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SYNTHESIS AND CHARACTERIZATION OF SOME NEW TRANSITION METAL COMPLEXES OF THE SCHIFF BASE DERIVED FROM QUINOXALINE-2-CARBOXALDEHYDE AND 2-AMINOPHENOL

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ABSTRACT

Some new transition metal complexes of the Schiff base quinoxaline-2-carboxalidene-2-aminophenol (HQAP) have been synthesized and characterized by elemental analyses, conductance and magnetic measurements and IR and UV-Visible spectral studies. The complexes have the following empirical formulae: $[Mn(QAP)_2]$, $[Fe(QAP)_2Cl]$, $[Co(QAP)_2]$, $[Ni(QAP)_2]$ and $[Cu(QAP)_2]$. A tetrahedral structure has been assigned for the manganese(II), cobalt(II), nickel(II) and copper(II) complexes. For the iron(III) complex an octahedral dimeric structure has been suggested.

INTRODUCTION

Quinoxalines are bicyclic, heterofused systems widely distributed in nature. Numerous synthetic quinoxalines are also reported. They are reported to have useful antibacterial, antiinflammatory, analgesic and tuberculostatic properties[1]. Quinoxalinoyl residues are present in several biologically active polypeptides such as levomycin, actinoleukin and echinomycin[2]. Quinoxaline derivatives play an important role in the synthesis of the antibiotic peptide triostin[3]. We thought it is worthwhile to synthesize a new Schiff base by the condensation of quinoxaline-2-carboxaldehyde with 2-aminophenol and its metal complexes. Aminophenols are also important to the pharmaceutical industry, since they have antibacterial and antitubercular action. Schiff bases obtained by the condensation of 2-aminophenol with some aldehydes and ketones have also been used widely as antituberculosis compounds and their importance is mainly due to their ability to form metal chelates[4-6]. In the present communication, we report the synthesis and characterization of some new transition metal complexes of the Schiff base, quinoxaline-2-carboxalidene-2- aminophenol (HQAP).

RESULTS AND DISCUSSION

The formation of the complexes can be represented by the equations shown below:

$$2\text{HQAP} + \text{M(CH}_3\text{COO)}_2 \xrightarrow[\text{reflux}]{\text{ethanol}} [\text{M(QAP)}_2] + 2\text{CH}_3\text{COOH}$$

(M=Mn(II), Co(II), Ni(II) and Cu(II))

$$2\text{HQAP} + \text{FeCl}_3 \xrightarrow[\text{reflux}]{\text{ethanol}} [\text{Fe(QAP)}_2\text{Cl}] + 2\text{HCl}$$

The complexes were found to be stable in air and non-hygroscopic. The complexes are soluble in DMF and DMSO and

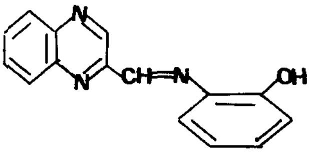

Fig. 1. Structure of the Ligand (HQAP)

partially soluble in ethanol, methanol, acetonitrile, nitrobenzene and chloroform. The analytical data (Table I) show that these complexes have the following empirical formulae: $[Mn(QAP)_2]$, $[Fe(QAP)_2Cl]$, $[Co(QAP)_2]$, $[Ni(QAP)_2]$ and $[Cu(QAP)_2]$. The very low molar conductance values of the complexes in methanol and nitrobenzene indicate non-electrolytic nature of the complexes[7]. Magnetic moment values are in agreement with a tetrahedral structure for the cobalt(II), nickel(II) and copper(II) complexes[8]. The lowering in μ_{eff} (3.5 B.M) in the nickel(II) complex may be due to the effect of covalency or distortion from a tetrahedral structure[9]. In the case of the manganese(II) complex, no conclusion can be drawn as the same magnetic moment value can be expected for both octahedral and tetrahedral complexes. For the iron(III) complex the value is 5.3 B.M. It is less than that expected for spin-free octahedral complexes, indicating a bridged structure for this complex where antiferromagnetic coupling is operative[10-12].

Electronic Spectra

In the electronic spectra of all the complexes a broad band is observed around 30000 cm^{-1}. This band is seen to be sensitive to

Table I
Physical and Analytical Data

Complex Mol.formula (Emp.formula)	Emp.formula weight	Colour	Yield	C(%) Found (Calc.)	H(%) Found (Calc.)	N(%) Found (Calc)	M(%) Found (Calc)	Cl(%) Found (Calc.)	M.P (°C) (Calc.)
[Mn(QAP)$_2$] ($MnC_{30}H_{22}N_6$)	550.9	Purple	60	61.47 (61.72)	4.28 (4.51)	14.14 (14.60)	9.45 (9.94)	—	>230
[Fe(QAP)$_2$Cl] ($FeC_{30}H_{22}N_6Cl$)	589.3	Black	64	51.19 (51.88)	3.45 (3.78)	11.74 (12.04)	8.90 (9.01)	6.50 (6.42)	>230
[Co(QAP)$_2$] ($CoC_{30}H_{22}N_6$)	554.9	Purple	67	62.96 (63.54)	4.48 (4.99)	14.80 (14.96)	10.38 (10.58)	—	>230
[Ni(QAP)$_2$] ($NiC_{30}H_{22}N_6$)	554.7	Violet	64	64.37 (64.87)	4.22 (4.80)	15.42 (15.95)	8.92 (8.92)	—	>230
[Cu(QAP)$_2$] ($CuC_{30}H_{22}N_6$)	559.5	Brown	65	52.28 (52.61)	3.24 (3.56)	12.17 (12.85)	9.99 (10.35)	—	>230

Table II

Magnetic and Electronic Spectral Data of the Complexes

Compound	μ_{eff} (B. M)	Absorption max. (cm^{-1})	Tentative Assignments
[Mn(QAP)$_2$]	5.7	47500	Intraligand teansition
		40430	Intraligand transition
		28790	Charge transfer transition
		18270	$^6A_1 \longrightarrow {}^4T_1(G)$
[Fe(QAP)$_2$Cl]	5.3	47505	Intraligand transition
		42220	Intraligand transition
		31400	Charge transfer transition
[Co(QAP)$_2$]	4.5	46340	Intraligand transition
		40430	Intraligand transition
		27940	Charge transfer transition
		18630	$^4A_2 \longrightarrow {}^4T_1(P)$
		6250	$^4A_2 \longrightarrow {}^4T_1(F)$
[Ni(QAP)$_2$]	3.5	47500	Intraligand transition
		39580	Intraligand transition
		27940	Charge transfer transition
		17120	$^3T_1(F) \longrightarrow {}^3T_1(P)$
		5150	$^3T_1(F) \longrightarrow {}^3A_2$
[Cu(QAP)$_2$]	2.2	46910	Intraligand transition
		40860	Intraligand transition
		31670	Charge transfer transition
		16600	$^2T_2 \longrightarrow {}^2E$

the solvent and it is observed at 28790 cm^{-1}, 28325 cm^{-1} and 27641 cm^{-1} in ethanol, DMSO and DMF, respectively, in the case of the manganese(II) complex. This band can be assigned to ligand to metal charge-transfer transition as this band is seen to make a red shift in more polar solvents[13]. A similar change is observed in the case of the other complexes also. The absorptions observed around 40000 cm^{-1} and 47000 cm^{-1}, are due to electronic transitions within the ligand[14]. The electronic transitions from the $^6A_1$ ground term of manganese(II) to higher energy terms are spin-forbidden. However, a band is observed at 18270 cm^{-1} in the electronic spectrum of the present manganese(II) complex. This is probably due to spin-orbit interaction which makes this transition allowed. In the tetrahedral environment it appears as a weak band[15]. So the band appearing at 18270 cm^{-1} in the electronic spectrum of the present complex is assignable to the transition $^6A_1 \longrightarrow {}^4T_1(G)$ and is consistent with a tetrahedral geometry[16,17] for manganese(II) ion.

The band appearing at 18630 cm^{-1} in the spectrum of the cobalt(II) complex can be assigned to the transition $^4A_2 \longrightarrow {}^4T_1(P)$ which is typical of tetrahedral cobalt(II) complexes. For the nickel(II) complex the band occuring at 17120 cm^{-1} is assigned to the spin forbidden transition $^3T_1(F) \longrightarrow {}^3T_1(P)$ due to the tetrahedral structure around nickel(II). For the copper(II) complex there is a very broad band in the region 16600 cm^{-1} which can be attributed to the $^2T_2 \longrightarrow {}^2E$ transition, supporting a distorted tetrahedral configuration.

The low-energy bands expected for tetrahedral complexes are seen around 5000 cm^{-1} in the spectra of the cobalt and nickel complexes and are due to the $^4A_2 \longrightarrow {}^4T_1(F)$ and $^3T_1(F) \longrightarrow {}^3A_2$ transitions[13], respectively.

Infrared Spectra

The infrared spectral data show that HQAP acts as a bidentate ligand and it coordinates through the phenolic oxygen and azomethine nitrogen atoms. Most of the bands due to the free ligand are present in the spectra of the complexes. The strong OH stretching band at 3379 cm^{-1} of HQAP is absent in the spectra of the complexes, which suggests that the phenolic oxygen atom is coordinated to the metal atom in the ionized form. The coordination of the phenolic oxygen atom in all the complexes is further supported by the fact that the strong band observed at 1280 cm^{-1} in the spectrum of the ligand, which is attributed to the phenolic C-O stretching vibration, undergoes a shift to higher wave numbers ($\Delta\nu$ = 20 cm^{-1}) in the spectra of the complexes[18,19]. The ν(C=N) band of the azomethine linkage appears at 1672 cm^{-1} in the spectrum of the ligand. This band is shifted to 1630 cm^{-1} in the spectra of the complexes, indicating that the azomethine nitrogen is involved in bonding[20].

EPR Spectra

The EPR spectrum (Fig.2) of $[Cu(QAP)_2]$ was recorded in ethanol at liquid nitrogen temperature. Kneubuhl's procedure[21] was used to calculate the *g* values. Three *g* values (g_1= 1.81, g_2= 2.07,

Table III

(Relevant IR Absorption Frequencies of HQAP and its Complexes (cm^{-1})

Compound	ν(O–H)	ν(C=N)	ν(C–O)	ν(C–N)	ρCH	δCH(Ph)
HQAP	3379	1701	1282	1126	883	758
[Mn(QAP)$_2$]	—	1635	1296	1132	881	769
[Fe(QAP)$_2$Cl]	—	1635	1300	1130	881	764
[Co(QAP)$_2$]	—	1630	1294	1126	881	771
[Ni(QAP)$_2$]	—	1637	1290	1126	883	760
[Cu(QAP)$_2$]	—	1628	1300	1128	880	760

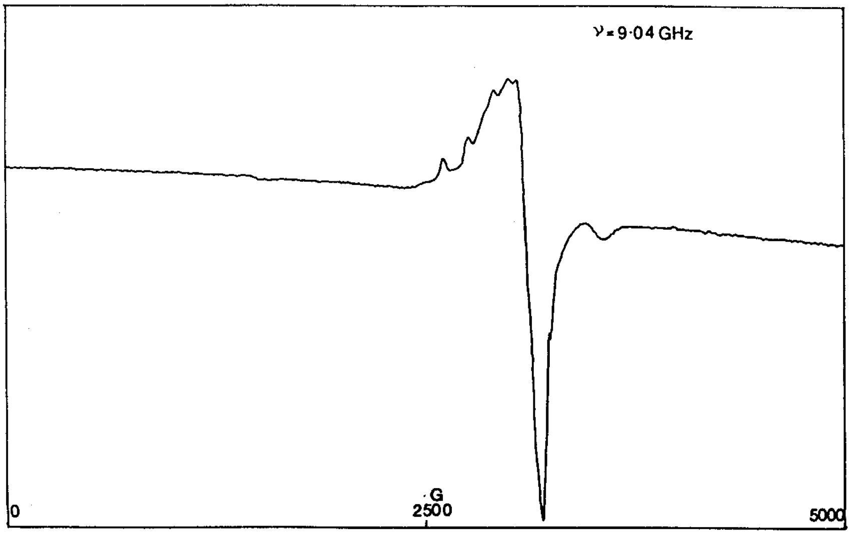

Fig. 2. EPR Spectrum of [Cu(QAP)$_2$] at Liquid Nitrogen Temparature

g_3=2.26; A_3=144 G) were observed for the present copper(II) complex which may be due to distortion from the tetrahedral structure.

Based on the above physicochemical studies, the structures shown in Fig.3 may be assigned to the complexes.

EXPERIMENTAL

Quinoxaline-2-carboxaldehyde was prepared as described elsewhere[22]. All other reagents were of analytical grade purity.

Synthesis of the Ligand

The ligand (HQAP) was prepared by mixing an ethanolic solution (100 mL) of quinoxaline-2-carboxaldehyde (0.01 mol, 1.58 g) and 2-aminophenol (0.01 mol, 1.09 g) in ethanol (100 mL). The solution was refluxed for 1 h. The ligand separated out was filtered and dried *in vacuo* over anhydrous calcium chloride. (Yield: 70 %, 1.7 g, M.P.: 180 ^{0}C).

Preparation of the Complexes

The complexes of manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) were prepared by the following general procedure:

An ethanolic solution of the Schiff base (HQAP) (0.01 mol, 2.49 g) in ethanol (100 mL) was mixed with the corresponding metal salt solution in ethanol (0.005 mol - 1.22 g of $(CH_3COO)_2Mn.4H_2O$; 0.81 g of anhydrous $FeCl_3$; 1.25 g of $(CH_3COO)_2Co.4H_2O$; 1.24 g of $(CH_3COO)_2Ni.4H_2O$ or 0.99 g of $(CH_3COO)_2Cu.H_2O$). The solution was refluxed for 2 h. The volume of the resulting solution was reduced by evaporation and the solution was cooled in a freezer for 1 h.

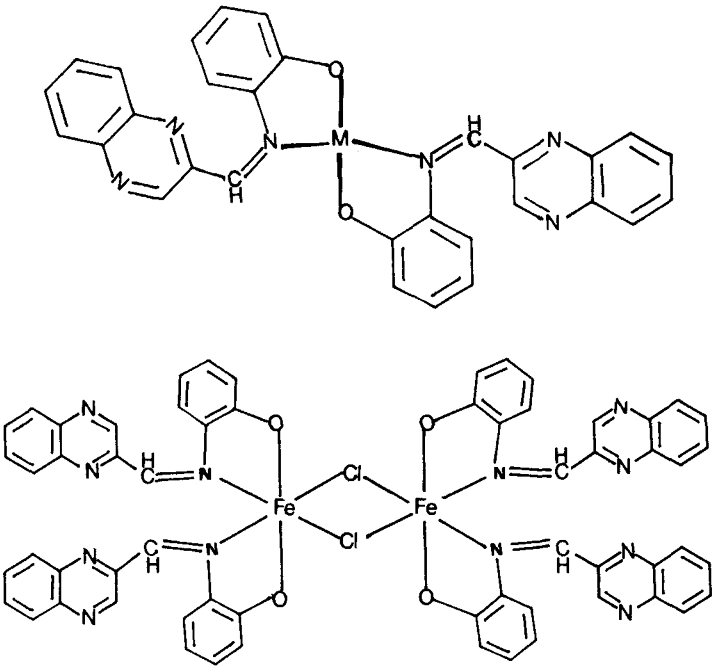

Fig. 3. Suggested Structures of the Complexes (where M = Mn(II), Co(II), Ni(II) and Cu(II))

The crystalline complex separated out was filtered, washed with ether and dried *in vacuo* over anhydrous calcium chloride. (Yields: 60-70 %, 1.6-1.9 g, M.P.: >230 ^{0}C).

Analytical Methods

Metal and chlorine analyses were carried out using standard procedures[23]. Microanalyses for carbon, hydrogen and nitrogen were done on an Heraeus CHN elemental analyzer. Magnetic susceptibility measurements were carried out at 300 K by the Gouy method using $Co[Hg(SCN)_4]$ as the standard. Infrared spectra of the ligand and the complexes were taken as KBr discs on a Shimadzu 8101 FTIR spectrophotometer. Electronic spectra of the complexes were taken in methanol in the region 1000-200 nm on a Shimadzu 160 A UV-Visible spectrophotometer. The near IR spectrum of the complexes in the region 2000-1000 nm were recorded with a Hitachi U-3410 spectrophotometer.

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