Polyhedron Vol. 9, No. 6, pp. 805–811, 1990
Printed in Great Britain

0277–5387/90 $3.00+.00
Pergamon Press plc

ESR AND OTHER SPECTRAL STUDIES ON COPPER(II) COMPLEXES WITH 2,3-DISUBSTITUTED QUINAZOLINE-(3H)-4-ONES

B. PRABHAKAR and P. LINGAIAH*

Department of Chemistry, Kakatiya University, Warangal, Andhra Pradesh, India

and

K. LAXMA REDDY

Department of Chemistry, Regional Engineering College, Warangal 506 004, India

(*Received* 24 *May* 1989; *accepted* 18 *October* 1989)

Abstract—A number of copper(II) complexes of some tridentate O—N—O donors and bidentate O—O and O—N donors in the form of 2,3-disubstituted quinazolin-(3H)-4-ones have been synthesized and characterized based on analytical, conductivity, magnetic, IR, electronic and ESR spectral data. The reaction between copper(II) acetate and tridentate O—N—O donor ligands such as 2-(R)-3-(X)-substituted quinazoline-(3H)-4-ones, where R = methyl/phenyl and X = 2′-hydroxyphenylamino (MHBQ/PHBQ), yielded neutral complexes of the type Cu(O—N—O)$_2$. The bidentate O—O or O—N donor ligands like 2-(R)-3-(X)-substituted quinazoline-(3H)-4-ones, where R = methyl/phenyl and X = carboxymethyl (MCMQ/PCMQ), furylamino (MFQ/PFQ), acetamino (MAQ/PAQ), uramino (MUQ/PUQ) and thiouramino (MTUQ/PTUQ), yielded neutral complexes of the type Cu(O—O)$_2$ or Cu(O—N)$_2$(CH$_3$COO)$_2$. The IR spectral data of the metal complexes indicate that the ligands like MHBQ and PHBQ act as uninegative tridentate, MCMQ and PCMQ act as uninegative bidentate and MFQ, PFQ, MAQ, PAQ, MUQ, PUQ, MTUQ and PTUQ act as neutral bidentate ligands. The reflectance spectral studies of these complexes indicate that they contain square-planar or tetragonal geometry around copper(II).

Quinazolones contain both an oxygen on the ring and a nitrogen and oxygen on the substituent at the three-position (Structure I) as donor centres in the proper orientation to chelate with the metal ion. The chelating tendency of these compounds is not very well documented except for a few publications involving similar ligands.[1–4] Spectral studies of copper(II) complexes are of great interest because their ground states orbitally degenerate in regular geometries and non-degenerate in distorted geometries, since an orbitally degenerate configuration is susceptible to a Jahn–Teller distortion. As a result, the ESR studies of copper(II) complexes yield valuable information regarding the nature of bonding between the metal ion and donor atom. Basically, the interpretation of the ESR spectrum of an isolated transition metal ion yields values for two types of parameter: (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. In order to discover the nature of the interaction of these ligands with the copper(II) ion, the present study was undertaken. In this paper, complexes of copper(II) with 2-(R)-3-(X)-substituted quinazolin-(3H)-4-ones, where R = methyl/phenyl and X = carboxymethyl (MCMQ/PCMQ), 2′-hydroxy benzylamino (MHBQ/PHBQ), furylamino (MFQ/PFQ), acetamino (MAQ/PAQ), uramino (MUQ/PUQ) and thiouramino (MTUQ/PTUQ), are discussed.

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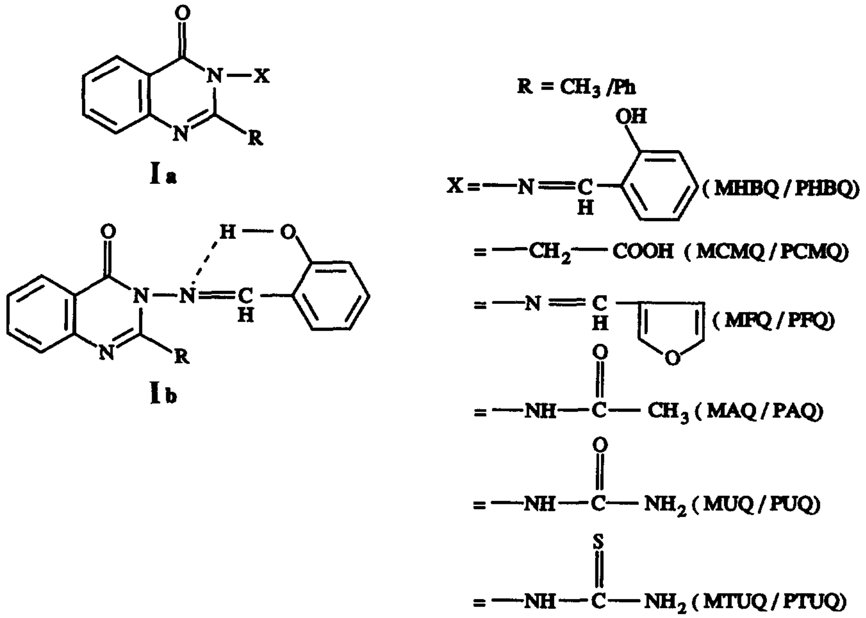
* Author to whom correspondence should be addressed.



Structure **Ia** and **b**. Structures of the ligands.

EXPERIMENTAL

All the chemicals used were of AR grade. The ligands were prepared by literature methods.[5,6] The purity of these compounds was checked by TLC and melting point determinations.

Preparation of complexes

Copper acetate solution (1 mmol) in acetone was added dropwise to a solution (3 mmol) in acetone with constant stirring. The reaction mixture was refluxed on a water bath for 60–120 min and cooled. The solid thus obtained was filtered and washed several times with water and acetone until the washings were free from excess ligands. These complexes were finally dried *in vacuo* over fused calcium chloride. All the copper(II) complexes are crystalline powders, light or dark green in colour. They are stable to room temperature, non-hygroscopic and insoluble in common organic solvents like methanol, ethanol, acetone and CCl_4, but appreciably soluble in DMF and DMSO.

Physical measurements

The analytical data (C, H, N) for the ligands and their metal complexes were obtained from the Microanalytical Laboratory, Calcutta University, Calcutta, India. The metal content of the complexes after heating to decomposition temperatures was determined using standard procedures. Molar conductivities of the complexes in DMF were measured using a Digisun digital conductivity meter, Model-DI-909 with a 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 calibrant. Diamagnetic corrections were applied using Pascal's constants. The TGA and DTA curves of the complexes were recorded on a Leeds and Nathrup DTA unit (U.S.A.), using calcined alumina as reference material. The experiments were carried out in an atmosphere of static air using Pt/Rh thermocouples, and the rate of heating was maintained at 6°C min^{-1}. The IR spectra of the ligands and their complexes in Nujol and KBr, in the range 4000–200 cm^{-1}, were recorded on a Perkin–Elmer IR spectrophotometer, Model-283. The UV and visible spectra of the complexes in DMF were recorded on a Shimadzu multipurpose recording spectrometer, Model MPS-5000. The reflectance spectra of the complexes were measured on a Perkin–Elmer Lambda-15 spectrophotometer. The ESR spectra of the complexes in solid state and in DMF solutions at liquid nitrogen temperature were recorded on a Varian E-4, X-band spectrometer.

RESULTS AND DISCUSSION

The analytical and physical data for the complexes are listed in Table 1. On the basis of analytical data the metal complexes are found to have 1 : 2 (metal–ligand) stoichiometry and some complexes are also associated with two acetate molecules. The molar conductance values of the complexes in DMF at 10^{-3} M concentrations are low (10–20 Ω^{-1} cm^2

Table 1. Analytical and thermal data of copper(II) complexes

Sl. No.	Complex	Found (Calc.) % Cu	C	N	H	S	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Decomposition temperature (°C)
1	$[Cu(MCMQ)_2]$	12.7	52.8	11.2	4.0	—	17	300
		(12.7	52.8	11.2	4.0)			
2	$[Cu(PCMQ)_2]$	10.2	61.6	9.0	3.8	—	20	305
		(10.2	61.5	8.9	3.8)			
3	$[Cu(MHBQ)_2]$	10.2	62.9	13.6	3.8	—	15	340
		(9.9	61.0	13.1	3.2)			
4	$[Cu(PHBQ)_2]$	8.5	67.8	11.3	3.8	—	10	335
		(8.1	67.0	10.9	3.1)			
5	$[Cu(MFQ)_2(CH_3COO)_2]$	9.1	55.9	12.2	4.1	—	10	320
		(9.1	55.8	12.2	4.0)			
6	$[Cu(PFQ)_2(CH_3COO)_2]$	7.8	62.1	10.3	3.9	—	17	310
		(7.7	62.1	10.3	3.9)			
7	$[Cu(MAQ)_2(CH_3COO)_2]$	10.3	50.7	13.6	4.5	—	16	310
		(10.2	50.5	13.6	4.5)			
8	$[Cu(PAQ)_2(CH_3COO)_2]$	8.6	58.4	11.3	4.3	—	12	315
		(8.5	58.4	11.3	4.3)			
9	$[Cu(MUQ)_2(CH_3COO)_2]$	10.2	46.7	18.1	4.2	—	18	320
		(10.2	46.6	18.1	4.2)			
10	$[Cu(PUQ)_2(CH_3COO)_2]$	8.5	55.1	15.1	4.0	—	12	328
		(8.4	55.0	15.1	4.0)			
11	$[Cu(MTUQ)_2(CH_3COO)_2]$	9.7	44.4	17.2	4.0	9.9	13	318
		(9.7	44.3	17.2	4.0)	(9.8)		
12	$[Cu(PTUQ)_2(CH_3COO)_2]$	8.9	57.5	15.8	4.2	9.0	11	330
		(8.8	57.4	15.7	4.2)	(9.0)		

mol^{-1}) suggesting that they are non-electrolytes.[7]

Decomposition temperatures of the complexes, determined from their thermograms, are given in Table 1. The complexes are thermally stable up until 200°C and are not hydrated. This fact is further confirmed by their DTA curves which do not give endothermic peaks in the 150–200°C region. The sharp decomposition associated with the loss of ligand starts above 230°C. The final products of decomposition above 600°C in all the complexes correspond to metallic oxide. The decomposition temperatures of the complexes are a measure of their thermal stability. The ligands under study form complexes of varying stability in the order MCMQ $<$ PCMQ $<$ PFQ $\simeq$ MAQ $<$ PAQ $<$ MTUQ $<$ MFQ $\simeq$ MUQ $<$ PUQ $<$ PTUQ $<$ PHBQ $<$ MHBQ.

Despite the large amount of work on thermogravimetry, considerable difficulties still exist in rationalizing the increase or decrease in thermal stability of complexes with different ligands. The literature contains various explanations of the relative order of thermal stability of the complexes. For example, thermal stability is said to increase with an increase in π-electron delocalization, the size of the molecule and also the nature of the rings formed.[8] The relative order of stability observed for the present complexes may be accounted for by such factors.

Important IR absorption frequencies of ligands and their complexes, along with their assignments, are listed in Table 2. A strong band corresponding to ν(C=O) of the quinazolone ring at 1700 cm^{-1} is shifted to lower wavenumbers by 40–50 cm^{-1} in the IR spectra of all the complexes, indicating that the carbonyl oxygen is invariably coordinated to copper(II).[9] The bands due to ν(OH) observed in the spectra of MHBQ, PHBQ,[10] MCMQ and PCMQ[11] disappeared completely in the spectra of their complexes confirming the coordination of these ligands by deprotonation. The band at 1640 cm^{-1} due to ν(C=N) of quinazolone remains unaltered in the spectra of complexes, whereas the band at 1600 cm^{-1} due to the benzylamino/furylamino group undergoes a lower shift of 40–50 cm^{-1}, suggesting coordination through this nitrogen.[12]

The ν(N—H) frequency observed at 3300 cm^{-1} in MAQ, PAQ, MUQ, PUQ, MTUQ and PTUQ has shifted to a lower region ($\Delta\nu$ = 50 cm^{-1}) in the

Table 2. Infrared spectral data (cm^{-1}) and their assignment of copper(II) complexes

Complex	ν(C=O)	ν(N—H)	ν(O—H)/NH_2	ν(C=N)	ν(Cu—O)	ν(Cu—N)
1	1650	—	—	1635	450, 430	—
	(1700)		(2500)[a]	(1640)		
2	1635	—	—	1640	430, 420	—
	(1690)		(2500)[a]	(1640)		
3	1640	—	—	1570	400, 450	500
	(1680)		(3150)	(1610)		
4	1640	—	—	1570	410, 440	500
	(1690)		(3200)	(1610)		
5	1650	—	—	1560	420	470
	(1700)			(1610)		
6	1650	—	—	1560	420	490
	(1700)			(1600)		
7	1660	3260	—	1640	440, 420	460
	(1680)	(3300)		(1640)		
8	1655	3240	—	1635	430, 420	460
	(1690)	(3300)		(1640)		
9	1640	3230	3390[b]	1630	435	500
	(1690)	(3280)	(3400)	(1630)		
10	1640	3260	3390[b]	1630	435	490
	(1700)	(3310)	(3400)	(1630)		
11[c]	1635	3280	3390[b]	1640	430	490
	(1690)	(3320)	(3390)	(1640)		
12[c]	1640	3270	3390[b]	1635	440	480
	(1700)	(3320)	(3390)	(1640)		

Values presented in parentheses are of the free ligand bands.

[a] OH of carboxyl group.

[b] Stretching frequency of NH_2 group.

[c] (C=S) of thiouramino group observed at 860 cm^{-1} in MTUQ and PTUQ and at 850 cm^{-1} in their complexes.

complexes, indicating the involvement of the imino-nitrogen in coordination,[13] whereas the bands due to $\nu(NH_2)$[14] (MUQ, PUQ, MTUQ and PTUQ), ν(C=O) (MAQ, PAQ, MUQ and PUQ)[5] and ν(C=S) (MTUQ and PTUQ)[15] at 3400, 1660 and 860 cm^{-1}, respectively, remain unchanged in the complexes, indicating the non-participation of the N/O/S of these groups in coordination. The presence of acetate ion in the coordination sphere in some complexes is also confirmed from their IR data.[16] The mode of coordination is further supported by the appearance of ν(Cu—O) and ν(Cu—N) bands around 400 and 500 cm^{-1}, respectively.[17,18]

The electronic spectral data along with the assignments are presented in Table 3. All the ligands exhibit strong bands around 35,000 and 32,000 cm^{-1} which may be assigned to $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions, respectively. The reflectance spectra of all the copper(II) complexes, except those complexes of MCMQ and PCMQ, exhibit one broad band around 16,000 cm^{-1}, and complexes **3**, **4**, **6** and **7** also show one shoulder around 13,000 cm^{-1}. Due to the Jahn–Teller effect, tetragonal copper(II) complexes involve three transitions, *viz.* ${}^2B_{2g} \leftarrow {}^2B_{1g}$, ${}^2E_g \leftarrow {}^2B_{1g}$ and ${}^2A_{1g} \leftarrow {}^2B_{1g}$, but bands due to these transitions usually overlap to give a broad absorption band. Based on earlier reports, the present complexes are tentatively assigned tetragonal geometry.[19–21] However, the copper(II) complexes of MCMQ and PCMQ display two bands around 15,000 and 20,000 cm^{-1} which may be due to ${}^2B_{2g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$ transitions and are also tentatively assigned square-planar geometry.[22]

All the copper(II) complexes are paramagnetic and possess magnetic moment values equivalent to one unpaired electron. The value is found to be less than 1.9 BM indicating the complexes have tetragonal or square-planar arrangements around the copper(II) ion.[23] But the excess over the spin-only value of 1.73 BM observed (Table 3) in these complexes might be due to spin-orbit coupling.

The ESR spectra of the copper(II) complexes of MFQ and PFQ at liquid nitrogen temperature in

Table 3. Magnetic and electronic spectral data of copper(II) complexes

Complex	μ_{eff} (BM)	Electronic spectral bands	(cm^{-1})
1	1.82	15,000, 20,000	31,000, 35,000
2	1.82	15,500, 21,000	31,000, 34,000
3	1.82	13,200, 16,000, 31,000	34,000
4	1.83	13,100, 16,000, 32,000	35,000
5	1.82	16,500,[a] 30,000	34,000
6	1.81	13,000, 16,500, 31,000	34,500
7	1.83	13,150, 16,500, 31,000	33,000
8	1.82	16,000,[a] 30,000	34,000
9	1.82	15,800,[a] 29,000	34,000
10	1.81	15,900,[a] 30,000	35,000
11	1.81	16,000,[a] 31,000	36,000
12	1.82	16,200,[a] 31,000	35,000

[a] Broad band indicating overlapping of different transitions.

the solid state and in solutions are given in Figs 1 and 2. The ESR spectral and bonding parameters are listed in Table 4.

The ESR spectra of all the copper(II) complexes in the solid state at liquid nitrogen temperature show two peaks, one of intense absorption at high field and the other of less intensity at low field. From these peaks $g_{\parallel}$ and $G_{\perp}$ have been calculated. However, the ESR spectra of all the copper(II) complexes in solution 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.

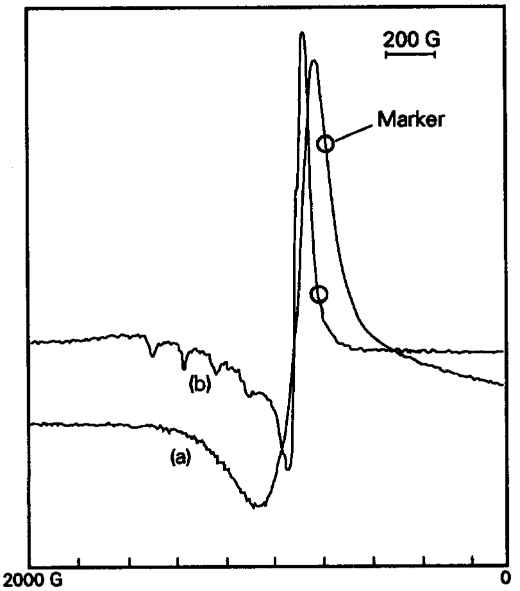


Fig. 1. ESR spectra of copper(II) MFQ complexes at liquid nitrogen temperature: (a) in the solid state; (b) in solution.

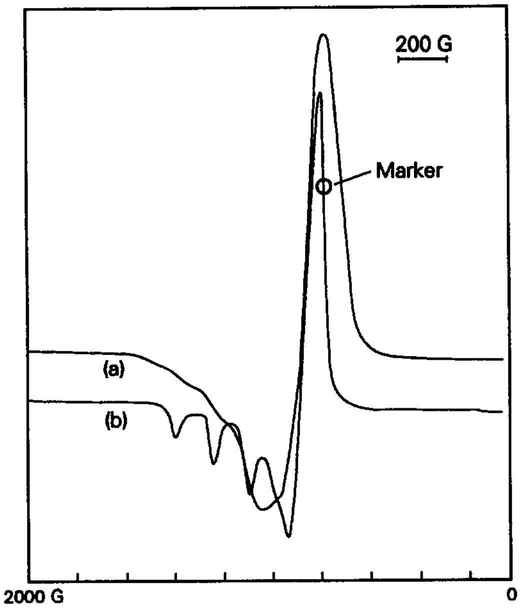


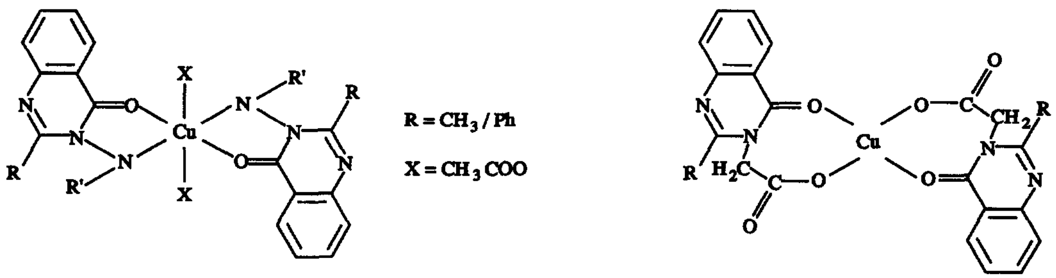
Fig. 2. ESR spectra of copper(II) PFQ complexes at liquid nitrogen temperature: (a) in the solid state; (b) in solution.

The $g_{\parallel}$ and $g_{\perp}$ values have been calculated using Kneubuhl's method.[24] $A_{\parallel}$ and $A_{\perp}$ values were calculated by using one third of the line widths at half maximum and A_0 as 1/3 $(A_{\parallel}+2A_{\perp})$ and g_0 as 1/3 $(g_{\parallel}+2g_{\perp})$.[25] No bands corresponding to Ms $= \pm 2$ transitions were observed in the spectra, ruling out any Cu—Cu interaction.

The g tensor values of copper(II) complexes can be used to derive the ground state.[26] 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 $g_{\parallel} > g_{\perp}$.

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

	Spectral parameter					
Complex	$g_\parallel$	$g_\perp$	g_0	$A_\parallel \times 10^4$ (cm^{-1})	$A_\perp \times 10^4$ (cm^{-1})	$A_0 \times 10^4$ (cm^{-1})
1	2.14	2.03	2.06	—	—	—
2	2.13	2.03	2.06	—	—	—
3	2.24	2.06	2.12	—	—	—
4	2.23	2.05	2.11	—	—	—
5	2.20	2.05	2.10	173	74	107
6	2.18	2.04	2.08	142	68	92
7	2.23	2.05	2.11	—	—	—
8	2.22	2.04	2.10	—	—	—
9	2.20	2.05	2.10	167	87	113
10	2.21	2.05	2.10	173	56	95
11	2.20	2.05	2.10	143	99	113
12	2.21	2.05	2.10	173	80	111



IIa **IIb**

Structure **IIa**: Copper(II) complexes of the (O—N) donor ligands; **IIb**: copper(II) complexes of the (O—O) donor ligands.

In a compressed octahedron, on the other hand, the unpaired electron lies in the 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 complexes also show anisotropic ESR spectra with $g_\parallel > g_\perp$ characteristic of tetragonal or square-planar geometry. Recalling the complexes with the $d_{x^2-y^2}$ ground state, strong interactions along the z axis are accompanied by an 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.[27] Both these effects tend to increase the values of $g_\parallel$.

$g_\parallel$ 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.[28] It is clear from Table 4 that the value of $g_\parallel$ obtained is less than 2.3 indicating covalent character of the metal–ligand bond.

Based on the foregoing data all the copper(II) complexes are assigned to the tetragonal or square-planar geometry and are shown in structures **IIa** and **b**.

Acknowledgements—The authors thank the Head, IIT, Bombay, for providing facilities for recording ESR spectra. One of us (B.P.) is grateful to CSIR, New Delhi, for the award of a SRF.

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