Pak J Sci Ind Res 1999 ***42*** *(2) 83-85*

COMPLEXES OF Co (II), Ni (II), Cu (II), Zn (II), Cd (II) AND Hg (II) WITH ON-NO DONOR TETRADENTATE LIGAND

Bipin B Mahapatra* and A S P Mishra

Department of Chemistry, G M Autonomous College Samhalpur - 768 004, India

(Received 16 September 1997; accepted 29 May 1998)

Fifteen complexes of composition [MLX_2] have been prepared where M=Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II); X=Cl^-, NO^-_3, SCN^-; L=1,9- dibenzoyl - 2,8-di (p-methoxy phenyl) -3,7- diazanonane. The ligand possesses ON - NO donor atoms and forms mononuclear complex compounds with the above metal ions. The complexes have been characterised to be either octahedral or distorted octahedral basing upon conductance, magnetic susceptibility, IR, electronic, NMR and ESR spectra apart from x-ray diffraction data.

Key words **:** Metal complex, Tetradentate ligand.

Introduction

The pharmacological properties of chalcone and its derivatives (Getehouse *et al* 1958; Addition and logan 1964) made us interested to synthesize some new multidentate chalcone derivatives for complexation with some divalent metal ions. In our earlier work (Allan *et al* 1964; Lever 1968) we have reported a number of mono and dimeric complexes using new multidentate chalcone derivaties having ON-NO, OOO, ONO, OONNOO donor atoms. The present work describers the synthesis of a new ON-NO donor tetradentate chalcone derivative and its fifteen monoNuclear complexes with Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II) ions.

Experimental

Acetophenone, anisaldehyde, 1, 3-diaminopropane, sodium hydroxide, potassium carbonate, diethyl ether, cyclohexane were all BDH or E. Merck grade. Ethanol and metal salts were reagent grade chemicals. p- methoxy benzal acetophenone was prepared following a similar procedure of the preparation of benzal acetophenone (Ballhausend 1904). To prepare 1,9-dibenzoyl-2,8-di (methoxy phenyl) -3,7-diazanonane a mixture of p-methoxy benzal acetophenone (0.2 mol) and 1,3- diaminopropane (0.1 mol) in cyclohexane-ether (50 ml) was refluxed for 6 h in presence of K_2CO_3 (4g). It was then cooled filtered and kept in refrigerator [Found C, 76.0% H, 6.8% N, 4.9%; Calcd. C, 76.34% H, 6.96% N, 5.09%].

The metal complexes have been prepared by refluxing the ethanolic solution of metal salts with ligand in situ over a heating mantle for more than 2 h. Some metal complexes separated out during reflux and some appeared on keeping the solution in refrigerator for about 48 h. They were then filtered, washed with ethanol and ether and dried in vaccum.

The elemental analyses were done by standard procedures. Conductance was measured by a conductivity bridge in 10^{-3} M DMSO 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 PE- 983/781 spectrophotometer, electronic spectra (10^{-2} M DMSO) on a Hilger and Watt Uvispeck spectrophotometer, ESR on a EPR E-112 spectrometer at room temperature and NMR spectrum was scanned using an NMR spectrophotometer model JEOL-GSX 400. XRD of a cadmium complex was recorded on an X-ray diffractometer, M/s Philips, Holland.

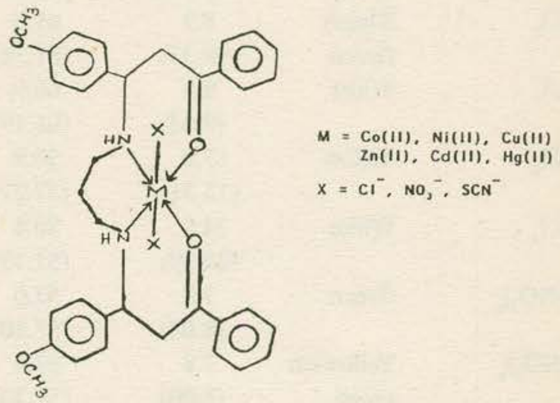

Fig 1. Complexes of Co(II), Ni(II), Cu(II), Zn(II) Cd(II) and Hg(II) with ON-NO donor tetradentate ligand.

Results and Discussion

The complexes reported here are of the type [ML X_2], where

---

*Author for correspondence

M=Co (II), Ni (II) Cu (II), Zn (II), Cd (II) and Hg (II); X=Cl, NO_3, SCN; L=1,9-dibenzoyl-2,8-di (p-methoxy phenyl-3,7-diazanonane. All the complexes are found to be non-electrolytes. ΔM being very low (2.7-3.3 Ω^{-1} cm^2 mol^{-1}).

In the IR spectra of the complexes the bands observed at ca 1650-1670 cm^{-1} and ca 3350 cm^{-1} can be ascribed to ν(C=O) and ν(NH) vibrations respectively indicating the bonding of the ligand to metal ions through carbonyl oxygen and secondary amino nitrogen atoms. Furthermore the co-ordination of oxygen and nitrogen atoms of the ligand to the metal ions is confirmed by the appearance of ν(M-O) and ν(M-N) at ~ 490 cm^{-1} and ~ 530 cm^{-1} respectively. (Hideg and Lloyd 1970) (Table 1)

In the nitrato complexes under report, strong bands are observed at 1405 cm^{-1} and 1280 cm^{-1} and the difference Δν of 125 cm^{-1} is suggestive of unidentate co-ordination of nitrate groups. It is observed that for M-NCS bonding νCN and νCS appear to fall in the range 2080-2040 cm^{-1} and 860-780 cm^{-1} respectively and for M-SCN bonding the corresponding bands are observed at 2120 - 2080 cm^{-1} and 720-680 cm^{-1}. In case of cobalt, nickel and copper complexes, the νCN and νCS appear in ca 2060 and 840 cm^{-1} respectively suggesting M-NCS bonding and in case of cadmium and mercury complexes, the νCN and νCS appear at ca 2100 and 700 cm^{-1} respectively indicating M-SCN type of bonding of thiocyanate groups. In the nitrato complexes under report strong bands are observed at 1405 and

Table 1

Analytical and IR spectral data of the complexes

Compound	Colour	Analytical Found/(Calcd.) M	C	H	N	ν(C=O) ν(N-H)	ν(M-o) ν(M-N)
$CoLC1_2$	Pink	8.4	61.4	5.4	4.0	1650/3150	490/530
		(8.66)	(61.77)	(5.63)	(4.12)		
$NiLCl_2$	Yellowish	8.4	61.5	5.4	3.9	1660/3200	495/535
	green	(8.63)	(61.79)	(5.63)	(4.12)		
$CuLCl_2$	Bluish	8.9	61.0	5.4	3.8	1670/3150	490/525
	Green	(9.27)	(61.36)	(5.59)	(4.09)		
$ZnLCl_2$	White	9.3	60.9	5.3	3.9	1665/3200	495/530
		(9.52)	(61.19)	(5.58)	(4.08)		
$CdLCl_2$	Yellow	15.0	56.9	5.0	3.6	1660/3200	490/525
		(15.31)	(57.27)	(5.22)	(3.82)		
$HgLCl_2$	White	24.0	50.8	4.5	3.2	1665/3200	495/530
		(24.39)	(51.13)	(4.66)	(3.41)		
$CoL(NO_3)_2$	Green	7.8	57.0	5.0	7.4	1650/3200	490/520
		(8.03)	(57.30)	(5.22)	(7.64)		
$NiL(NO_3)_2$	Yellowish	7.8	57.0	5.0	7.5	1650/3200	490/520
	green	(8.00)	(57.32)	(5.22)	(7.64)		
$CuL(NO_3)_2$	Green	8.3	56.5	5.0	7.3	1660/3150	495/530
		(8.61)	(56.94)	(5.19)	(7.59)		
$CdL(NO_3)_2$	White	14.0	53.0	4.7	7.0	1670/3150	490/530
		(14.28)	(53.41)	(4.87)	(7.12)		
$CoL(SCN)_2$	Bluish	8.0	60.9	5.0	7.5	1670/3200	494/525
	green	(8.12)	(61.23)	(5.28)	(7.72)		
$NiL(SCN)_2$	Yellowish	7.9	60.9	5.1	7.6	1670/3200	495/530
	green	(8.09)	(61.25)	(5.28)	(7.72)		
$CuL(SCN)_2$	Yellow	8.5	60.5	5.1	7.5	1660/3150	490.525
		(8.70)	(60.84)	(5.24)	(7.67)		
$CdL(SCN)_2$	Yellow	14.2	56.8	4.8	7.0	1670/3200	495/530
		(14.42)	(57.03)	(4.92)	(7.19)		
$HgL(SCN)_2$	Grey	23.0	50.9	4.2	6.2	1665/3205	490/525
		(23.12)	(51.23)	(4.42)	(6.46)		

1275 cm^{-1} and the difference $\Delta\nu$ of 130 cm^{-1} suggests unidentate co-ordination of nitrate groups (Ferraro 1971; Nakamoto 1978; Mahapatra *et al* 1995; Mahapatra and Mishra 1995; Mahapatra and Behera 1997; Mahapatra and Mishra 1997).

In the electronic spectra of cobalt (II) complexes the absorption bands observed at ~ 8510 ~ 18485 ~ 21240 and ~ 32100 cm^{-1} can be attributed to $^4T_{1g}$ (F)-------> $^4T_{2g}$ (F) -------> $^4A_{2g}$ (F) -------> $^4T_{1g}$ (P) and CT transition respectively. The calculated spectral parameters Dq =997.5, B=946.3, β_{35} = 0.974, $V_2/V_1 = 2.17$ and σ=2.67 are in conformity with an octahedral configuration. (Nieman and Kivelson 1961). This formulation is supported by high μ_{eff} values. The electronic spectra of Ni(II) complexes shows bands at 10960, ~ 18320, ~ 26235 and ~ 31560 cm^{-1} assignable to $^3A_{2g}$ (F)------> $^3T_{2g}$ (F) ------> $^3T_{1g}$ (P) and CT transition respectively in tetragonally distorted octahedral field (Rao *et al* 1970). The spectral parameters Dq=1096, B=778.3, B_{35}=0.748, v_2/v_1=1.672 and δ=33.69 are supportive of the configuration. The high μ_{eff} values are also suggestive of this stereochemistry. All the Copper (II) complexes exhibit a broad band at 13,600-14,250 cm^{-1} due to ^2E_g -------> $^2T_{2g}$ transition indicating a distorted octahedral configuration for the complexes. (Tomlin son and Hathway 1968, Jairama and Souza 1986). The ESR spectrum of the copper (II) complex was recorded at X-band. The g values of the complexes (g_I=2.0386 and g_{11}= 2.1890) and its spectrum indicate that the symmetry around Copper (II) is axial (two values tensor) i.e. symmetry is tetragonal. The g_{11} value <2.3 indicates that the complex is largely covalent (Tramer 1962) and has mixed Cu-N and Cu-O bands (Sacconi 1961; Yamada 1966). The axial symmetry parameter G calculated for the complex from the relation $(G=g_{11}-2) / (g_I-2)$ is found to be 4.8 which suggests the absence of exchange interation. The value of $g_{11} > g_I$ shows that the unpaired electron is localised in $dx^2\text{-}y^2$ orbital. The spin-orbit coupling constant (λ^1) can be obtained from the relation gav = 2.00m[1-($2\lambda^1/10D_q$)]. The g_{av} value is obtained from the relation $g_{av} = 1/3\ (g_{11} + 2\ g_I)$ and $10D_q$ from the electronic spectrum. The value (λ^1) for the complex (-308.71) is found to be lower than the free ion (-830) which suggests a considerable overlapping of the orbital.

The X-ray diffraction study (Powder pattern) of the cadmium complex [$CdLCl_2$] has been indexed in the X-ray diffractometer and the unit cell parameters have been claculated with the help of a computer. Basing upon the data like A,B,C, α,β,γ and volume of the unit cell, the complex is suggested to be monoclinic in nature (Table-2).

Table 2

X-Ray diffraction data of the complex [$CdLCl_2$]

A	B	C	∝	β	γ	Volume
12.147	17.917	10.593	94.479	93.700	87.272	2291.47
12.153	26.442	11.509	90.000	93.642	90.000	3690.69
18.652	15.879	10.555	90.000	95.201	90.000	3113.25

The ^{1}H n.m.r. spectrum of the copper complex has been scanned using DMSO d^6 as solvent and TMS as internal standard. The complex pattern displayed at δ = 7.01 - 8.14 (ppm) is due to eighteen phenyl protons. The sharp peak at δ = 3.35 indicates the presence of two -NH protons and at δ=2.68 six methoxy protons. The sharp observed at δ = 3.83 is assignable to ten methylene protons. The peak appeared at δ = 2.51 suggests the presence of two -CH-protons.

The Zn (II), Cd (II) and Hg (II) complexes are assigned to have octahedral geometry basing upon the analytical and IR spectral data. Hence the new chalcone derivative behaves as ON-NO donor tetradentate ligand by co-ordinating to the metal ions through its two carbonyl oxygen and two secondary nitrogen atoms.

References

Addition C C, Logan N 1964 *Chem Radio Chemistry* **6** 95.

Allan J R, Brown D H, Nutal R H, Sharp D W A 1964 *J Inorg Nucl Nucl Chem* **26** 1895.

Ballhausen C J, Hare C R 1904 *J Chem Phys* **40** 788.

Ferraro J R 1971 *Low frequency vibration of inorganic and co-ordination compounds*. Plenum press New York.

Getehouse B M, Livingstone S E, Nyholm R S 1958 *J Inorg Nucl Chem* **8** 75.

Hideg K, Lloyd D 1970 *J Chem Soc C* 3441 1971.

Jairama, Souza M V D 1986 *Indian J Chem* **25**A 183.

Lever A B P 1968 *Inorganic electronic spectroscopy* Elsevier Amsterdam.

Mahapatra B B, Raval M K, Behera A K 1995 *Asian J Chem* **7** 429.

Mahapatra B B, Mishra A S P 1995 *Usc Phy Sc* **7** (2) 153.

Mahapatra BB, Behera AK 1997 *Indian Journal of Chemistry* **35** (A) 154.

Mahapatra B B, Mishra A S P 1997 *Usc Phy Sc* **9** (2) 285.

Nieman F, Kivelson D 1961 *J Chem Phys* **35** 149.

Rao AV, Subarao N V S 1970 *Prodc Indian Acad Sci* **72** (A) 24.

Sacconi L 1961 *J Inorg Chem* **19** 73.

Tramer A 1962 *J Chem Phys* **59** 231.

Tomlinson A A G, Hathway BJ 1968 *J Chem Soc* **A** 1685.

Yamada S 1966 *Coord Chem Rev* **1** 415.