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Synthesis, thermal, spectral and magnetic studies of complexes of Co(II), Ni(II), Cu(II), Ru(II), Pd(II) and Pt(II) with 2, 3-disubstituted quinazolin-(3H)-4-ones

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Abstract. A number of complexes of Co(II), Ni(II), Cu(II), Ru(II), Pd(II) and Pt(II) with 2-methyl-3-(carboxy methyl) quinazolin (3H)-4-one (MCMQ) and 2-phenyl-3-(carboxy methyl) quinazolin (3H)-4-one (PCMQ) have been synthesized and characterized by analytical, conductivity, thermal, magnetic, infrared, electronic, proton magnetic resonance and electron spin resonance spectral data. Based on analytical data, the stoichiometry and the association with other molecules of the complexes have been determined. Conductivity data show that all these complexes are nonelectrolytes. Infrared and PMR spectral data indicate that both the ligands are uninegative bidentate with all the metal ions. Based on electronic spectral data, the geometries of the complexes have been indicated. Electronic spectral parameters for Co(II) and Ni(II) and ESR parameters for Cu(II) complexes have been calculated and relevant conclusions have been drawn with respect to the nature of bonds present in them.

Keywords. Quinazolones, uninegative bidentate ligands; octahedral geometry; bivalent metal complexes.

1. Introduction

Biologically and pharmacologically active ligands like 2-methyl-3-(carboxy (methyl)quinazoline-(3H)-4-one (MCMQ) and 2-phenyl-3-(carboxy methyl)quinazoline-(3H)-4-one (PCMQ) represented in figure 1 contain both an oxygen/nitrogen on the ring and an oxygen on the substituent at the 3-position as donor centres in the proper

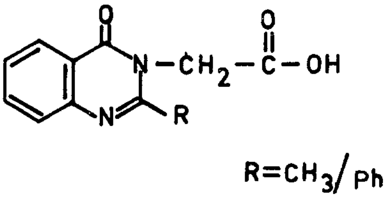

Figure 1. Structure of 2-(substituted)-3-carboxy methyl quinazolin-(3H)-4-one.

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orientation to chelate with the metal ions. Upon coordination to a metal ion the compounds undergo some changes in their electronic structure, which might in turn alter their pharmacological activity. In view of this, it was considered important to study the interaction of 2,3-disubstituted quinazolones with Co(II), Ni(II), Cu(II), Ru(II), Pd(II) and Pt(II) ions. We report here the synthesis and characterisation of these complexes based on analytical, conductivity, thermal, magnetic, infrared, electronic, PMR and ESR data.

2. Materials and methods

2.1 *Materials*

Anthranilic acid, acetic anhydride, benzoyl chloride, glycine and the organic solvents used were of BDH/AR grade. The metal salts used for the preparation of the complexes were of AR grade. Ruthenium trichloride, palladium and platinum dichlorides were obtained from Johnson Matthey Chemicals, (England). The ligands MCMQ and PCMQ were prepared as reported in literature and their purities were checked by TLC and melting point determinations (Soliman and Soliman 1973). The complex $RuCl_2(DMSO)_4$ was prepared by the published method (Evans *et al* 1973).

2.2 *Preparation of metal complexes*

In the preparation of the Co(II), Ni(II) and Cu(II) complexes the following general procedure was adopted. Metal acetate solution (1 m mol) in methanol was added dropwise to a solution of the ligand in acetone ($\approx$ 3 m mol) with constant stirring. In all the cases, the ligand concentration was taken in slight excess of the 1:3 metal–ligand molar ratio. The reaction mixture was refluxed on a water bath for 30–60 min. The complexes separated out on cooling and were filtered through a sintered glass crucible (G_4) and were washed with methanol several times and finally with acetone. The complexes were dried *in vacuo* over fused calcium chloride.

Complexes of Pd(II) and Pt(II) were prepared as follows: 1 g of metal(II) chloride was dissolved in 1 ml concentrated hydrochloric acid and diluted to 100 ml to give a 0·1 M solution. The metal chloride solution (0·1 mol) was treated with an equal volume of water. To this solution was added the ligand in acetone (0·3 mol) (30 ml) drop-by-drop with constant stirring. The reaction mixture was refluxed on a water bath for about 30–60 min. The complex separated out in a neutral medium on cooling. It was filtered through a sintered glass crucible and washed with hot water and acetone. The complexes were dried *in vacuo* over fused calcium chloride.

The following procedure was used for the preparation of Ru(II) complexes. The complex, $RuCl_2(DMSO)_4$ (0·2 g), was suspended in toluene (30 ml) and refluxed for one hour with about three moles excess of the ligand in acetone (10 ml). During the period of refluxing the whole suspension dissolved resulting in a clear solution, which was then evaporated under reduced pressure to remove the excess solvent. The residue was treated with diethyl ether when the solid complex precipitated. This was filtered off, washed several times with diethyl ether, dried and recrystallised from ethanol–ether to give a pure complex.

2.3 *Physical measurements*

Analytical data (C, H, N) for the ligands and their metal complexes were obtained from the Microanalytical Laboratory, Calcutta University, Calcutta. The metal content in the complexes after heating to decomposition temperatures were determined by the authors using standard procedures (Vogel 1961). The conductance measurements of the complexes in dimethyl formamide were made at a concentration of 10^{-3} M, using a Digisum Digital Conductivity-meter, Model-DI-909 with Philips dip-type conductivity cell. The magnetic measurements of the complexes in the solid state were made on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constants. TGA and DTA curves of the complexes were recorded on a Leeds and Nathrup DTA unit (USA) using calcined alumina as the reference material. The experiments were carried out in the presence of air using Pt/Rh thermocouples in a Robert–Grimshaw type ceramic sample holder. The infrared spectra in the range 4000–200 cm^{-1} of the ligands and their metal complexes in nujol and KBr were recorded making use of a Perkin–Elmer infrared spectrophotometer, Model-283. The UV and visible spectra in DMF were recorded in a Shimadzu Multipurpose Recording spectrophotometer, Model-MPS-5000. Jeol 100 MHz spectrophotometer was used for recording PMR spectra and a Varian E-4 X-band spectrophotometer for recording the ESR spectra of Cu(II) complexes.

3. Results and discussion

All the complexes are stable at room temperature, nonhygroscopic, insoluble in water and many of the common organic solvents, but soluble in DMF and DMSO. The analytical and physical data of the complexes are listed in table 1. The analytical data of the complexes indicate that the metal to ligand molar ratio is 1:2 and that the complexes of Co(II) and Ni(II) are associated with two water molecules each, and Ru(II) complexes with two DMSO groups. The molar conductance values of the complexes in DMF are in the range 12–22 $mhos\,cm^2\,mol^{-1}$, indicating their non-electrolytic nature (Geary 1971).

3.1 *Thermal study*

It is known from the TGA and DTA curves that all the complexes except those of Co(II) and Ni(II) complexes are thermally stable upto 220°C indicating that they are not hydrated. The TGA of Co(II) and Ni(II) complexes show weight loss in the temperature range 140–180°C corresponding to two water molecules. The expulsion of water from the complexes in this temperature range also indicates that they are present inside the coordination sphere (Nikoleeve *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 230°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 proposed on the basis of analytical data.

Table 1. Analytical and physical data of the complexes.

Complex	Colour	M.P. (°C)[a]	Analysis (%)[b] M	C	N	H	S	Molar conductance (mho cm^2 mol^{-1})
[Co(MCMQ)$_2$(H$_2$O)$_2$]	Brick red	307	11·09 (11·05)	49·72 (49·68)	10·54 (10·50)	4·52 (4·49)	—	18
[Co(PCMQ)$_2$(H$_2$O)$_2$]	Red	305	8·99 (8·95)	58·63 (58·60)	8·55 (8·51)	4·27 (4·25)	—	15
[Ni(MCMQ)$_2$(H$_2$O)$_2$]	Brown	320	11·05 (11·01)	49·74 (49·69)	10·55 (10·51)	4·52 (4·48)	—	12
[Ni(PCMQ)$_2$(H$_2$O)$_2$]	Dark brown	318	8·96 (8·92)	58·65 (58·62)	8·55 (8·52)	4·27 (4·25)	—	20
[Cu(MCMQ)$_2$]	Green	310	12·71 (12·68)	52·84 (52·80)	11·21 (11·17)	4·00 (3·96)	—	17
[Cu(PCMQ)$_2$]	Light green	315	10·19 (10·16)	61·58 (61·52)	8·98 (8·91)	3·84 (3·81)	—	22
[Ru(MCMQ)$_2$(DMSO)$_2$]	Snuff	300	14·58 (14·54)	45·01 (45·00)	8·07 (8·01)	4·61 (4·55)	9·23 (9·20)	14
[Ru(PCMQ)$_2$(DMSO)$_2$]	Snuff	320	12·36 (12·31)	52·87 (52·82)	6·85 (6·81)	4·40 (4·36)	7·83 (7·81)	19
[Pd(MCMQ)$_2$]	Yellow	312	19·61 (19·56)	48·67 (48·62)	10·32 (10·30)	3·68 (3·64)	—	15
[Pd(PCMQ)$_2$]	Yellow	318	15·96 (15·92)	57·62 (57·60)	8·40 (8·36)	3·60 (3·56)	—	20
[Pt(MCMQ)$_2$]	Black	310	30·91 (30·87)	41·83 (41·80)	8·87 (8·85)	3·16 (3·10)	—	12
[Pt(PCMQ)$_2$]	Black	315	25·83 (25·80)	50·85 (50·81)	7·41 (7·35)	3·17 (3·14)	—	14

[a] All the complexes decompose above the temperature cited; [b] calculated values in parentheses.

3.2 *Infrared spectra*

Important absorption frequencies of ligands and complexes along with their assignments are listed in table 2.

In the IR spectra of the ligands, a strong band corresponding to $\nu(C{=}O)$ of the quinazolone ring is observed at 1690 cm^{-1}. This band is shifted to lower wavenumbers by 35–50 cm^{-1} in the spectra of all the complexes indicating that the carbonyl oxygen is invariably involved in coordination with all the metals (Sahai *et al* 1982). The ligands also contain a carboxylic group at the 3-position of the quinazolone ring. The characteristic $\nu(OH)$ is observed as a broad band at 2500 cm^{-1} in both the ligands and disappears completely in their complexes indicating the participation of the oxygen of the carboxyl group in the coordination (Singh *et al* 1980). Changes observed in $\nu_{as}(COO)$ and $\nu_s(COO)$ bands due to the coordination of the carboxylate group to the metal ions in all the complexes are consistent with earlier observations (Laxma Reddy *et al* 1984). Both ligands also contain one (C=N) group of the quinazolone ring. The stretching frequency of this group appears at 1640 cm^{-1} in the free ligands and in the complexes indicating that the nitrogen is not involved in the coordination (Prabhakaran and Patel 1972).

In addition, Co(II) and Ni(II) complexes show broad, medium intense peaks between 3500–3300 cm^{-1} which may be attributed to the OH-stretching frequency of water in the complexes. These complexes also show bands at 1600 and 800 cm^{-1} due to HOH bending and rocking (ρH_2O), respectively, indicating the presence of coordinated water (Nakamoto 1978). Presence of DMSO in the Ru(II) complexes was characterised by its $\nu(S{=}O)$, which decreases when it is coordinated through oxygen and increases upon binding to the metal through sulphur (Reynolds 1970). The IR spectra of Ru(II) complexes exhibit bands due to $\nu(S{=}O)$ in the region 1050–1100 cm^{-1} corresponding to the S-bonded DMSO groups (Evans *et al* 1973).

The participation of oxygen in coordination in all the complexes and also of sulphur

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

Compound	Infrared assignment (cm^{-1})			
	$\nu(OH)$	$\nu(C{=}O)$	$\nu(C{=}N)$	$\nu(M{-}O)$
MCMQ	2500	1690	1640	—
$[Co(MCMQ)_2 2H_2O]^a$	3400^a	1650	1635	430, 400
$[Ni(MCMQ)_2 2H_2O]^a$	3450^a	1640	1640	440, 410
$[Cu(MCMQ)_2]$	—	1650	1640	450, 430
$[Ru(MCMQ)_2(DMSO)_2]$	—	1630	1640	420, 310^b
$[Pd(MCMQ)_2]$	—	1655	1645	440, 400
$[Pt(MCMQ)_2]$	—	1650	1635	450, 410
PCMQ	2500	1690	1640	—
$[Co(PCMQ)_2 2H_2O]$	3350^a	1650	1635	430, 410
$[Ni(PCMQ)_2 2H_2O]$	3350^a	1650	1640	430, 420
$[Cu(PCMQ)_2]$	—	1635	1640	450, 420
$[Ru(PCMQ)_2(DMSO)_2]$	—	1635	1640	420, 330^b
$[Pd(PCMQ)_2]$	—	1635	1640	460, 420
$[Pt(PCMQ)_2]$	—	1640	1640	460, 430

[a] The band is due to $\nu(OH)$ of coordinated water; [b] The band is due to $\nu(Ru{-}S)$.

in Ru(II) complexes is further confirmed by the presence of nonligand bands in their far-infrared spectra. The bands observed around 400 and 300 cm^{-1} in the complexes may be due to ν(M–O) and ν(M–S) respectively (Laxma Reddy *et al* 1984).

3.3 *PMR spectra*

PMR spectra were recorded for Ru(II), Pd(II) and Pt(II) complexes. The spectra of these complexes bear general resemblance to those of the free ligands, nevertheless some differences are evident because of coordination. A strong absorption due to the –OH group of carboxylic acid appeared at 10·5δ in the free ligands and totally disappears in the complexes, confirming the coordination of oxygen with deprotonation (Laxma Reddy *et al* 1986). A single intense signal in the region 3·0–3·5δ in Ru(II) complexes with a downfield shift of about 0·7–0·9 ppm from that of free DMSO, indicates the presence of S-bonded DMSO ligands in the complexes (Evans *et al* 1973). Both the ligands and their complexes show signals in the region 7·1–8·9δ which are due to aromatic protons. A signal in the region 2·4–2·8δ in MCMQ and its complexes has been assigned to methyl protons.

3.4 *Electronic spectra*

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

The ligands exhibit strong bands around 34,000 cm^{-1} and 31,000 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 8300, 17,000 and 21,000 cm^{-1} which may be assigned to the spin-allowed transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ respectively, characteristic of octahedral geometry around Co(II) (Matthews and Walton 1971). Nickel(II) complexes also exhibit three bands in their electronic spectra around 9000, 15,000 and 24,000 cm^{-1} and these have respectively been assigned to the transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ characteristic of octahedral geometry (Sacconi 1968). The octahedral geometry of Co(II) and Ni(II) complexes is further supported by the ratio ν_2/ν_1 which lies around 2·2 and 1·65, respectively. The ratio ν_2/ν_1 obtained for the complexes is lower than that of regular octahedral aquo complexes which may be due to the asymmetric environment around Co(II) and Ni(II).

Various ligand field parameters, such as the ligand field splitting energy ($10D_q$), Racah-interelectronic 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) (Lever 1968). The calculated $10D_q$ 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 the free ion value which is an indication of orbital overlap and delocalization of d-orbitals. The β-values obtained are less than one suggesting a considerable amount of covalent character in the metal–ligand bonds.

Generally, electronic spectra of Cu(II) complexes with square-planar geometry display two bands around 15,000 and 20,000 cm^{-1} which may be due to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions (Werden *et al* 1966). The present Cu(II) complexes exhibit a broad band centred at 17,000 cm^{-1} and thus are assigned square-planar geometry.

Two bands are observed at 20,000 and 24,000 cm^{-1} in Ru(II) complexes which may

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

Complex	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_2/ν_1	$10D_q$ (cm^{-1})	B (cm^{-1})	β	LFSE (k cal mol^{-1})	μ_{eff} (BM)	
									Expt.	Calc.
[Co(MCMQ)$_2$2H$_2$O]	8300	17,100	19,900	2·06	8800	806·7	0·71	20·19	4·98	5·01
[Co(PCMQ)$_2$2H$_2$O]	8300	17,000	20,000	2·04	8700	806·7	0·71	20·11	5·03	5·01
[Ni(MCMQ)$_2$2H$_2$O]	8800	14,800	24,200	1·68	6000	840·0	0·80	20·57	3·16	3·18
[Ni(PCMQ)$_2$2H$_2$O]	9000	14,900	24,000	1·65	5900	793·4	0·76	20·91	3·16	3·18
[Cu(MCMQ)$_2$]	—	17,000[a]	—	—	—	—	—	—	1·82	1·81
[Cu(PCMQ)$_2$]	—	16,900[a]	—	—	—	—	—	—	1·82	1·82
[Ru(MCMQ)$_2$(DMSO)$_2$]	—	20,000	24,000	—	—	—	—	—	Diamagnetic	
[Ru(PCMQ)$_2$(DMSO)$_2$]	—	20,000	24,250	—	—	—	—	—	Diamagnetic	
[Pd(MCMQ)$_2$]	—	15,500	20,150	—	—	—	—	—	Diamagnetic	
[Pd(PCMQ)$_2$]	—	15,000	20,200	—	—	—	—	—	Diamagnetic	
[Pt(MCMQ)$_2$]	—	21,150	25,000	—	—	—	—	—	Diamagnetic	
[Pt(PCMQ)$_2$]	—	21,200	24,500	—	—	—	—	—	Diamagnetic	

[a] Broad band indicating overlapping of different transitions

be due to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively, characteristic of octahedral geometry (Laxma Reddy *et al* 1986). Absence of splitting of the lower energy band in the electronic spectra of Ru(II) complexes indicates that there is no tetragonal distortion (Seetha Rama Rao *et al* 1988). The Pd(II) complexes show two bands around 15,000 and 20,000 cm^{-1} which may be due to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ transitions respectively characteristic of square-planar geometry (Seetha Rama Rao *et al* 1988). Platinum(II) complexes also exhibit two bands at 21,000 and 24,000 cm^{-1} characteristic of square-planar geometry (Prabhakar *et al* 1988).

3.5 *Magnetic moment*

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

The magnetic moment values obtained for the complexes of Co(II) indicate that they are of the octahedral type. In octahedral geometry the ground term is ${}^4T_{2g}$ 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. In an attempt to correlate the spectral and magnetic properties, μ_{eff} values have been calculated and are in agreement with experimental values suggesting considerable orbital contribution (Figgis 1966). All the Ni(II) complexes are found to be paramagnetic and to have a magnetic moment corresponding to octahedral geometry (Khulbe *et al* 1981). μ_{eff} values have also been calculated using $10\,D_q$ (Figgis 1966) and are in good agreement with experimental values indicating a small orbital contribution due to spin-orbit (SO) mixing of the ground state ${}^3A_{2g}$ with the first excited state ${}^3T_{2g}$. This also indicates the validity of the ligand field parameters $10\,D_q$, B and the $\mu_{\text{eff}}^{\text{expt}}$. All the Cu(II) complexes are paramagnetic and possess magnetic moments equivalent to one unpaired electron. However, the values are found to be less than 1·90 BM indicating that the complexes are of the tetragonal type. The excess over the spin-only value of 1·73 BM observed in the present complexes might be due to spin-orbit coupling in which case the μ_{eff} values have been calculated using the equation (Figgis 1966),

$$\mu_{\text{eff}}^{\text{cal}} = \mu_{\text{eff}}^{\text{SO}}(1 - 2\lambda/10\,D_q)$$

where λ is the spin-orbit coupling constant of the metal ion in the complexes. The experimental values are in good agreement with the calculated ones and also further support the tetragonal geometry proposed on the basis of electronic spectral data. All the Ru(II), Pd(II) and Pt(II) complexes are found to be diamagnetic and this is confirmed by the absence of a peak in their ESR spectra.

3.6 *ESR spectra*

ESR studies of the Cu(II) complexes are of much interest because their ground states are orbitally degenerate in regular geometries and non-degenerate in distorted geometries, since an orbitally degenerate configuration is susceptible to a Jahn–Teller distortion (Jahn and Teller 1937). Basically, the interpretation of the ESR spectrum of an isolated transition metal ion yields values for two kinds of parameters: (1) the spectroscopic splitting constants (g-values) which describe the frequencies between the different electron spin states and (2) the hyperfine coupling constants (A) which give a measure of electron spin–nuclear spin interactions. These parameters are affected by the presence of ligands around the central metal ion.

The ESR spectra of the Cu(II) complex of MCMQ at room temperature and at liquid nitrogen temperature are given in figures 2 and 3. The ESR parameters are listed in table 4. The ESR spectra of Cu(II) complexes in the solid state at liquid nitrogen temperature exhibit a set of four well-resolved peaks in the low-field region and intense unresolved peaks in the high-field region. From these well-resolved peaks the values of $g_\parallel$ and $A_\parallel$ have been calculated (Kneubuhl 1960). The $g_\perp$ and $A_\perp$ values have been calculated from the unresolved peaks in the high field region. The ESR spectra of Cu(II) complexes in the solid state at room temperature show only one peak from which the g_{av} has been calculated (Kneubuhl 1960).

The g tensor values of Cu(II) complexes can be used to derive the ground state (Ballhausen 1962). In elongated octahedral (tetragonal) and square-planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbitals 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 a d_{z^2} orbital giving ${}^2A_{1g}$ as the 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 states, 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 the $d_{x^2-y^2}$ transition (Smith 1970). Both these 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 the covalent character of the

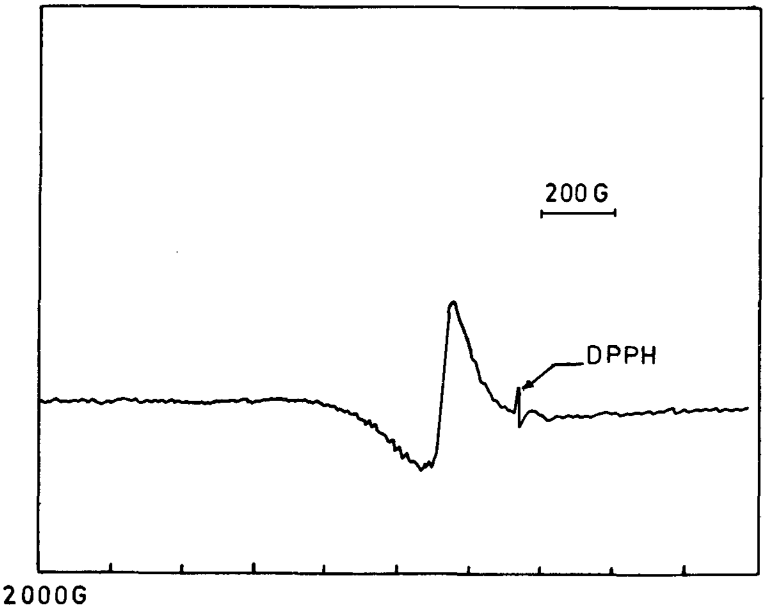

Figure 2. ESR spectrum of Cu(II) complex of MCMQ at room temperature.

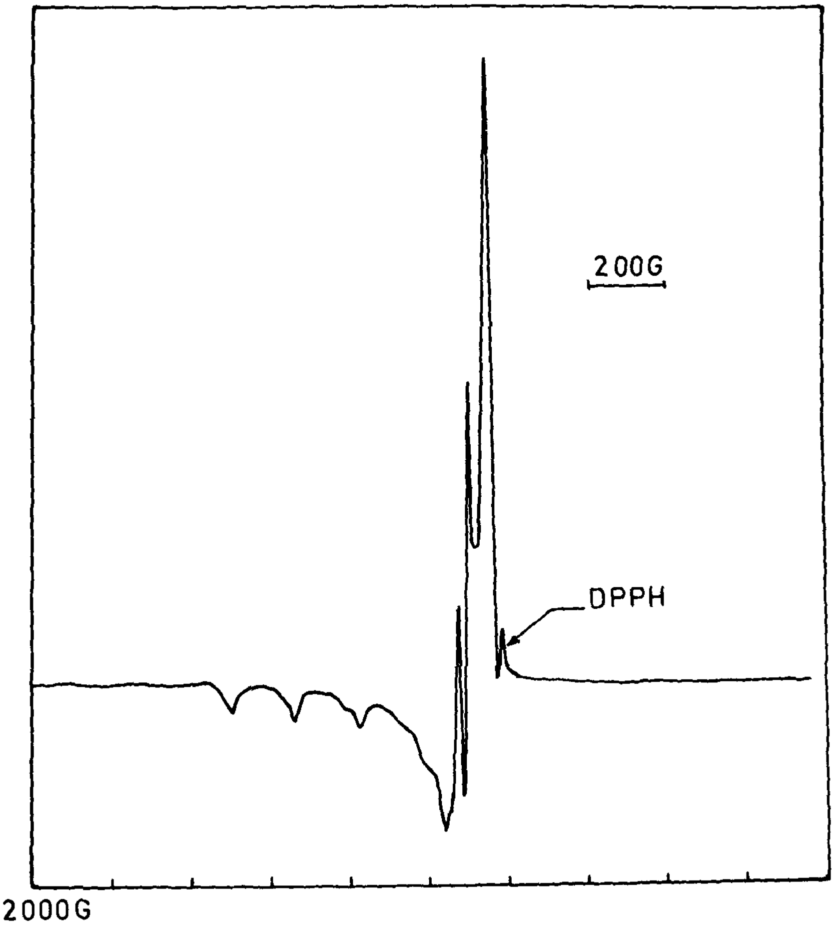

Figure 3. ESR spectrum of Cu(II) complex of MCMQ at liquid nitrogen temperature.

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

ESR parameter	[Cu(MCMQ)$_2$]	[Cu(PCMQ)$_2$]
$g_{\parallel}$	2·14	2·13
$g_{\perp}$	2·03	2·03
g_{av}	2·06	2·06
$A_{\parallel}$	0·26	0·27
$A_{\perp}$	0·16	0·16
α^2	0·27	0·27
β^2	1·23	1·14
γ^2	0·99	0·99
$r_{\parallel}^2$	0·33	0·30
$r_{\perp}^2$	0·26	0·27
G	4·97	4·61
λ	280	260

metal–ligand bond. The theoretical hyperfine parameters ($A_\parallel$ and $A_\perp$) have been calculated using the expressions (Maki and McGarvey 1958),

$$A_\parallel = P - (4\alpha^2/7) - K + (g_\parallel - 2{\cdot}0023) + (3/7)(g_\perp - 2{\cdot}0023),$$

$$A_\perp = P + (2\alpha^2/7) - K + (11/14)(g_\perp - 2{\cdot}0023),$$

where $P = 0{\cdot}036$ and $K = 0{\cdot}30$ are the spin-orbit interaction factor and Fermicontact term, respectively.

The metal–ligand σ bonding parameter α^2, has been calculated using the following relationship (Narayana *et al* 1975).

$$g_{\mathrm{av}} = 2{\cdot}0023 - 4\lambda\alpha^2/\Delta E.$$

The value ΔE is obtained from the electronic spectra and λ is the spin-orbit coupling constant of free metal ion ($-828\,\mathrm{cm}^{-1}$). Using the $g_\parallel$, $g_\perp$, P, K and α values the $A_\parallel$ and $A_\perp$ values have been calculated and are in good agreement with the experimental values.

The axial symmetry parameter G is defined as $(g_\parallel - 2{\cdot}0023)/(g_\perp - 2{\cdot}0023)$ and shown to be a measure of the exchange interaction between copper centres in polycrystalline solids (Procter *et al* 1988). 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, 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 0·3–0·4 indicating the presence of appreciable in-plane covalency. As $r_\parallel^2 > r_\perp^2$ in all the complexes, this indicates that the ligands are of the out-of-plane π-bonded type (Hathaway 1973). The spin-orbit coupling constant for the complexes is found to be 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 of the complexes $\mu^2 = (3/4)|g|^2$ and the calculated values are in good agreement with experimental ones.

Based on their stoichiometry, conductance, magnetic, infrared, PMR and electronic data, all the Co(II), Ni(II), Ru(II) complexes are tentatively assigned octahedral geometries while Cu(II), Pd(II) and Pt(II) complexes possess square-planar geometries with each bidentate chelate forming a seven-membered ring as shown in figure 4.

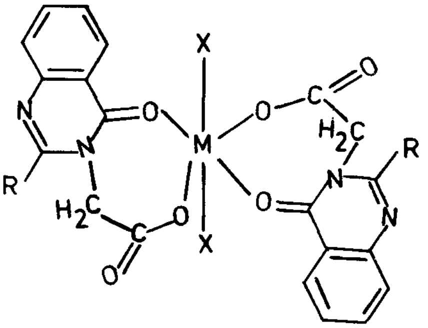

Figure 4. Structure of complexes of Co(II), Ni(II), Cu(II), Ru(II), Pd(II) and Pt(II). When M is Co(II) or Ni(II), X = H_2O; when M = Ru(II), X = DMSO; when M = Cu(II), Pd(II) or Pt(II), there is no X.

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