

Synthesis and characterization of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II) complexes with 1,8-dibenzoyl-2,7-diphenyl-3,6-diazaoctane and 1,9-dibenzoyl-2,8-diphenyl-3,7-diazanonane

B B Mahapatra* & A K Behera

P G Department of Chemistry, G M College, Sambalpur

Received 24 March 1995; revised 13 June 1995;
accepted 14 August 1995

A few complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been synthesized and characterised by analytical, magnetic susceptibility, conductance, IR, electronic, ESR spectra and X-ray powder diffraction data. It is observed that both the ligands, 1,8-dibenzoyl-2,7-diphenyl-3,6-diazaoctane and 1,9-dibenzoyl-2,8-diphenyl-3,7-diazanonane, behave as ONNO tetradentate donors.

Chalkones have been found to possess immense pharmacological properties^{1,2}. There seems to be no work reported on the metal complexes using the tetradentate ligands obtained from the Michael type of addition reactions of chalkones with diamines. So, it was thought worthwhile to prepare ONNO donor ligands and their complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions.

Experimental

Acetophenone, benzaldehyde, 1,2-diaminoethane, 1,3-diaminopropane, sodium hydroxide, potassium carbonate, diethylether, perchloric acid used were of BDH or E Merck grade. Ethanol and metal salts were reagent grade chemicals. Benzalacetophenone was prepared according to the literature procedure³.

Preparation of 1,8-dibenzoyl-2,7-diphenyl-3,6-diazaoctane (L) and 1,9-dibenzoyl-2,8-diphenyl-3,7-diazanonane (L¹)

A mixture of benzilideneacetophenone (0.2 mol) and 1,2-diaminoethane or 1,3-diaminopropane (0.1 mol) in cyclohexane-ether (50 ml) was refluxed for 6 h in the presence of K_2CO_3 (4 mg) K_2CO_3 . The mixture was then cooled, filtered and kept in refrigerator [Found: C, 80.5, H, 6.6; N,

5.7; Reqd. for $\text{C}_{32}\text{H}_{32}\text{O}_2\text{N}_2$ (L), C, 80.67; H, 6.72; N, 5.88%]; [Found: C, 80.7; H, 6.8; N, 5.5; Reqd. for $\text{C}_{33}\text{H}_{34}\text{O}_2\text{N}_2$ (L¹); C, 80.81; H, 6.93; N, 5.71%].

Preparation of the complexes

The metal complexes were prepared by refluxing ethanolic solution of metal salts with the ligands (L & L¹) over a heating mantle for 2 h. Some metal complexes separated out immediately during reflux and some separated after keeping in a refrigerator for 24-36 h. They were then filtered, washed with ethanol following by ether and dried *in vacuo*.

The elemental analyses were determined by standard procedures. Conductance was measured by conductivity bridge in $10^{-3}M$ DMF solution of the complexes. Magnetic susceptibility measurements of the solid samples were carried out at room temperature by Gouy method. IR spectra (KBr) were recorded on a Perkin-Elmer 398 and Bruker TFS 66V FT-IR spectrophotometers, electronic spectra ($10^{-2}M$ DMF) on a Hilger and Watt Uvispeck spectrophotometer and ESR on an E-4 ESR spectrometer at room temperature. XRD of the complex $(\text{NiL}^1(\text{SCN})_2]$ was recorded in PW 1130/100 model X-ray diffractometer, M/s Phillips, Holland.

Results and discussion

Based upon the analytical and conductance data, the complexes have the composition $[\text{ML}/\text{L}^1\text{X}_2]$; [where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II); L = 1,8-dibenzoyl-2,7-diphenyl-3,6-diazaoctane, L¹ = 1,9-dibenzoyl-2,8-diphenyl-3,7-diazanonane; X = Cl^- , Br^- , SCN^- , NO_3^- , ClO_4^-]. All the twenty six complexes are found to be non-electrolytic in nature (Table 1).

In the IR spectra of the complexes, the bands appearing at 1620 and 3150 cm^{-1} can be ascribed to $\nu(\text{C}=\text{O})$ and $\nu(\text{NH})$ vibrations respectively indicating the bonding of both the ligands to the metal ions through the carbonyl oxygen and secondary amino nitrogen atoms. Furthermore, the coordination of oxygen and nitrogen atoms of the ligands to the metal ions is confirmed by the observation of $\nu_{(\text{M}-\text{O})}$ and $\nu_{(\text{M}-\text{N})}$ at ~ 525 and ~ 325 cm^{-1} respectively^{4,5}.

It is observed that for M-NCS bonding, ν_{CN} and ν_{CS} appear to fall in the range 2080-2040

Table 1—Characterization data of the complexes

Compound Colour	Found (Calcd.), %				Λ_M $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	μ_{eff} B.M.
	M	C	H	N		
L Yellow	— (9.72)	80.5 (80.67)	6.6 (6.72)	5.7 (5.88)	—	—
L' Yellow	— (9.62)	80.7 (80.81)	6.8 (6.93)	5.5 (5.71)	—	—
[CoL'Cl ₂] Brown	9.4 (9.72)	63.1 (63.38)	5.2 (5.28)	4.6 (4.62)	5.3	5.05
[CoL'Cl ₂] Reddish brown	9.3 (9.50)	63.6 (63.88)	5.5 (5.48)	5.4 (5.52)	6.1	5.00
[NiLCl ₂] Violet	9.6 (9.62)	63.2 (63.40)	5.1 (5.28)	4.4 (4.62)	5.8	2.95
[NiL'Cl ₂] Violet	9.2 (9.47)	63.8 (63.90)	5.4 (5.49)	4.4 (4.52)	5.5	3.02
[CuLCl ₂] Light green	10.3 (10.40)	62.7 (62.90)	5.1 (5.24)	4.5 (4.59)	4.9	1.80
[CuL'Cl ₂] Blue	9.9 (10.17)	63.3 (63.41)	5.5 (5.44)	4.3 (4.48)	4.6	1.82
[ZnLCl ₂] White	10.5 (10.67)	62.5 (62.70)	5.0 (5.22)	4.3 (4.57)	5.7	—
[CdLCl ₂] Yellow	17.0 (17.04)	58.2 (58.23)	4.7 (4.85)	4.0 (4.24)	4.5	—
[HgLCl ₂] Yellow	26.5 (26.82)	51.3 (51.37)	4.1 (4.28)	3.4 (3.74)	6.8	—
[CoLBr ₂] Pink	8.2 (8.47)	55.2 (55.25)	4.5 (4.60)	3.8 (4.02)	7.1	5.08
[CoL'Br ₂] Pink	8.2 (8.31)	55.6 (55.85)	4.6 (4.79)	3.6 (3.94)	4.9	4.95
[ZnLBr ₂] Yellow	9.1 (9.32)	54.6 (54.74)	4.4 (4.56)	3.7 (3.99)	7.3	—
[CoL(NO ₃) ₂] Brown	8.8 (8.94)	58.2 (58.27)	4.7 (4.86)	8.3 (8.49)	4.7	4.98
[CoL'(NO ₃) ₂] Pink	8.6 (8.75)	58.5 (58.85)	4.9 (5.05)	8.2 (8.32)	6.3	5.02
[NiL(NO ₃) ₂] Green	8.7 (8.91)	58.2 (58.30)	4.6 (4.86)	8.3 (8.50)	5.4	3.00
[CuL(NO ₃) ₂] Green	9.3 (9.57)	57.6 (57.87)	4.7 (4.82)	8.2 (8.44)	5.1	1.85
[CdL(NO ₃) ₂] Yellow	15.6 (15.77)	53.8 (53.90)	4.5 (4.49)	7.8 (7.86)	4.6	—
[CoL(ClO ₄) ₂] Pink	7.8 (8.02)	52.1 (52.32)	4.1 (4.36)	3.7 (3.81)	5.5	5.06

Contd.

Table 1—Characterization data of the complexes—Contd

Compound Colour	Found (Calcd.), %				Λ_M $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	μ_{eff} B.M.
	M	C	H	N		
[NiL(ClO ₄) ₂] Reddish	7.8 (8.00)	52.2 (52.33)	4.2 (4.36)	3.7 (3.81)	6.8	2.92
[CuL(ClO ₄) ₂] Green	8.3 (8.59)	51.8 (51.99)	4.3 (4.33)	3.6 (3.79)	5.7	1.79
[CoL(SCN) ₂] Brown	8.8 (9.05)	62.5 (62.67)	4.8 (4.92)	8.4 (8.60)	6.2	5.04
[CoL'(SCN) ₂] Brown	8.6 (8.86)	62.9 (63.16)	5.0 (5.11)	8.2 (8.42)	6.5	4.96
[NiL(SCN) ₂] Violet	8.8 (9.02)	62.6 (62.70)	4.8 (4.92)	8.4 (8.60)	5.1	2.98
[NiL'(SCN) ₂] Blue	8.6 (8.83)	62.8 (63.18)	4.8 (5.12)	8.3 (8.42)	5.4	3.08
[CuL(SCN) ₂] Green	9.5 (9.69)	62.0 (62.24)	4.7 (4.88)	8.3 (8.54)	4.7	1.81
[CuL'(SCN) ₂] Brown	9.3 (9.48)	62.6 (62.73)	4.9 (5.08)	8.2 (8.36)	5.2	1.83

L = 1,8-dibenzoyl-2,7-diphenyl-3,6-diazaoctane; L' = 1,9-dibenzoyl-2,8-diphenyl-3,7-diazanonane

cm^{-1} and $860\text{--}780 \text{ cm}^{-1}$ respectively and for M-SCN bonding, the corresponding bands are observed at $2120\text{--}2080$ and $720\text{--}680 \text{ cm}^{-1}$. In case of cobalt, nickel and copper complexes the ν_{CN} and ν_{CS} appear at 2050 and 820 cm^{-1} respectively suggesting the M-NCS type of bonding of the thiocyanate group⁶.

In nitrate complexes under study, strong bands are observed at 1400 and 1275 cm^{-1} and the difference $\Delta\nu$ of 125 cm^{-1} suggest unidentate coordination of nitrate groups⁷⁻⁹. In the cobalt, nickel and copper perchlorate complexes under investigation, the three absorption bands at ~ 1100 , ~ 1080 and $\sim 980 \text{ cm}^{-1}$, strongly support monodentate coordination of perchlorate group^{10,11}.

In the electronic spectra of cobalt(II) complexes, the absorption bands, at $\sim 8465(10)$, $\sim 18,490(21)$ and $\sim 21,120(35) \text{ cm}^{-1}$ have been attributed to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $\rightarrow {}^4A_{2g}(F)$ and $\rightarrow {}^4T_{1g}(P)$ transitions respectively in conformity with an octahedral configuration^{12,13}. This is supported by high μ_{eff} values as well¹¹. All the copper (II) complexes show a broad band at $\sim 13,700\text{--}14,350 \text{ cm}^{-1}$ due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition indicating a distorted-octahedral stereochemistry of the complexes¹⁴. The electronic spectra of the nickel complexes show bands at $\sim 8950(6.0)$, $\sim 18,250(9.4)$, $\sim 26,450(17.0)$ and $\sim 28,350 \text{ cm}^{-1}$ assignable to

Table 2—X-ray diffraction data of the complex [NiL'(SCN)₂]

2 θ	Unit cell dimensions in Å	Cell volume Å ³	Probable geometry
3.74638	a = 6.52 ± 0.008	125.601 \pm 0.456	Monoclinic
3.52712	b = 4.65 ± 0.005		
3.15981	c = 4.27 ± 0.014		
2.54689	$\alpha = 89.77 \pm 0.251$		
2.32390	$\beta = 90.33$		
2.18856	$\gamma = 90.00 \pm 0.001$		
2.04690			
1.88614			
1.55955			

${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $\rightarrow {}^3T_{1g}(F)$, $\rightarrow {}^3T_{1g}(P)$ and CT transitions respectively in tetragonally distorted octahedral field. The high μ_{eff} values of the complexes support this stereochemistry^{15,16}.

The ESR spectrum of the complex [CuL(SCN)₂] was recorded at X-band at room temperature. The 'g' values of the complex $g_1 = 2.0555$, $g_2 = 2.1035$ and $g_3 = 2.1754$ and its spectrum indicate that the symmetry around copper(II) is axial (two values tensor) i.e. the symmetry is tetragonal. The 'R' value is found to be 0.66 which shows that the ground state of the complex is $d_{x^2-y^2}$. The axial symmetry parameters 'G' (2.2) indicates exchange interaction among the magnetically equivalent

Cu(II) ions in the unit cell. The g -value < 2.3 indicates that the complex is largely covalent¹⁷ and mixed Cu–N and Cu–O bond¹⁸.

The X-ray diffraction study (powder pattern) of the complex $[\text{NiL}^1(\text{SCN})_2]$ has been interpreted and the unit cell parameters like a , b , c , α , β and τ and the volume of the unit cell have been calculated with help of a computer (Table 2). Based upon these data, the complex is suggested to be monoclinic in nature.

The Zn(II), Cd(II) and Hg(II) complexes are suggested to be six-coordinated probably having octahedral stereochemistry based upon the analytical, IR and conductance data.

References

- 1 Bibhute Y B & Wadje S S, *Indian J Expt Biol*, 14 (1976) 739.
- 2 Rao A V & Subbarao N V S, *Proc Indian Acad Sci*, 72A (1970) 24.
- 3 Hideg K & Lloyd D, *Chem Commun*, (1970) 929; *J Chem Soc C*, (1971) 3441.
- 4 Ferraro J R, *Low frequency vibration of inorganic and coordination compounds* (Plenum Press, New York), 1971.
- 5 Nakamoto K, *Infrared spectria of inorganic and coordination compounds*, 2nd Edn (John Wiley, New York), 1963, 75.
- 6 Tramer A, *J chem Phys*, 59 (1962) 231.
- 7 Gatehouse B M, Livingstone S E & Nyholm R S, *J inorg nucl Chem*, 8 (1958) 75.
- 8 Addison C C & Logan N, *Adv Inorg Chem Radiochem*, 6 (1964) 95.
- 9 Karayannis N M, Mikulski C M, Pytlewski L L & Labes M M, *J inorg nucl Chem*, 34 (1972) 3139.
- 10 Gopalakrishna J, Pani A & Patel C C, *Bull Chem Soc Japan*, 48 (1967) 791.
- 11 Hathaway B J & Underhill A E, *J chem Soc*, (1961) 3091.
- 12 Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam) 1968.
- 13 Allan J R, Brown D H, Nuttal R H & Sharp D W A, *J inorg nucl Chem*, 26 (1964) 1895.
- 14 Yamada S, *Coord chem Rev*, 1 (1966) 415; Sacconi L, *J inorg nucl chem*, 19 (1961) 73.
- 15 Lever A B P, *Chem Rev*, 3 (1968) 119.
- 16 Ballhausen C J & Hare C R, *J chem Phys*, 40 (1984) 788.
- 17 Nieman F & Kivelson D, *J chem Phys*, 35 (1961) 149.
- 18 Tomlinson A A G & Hathaway B J, *J chem Soc A*, (1968) 1685.