

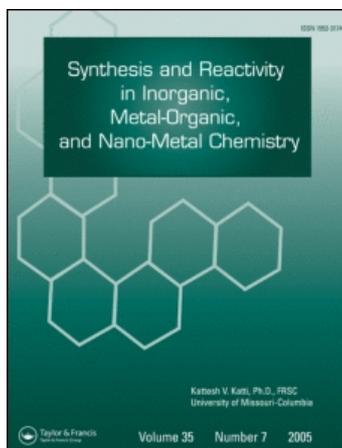
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Studies on Some Transition Metal Complexes of Schiff Bases Derived from Quinoxaline-2-carboxaldehyde

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ABSTRACT

Two series of transition metal complexes of Schiff bases derived from quinoxaline-2-carboxaldehyde with semicarbazide (QSC) and furfurylamine (QFA) were synthesised and characterised by elemental analyses, molar conductance and magnetic susceptibility measurements, IR, electronic and EPR spectral studies. The QSC complexes have the general formula $[M(QSC)Cl_2]$. A tetrahedral structure has been assigned for the Mn(II), Co(II) and Ni(II) complexes and a square-planar structure for the Cu(II) complex. The QFA complexes have the formula $[M(QFA)_2Cl_2]$. An octahedral structure has been assigned for these complexes. All of the complexes exhibit catalytic activity towards the oxidation of 3,5-

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di-*tert*-butylcatechol (DTBC) to 3,5-di-*tert*-butylquinone (DTBQ) using atmospheric oxygen. The cobalt(II) complex of the ligand QFA was found to be the most active catalyst.

Key Words: Quinoxaline-2-carboxaldehyde; Semicarbazide; Furfurylamine; Schiff base; Manganese(II); Cobalt(II); Nickel(II); Copper(II); Transition metal complexes; 3,5-Di-*tert*-butylcatechol; Catalytic oxidation.

INTRODUCTION

Interest in the design and synthesis of new metal complexes is partially derived from their existence in biological systems and for their potential to act as catalysts for numerous chemical reactions.^[1] The electronic and geometric features of the ligand impart on the metal ion the specific properties that facilitate the binding of small molecules and catalytic action. Liquid-phase catalytic oxidation of catechol and its derivatives has been the subject of considerable interest, as it is important in understanding the chemistry of pyrocatechase enzymes and oxidases. Nitrogen donor ligands have found extensive use in biological systems.^[2] Quinoxalines and its derivatives have interesting biological applications and are present in several biologically active polypeptides.^[3] Schiff bases with an electron-withdrawing heterocyclic ring system derived from quinoxaline-2-carboxaldehyde would be interesting as their ligand field strengths are expected to be weaker than the Schiff bases containing only aromatic rings, like naphthaldehyde. Owing to the importance of the above ligand and as part of our earlier studies on similar types of systems,^[4,5] we report here the structural and catalytic activity studies of two series of complexes of Schiff bases (Figure 1) derived from quinoxaline-2-carboxaldehyde.

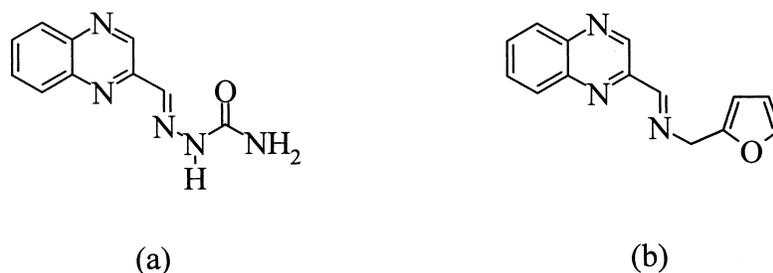


Figure 1. (a) Structure of the ligand QSC, (b) structure of the ligand QFA.

EXPERIMENTAL

Materials

MnCl₂·4H₂O (E. Merck), CoCl₂·6H₂O (E. Merck), NiCl₂·6H₂O (BDH), CuCl₂·2H₂O (E. Merck), semicarbazide hydrochloride (BDH) and 2-furfurylamine (E. Merck) were used as received. DTBC used in the catalytic experiments was obtained from Sigma–Aldrich. All other reagents used were either of 99% purity or were purified by known laboratory procedures.^[6] The synthesis of quinoxaline-2-carboxaldehyde was carried out by the literature method.^[7,8]

Synthesis of Ligands

Quinoxaline-2-carboxaldehydesemicarbazone (QSC)

The ligand (QSC) was prepared by mixing an ethanolic solution (100 mL) of quinoxaline-2-carboxaldehyde (0.01 mol, 1.58 g) and semicarbazide hydrochloride (0.01 mol, 1.11 g) in methanol (100 mL) and stirring the solution for fifteen minutes. The ligand separated out, was filtered and washed with ethanol. It was then dried in vacuo over anhydrous calcium chloride; Yield, 62%, m.p. 230 °C.

Quinoxaline-2-carboxalidene-2-furfurylamine (QFA)

The ligand QFA was prepared by mixing a solution of quinoxaline-2-carboxaldehyde (0.01 mol, 1.58 g) in diethyl ether (50 mL) with furfurylamine (0.01 mol, 0.97 g) and refluxing the solution for fifteen minutes. The solid ligand obtained was filtered, washed with ether and dried in vacuo over anhydrous calcium chloride; Yield, 51%, m.p. 200 °C.

Preparation of Complexes

QSC Complexes

The QSC complexes were prepared by heating a solution of the ligand (0.02 mol, 4.3 g) in acetic acid (25 mL) on a water bath, and then mixing with a solution of the corresponding metal salt (0.01 mol; 1.98 g MnCl₂·4H₂O, 2.37 g CoCl₂·6H₂O, 2.37 g NiCl₂·6H₂O or 1.7 g CuCl₂·2H₂O). The complexes separated out on cooling were filtered, washed with chloroform and dried over anhydrous CaCl₂. The complexes were recrystallised from methanol; Yields, 60–70%.



QFA Complexes

The QFA complexes were synthesized by the following general procedure. The ligand (0.02 mol, 4.74 g) dissolved in acetone (30 mL) was mixed with a solution of the corresponding metal salt (0.01 mol; 1.98 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 2.37 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 2.37 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or 1.7 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in the minimum quantity of methanol and the resultant solution was then refluxed for about thirty minutes. The solution was mixed with an excess of diethyl ether when the complexes separated out. They were filtered, washed with diethyl ether and dried over anhydrous calcium chloride and recrystallised from acetone; Yields, 45–50%; m.p. >250 °C.

Analytical Methods

All of the complexes were analysed for their metal and halide contents by conventional methods.^[9] Chloride was determined by peroxide fusion of the sample followed by titration using Volhard's method. In all of the cases, the organic part of the complexes was completely destroyed before the determination of the metal ions. Microanalyses for carbon, hydrogen and nitrogen were done on a Heraeus CHN elemental analyser. Molar conductances of the complexes were determined at 28 ± 1 °C using a conductivity bridge (Century 601) with a dip-type cell and a platinised platinum electrode. The magnetic susceptibility measurements were done at room temperature (28 ± 1 °C) on a simple Gouy-type magnetic balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibration agent. Electronic spectra of the ligands and the complexes were measured in methanol and in the solid state (using a paste with Nujol) in the 200–1100 nm range on a Shimadzu UV-Vis 160-A spectrophotometer. The near-infrared (NIR) spectra of complexes in the region 2000–1000 nm were recorded on a Hitachi U-3410 spectrophotometer. The infrared spectra of the ligands and the complexes were recorded in the region 400–4000 cm^{-1} both as Nujol mulls and as KBr discs on a Shimadzu 8101 FTIR spectrophotometer. The far-infrared (FIR) spectra of the complexes were recorded in the 50–750 cm^{-1} range. The X-band electron paramagnetic resonance (EPR) spectra of the copper(II) complexes were measured in dimethyl sulfoxide (DMSO) or methanol at liquid nitrogen temperature (LNT) using a Varian E-112 X/Q band spectrophotometer.

Catalytic Experiments

DMSO was selected as solvent in order to avoid vaporization during the experiment. The solvent was made 0.1 molar with respect to tri-



ethylamine (15 mL/L of DMSO) to increase the basicity of the solvent. The DTBC solution (0.22 g in 90 mL solvent) was prepared afresh before each experiment in order to avoid slow aerial oxidation. The same solvent was used to prepare the catalyst solution (100 mL). A catalyst to substrate ratio 1:10 was used for the present study.

The catalytic oxidations were carried out in a 250 mL beaker using atmospheric oxygen as oxidant. The reaction was initiated by mixing the catalyst solution and the DTBC solution. The course of the reaction was monitored by measuring the change in absorbance of the product at 400 nm. A solution of the catalyst with the same concentration as that of the reaction mixture was used as the reference. The rate of conversion was obtained from the concentration versus time data by a computerized technique.^[10] The concentration of the DTBC undergoing oxidation in moles being derived from the molar extinction coefficient (ϵ) value of DTBQ.

RESULTS AND DISCUSSION

The isolated complexes are non-hygroscopic, amorphous powders and are stable in air. The QSC complexes are appreciably soluble in methanol, ethanol, acetonitrile, DMSO and dimethylformamide (DMF). The analytical data (Table 1) show that the QSC complexes have the general formula $M(QSC)Cl_2$. Molar conductance values (Table 2) show that they are non-electrolytes in methanol which suggests the formula of the complexes to be $[M(QSC)Cl_2]$ ($M = Mn(II), Co(II), Ni(II)$ or $Cu(II)$). The QFA complexes are highly soluble in methanol, ethanol, dichloromethane, acetonitrile, DMF and DMSO and have the general formula $M(QFA)_2Cl_2$. The molar conductance values show that the QFA complexes are non-electrolytes in nitrobenzene which indicates that the formula of the complexes is $[M(QFA)_2Cl_2]$ ($M = Mn(II), Co(II), Ni(II)$, or $Cu(II)$).

NMR Spectra

The 1H NMR spectrum of the ligand QSC shows a one proton singlet at δ 9.7 due to the azomethine proton, a multiplet in the aromatic region at δ 7.8 to 8.9 due to the quinoxaline ring and a broad peak around δ 3.4 which may be due to the three protons in the NH and NH_2 groups.

The 1H NMR spectrum of the ligand QFA shows a singlet at δ 9.7 due to the azomethine proton, a multiplet in the range δ 6.9 to 9.0 due to quinoxaline and furan rings and a two proton singlet at 1.6 due to the CH_2 group.



Table 1. Physical and analytical data.

Complex (empirical formulae)	Percentages found (calculated) (%)							Formula weight	Yield (%)	M.p. (°C)
	C	H	N	M	Cl					
QSC (C ₁₀ H ₆ N ₅ O)	55.68 (55.81)	3.91 (4.18)	31.98 (32.56)					215	62	230
[Mn(QSC)Cl ₂]	34.80	2.38	20.20	16.09	20.50			340.84	68	315
(C ₁₀ H ₆ Cl ₂ MnN ₅ O)	(35.20)	(2.64)	(20.50)	(16.10)	(20.80)					
[Co(QSC)Cl ₂]	34.50	2.50	19.90	16.89	20.33			344.83	69	290
(C ₁₀ H ₆ Cl ₂ CoN ₅ O)	(34.80)	(2.60)	(20.30)	(17.10)	(20.56)					
[Ni(QSC)Cl ₂]	34.60	2.40	20.10	16.90	20.04			344.59	61	305
(C ₁₀ H ₆ Cl ₂ N ₅ NiO)	(34.82)	(2.61)	(20.31)	(17.03)	(20.57)					
[Cu(QSC)Cl ₂]	33.90	2.30	19.80	17.95	19.98			349.44	70	320
(C ₁₀ H ₆ Cl ₂ CuN ₅ O)	(34.34)	(2.57)	(20.03)	(18.20)	(20.29)					
QFA (C ₁₄ H ₁₁ N ₃ O)	70.76 (70.88)	4.38 (4.64)	17.68 (17.72)					237	40	200
[Mn(QFA) ₂ Cl ₂]	55.88	3.62	13.95	8.97	11.64			599.84	45	320
(C ₂₈ H ₂₂ Cl ₂ MnN ₆ O ₂)	(56.01)	(3.67)	(14.00)	(9.16)	(11.80)					
[Co(QFA) ₂ Cl ₂]	55.55	3.62	13.60	9.69	11.70			603.83	50	330
(C ₂₈ H ₂₂ Cl ₂ CoN ₆ O ₂)	(55.64)	(3.64)	(13.91)	(9.72)	(11.75)					
[Ni(QFA) ₂ Cl ₂]	55.43	3.62	13.79	9.64	11.65			603.59	46	210
(C ₂₈ H ₂₂ Cl ₂ N ₆ NiO ₂)	(55.67)	(3.65)	(13.91)	(9.72)	(11.75)					
[Cu(QFA) ₂ Cl ₂]	54.97	3.55	13.63	10.41	11.54			608.44	49	292
(C ₂₈ H ₂₂ Cl ₂ CuN ₆ O ₂)	(55.20)	(3.62)	(13.80)	(10.44)	(11.65)					



Table 2. Molar conductance and magnetic data.

Complex	Color	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	Magnetic moment (B.M.)
[Mn(QSC)Cl ₂]	Brownish yellow	19.2	5.8
[Co(QSC)Cl ₂]	Brownish yellow	13.0	4.5
[Ni(QSC)Cl ₂]	Brownish yellow	2.6	4.0
[Cu(QSC)Cl ₂]	Light brown	2.2	1.9
[Mn(QFA) ₂ Cl ₂]	Brown	1.0	5.8
[Co(QFA) ₂ Cl ₂]	Brown	1.0	5.1
[Ni(QFA) ₂ Cl ₂]	Black	2.4	3.0
[Cu(QFA) ₂ Cl ₂]	Brown	4.8	2.0

Infrared Spectra

QSC Complexes

The IR spectral data (Table 3) show that QSC acts as a bidentate ligand, coordinating through the azomethine and ring nitrogen atoms. The ligand exhibits a band around 1710 cm⁻¹, which might be due to a combination of $\nu(\text{C}=\text{N})$ of the azomethine group and $\nu(\text{C}=\text{O})$ of the semicarbazone. In the spectra of the complexes, $\nu(\text{C}=\text{N})$ appears as a strong peak at 1670 cm⁻¹, which indicates the participation of the azomethine nitrogen in bonding to the metal atom.^[11] The ligand exhibits a strong band around 1585 cm⁻¹ which might be due to the $\nu(\text{C}=\text{N})$ frequency of the quinoxaline ring.^[12] This band is shifted to 1545 cm⁻¹ in the spectra of the complexes showing that the ring nitrogen is involved in coordination to the metal atom in all cases. The far-IR spectra of the complexes show two

Table 3. Infrared spectral bands of QSC and its complexes.

Ligand	[Mn(QSC)Cl ₂]	[Co(QSC)Cl ₂]	[Ni(QSC)Cl ₂]	[Cu(QSC)Cl ₂]	Assignments
3300 m	3300 m	3295 m	3295 m	3300 m	$\nu(\text{N}-\text{H})$
1710 s	1708 w	1710 w	1708 w	1708 w	$\nu(\text{C}=\text{O})$
1710 s	1676 s	1677 s	1678 s	1680	$\nu(\text{C}=\text{N})$ azomethine
1585 s	1544 m	1539 m	1541 m	1539 m	$\nu(\text{C}=\text{N})$ ring
761 s	760 sh	760 s	760 sh	760 sh	$\delta(\text{C}-\text{H})$ (Ph)
-	245 m	251 m	252 m	251 w	$\nu(\text{M}-\text{Cl})$
-	422 m	424 m	427 m	419 m	$\nu(\text{M}-\text{N})$



Table 4. Infrared spectral bands of QFA and its complexes.

Ligand	[Mn(QFA) ₂ Cl ₂]	[Co(QFA) ₂ Cl ₂]	[Ni(QFA) ₂ Cl ₂]	[Cu(QFA) ₂ Cl ₂]	Assignment
1675 s	1645 s	1645 s	1640 s	1640 s	$\nu(\text{C}=\text{N})$ azomethine
1584 s	1544 m	1539 m	1541 m	1539 m	$\nu(\text{C}=\text{N})$ ring
761 s	760 sh	760 s	760 sh	760 sh	$\delta(\text{C}-\text{H})$ (Ph)
–	302 w	310 w	305 w	303 w	$\nu(\text{M}-\text{Cl})$
–	411 w	415 w	415 w	414 w	$\nu(\text{M}-\text{N})$

bands at 250 cm^{-1} and 420 cm^{-1} which are attributed to the M–Cl and M–N stretching vibrations, respectively.^[13,14]

QFA Complexes

The IR data (Table 4) show that the ligand QFA exhibits a strong band at 1675 cm^{-1} corresponding to $\nu(\text{C}=\text{N})$ of the azomethine group. This band is found to be shifted to 1640 cm^{-1} in all the complexes, indicating the coordination of the azomethine group of the ligand.^[15] The $\nu(\text{C}=\text{N})$ band of the quinoxaline ring which appears at 1584 cm^{-1} in the ligand undergoes a red-shift to around 1560 cm^{-1} in the spectra of all the complexes,^[12] indicating that the ring nitrogen atom is also coordinated to the metal. These results suggest that the ligand QFA acts as a bidentate ligand in all the complexes coordinating through the azomethine nitrogen and quinoxaline ring nitrogen atoms. In the far-IR spectra of the QFA complexes, two weak bands are observed around 300 cm^{-1} and 410 cm^{-1} which tentatively are assigned to $\nu(\text{M}-\text{Cl})$ and $\nu(\text{M}-\text{N})$, respectively.^[13,14]

Electronic Spectra

The electronic spectra of all the complexes were recorded in methanol and in the solid state. The observed bands and their tentative assignments are given in Table 5.

QSC Complexes

The electronic transitions from ${}^6\text{A}_1$ ground state of manganese(II) to higher energy states are spin-forbidden and these transitions are not observed in the spectrum of the manganese(II) complex of the ligand QSC.^[16] The electronic spectrum of the cobalt(II) complex of QSC shows absorption bands at $18,650\text{ cm}^{-1}$ which is in accordance with the transition



Table 5. Electronic spectral data of the QSC complexes.

Complex	λ (cm ⁻¹)	log ϵ (ϵ in L mol ⁻¹ cm ⁻¹)	Tentative assignments
[Mn(QSC)Cl ₂]	46,800	4.36	n → π^*
	40,000	4.09	n → π^*
	32,350	3.75	Charge transfer
	28,940	3.39	Charge transfer
[Co(QSC)Cl ₂]	46,600	4.46	n → π^*
	39,680	3.67	n → π^*
	28,200	3.25	Charge transfer
	18,650	1.53	⁴ A ₂ (F) → ⁴ T ₁ (P)
[Ni(QSC)Cl ₂]	6,960	0.95	⁴ A ₂ (F) → ⁴ T ₁ (F)
	45,830	4.40	n → π^*
	40,740	4.27	n → π^*
	28,170	3.35	Charge transfer
[Cu(QSC)Cl ₂]	14,860	1.77	³ T ₁ (F) → ³ T ₁ (P)
	6,930	0.94	³ T ₁ (F) → ³ A ₂ (F)
	49,510	4.28	n → π^*
	40,700	4.14	n → π^*
	31,450	3.35	Charge transfer
	28,200	3.25	Charge transfer
	18,870	1.69	B _{1g} → ² E _g

⁴A₂ → ⁴T₁(P), supporting a tetrahedral structure.^[17] A low-energy band at 6,960 cm⁻¹, attributable to the ⁴A₂ → ⁴T₁(F) transition also supports a tetrahedral configuration.^[18] In the case of the nickel(II) complexes, two transitions are observed, at 14,860 cm⁻¹ and 6,930 cm⁻¹, which indicate a tetrahedral geometry around the nickel(II) ion.^[19] Tetragonal copper(II) complexes are expected to show the transitions ²B_{1g} → ²A_{1g}, ²B_{1g} → ²B_{2g} and ²B_{1g} → ²E_g, but bands due to these transitions usually overlap to give one broad absorption band.^[19] The electronic spectrum of the present copper(II) complex exhibits a broad band centered at 18,870 cm⁻¹, indicating a tetragonal configuration around the copper(II) ion. Furthermore, the spectra of all QSC complexes exhibit strong bands in the region around 40,000 cm⁻¹ and 45,000 cm⁻¹ which might be due to the n- π^* transitions and the strong bands around 32,000 cm⁻¹ and 28,000 cm⁻¹ might be assigned to charge transfer transitions.^[18,20]

QFA Complexes

The manganese(II) complex of the ligand QFA shows a weak band around 21,670 cm⁻¹ which might be due to the ⁶A_{1g} → ⁴T_{2g}(G) transition of



Table 6. Electronic spectral data of the QFA complexes.

Complex	λ (cm ⁻¹)	log ϵ (ϵ in Lmol ⁻¹ cm ⁻¹)	Assignments
[Mn(QFA) ₂ Cl ₂]	46,000	4.36	n → π^*
	37,000	4.29	n → π^*
	33,300	3.37	Charge transfer
	21,670	0.89	⁶ A _{1g} → ⁴ T _{2g} (G)
[Co(QFA) ₂ Cl ₂]	47,600	4.15	n → π^*
	42,000	4.05	n → π^*
	32,350	3.45	Charge transfer
	27,170	3.43	Charge transfer
[Ni(QFA) ₂ Cl ₂]	22,000	1.44	⁴ T _{1g} (F) → ⁴ T _{1g} (P)
	46,730	4.35	n → π^*
	42,370	4.22	n → π^*
	30,660	3.40	Charge transfer
[Cu(QFA) ₂ Cl ₂]	17,600	1.37	³ A _{2g} (F) → ³ T _{1g} (F)
	40,000	4.43	n → π^*
	28,000	3.53	Charge transfer
	27,000	3.25	Charge transfer
	11,800	0.99	d-d transition

the octahedral Mn(II) ion.^[21] In the electronic spectrum of Co(II) complex the d-d transitions are almost masked by the high-intensity charge transfer bands. However, a shoulder is observed around 22,000 cm⁻¹ which may be assigned to the ⁴T_{1g}(F) → ⁴T_{1g}(P) transition of octahedral Co(II) complexes. The spectrum of the nickel(II) complex exhibits a band at 17,600 cm⁻¹ which is in accordance with the transition ³A_{2g} → ³T_{1g}(F), characteristic of an octahedral stereochemistry around the Ni(II) ion.^[22] A broad d-d band is observed at 11,800 cm⁻¹ for the copper(II) complex which has been reported for many octahedral copper(II) complexes.^[19] In the spectra of all complexes strong bands are observed around 40,000 cm⁻¹ due to n → π^* transitions. In addition, strong peaks are observed in the region 27,000–33,000 cm⁻¹ which may be assigned to the charge transfer transitions.

Magnetic Susceptibility Measurements

The magnetic moment values of all the complexes are shown in Table 2. The μ_{eff} value of 5.8 B.M. for the QSC complex of manganese(II), corresponds to the presence of five unpaired electrons.^[23] Magnetic moment values of 4.5 B.M. and 4.0 B.M. for the cobalt(II) and nickel(II) complexes of QSC suggest a tetrahedral structure for these complexes.^[24]



The copper(II) complex exhibits a magnetic moment value of 1.9 B.M., corresponding to one unpaired spin.

The manganese(II) complex of the ligand QFA exhibits a magnetic moment of 5.8 B.M., which corresponds to the presence of five unpaired electrons. The room temperature magnetic moments of the cobalt(II) and nickel(II) complexes of this ligand are 5.1 B.M. and 3.0 B.M., respectively, which suggests an octahedral stereochemistry around the metal ion.^[25] The copper(II) complex of QFA exhibits a magnetic moment of 2.2 B.M., which indicates the presence of an unpaired spin.^[26]

EPR Spectra

The EPR spectrum (Figure 2) of $[\text{Cu}(\text{QSC})\text{Cl}_2]$ was recorded in DMSO at LNT. The g and A value obtained are $g_{\parallel} = 2.33$, $g_{\perp} = 2.16$ and $A_{\parallel} = 145$ G. The trend $g_{\parallel} > g_{\perp}$, observed for this complex, indicates that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital of the copper(II) ion and the spectral features are characteristic of axial symmetry.^[27] Further, $g_{\text{av}} = 2.21$ and $\alpha^2 = 0.83$. The value of α^2 indicates the covalent nature of the metal–ligand bonding.

The EPR spectrum (Figure 3) of the complex $[\text{Cu}(\text{QFA})_2\text{Cl}_2]$ was taken in methanol at liquid nitrogen temperature. The g and A values obtained are $g_{\parallel} = 2.41$, $g_{\perp} = 2.08$ and $A_{\parallel} = 120$. The g and A values obtained indicate an axial symmetry for this complex.^[28] The g_{av} and α^2 values were calculated to be equal to 2.19 and 0.81, respectively. The α^2 value of the present complex supports the covalent nature of the complex.

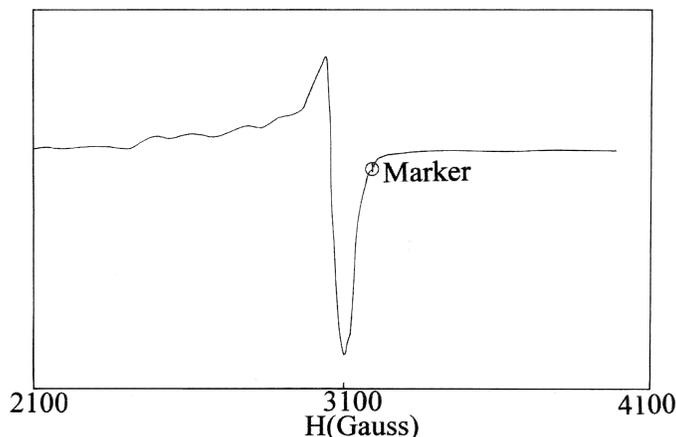


Figure 2. EPR spectrum of $[\text{Cu}(\text{QSC})\text{Cl}_2]$.



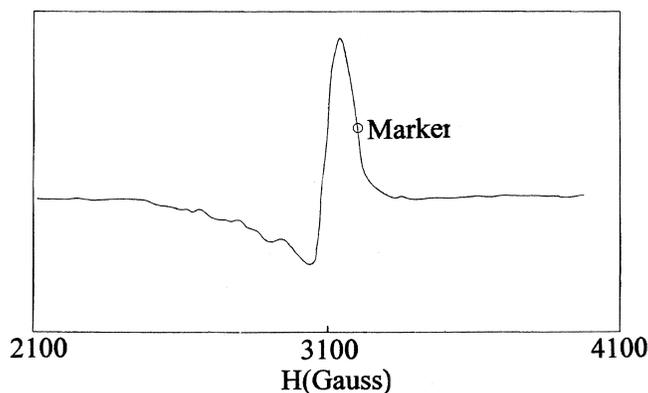


Figure 3. EPR spectrum of $[\text{Cu}(\text{QFA})_2\text{Cl}_2]$.

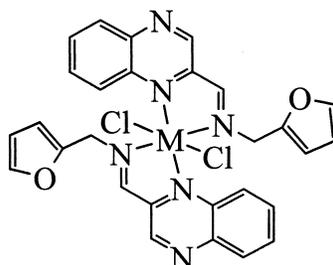
Based on the above studies the following structures (Figures 4 and 5) are proposed for the complexes.

Catalytic Activity Studies

The oxidation reaction of DTBC was found to be negligible even in the presence of the metal complex catalyst. However on adding the amine, the reactions acquired a measurable rate. Therefore, in all experiments triethylamine was added. DTBC may be partially dissociated in the presence of amine so that it can easily interact with metal complexes. In order to form the ternary complex, the prerequisite is that the catalyst should have vacant coordination sites. Surprisingly, even the octahedral complexes show some activity in the reaction. It may be proposed that on the approach of a DTBC molecule some of the labile metal ligand bonds



Figure 4. Suggested structure of the QSC complexes.



(M = Mn, Co, Ni or Cu)

Figure 5. Suggested structure of the QFA complexes.

Table 7. Rate of conversion data of the complexes in the oxidation of DTBC \rightarrow DTBQ.

Complex	Weight of catalyst in 100 mL solution	Rate of conversion (mol dm ⁻³ s ⁻¹)
[Mn(QSC)Cl ₂]	0.0155	7.04×10^{-4}
[Co(QSC)Cl ₂]	0.0104	1.31×10^{-3}
[Ni(QSC)Cl ₂]	0.0158	2.63×10^{-4}
[Cu(QSC)Cl ₂]	0.0181	4.69×10^{-4}
[Mn(QFA) ₂ Cl ₂]	0.0171	4.88×10^{-4}
[Co(QFA) ₂ Cl ₂]	0.0084	7.78×10^{-4}
[Ni(QFA) ₂ Cl ₂]	0.0139	2.61×10^{-4}
[Cu(QFA) ₂ Cl ₂]	0.0210	4.30×10^{-4}

dissociate and give way to the formation of a ternary complex. The reaction mechanism assumed here includes the associative oxygen species adsorbed to metal ions. The cobalt complexes were found to have higher activity than the others. The greater dioxygen affinity of this metal may be the reason for this observation. The intramolecular electron transfer within such a ternary complex (DTBC-ML-O₂) generates the corresponding quinone. The results of the studies are given in Table 7. The rate of conversion data indicates that all the complexes are catalytically active in the oxidation DTBC \rightarrow DTBQ. The [Co(QSC)Cl₂] complex is the most active catalyst. In many reactions reported earlier, it has been shown that the dissociation of one or two bonds of the chelate may be the rate determining step in the catalysed reaction.^[29]



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