method for the Synthesis of the Complexes

To a solution of 0.01 mol of the ligand in about 25–30 ml of absolute alcohol was added 0.005 mol of metal(II) chloride in about 25 ml of alcohol with constant stirring. The reaction mixture was further stirred for another ½ hr and allowed to stand overnight. Separated complexes were filtered, washed successively with 5 ml portions of dry alcohol and dry ether and dried in vacuo over fused calcium chloride. The dried samples were powdered and purified by Soxhlet extraction with dry alcohol.

RESULTS AND DISCUSSION

Cobalt(II), nickel(II) and copper(II) complexes are blue, brown and greenish in colour respectively. These are soluble in water, DMF, DMSO and are insoluble in benzene, nitrobenzene, chloroform and carbon tetrachloride. The analytical, magnetic susceptibility data are detailed in Table 1. The analytical data suggest that these complexes have 1 : 2 stoichiometry of the type ML_2Cl_2. The molar conductance values of the complexes in water at the concentration 10^{-3} M fall in the range of 160–190 ohm^{-1} cm^2 mol^{-1}; thus these complexes show 1 : 1 electrolytic behaviour in water.

Important infrared bands along with their assignments are listed in Table 2.

A broad band of medium intensity around 3350 cm^{-1} is assigned to the ν(NH) vibrations in view of previous assignments[13–16]. The band in the region around 1660 cm^{-1} is regarded as due to ethylenic ν(C=C). A medium intensity band appearing around 1630 cm^{-1} is regarded as due to the ν(C=N) vibrations[13–16]. On complexation we observe the ν(NH) band appears in the region 3300–3100 cm^{-1} as a medium intensity split band. The band due to ν(C=N) shifts and appears in the region 1610–1600 cm^{-1} indicating the involvement of both NH and C=N in the complex formation. The band due to ν(C=C) appears around 1640 cm^{-1} as a medium intensity band. In addition to these we have noticed medium intensity bands in the 480–450 cm^{-1} and 380–350 cm^{-1} regions attributable to the ν(M–N) vibrations[13–16]. Appearance of medium intensity bands in the 300–200 cm^{-1} region may be regarded as due to the ν(M–Cl) vibrations in view of the previous literature[13–16].

Electronic spectra of the complexes have been studied in donor solvents such as DMF, DMSO and pyridine. Cobalt(II) complexes exhibit high intensity multicomponent bands in the region 16129–14705 cm^{-1}, characteristic of cobalt(II) complexes having tetrahedral configuration and is

TABLE 1

ANALYTICAL, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRAL DATA OF THE COMPLEXES

Sl. No.	Empirical formulae	% Found (Calc.)			Magnetic Suscept. B.M.	Molar Extn. Coefficient	
		N	Cl	M		λ	ε
1.	$(I)_2CuCl_2$ $(C_{11}H_{12}N_2)_2CuCl_2$	11.5 (11.7)	14.7 (14.8)	13.5 (13.3)	2.21	19230	1990
2.	$(II)_2CuCl_2$ $(C_{12}H_{14}N_2)_2CuCl_2$	10.0 (10.1)	14.1 (14.0)	12.2 (12.5)	2.06	19048	1890
3.	$(III)_2CuCl_2$ $(C_{11}H_{11}N_2Cl)_2CuCl_2$	10.4 (10.2)	26.1 (25.9)	11.5 (11.5)	2.14	18867	1790
4.	$(IV)_2CuCl_2$ $(C_{11}H_{11}N_3O_2)_2CuCl_2$	15.0 (14.8)	12.4 (12.5)	10.0 (10.2)	1.77	19230	1880
5.	$(I)_2CoCl_2$ $(C_{11}H_{12}N_2)_2CoCl_2$	11.6 (11.8)	15.2 (15.0)	12.3 (12.4)	4.24	16393 14705	490 640
6.	$(II)_2CoCl_2$ $(C_{12}H_{14}N_2)_2CoCl_2$	11.4 (11.2)	14.3 (14.1)	11.9 (11.7)	3.96	16660 14705	500 700
7.	$(III)_2CoCl_2$ $(C_{11}H_{11}N_2Cl)_2CoCl_2$	10.2 (10.3)	26.3 (26.2)	10.8 (10.8)	4.32	16393 14492	500 750
8.	$(IV)_2CoCl_2$ $(C_{11}H_{11}N_3O_2)_2CoCl_2$	15.0 (14.9)	12.9 (12.6)	10.6 (10.4)	3.77	17000 14705	510 640
9.	$(I)_2NiCl_2$ $(C_{11}H_{12}N_2)_2NiCl_2$	12.0 (11.8)	15.1 (15.0)	12.4 (12.4)	3.91	21739	750
10.	$(II_2)NiCl_2$ $(C_{12}H_{14}N_2)_2NiCl_2$	11.2 (11.2)	14.3 (14.2)	11.6 (11.7)	3.98	21739	720
11.	$(II)_2NiCl_2$ $(C_{11}H_{11}N_2Cl)_2NiCl_2$	10.3 (10.2)	26.5 (26.2)	10.7 (10.8)	3.76	22727	740
12.	$(IV)_2NiCl_2$ $(C_{11}H_{11}N_3O_2)_2NiCl_2$	15.1 (14.9)	12.8 12.6)	10.6 (10.4)	4.08	22727	760

attributed to $4A_2 \rightarrow 4T_1(P)$ transition.[17]. Hence, cobalt(II) complexes may have tetrahedral configuration. Nickel(II) complexes display two bands of high intensity in the region 16393–14705 cm^{-1}. It is documented in the literature[17] that tetrahedral nickel(II) complexes show high intensity bands in the region 16129–13889 cm^{-1} and these are attributed to $3T_1(F) \rightarrow 3T_1(P)$ transition. Copper(II) complexes exhibit broad band maxima around 18000 cm^{-1} due to d–d transitions. This agrees very well with the well characterised square-planar complexes of copper(II). In nujol spectra, this band appears around 19230 cm^{-1}. Thus it is obvious

TABLE 2

IMPORTANT INFRARED FREQUENCIES (cm^{-1}) OF THE LIGANDS, FEW REPRESENTATIVE COMPLEXES AND THEIR ASSIGNMENTS

Ligands/ complexes	ν(NH)	ν(C=C)	ν(C=N)	ν(C=C) aromatic	ν(M–N)	ν(M–Cl)
Ligands						
I	3500br 3350br	1650s	1630m	1570m 1540sh 1520s	—	—
II	3500br 3400br	1660m	1640m	1580m 1540sh 1520s	—	—
III	3500br 3400br	1660s	1640m	1570m 1520s	—	—
IV	3400br	1660m	1620m	1580m 1560w 1520s	—	—
Complexes						
$\mathrm{I_2CoCl_2}$	3300br	1630s	1600s	1580sh 1550w 1525sh 1510s	540w 500w 470s 410sh	280sh 260s
$\mathrm{II_2CoCl_2}$	3350br 3150w	1650s	1610s	1590s 1585sh 1530s	410sh 300sh	290s 270s
$\mathrm{I_2NiCl_2}$	3350br 3150w	1650s	1610s	1580sh 1560w 1540w 1520s	590w 510s 390w 375s 340sh	290s 270s
$\mathrm{III_2NiCl_2}$	3350br 3150w	1650s	1610s	1580sh 1560w 1540w 1520s	590w 510s 390w 375s 340sh	290s 270s
$\mathrm{I_2CuCl_2}$	3300s 3250s	1640br	1620s	1580s 1560w 1540w 1510sh	540s 500w 470w 300sh	280s 270s
$\mathrm{II_2CuCl_2}$	3300s 3250s	1640br	1620s	1580s 1560w 1540w 1510sh	540s 500w 470w 300sh	280s 270s

that in donor solvents copper(II) complexes have undergone axial addition. This offers an additional proof for copper(II) being square-planar.

All the cobalt(II) complexes show the magnetic moments in the range 3.77–4.32 B. M. It is documented in the literature[18] that tetrahedral cobalt(II) complexes display magnetic moments in the range of 3.80–4.77 B.M. Hence, it may be concluded that cobalt(II) has tetrahedral configuration in these complexes. Nickel(II) complexes exhibit magnetic moments in the range 3.76–3.98 B.M. These values very well reconcile with the magnetic moments for tetrahedral nickel(II) complexes[18,19], *viz.*, 3.5–4.2 B. M. Hence, in these complexes nickel(II) has tetrahedral configuration. The magnetic moments obtained for copper(II) complexes fall in the range 1.77–2.21 B. M. typical of spin only value for one unpaired electron. The data suggest that the complexes are devoid of spin-spin interaction. However, one cannot set a compromise between the magnetic moments and geometry in the case of copper(II). However, in view of the electronic spectra it may be concluded that these may have square-planar configuration.

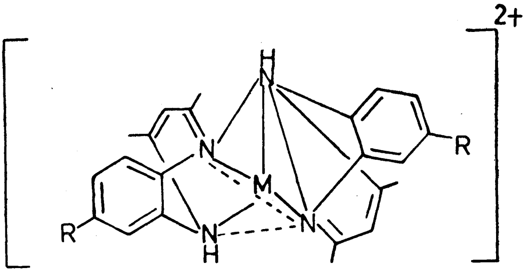
X-ray powder patterns for a few typical complexes reveal that they are in cubic crystal structure. The $\sin^2 \theta$ and a^2 values are presented in Table. 3.

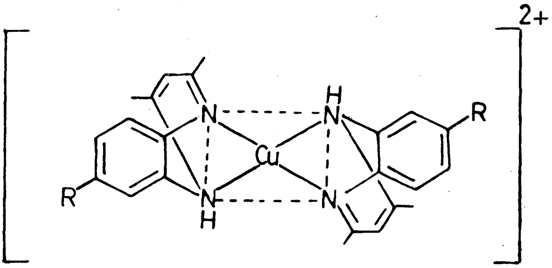
TABLE 3

X-RAY DIFFRACTION DATA OF FEW COMPLEXES

Complex	d	$\sin^2 \theta$	N	hkl	a
I_2CoCl_2	9.4511	0.0815	6	211	23.15
	8.0956	0.0950	8	220	22.90
	6.2983	0.1223	13	320	22.71
	5.4007	0.1426	18	411, 330	22.91
	4.0407	0.1906	32	440	22.85
II_2CuCl_2	9.7536	0.0789	6	211	23.90
	8.5114	0.0905	8	220	24.07
	7.9540	0.0968	9	300, 221	23.86
	6.1823	0.1245	16	400	24.72
	5.5160	0.1396	19	331	24.04

All these informations suggest the following structures for these complexes:





M = Co(II) or Ni(II)

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