

Synthesis and characterisation of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) bis- chelates of 8-quinolinyl oxyacetic acid and a few mixed ligand complexes of Cu(II) with 8-quinolinyl oxyacetic acid

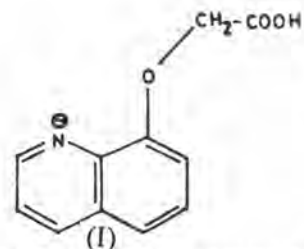
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Manganese(II), cobalt(II), nickel(II) and zinc(II) complexes of the type $[M(EHQ)_2(H_2O)_2]$ and $Cu(EHQ)_2$ with the ligand 8-quinolinyl oxyacetic acid (EHQH) have been isolated and characterized on the basis of elemental analyses, spectral, magnetic and thermal data. Copper(II) mixed ligand complexes of the type $[Cu(EHQ)L(H_2O)]$, where LH = 8-hydroxyquinoline(oxineH) / 1-acetyl-2-naphtholoxime (OATNOH) / salicylaldehyde phenylhydrazone (SalphH) have also been characterised similarly.

The mode of bonding of aryloxyacetic acids with metal ions, particularly with copper(II) seems interesting. In the copper(II) complex of phenoxyacetic acid, the ligand behaves like a bidentate ligand coordinating through ethereal oxygen and a carboxylato-oxygen as established by X-ray studies^{1,2}. With 1-naphthoxyacetic acid, Cu(II) forms an octahedral complex wherein the aryloxyacetic acid behaves as a monodentate ligand³, but in the case of 2-naphthoxyacetic acid, Cu(II) forms a binuclear complex^{4,5}, similar to cupric acetate monohydrate. With regard to lanthanide(III) ions all the above three ligands, namely, phenoxyacetic acid, 1-naphthoxyacetic acid and 2-naphthoxyacetic acid as well as 8-quinolinyl oxyacetic acid form bidentate chelates wherein the two oxygen atoms of the carboxylato group are involved in bonding^{6,7}. Since 3d ions are not hard acids like lanthanide(III) ions, the imine-N of EHQH may itself involve in bonding. Keeping this in view, we have prepared bis-chelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 8-quinolinyl oxyacetic acid (I) and three mixed ligand



complexes using 8-quinolinyl oxyacetic acid as the primary ligand, and 8-hydroxyquinoline or salicylaldehyde phenylhydrazone or 1-acetyl-2-naphtholoxime as the secondary ligand.

Experimental

All the metal(II) acetates employed were of analar grade. The ligands were prepared by the known procedures⁷.

Preparation of bis-chelates

To a solution of 8-quinolinyl oxyacetic acid (2.03 g, 10 mmol) in aqueous ethanol (1:1, 250 ml) was added a solution of metal(II) acetate (5 mmol) in aqueous ethanol (1:1, 200 ml). The precipitated complex was suction-filtered, washed with aqueous ethanol (1:1), dried in air and then *in vacuo* over anhydrous calcium chloride.

Preparation of the mixed ligand complexes

To a solution of 8-quinolinyl oxyacetic acid (10 mmol) and 8-hydroxyquinoline / 1-acetyl-2-naphtholoxime / salicylaldehyde phenylhydrazone (10 mmol) in aqueous ethanol (1:1, 400 ml), was added a solution of copper(II) acetate (10 mmol) in aqueous ethanol (1:1, 400 ml). The complex settled was suction-filtered, washed with aqueous ethanol (1:1), dried in air and then *in vacuo* over anhydrous calcium chloride.

The purity of the mixed ligand complexes was confirmed by TLC. The metal contents of the complexes were estimated by incinerating them to the oxides. The conductivity measurements were made using a Toshniwal conductivity meter with a dip-type cell fitted with a platinised platinum electrode (cell constant, 0.734), using approximately $1 \times 10^{-3} M$

solution of the complexes. The magnetic susceptibility measurements were carried out using solid samples on a simple Gouy type magnetic balance at room temperature (303-308 K). The infrared spectra of all the complexes and ligands were recorded as KBr pellets on a Perkin-Elmer 527 Infrared spectrophotometer ($200-4000\text{ cm}^{-1}$). The electronic spectral measurements of the complexes were made in chloroform solution with a Shimadzu UV-visible spectrophotometer (UV-160).

Results and discussion

The results of elemental analysis and magnetic moment data of the complexes are given in Table 1. All the complexes are insoluble in water, but soluble in solvents like chloroform or DMF. The complexes are non-conducting as shown by the molar conductance values which lie in the range $2-8\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$.

The isothermal heating at 120°C indicated mass loss corresponding to two water molecules for the bis-chelates of Ni(II), Co(II) and Mn(II) whereas the corresponding Zn(II) complex revealed mass loss for two water molecules at 80°C . Similar mass loss corresponding to the presence of water molecules was not observed for copper(II) bis-chelate, which

suggests the absence of either coordinated or hydrated water molecules. All the three copper(II) mixed ligand complexes indicated mass loss corresponding to one water molecule at $115-120^\circ\text{C}$.

All the copper(II) complexes showed μ_{eff} values in the range 1.80-1.82 B.M. The Mn(II), Co(II) and Ni(II) bis-chelates showed μ_{eff} values 5.85, 4.95, and 3.01 B.M. respectively, suggesting octahedral nature for these complexes. The Zn(II) bis-chelate is diamagnetic as expected

In the case of carboxylato complexes, attempts have been made to relate values of the carbon-oxygen stretching frequencies to the nature of the carboxylate coordination. The unidentate coordination removes the equivalence of two oxygen atoms. If the carbon-oxygen bond orders are appreciably affected, a pseudo-ester configuration is obtained. This should increase $\nu_{\text{as}}(\text{COO})$ and decrease $\nu_{\text{s}}(\text{COO})$ thereby increasing the separation between the two carboxylato stretching frequencies relative to the values for the free carboxylate ion, usually taken as those of the sodium or potassium salts⁸.

Infrared spectrum of sodium salt of 8-quinolinyl-oxoacetic acid exhibits $\nu_{\text{as}}(\text{COO})$ at 1605 cm^{-1} and $\nu_{\text{s}}(\text{COO})$ at 1405 cm^{-1} . The infrared spectra of Mn(II), Co(II), Ni(II) and Zn(II) complexes exhibit

Table 1 — Analytical and magnetic moment data of complexes

Compound	Found (Calc.), %				μ_{eff} (B.M)
	Metal	C	H	N	
1. Cu(EHQ) ₂	13.45 (13.60)	56.02 (56.46)	3.36 (3.42)	6.01 (5.98)	1.80
2. Cu(EHQ)(oxine)(H ₂ O)	14.62 (14.86)	56.45 (56.13)	3.44 (3.74)	6.42 (6.55)	1.82
3. Cu(EHQ)(OATNO)(H ₂ O)	12.96 (13.14)	56.82 (57.08)	4.27 (4.13)	5.98 (5.79)	1.82
4. Cu(EHQ)(Salph)(H ₂ O)	12.62 (12.85)	57.96 (58.23)	4.35 (4.24)	8.21 (8.49)	1.80
5. Co(EHQ) ₂ (H ₂ O) ₂	11.65 (11.81)	52.62 (52.91)	3.96 (4.00)	5.52 (5.61)	4.95
6. Ni(EHQ) ₂ (H ₂ O) ₂	11.52 (11.77)	52.58 (52.93)	3.98 (4.01)	5.58 (5.61)	3.01
7. Zn(EHQ) ₂ (H ₂ O) ₂	13.15 (12.93)	52.04 (52.23)	3.94 (3.95)	5.51 (5.54)	dia
8. Mn(EHQ) ₂ (H ₂ O) ₂	10.95 (11.09)	52.98 (53.34)	4.08 (4.04)	5.59 (5.65)	5.85

EHQH = 8-quinolinyl-oxoacetic acid, oxine H = 8-hydroxyquinoline, OATNOH = 1-acetyl-2-naphtholoxime, SalphH = salicylaldehydophenylhydrazone

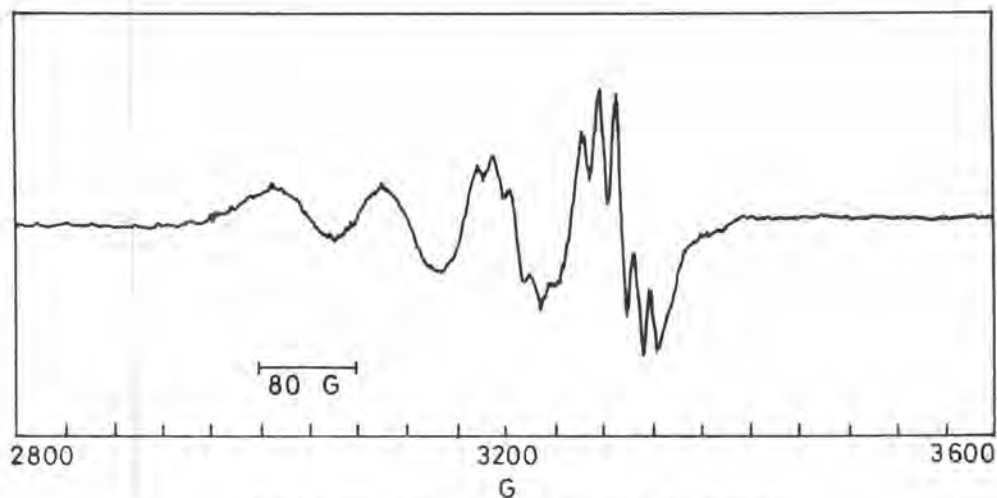
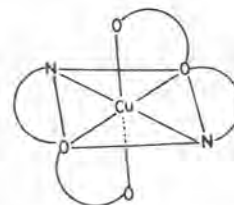


Fig.1 — ESR spectrum of Cu(EHQ)(OATNO)(H₂O)

$\nu_{as}(\text{COO})$ at 1573, 1573, 1572 and 1565 cm^{-1} respectively; and $\nu_s(\text{COO})$ at 1420, 1420, 1415 and 1415 cm^{-1} respectively. These values suggest bidentate chelating mode of coordination for these complexes⁹⁻¹¹. A broad band around 3200-330 cm^{-1} is observed for all these complexes indicating the presence of water molecules in these complexes.

The infrared spectrum of bis(8-quinolinyl-oxoacetato) copper(II), exhibits $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ at 1625 and 1395 cm^{-1} respectively. These values when compared with the values of corresponding sodium salt suggest the monodentate coordination of the carboxylato group⁸. It was not possible to assign unambiguously the $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ modes for the mixed ligand complexes. However, the three mixed ligand complexes exhibit a broad band around 3400 cm^{-1} indicating the presence of water molecule in these complexes.

The electronic absorption spectra of bis(8-quinolinyl-oxoacetato) copper(II) [Cu(EHQ)₂], (8-quinolinyl-oxoacetato) (8-hydroxyquinolinato) aquo-copper(II) [Cu(EHQ)(oxine)(H₂O)], (8-quinolinyl-oxoacetato) (1-acetyl-2-naphtholato-oximate) aquo-copper(II) [Cu(EHQ)(OATNO)(H₂O)], (8-quinolinyl-oxoacetato) (salicylaldehyde-phenylhydrazonato) aquo-copper(II) [Cu(EHQ)(Salph)(H₂O)], exhibit absorption bands at 15290, 14925, 15674, 14771 cm^{-1} , respectively corresponding to the transitions ${}^2B_{1g} \rightarrow {}^2B_{2g}, {}^2E_g$ in a D_{4h} environment. For the cobalt complex of EHQH, namely, Co(EHQ)₂(H₂O)₂, the expected transition [${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$] in the visible region is masked by the



axial oxygen = ether oxygen
equatorial oxygen = carboxylato oxygen
(II)

intense charge-transfer band in the UV region. The Ni(II) complex of EHQH, Ni(EHQ)₂(H₂O)₂ exhibits a shoulder around 15385 cm^{-1} on the low energy side of the charge-transfer band which may be assigned to the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in an octahedral environment. The manganese(II) complex of 8-quinolinyl-oxoacetic acid shows no definite band in the visible region as is common for high-spin octahedral complexes.

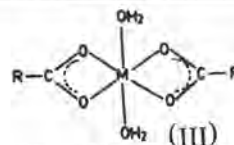
The EPR spectra of all the four copper(II) complexes were taken in chloroform solution at room temperature as well as at liquid nitrogen temperature. The X-band EPR spectra of these complexes in chloroform solution at ambient temperature exhibit the four copper hyperfine lines. For all the four copper complexes the N-shf structure is well resolved into five lines in the fourth line of copper hyperfine lines, with N_1 value of 12 G. But with the complex [Cu(EHQ)(OATNO)(H₂O)], the N-shf structure is well resolved into five lines, also in the third line of copper hyperfine lines (Fig.1). This indicates the presence of two equivalent imine N donors. Even though the electronic environment of both the imine

Table 2 — EPR data for copper complexes (CHCl₃/RT & LNT)

Complex	g_0	$A_0 \times 10^4$ (cm ⁻¹)	$g_{ }$	g_{\perp}	$A_{ } \times 10^4$ (cm ⁻¹)	$A_{\perp} \times 10^4$ (cm ⁻¹)	$g_{ }/A_{ }$
Cu(EHQ) ₂	2.087	81	2.235	2.067	205	49	109
Cu(EHQ)(oxine)(H ₂ O)	2.092	85	2.247	2.065	192	64	117
Cu(EHQ)(OATNO)(H ₂ O)	2.092	83	2.238	2.079	185	52	121
Cu(EHQ)(Salph)(H ₂ O)	2.099	82	2.245	2.056	196	50	115

nitrogens is not the same, it could not be differentiated in RT solution spectra. The frozen solution spectra are axial. The g_{11} value observed is less than that for CuO₄(2.28 - 2.40)¹² and greater than that for CuN₄ indicating the presence of CuN₂O₂ chromophore which is consistent with the electronic spectral data. The diagonal shifting of A_{11} and g_{11} values by tetrahedral distortion arising from the dependence of g_{11} on the dihedral angle ω (a measure of distortion) may be conveniently expressed by the quotient¹³ g_{11}/A_{11} . This quotient ranges from 105 to 135 cm for square-planar structure, the CuS₄ center being at the higher end of this range. For the present complexes, the quotient is in the range 109-121, indicating that the CuN₂O₂ chromophore is strictly square-planar. Thus the following structure (II) may be assigned for the bis-chelate of copper(II). The EPR data of the four complexes are presented in Table 2.

From the above discussion, it is interesting to note that 8-quinolinylxyacetic acid behaves as a tridentate ligand in the copper(II) complexes in contrast to lanthanide chelates wherein it acts as a bidentate ligand. Thermal studies indicate the presence of one coordinated water molecule in the mixed-ligand complexes. IR data suggest monodentate coordination of the carboxylato group for the bis-chelate of copper(II) similar to Cu(II) phenoxyacetato complex. EPR spectral data reveal the presence of square-planar CuN₂O₂ chromophore, as seen from the g_{11} and A_{11} values. These conclusions are in conformity with the λ_{max} values (14700 - 15700 cm⁻¹) of the complexes. It could also be inferred that the ligand 8-quinolinylxyacetic acid forms complexes with Mn(II), Co(II) and Ni(II) with the following structure (III).



The above structure is supported by spectral and magnetic moment studies. The Zn(II) complex of EHQH may be tetrahedral with two coordinated water molecules. The non-ionic nature of all the complexes studied is revealed by their low molar conductance values.

Acknowledgement

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