Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 100, No. 5, October 1988, pp. 363–373.
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Synthesis and structural studies of complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with substituted chalcones

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MS received 18 December 1987; revised 16 May 1988

Abstract. Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 3-(2-pyridyl)-1-(2-hydroxy phenyl)-2-propen-1-one (PHPO), 3-(1-naphthyl)-1-(2-hydroxy phenyl)-2-propen-1-one (NHPO) and 3-(3,4-dimethoxy phenyl)-1-(2-hydroxy phenyl)-2-propen-1-one (DMPHPO) have been synthesized and characterized by analytical, conductivity, thermal, magnetic, infrared, electronic and electron spin resonance data. Based on analytical data the stoichiometry of the complexes has been found to be 1 : 2. The conductivity data show that all these complexes are non-electrolytes. The infrared spectral data indicate that the ligand PHPO acts as uninegative tridentately towards Co(II) and Ni(II) and bidentately with Cu(II), Zn(II) and Cd(II). Ligands like NHPO and DMPHPO act as uninegative bidentately with all the metal ions. The electronic spectral data suggest that all the Co(II) complexes and Ni(II) of PHPO complex are octahedral and all the Cu(II) and Ni(II) of NHPO and DMPHPO complex are square-planar. The complex of Zn(II) and Cd(II) are tetrahedral. ESR parameters of Cu(II) complexes have been calculated and relevant conclusions have been drawn with respect to the nature of bonds present in them.

Keywords. Chalcones; complexes; IR spectra; electronic spectra; ESR spectra.

1. Introduction

Biologically active ligands like 2′-hydroxy chalcones contain two coordinating sites and are reported to be mononegative bidentate towards Cu(II) (Seshadri Naidu and Raghava Naidu 1979). We also studied the coordinating behaviour of some substituted chalcones and found that they act as mononegative tridentate towards Co(II), Ni(II) and Ru(II) and bidentate towards Pd(II), Pt(II) and Zn(II) (Seetharama Rao *et al* 1985). Although chalcones exhibit diverse coordinating behaviour towards different metal ions, studies oriented towards the complexing behaviour of these compounds by way of synthesis and characterization of their metal complexes are limited. The dearth of studies made in this direction has prompted the author to undertake the present work. The ligands selected in the preparation of metal complexes are 3-(2-pyridyl)-1-(2-hydroxyphenyl)-2-propen-1-one (PHPO), 3-(1-naphthyl)-1-(2-hydroxyphenyl)-2-propen-1-one (NHPO) and 3-(3,4-dimethoxy phenyl)-1-(2-hydroxyphenyl)-2-propen-1-one (DMPHPO). As these compounds possess three donor atoms, they may be monodentate, bidentate or tridentate in

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different metal complexes. In order to determine the nature of the interaction of these ligands with different metal ions like Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), we have used them for the syntheses of their complexes. The complexes have been characterized on the basis of analytical data, conductivity measurements, magnetic susceptibility, thermal analysis and infrared, electronic and electron spin resonance (ESR) spectral data. With these data at hand relevant conclusions can be drawn with respect to the geometry of the complexes and the nature of bonding present in them.

2. Materials and methods

2.1 *Materials*

o-Hydroxy acetophenone, pyridine-2-aldehyde, 1-naphthaldehyde and veratraldehyde were obtained from M/s Chempure Chemicals Limited, Bombay. The metal salts used for the preparation of complexes were of Analar grade. All organic solvents used were BDH-Analar grade. The ligands PHPO, NHPO and DMPHPO were prepared as reported in the literature (Asahina 1944; Geissman and Clinton 1946).

2.2 *Preparation of metal complexes*

In the preparation of all the Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes, the following general procedure was adopted. Metal salt solution (30 ml) in methanol was added dropwise to a solution (60 ml) of the ligand in methanol with constant stirring. However, ligands like NHPO and DMPHPO were dissolved in toluene and mixed with metal salt solution. In all the cases, the ligand concentration was in slight excess of the 1 : 3 metal–ligand molar ratio. The reaction mixture was refluxed on a water-bath for 60–90 minutes. The complex separated out on cooling. It was then filtered through a sintered glass crucible (G_4) and the residue was washed several times with hot methanol until the washings were free of the excess ligand. The complexes of NHPO and DMPHPO were also washed with acetone. These complexes were finally dried under vacuum over fused calcium chloride.

2.3 *Physical measurements*

The analytical data (C, H, N) for the ligands and their metal complexes were obtained from the Microanalytical Laboratory, Calcutta University. The metal content in the complexes after heating to decomposition was determined by the author using standard procedures (Vogel 1961). Conductance measurements of the complexes in dimethyl formamide were made at a concentration of 10^{-3} M using a Digisun Digital Conductivity Meter, Model-DI-909 with Philips dip type conductivity cell. The magnetic susceptibility measurements of the complexes in the solid state were made on a Guoy balance at room temperature using $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constant. DTA curves of complexes were recorded on a Leeds and Nathrup DTA unit (USA) using calcined alumina reference material. The experiments were carried out in a static air atmosphere using Pt/Rh thermocouples, while the rate of heating was maintained at 6°C per minute. The infrared spectra of the ligands and their metal complexes in nujol and as KBr pellets in the range 4000–200 cm^{-1} were recorded making use of a Perkin–Elmer infrared spectrophotometer, Model-283. Ultraviolet and visible spectra in DMF were recorded on a Shimadzu Multipurpose Recording Spectrophotometer, Model-MPS-5000. For want of neat solubility of the complexes in DMF, quantitative spectra could not be recorded. A Varian E-4 X-band spectrophotometer was used for recording the solid state ESR spectra of the Cu(II) complexes at room temperature.

3. Results and discussion

All the complexes are stable at room temperature, non-hygroscopic, insoluble in water and many of the common organic solvents, but soluble in DMF and DMSO. The analytical data of the complexes (table 1) indicate that their stoichiometry may be represented as 1 : 2 metal to ligand. Some of the complexes like Co(II) with NHPO and DMPHPO are also further associated with two moles of water mole-

Table 1. Analytical and conductivity data of the complexes.

Complex	Found (Calc.) (%)				Molar conductance (Ohm^{-1} cm^2 mol^{-1})
	Metal	C	H	N	
$[Co(PHPO)_2]$	12·36	64·14	3·99	5·62	13
	(12·25)	(64·87)	(3·74)	(5·82)	
$[Co(NHPO)_2$ $2H_2O]$	9·88	71·86	4·12	—	10
	(9·20)	(71·15)	(4·68)		
$[Co(DMPHPO)_2$ $2H_2O]$	9·56	61·86	5·26	—	8
	(8·92)	(61·73)	(5·14)		
$[Ni(PHPO)_2]$	12·92	64·36	2·82	5·84	10
	(12·21)	(64·90	(3·75)	(5·83)	
$[Ni(NHPO)_2]$	9·12	74·92	4·32	—	8
	(9·71)	(75·41)	(4·30)		
$[Ni(DMPHPO)_2]$	9·92	65·82	4·72	—	14
	(9·40)	(65·31)	(4·80)		
$[Cu(PHPO)_2]$	13·82	64·82	3·72	5·56	12
	(13·09)	(64·26)	(3·71)	(5·77)	
$[Cu(NHPO)_2]$	10·22	74·96	4·82	—	5
	(10·43)	(74·81)	(4·27)		
$[Cu(DMPHPO)_2]$	9·56	64·56	4·82	—	10
	(10·10)	(64·81)	(4·77)		
$[Zn(PHPO)_2]$	13·92	65·82	3·72	5·86	10
	(13·41)	(64·02)	(3·69)	(5·75)	
$[Zn(NHPO)_2]$	10·82	74·92	4·34	—	10
	(10·69)	(74·59)	(4·25)		
$[Zn(DMPHPO)_2]$	10·66	64·92	4·82	—	12
	(10·35)	(64·62)	(4·75)		
$[Cd(PHPO)_2]$	21·95	59·12	3·52	5·46	13
	(21·03)	(58·38)	(3·37)	(5·24)	
$[Cd(NHPO)_2]$	16·56	69·56	4·12	—	12
	(17·07)	(69·26)	(3·95)		
$[Cd(DMPHPO)_2]$	16·66	59·86	4·46	—	10
	(16·57)	(60·14)	(4·42)		

cules. The molar conductance values of the complexes in DMF are in the range 8–15 Ohm^{-1} cm^2 mol^{-1} suggesting their non-ionic nature (Geasy 1971).

3.1 *Thermal study*

It is known from the DTA curves that all the complexes except those of Co(II) with NHPO and DMPHPO are thermally stable upto 250°C indicating that they are not hydrated. The TGA of the Co(II) complexes of NHPO and DMPHPO show a weight loss corresponding to two water molecules in the temperature range 140–160°C. The expulsion of water from the complex in this temperature range also indicates that they are present inside the coordination sphere (Nikolaev *et al* 1969). This is also confirmed by the presence of endothermic peaks in the DTA curves in the same temperature range. The thermograms of all the complexes show sharp decomposition associated with the loss of the organic part above 250°C. It is clear that the final products of decomposition as computed from the thermograms correspond, in each case, to metallic oxides. The analysis of the thermograms of the complexes by way of identifying their components offers further support to the composition of the complexes as proposed on the basis of analytical data. Further, all the complexes are thermally stable to varying degrees. Taking the decomposition temperatures of the complexes as a measure of their thermal stability, the order of ligands that form stable complexes is: PHPO > NHPO > DMPHPO. Despite the large amount of work done on differential thermogravimetry, considerable difficulty still exists in assigning definite reasons for the increase or decrease in thermal stability of complexes with different ligands. The relative order of stability observed in the present complexes may be explained in terms of the increase in the number of metal oxygen bonds through π-electron delocalization, the size of the molecule and the number of rings formed (Seshadri Naidu and Raghava Naidu 1977).

3.2 *Infrared spectra*

Important absorption frequencies of ligands and complexes along with their assignments are presented in table 2. The infrared spectra of ligands and their complexes were recorded in nujol and KBr. The – OH stretching frequency is not observed in all the ligands. This may be due to the strong hydrogen bonding with the oxygen of carbonyl group (Nakanishi Koji 1964). However, a strong absorption band is observed in all the ligands for O–H deformation at 1330–1370 cm^{-1} (Ramaswamy *et al* 1967). The disappearance of this band in the spectra of the metal complexes indicates complex formation by deprotonation of OH. In the IR spectra of all the ligands, the intense band observed at 1630 cm^{-1} is attributed to stretching vibration, $\nu(C{=}O)$ (Dhar and Gupta 1971). This band is shifted to lower wave numbers ($\Delta\nu$ = 50 cm^{-1}) in the spectra of the complexes indicating coordination through oxygen of the C=O group with the metal ion. The medium intensity bands appearing around 1570 cm^{-1} in the ligands are assigned to the aromatic $\nu(C{=}C)$ stretching vibrations and remain unshifted in the complexes indicates that there is no π-bond formation with the C=C group.

The ligand PHPO exhibits a strong band at 1660 cm^{-1} which may be assigned to the stretching vibration of the nitrogen of the pyridyl ring (Laxma Reddy *et al* 1986). The band remains unaltered in all the complexes of Co(II) and Ni(II) indi-

Table 2. Assignment of some important infrared spectral data of the compounds (cm^{-1}).

	Infrared assignments					
Compound	δ(OH)	ν(C=O)	ν(C=C)	ν(C=N)	ν(M–O)	ν(M–N)
PHPO	1350	1630	1560	1600	—	—
[Co(PHPO)$_2$]	—	1580	1560	1550	450,400	500
[Ni(PHPO)$_2$]	—	1580	1560	1550	450	520
[Cu(PHPO)$_2$]	—	1595	1560	1600	450,430	—
[Zn(PHPO)$_2$]	—	1850	1560	1600	430,400	—
[Cd(PHPO)$_2$]	—	1580	1560	1600	400,400	—
NHPO	1370	1640	1510	—	—	—
[Co(NHPO)$_2$2H$_2$O]	—	1580	1570	—	450,420	—
[Ni(NHPO)$_2$]	—	1590	1570	—	460,430	—
[Cu(NHPO)$_2$]	—	1595	1570	—	450,430	—
[Zn(NHPO)$_2$]	—	1590	1570	—	430,390	—
[Cd(NHPO)$_2$]	—	1590	1570	—	450,400	—
DMPHPO	1370	1640	1560	—	—	—
[Co(DMPHPO)$_2$ 2H$_2$O	—	1590	1560	—	450,400	—
[Ni(DMPHPO)$_2$]	—	1590	1560	—	450,420	—
[Cu(DMPHPO)$_2$]	—	1590	1560	—	470,400	—
[Zn(DMPHPO)$_2$]	—	1590	1570	—	430,390	—
[Cd(DMPHPO)$_2$]	—	1590	1560	—	450,400	—

cating that the nitrogen of the pyridyl group is not involved in coordination. However, the band is observed at 1550 cm^{-1} in the complexes of Co(II) and Ni(II) indicating the participation of nitrogen in M–L bond formation. The ligand DMPHPO also contains two methoxy groups on the phenyl ring. The presence of a ν(C–O) band at 1245 cm^{-1} both in the ligand and its metal complexes indicates the non-participation of the oxygen of the methoxy group in coordination (Pasto and Johnson 1969). In addition, the Co(II) complexes of NHPO and DMPHPO show broad, medium intense peaks occurring between 3450 and 3300 cm^{-1} which may be attributed to the O–H stretching frequency of water present in the complex. These complexes also show bands at 1630 and 800 cm^{-1} due to HOH bending and rocking (ρ H$_2$O) respectively indicating the presence of coordinated water (Nakamoto 1978).

The participation of nitrogen and oxygen in coordination is further evidenced by the presence of non-ligand bands in their far infrared spectra. The bands observed around 500 and 400 cm^{-1} in all the complexes may be due to ν(M–N) and ν(M–O) respectively (Laxma Reddy *et al* 1984).

3.3 *Electronic spectra*

Electronic spectral data of the complexes along with their assignments are given in table 3.

All the ligands exhibit strong bands around 36,000 cm^{-1} with a shoulder at 33,000 cm^{-1} which may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. Electronic spectra of Co(II) complexes display three bands around 8500, 17,000 and 20,000 cm^{-1} which may be assigned to the spin-allowed transitions

Table 3. Magnetic moment and electronic spectral data of complexes.

Complex	ν_1(cm^{-1})	ν_2(cm^{-1})	ν_3(cm^{-1})	ν_2/ν_1	10 Dq(cm^{-1})	B(cm^{-1})	'β'	LFSE (K cal mol^{-1})	μ_{eff}(B M) Expt.	μ_{eff}(B M) Calc.
[Co(PHPO)$_2$]	8700	18,250	20,950	2·10	9910	896	0·80	22·65	5·04	5·12
[Co(NHPO)$_2$ 2H$_2$O]	8800	17,985	21,480	2·04	9872	916	0·81	22·56	5·01	5·11
[Co(DMPHPO)$_2$ 2H$_2$O]	8510	17,600	20,400	2·06	9670	870	0·77	22·10	5·06	5·11
[Ni(PHPO)$_2$]	9300	15,200	24,900	1·63	9300	813	0·78	31·89	3·16	3·20
[Ni(NHPO)$_2$]	—	19,500	—	—	—	—	—	—	Diamagnetic	
[Ni(DMPHPO)$_2$]	—	20,500	—	—	—	—	—	—	Diamagnetic	
[Cu(PHPO)$_2$]	—	15,000	19,250	—	—	—	—	—	1·83	1·84
[Cu(NHPO)$_2$]	—	15,500	19,000	—	—	—	—	—	1·82	1·82
[Cu(DMPHPO)$_2$]	—	15,600	18,900	—	—	—	—	—	1·83	1·82

$^4T_{1g}(\mathrm{F}) \rightarrow {}^4T_{2g}(\mathrm{F})$ (ν_1), $^4T_{1g}(\mathrm{F}) \rightarrow {}^4A_{2g}(\mathrm{F})$ (ν_2) and $^4T_{1g}(\mathrm{F}) \rightarrow {}^4T_{1g}(\mathrm{P})$ (ν_3) respectively, characteristic of octahedral geometry around Co(II) (Matthews and Walton 1971).

Electronic spectra of the Ni(II) complex of PHPO exhibit three peaks in the regions 8900, 14,900 and 25,000 cm^{-1} and these have been respectively assigned to the transitions $^3A_{2g}(\mathrm{F}) \rightarrow {}^3T_{2g}(\mathrm{F})$ (ν_1), $^3A_{2g}(\mathrm{F}) \rightarrow {}^3T_{1g}(\mathrm{F})$ (ν_2) and $^3A_{2g}(\mathrm{F}) \rightarrow {}^3T_{1g}(\mathrm{P})$ (ν_3) characteristic of octahedral geometry. The octahedral geometry of the Co(II) and Ni(II) complexes of PHPO is further supported by the ratio of ν_2/ν_1 which lies around 2·10 and 1·63 respectively. The ratio of ν_2/ν_1 obtained for the complexes is lower than that of regular octahedral aquo complexes and may be due to the asymmetric environments around Co(II) and Ni(II). The electronic spectra of the Ni(II) complexes of NHPO and DMPHPO are characterised by broad peaks centred at 21,000 cm^{-1}. This has been assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, suggesting square planar geometry for Ni(II) complexes of NHPO and DMPHPO (Laxma Reddy *et al* 1985). Various ligand field parameters, such as the ligand field splitting energy (10 Dq), Racah-inter electronic repulsion parameter (B), covalent factor (β) and ligand field stabilization energy (LFSE) have been calculated for all the complexes of Co(II) and Ni(II) of PHPO (Lever 1968).

The calculated 10 Dq values of Co(II) and Ni(II) complexes suggest for the ligands a place between water and ammonia in the spectrochemical series. The B-values for the complexes are lower than free ion values which is an indication of orbital overlap and delocalization of d-orbitals. The β-values obtained are less than one suggesting the considerable covalent character of the metal–ligand bonds.

The electronic spectra of Cu(II) complexes with all the ligands display two bands around 15,000 and 20,000 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2Eg$ transition respectively, characteristic of square-planar geometry (Werden *et al* 1966).

3.4 *Magnetic moment*

The experimental and calculated magnetic moments of the complexes are given in table 3.

The values obtained for the complexes of Co(II) with all the ligands indicate that they are octahedral. In an attempt to correlate the spectral and magnetic properties, μ_{eff} has been calculated from Dq, B, E, C and A using the equations (Figgis 1966)

$$E^2 + (6\,Dq - 15B)E - 16\,Dq^2 - 90\,Dq\,B = 0,$$

$$C = (6\,Dq - E)/4\,Dq,$$

and $A = (1{\cdot}5 - C^2)/(1 + C^2)$.

A values have been calculated from the parameters $E(-6700)$ and $C(-0{\cdot}195)$. Using the A value(1·409) μ_{eff} has been calculated using the equation

$$\mu_{\mathrm{eff}}^{2} = \frac{\begin{array}{l} 3\,\{7(3-A)^2/5 + 12(2+A)^2/25\,AX + \\ +[2(11-2\mathrm{A})^2/45 + 76(2+A)^2/675\,AX]\exp(-5AX/2) + \\ +[(5+A)^2/9 \times 20(2+A)^2/27\,AX]\exp(-4AX)\} \end{array}}{3 + 2\exp(-5AX/2) + \exp(-4AX)}$$

where $X = \lambda/KT$, (λ = free ion spin-orbit coupling constant; K = Boltzmann constant, and T = temperature.)

In octahedral geometry, the ground term is ${}^4T_{1g}$ which is orbitally degenerate. This makes an orbital angular momentum contribution to the magnetic moment. Therefore, the present values are higher than the spin-only values. The experimental and calculated $\mu_{\rm eff}$ values are in good agreement suggesting considerable orbital contribution.

Ni(II) complexes of PHPO are shown to be paramagnetic and to have a magnetic moment corresponding to octahedral geometry (Khulbe *et al* 1981), whereas Ni(II) complexes of NHPO and DMPHPO are diamagnetic, characteristic of square-planar geometry (Sacconi 1968). The diamagnetism of these complexes is also confirmed from the ESR spectra which do not exhibit any resonance signal. In an attempt to correlate the spectral and magnetic data, the $\mu_{\rm eff}$ has also been calculated using 10 Dq (Figgis 1966). The calculated values are in good agreement with the experimental values indicating small orbital contribution due to spin-orbit mixing of the ground state ${}^3A_{2g}$ with the first excited state ${}^3T_{2g}$. This also indicates the validity of the ligand field parameters $10\,Dq$, B and the $\mu^{\rm expt}_{\rm eff}$

All the Cu(II) complexes are found to be paramagnetic and possess magnetic moment values, to the extent of one unpaired electron. Cu(II) complexes, in general, have $\mu_{\rm eff}$ values between 1·75 and 2·20 BM, and magnetic moments strictly cannot be used to distinguish between the stereochemistries of the complexes. Nevertheless, higher magnetic moments (2·20 BM) are attributed to distorted tetrahedral configurations and lower magnetic moments (< BM) are due to square-planar configurations (Laxma Reddy *et al* 1985). The present $\mu_{\rm eff}$ values for the complexes also further support the square-planar geometry proposed on the basis of electronic spectral data.

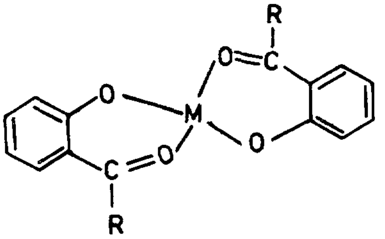
3.5 *Electron spin resonance study*

The ESR parameters are listed in table 4. The ESR spectra of Cu(II) complexes in the polycrystalline state show two peaks, one of intense absorption at high field and the other of less intensity at low field. From these peaks the values of $g_\parallel$ and $g_\perp$ have been calculated (Kneubuhl 1960). The g-values of Cu(II) complexes can be

Table 4. ESR spectral data of copper(II) complexes.

ESR spectral parameter	$[\mathrm{Cu(PHPO)_2}]$	$[\mathrm{Cu(NHPO)_2}]$	$[\mathrm{Cu(DMPHPO)_2}]$
$g_\parallel$	2·19	2·23	2·23
$g_\perp$	2·05	2·06	2·06
$\lvert g \rvert$	2·10	2·12	2·12
G	4·00	4·00	4·00
α^2	0·62	0·78	0·75
α'^2	0·48	0·31	0·34
β^2	0·65	0·62	0·64
γ^2	0·79	0·65	0·65
$r_\parallel^2$	0·40	0·48	0·48
$r_\perp^2$	0·49	0·51	0·49
λ	356	446	449

used to derive the ground state (Baulhausen 1962). In elongated octahedral and square-planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state with $g_{\parallel} > g_{\perp}$. In a compressed octahedron, on the other hand, the unpaired electron lies in the d_{z^2} orbital giving $^2A_{1g}$ as ground state with $g_{\perp} > g_{\parallel}$. From the observed values it is evident that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital. The complex also shows anisotropic ESR spectra with $g_{\parallel} > g_{\perp}$ characteristic of square-planar geometry. Recalling the complexes with $d_{x^2-y^2}$ ground state, strong interaction along the Z axis is to be accompanied by increase in the value of $g_{\parallel}$. Strong axial bonding leads to an increase in the length of the bond in the x–y plane which results in a decrease of both in-plane covalency and the energy of $d_{x^2-y^2}$ transition (Smith 1970). Both these



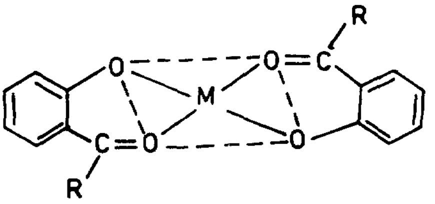
M = Cd(II), Zn(II)

R = –CH=CH–NC$_5$H$_5$ (PHPO)

–CH=CH–C$_{10}$H$_7$ (NHPO)

–CH=CH–C$_8$H$_9$O$_2$ (DMPHPO)

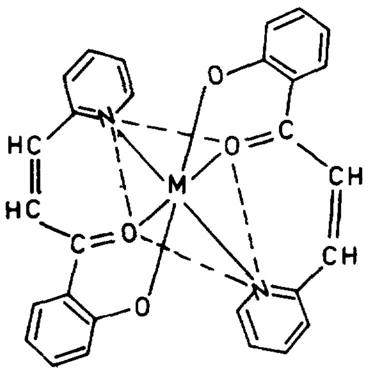
i) Tetrahedral complexes of Zn(II) and Cd(II)



M = Cu(II) –R = PHPO, NHPO or DMPHPO

= Ni(II) –R = NHPO or DMPHPO

ii) Square planar complexes of Cu(II), Ni(II)



M = Co(II), Ni(II)

iii) Octahedral complexes of Co(II), Ni(II) with PHPO

Figure 1. Structures of the complexes.

effects tend to increase the value of $g_{\parallel}$. The $g_{\parallel}$ is the most sensitive function for indicating the covalency, being 2·3 or more for ionic compounds and less than 2·3 for covalent compounds (Kivelson and Neimann 1961). It is clear from table 4 that $g_{\parallel}$ obtained is less than 2·3 indicating covalent character of the metal–ligand bond.

The axial symmetry parameter G defined as $(g_{\parallel} - 2{\cdot}0023)/(g_{\perp} - 2{\cdot}0023)$ is shown to be a measure of the exchange interaction between copper centres in the polycrystalline solids (Procter *et al* 1968). If the value of G is larger than 4, the exchange interaction is negligible while G values of less than 4 indicate considerable interaction in solid complexes. The present G values are found to be greater than 4, indicating that there is no exchange interaction in the solid state.

Further, orbital reduction parameters α^2, α^2, β^2, γ^2, $r_{\parallel}^2$, $r_{\perp}^2$ and λ have been calculated. The α^2 values for the present complexes fall in the range 0·4–0·6 indicating the presence of appreciable in-plane covalency. As $r_{\perp}^2 > r_{\parallel}^2$ in all the complexes, this indicates that the ligands are the in-plane π-bonded type (Hathaway 1973). The spin-orbit coupling constant for the complexes is less than that of the free metal ion ($\lambda_0 = -828\ \mathrm{cm}^{-1}$), suggesting considerable mixing of ground and excited terms. The g-values are also useful for calculating the magnetic moments (μ) of the complexes and calculated values are in good agreement with the experimental ones.

Based on their stoichiometry, conductance, magnetic, infrared and electronic data, all the Co(II) complexes and the Ni(II) complex of PHPO are tentatively assigned octahedral geometry while Ni(II) complexes of NHPO and DMPHPO and Cu(II) complexes are assigned square-planar geometry. Tetrahedral geometry is the most preferred structure for tetra coordinated Zn(II) and Cd(II) complexes. Based on the data obtained, tetrahedral geometry may be proposed for these complexes (figure 1).

Acknowledgements

The authors wish to thank the Regional Sophisticated Instrumentation Centre, IIT, Bombay, for providing ESR spectra. One of the authors (TSR) is thankful to the University Grants Commission for financial assistance.

References

Asahina T 1944 *Bull. Chem. Soc. Jpn.* **9** 133
Baulhausen C J 1962 *Introduction to ligand field theory* (New York: McGraw Hill) p. 134
Dhar D N and Gupta V P 1971 *Indian J. Chem.* **9** 818
Figgis B N 1966 *Introduction to ligand field* (New Delhi: Wiley Eastern) p. 265
Geasy M T 1971 *Coord. Chem. Rev.* **7** 81
Geissman T A and Clinton R O 1946 *J. Am. Chem. Soc.* **68** 697
Hathaway B J 1973 *Structure and bonding* (Berlin: Springer Verlag) vol. 14, p. 60
Khulbe R C, Bhoon Y K and Singh R P 1981 *J. Indian Chem. Soc.* **9** 940
Kivelson D and Neiman R 1961 *J. Chem. Phys.* **35** 149
Kneubuhl F K 1960 *J. Chem. Phys.* **33** 1074
Laxma Reddy K, SriHari S and Lingaiah P 1984 *Indian J. Chem.* **A23** 172
Laxma Reddy K, SriHari S and Lingaiah P 1985 *Indian J. Chem.* **A24** 318
Laxma Reddy K, Veera Reddy K and Lingaiah P 1986 *Polyhedron* **5** 1519
Lever A B P 1968 *Inorganic electronic spectroscopy* (Amsterdam: Elsevier) p. 142

Mathews and Walton R A 1971 *Inorg. Chem.* **10** 1443

Nakamoto K 1978 *Infrared and Raman spectra of inorganic coordination compounds* (New York: Wiley and Sons) p. 229

Nakanishi Koji 1964 *Infrared absorption spectroscopy* (Tokyo: Practical Nankolo Company Ltd) p. 167

Nikolaev A V, Myachina L I and Logvinenko V A 1969 *Thermal analysis* (New York: Academic Press) p. 779

Pasto D J and Johnson C R 1969 *Organic structure determination* (Englewood Cliffs, NJ: Prentice Hall) p. 372

Procter I M, Hathaway B J and Nicholis P 1968 *J. Chem. Soc. A* 1618

Ramaswamy K K, Jose C I and Sen D N 1967 *Indian J. Chem.* **5** 156

Sacconi L 1968 *Transition Met. Chem.* **4** 199

Seetharama Rao T, Laxma Reddy K, Swamy S J and Lingaiah P 1985 *Indian J. Chem.* **A24** 942

Seshadri Naidu R and Raghava Naidu R 1977 *Indian J. Chem.* **A15** 652

Seshadri Naidu R and Raghava Naidu R 1979 *J. Inorg. Nucl. Chem.* **41** 1625

Smith D N 1970 *J. Chem. Soc. A* 3108

Vogel A I 1961 *A text book of quantitative inorganic analysis* (London: Longman) p. 351, 429, 443 and 444

Werden B C, Billing E and Gray H B 1966 *Inorg. Chem.* **5** 78