Pergamon

Polyhedron Vol. 16, No. 17, pp. 2909–2916, 1997

0277–5387/97 \$17.00+0.00

PII: S0277-5387(97)00061-2

Spectroscopic and magnetic studies on some copper(II) complexes of antipyrine Schiff base derivatives

Kamal Z. Ismail,[a]* Ali El-Dissouky[a] and Aziza Z. Shehada[b]

[a] Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

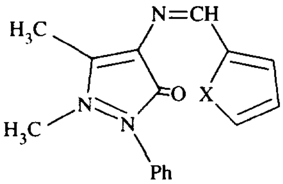
[b] Department of Chemistry, Faculty of Science Education, Alexandria University, Alexandria, Egypt

(Received 24 May 1996; accepted 4 February 1997)

Abstract—A new series of copper(II) complexes derived from 4-(2-thienyl-methylidene amino) antipyrine (TAAP) and 4-furfurylidene amino antipyrine (FAAP) have been synthesized. The complexes are formulated as $[(TAAP)Cu](ClO_4)_2$, $[(FAAP)_2Cu](ClO_4)_2$, $[(FAAP)Cu(OH)Br]$, $[L_2CuX_2]\cdot nH_2O$ and $[L_2Cu(NO_3)_2]$, L = TAAP or FAAP, X = Cl or Br and $n = 2$ or 1, based on their elemental analyses and infrared spectral data. The infrared data indicate the bidentate nature of both ligands in all complexes except in $[(TAAP)Cu](ClO_4)_2$ where the ligand acts as a tridentate chelating agent. The electronic and EPR spectral data are used to interpret the nature of bonding of the ligands with the copper(II) ion, ground state and ligand field strength. The room temperature magnetic moments indicate polymeric structure for $[(TAAP)CuX_2]\cdot nH_2O$, $[(TAAP)Cu](ClO_4)_2$, and $[(FAAP)Cu(OH)Br]$ and monomeric structure for the rest of the complexes. The biological activity studies of the complexes and the free ligands towards three gram-positive, seven gram-negative bacteria and three fungal species have been studied and the potential is related to the nature and structure of the complexes. © 1997 Elsevier Science Ltd

Keywords: antipyrine; Schiff base; copper(II); metal complexes; spectra; magnetism.

Because of their different coordination possibilities with metal ions and consequently their flexible complexing behavior, the synthesis and structural studies of pyrazole based ligands and their metal complexes has drawn the attention of many investigators [1–4]. The Schiff bases of 4-aminoantipyrine are considered to be pyrazolone derivatives and are reported to demonstrate biological [5], clinical [6], pharmacological [7] and analytical [8] applications. It is reported that some drugs showed increased activity when administered as metal chelate rather than as free organic compounds [9,10]. The aim of this work is to study the metal complexes of some new antipyrine Schiff bases along with their biological activity against some bacteria and fungi. Two Schiff bases of antipyrine with furfuraldehyde and the corresponding thiophenealdehyde, namely, 4-furfurylidine-aminoantipyrine (FAAP) and 4-(2-thienylmethylidine) aminoantipyrine (TAAP), structures [I] and [III], were synthesized. The metal complexes of both ligands with copper(II) ions were isolated and characterized using several physical techniques.



X = O, (FAAP) and X = S, (TAAP)
[I] [II]

EXPERIMENTAL

Synthesis of the organic compounds

The Schiff bases TAAP and FAAP were prepared by a dropwise addition, with stirring, of ethanolic

---

* Author to whom correspondence should be addressed.

solution (20 cm^3) of thiophene-2-carboxaldehyde (1.1 g, 0.01 mol) or furan-2-carboxaldehyde (1.0 g, 0.01 mol), Aldrich Chemical Company, Inc. U.S.A., to an ethanolic solution (25 cm^3) of 4-aminoantipyrine (2.1 g, 0.01 mol) respectively. The reaction mixture was refluxed on a water bath for 1–2 h. On cooling, the solid products were separated and filtered. Both Schiff bases were recrystallized from ethanol and dried *in vacuo* over P_4O_{10} to yield yellow crystals, m.p. 150 ± 1°C, and brown crystals, m.p. 200 ± 1°C, respectively. The purity of the prepared compounds was checked by TLC and elemental analysis.

Synthesis of the copper(II) complexes

The copper(II) complexes were prepared by refluxing a solution mixture in ethanol (20 cm^3 each) of the hydrated copper(II) salt (1.87 g, 1.70 g, 2.23 g, or 3.70 g; 0.01 mol of copper nitrate, chloride, bromide or perchlorate), Aldrich Chemical Company, Inc. U.S.A., and the corresponding Schiff base (6.2 g or 6.5 g; 0.022 mol of FAAP or TAAP, respectively). Reflux was continued, with stirring, for 0.5 to 3 h depending on the type of copper salt and the ligand used. On cooling to room temperature, the solid complexes were separated and collected by filtration, washed several times with ethanol and diethyl ether and dried *in vacuo* over P_4O_{10}. The purity of the prepared complexes was confirmed from their elemental analysis and melting points, shown in Table 1. Only listed complexes were isolated regardless of the molar ratio or the order of metal–ligand mixing.

Elemental analysis

Copper content of the prepared complexes were determined complexometrically [12] using standard EDTA solution. The carbon, hydrogen and nitrogen contents in each sample were estimated at the Microanalysis Unit, Faculty of Science, Cairo University, Cairo, Egypt. The analytical data along with some physical properties are summarized in Table 1.

Physical measurements

The infrared spectra were measured in the solid using the KBr disks technique on a Perkin-Elmer 1430-ratio recording spectrophotometer. The electronic absorption spectra were recorded both in Nujol and in solution (1 cm cell) using a Shimadzu 160 A UV-visible spectrophotometer. X-band EPR spectra of polycrystalline samples were recorded at room temperature using a Radiopan Varian spectrometer. Finally, magnetic susceptibility was, measured at room temperature employing the Faraday balance technique and the molar magnetic susceptibilities were corrected for diamagnetism of the constituent atoms using Pascal's constant [13].

Biological screening

The *in vitro* biological activities of the investigated compounds, Table 5, (2 mg per test) were screened against three gram-positive bacteria: *Bacillus subtilis*, *Sarcina lutea* and *Staphylococcus*; seven gram-negative bacteria: *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aerugenosa*, *Salmonella typhi*, *Serratia marcescens*, *Shigella sonnie* and *Proteus mirabilis*; in addition to three fungal species: *Aspergillus flarus*, *Penicillium chrysogenum* and *Candida albicans*, following the Disk-Diffusion techniques [11]. All plates were run in triplicate and the inhibition zones were measured. Dimethyl sulfoxide (DMSO) was used as antimicrobially inert solvent. Blank disks were moistened with DMSO.

Table 1. Microchemical analyses data, colour, melting points (°C) and room temperature magnetic moments (B.M.)

Compound	Colour	M.P. (± 1°C)	$\mu_{eff.}$	% Calculated (%Found) C	H	N	Cu
TAAP	Pale yellow	150	—	64.7(64.5)	5.1(5.0)	14.1(14.3)	—
$[(TAAP)CuCl_2]\cdot 2H_2O$	Brown	210	1.48	41.1(43.0)	4.1(4.0)	9.0(9.2)	13.6(13.8)
$[(TAAP)CuBr_2]\cdot H_2O$	Dark brown	230	1.44	34.5(34.9)	3.1(3.2)	7.5(7.3)	11.4(11.2)
$[(TAAP)Cu](ClO_4)_2$	Yellow	270	0.00	34.3(34.0)	2.7(2.7)	7.5(7.7)	11.4(11.6)
$[(TAAP)_2Cu(NO_3)_2]$	Dark brown	>300	1.84	49.1(48.7)	3.8(3.9)	10.7(10.8)	8.1(8.1)
FAAP	Yellow	200	—	68.3(68.4)	5.3(5.4)	14.9(14.9)	—
$[(FAAP)Cu(OH)Br]$	Dark brown	248	1.18	43.5(44.0)	3.6(3.7)	9.5(9.2)	14.4(14.2)
$[(FAAP)_2Cu](ClO_4)_2$	Brown	>300	1.88	46.6(47.0)	3.6(3.6)	10.2(10.4)	7.7(7.7)
$[(FAAP)_2Cu(NO_3)_2]$	Brown	290	1.78	51.2(51.6)	4.0(3.9)	14.9(14.7)	8.5(8.5)

RESULTS AND DISCUSSION

The elemental analysis data, color, melting points and the room temperature magnetic moment values of the complexes are given in Table 1. The complexes are air stable and freely soluble in DMSO, DMF, and pyridine but less soluble in ethanol and chloroform.

Infrared spectra

The infrared absorption bands of the organic compounds and their copper(II) complexes are listed in Table 2. The two absorption bands at 1642 and 1637 cm^{-1} are assigned $\nu_{C=O}$ in both TAAP and FAAP free ligands, respectively. The shift of such bands to lower wavenumber, *ca* 20–40 cm^{-1}, in the spectra of all metal complexes suggests the involvement of the pyrazolone oxygen in chelation [14,15]. The strong absorption bands located at 1596 and 1603 cm^{-1} in the spectrum of the free TAAP and FAAP ligands respectively, are attributed to $\nu_{-CH=N}$. These bands are shifted to 1553–1575 cm^{-1} and 1583–1587 cm^{-1} in the corresponding cooper complexes, respectively, indicating the involvement of the azomethine nitrogen in coordination to the copper ion [15–17]. Accordingly, both ligands act as bidentate chelating agents bonded to the copper ion *via* the azomethine nitrogen and the pyrazolone ring oxygen atoms in all isolated complexes except for $[(TAAP)Cu](ClO_4)_2$. In such a complex, the TAAP acts as a tridentate chelating ligand. The third coordination site is the thiophene sulfur atom as evident from the shift of the medium-strong absorption of the ν_{CSC} at 1332 cm^{-1} in free TAAP to 1316 cm^{-1} in the complex [18]. Assignment of the proposed coordination sites is further supported by the appearance of medium absorption bands at 352–396 cm^{-1} and 458–468 cm^{-1} (absent in the free TAAP and FAAP) which could be attributed to ν_{Cu-N} and ν_{Cu-O} respectively. The appearance of ν_{C-H} and δ_{C-H} of the methylene group at lower frequencies in the complexes compared to their positions in the free ligands could also be taken as evidence for the coordinating nature of the azometheine nitrogen. Free, uncoordinated, perchlorate ion has a T_d symmetry, whereas the symmetry is reduced to C_{3v} or C_{2v} if it acted as mono or bidentate, respectively. Such reduction in symmetry increases the number of vibrational modes and a metal–oxygen stretching frequency would also be expected in the far IR region [19]. The diagnostic infrared band frequencies of the polyatomic anion, Table 3, indicate the ionic nature of ClO_4 in all perchlorate containing complexes, the monodentate nature of NO_3 in $[L_2Cu(NO_3)_2]$, L = TAAP or FAAP, and the bridging nature of the OH in [(FAAP) Cu(OH)Br] [18,20]. The medium absorption bands at 292 and 236 cm^{-1} in the spectra of $[(TAAP)CuX_2] \cdot nH_2O$, X = Cl or Br and n = 2 or 1, are attributed to the terminal ν_{Cu-Cl} and ν_{Cu-Br}, respectively. The low frequency absorption bands at 224 and 205 cm^{-1} have been attributed to the stretching vibration of bridged chloride and bromide respectively. The spectrum of [(FAAP)Cu(OH)Br] displays a medium band at 229 cm^{-1} which could be assigned to a terminal Cu—Br bond. The strong and broad absorption band at 3450–3328 cm^{-1} in the spectra of $[(TAAP)CuX_2] \cdot nH_2O$ complexes is due to water of crystallization. The absence of coordinated water molecules is confirmed from the absence of the rocking,

Table 2. IR spectral data (cm^{-1}) for the free ligands and their copper(II) complexes

Compound	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-H}	ν_{C-H}	ν_{Cu-O}	ν_{Cu-N}	ν_{Cu-X}
TAAP	1642s	1596s	1451m 1420m	1252m			
$[(TAAP)Cu](ClO_4)_2$	1617vs	1575s	1440m 1410m	1219m	465w	390w	
$[(TAAP)CuCl_2] \cdot 2H_2O$	1608s	1565m	1442m 1428m	1214m	468m	386m	292m 224m
$[(TAAP)CuBr_2] \cdot H_2O$	1606s	1553s	1441m 1417m	1214m	460m	396m	236m 205
$[(TAAP)_2Cu(NO_3)_2]$	1612s	1563s	1442m 1426m	1212m	463m	388m	
FAAP	1637s	1603s	1447m 1420m	1263m			
[(FAAP)Cu(OH)Br]	1616s	1587s	1427m 1408m	1251m	458m	390m	229m
$[(FAAP)_2Cu](ClO_4)_2$	1612s	1583s	1426m 1409m	1254m	460m	382m	
$[(FAAP)_2Cu(NO_3)_2]$	1618s	1579s	1422m 1406m	1251m	456m	384m	

Table 3. Main IR spectral bands (cm^{-1}) for the polyatomic anions

Complex	Different vibrational modes of the poly anions
$[(TAAP)Cu](ClO_4)_2$	1140–1080 br(ν_3), 936 w(ν_1), 620 w(ν_4), T_d symmetry
$[(FAAP)_2Cu](ClO_4)_2$	1133–1082 br(ν_3), 942 w(ν_1), 628 w(ν_4), T_d symmetry
$[(TAAP)_2Cu(NO_3)_2]$	1380 br(ν_3), 830 s(ν_2), C_{2v} symmetry, 300 (ν_{Cu-N}) of NO_3
$[(FAAP)_2Cu(NO_3)_2]$	1372 br(ν_3), 824 s(ν_2), C_{2v} symmetry, 306 (ν_{Cu-N}) of NO_3
[([(FAAP)Cu(OH)Br]	3496 br(ν_{O-H}), 406 (ν_{Cu-OH})

twisting and wagging vibrational modes which are normally activated at 930–970 cm^{-1} and 600–660 cm^{-1} [21].

Magnetic and electronic spectral studies

Copper(II) ion, like all transition metal ions, is capable of forming coordination complexes with a variety of ligands. The stereochemistry of copper(II) complexes is dominated by the formation of nonregular structures involving significant bond length and bond angle distortions. The major responsibility for such behavior is the d^9-electron configuration and the operation of the Jahn–Teller effect. In the absence of X-ray crystallography, the correlation of electronic and magnetic properties of the complex to its structure will acquire some degree of uncertainty, specially if ligands are facultative polydentate [22].

Dimeric copper(II) complexes can range from normal paramagnetic ($\mu_{eff} = \mu_{S.O.}$) to ferromagnetic ($\mu_{eff} > \mu_{S.O.}$ and $2J = 0$–200 cm^{-1}), to antiferromagnetic but still paramagnetic ($\mu_{eff} < \mu_{S.O.}$ and $2J = 0$–200 cm^{-1}), to strongly antiferromagnetic ($2J > 300$ cm^{-1}) and diamagnetic. For antiferromagnetic systems, monobridging chromophores generally involve weak interaction, while dibridging systems are generally more strongly antiferromagnetic and in some cases diamagnetic [23].

Copper(II) complexes $[(TAAP)CuX_2] \cdot nH_2O$, $X = Cl$; $n = 2$, and $X = Br$; $n = 1$, respectively, have room temperature magnetic moments of 1.48 and 144 B.M., respectively. The complex [(FAAP)Cu(OH)Br] has a magnetic moment of 1.18 B.M. These observed values indicate some sort of molecular association that could be achieved through a direct copper–copper interaction and/or magnetic exchange interaction through a bridging ligand(s) [24,25]. Since the electronic spectra of these complexes, which will be discussed later, show no absorption in the region 26–27 kK due to Cu—Cu bonding, one should conclude that the observed magnetic moments are most probably due to magnetic exchange interaction through bridging ligands(s) [23,26].

The observed zero magnetic moment, at room temperature, for $[(TAAP)Cu](ClO_4)_2$ could be attributed to the reduction of copper(II) to copper(I) by the ligand. This phenomenon has been reported for several copper(II) complexes with sulfur containing ligands [23,26]. Since elemental analysis and electronic spectral data, to be discussed later, support the existence of copper(II), therefore our complex represents one of the few copper(II) complexes in which the paramagnetism is almost quenched at room temperature [23,26,27]. This magnetic behavior could be interpreted in terms of strong spin–spin interaction between the copper centers in the solid phase at room temperature. This interaction may take place either by the formation of σ or δ bond by the overlap of the two d-orbitals or through the overlap of the extended molecular orbitals of copper and one of the ligands donor orbitals [23]. Room temperature magnetic moments of 1.84, 1.88 and 1.78 B.M. were recorded for the complexes $[(FAAP)_2Cu](ClO_4)_2$, $[(TAAP)_2Cu(NO_3)_2]$, and $[(FAAP)_2Cu(NO_3)_2]$ respectively. Such values are characteristic of magnetically diluted copper(II) complexes. The electronic spectra, as Nujol mull, for the isolated compounds are listed in Table 4. The complexes $[(TAAP)CuX_2] \cdot nH_2O$, ($X = Cl$, $n = 2$; $X = Br$, $n = 1$) and [(FAAP)Cu(OH)Br] exhibit intense absorption bands in the regions 22.0–25.0 kK and 26.0–33.0 kK respectively. These bands are attributed to the intraligand (ligand localized) and LMCT transitions. The absorption bands at 16.1–16.4 kK and 11.6–11.8 kK are consistent with the copper(II) ion in a square pyramidal environment [27,28]. Assuming approximately a C_{4v} symmetry for these complexes, the absorption band at 16.1–16.4 kK can be considered to consist of two bands due to $^2B_1 \rightarrow {}^2E_1$ and $^2B_1 \rightarrow {}^2B_2$ transitions. The absorption at 11.6–11.8 kK is due to $^2B_1 \rightarrow {}^2A_1$ transition [26,27]. Solution absorption spectra of the complexes $[(TAAP)CuX_2] \cdot nH_2O$ in chloroform display only one broad band at 16.9 for $X = Cl$ and 16.7 kK for $X = Br$ along with the disappearance of the lower energy absorption. Both the spectral features and band position indicate unchanged structure in chloroform and rather consistent with C_{4v} symmetry. The observed blue shift of the band may be attributed to solute–solvent interaction and/or disproportionation of the complex followed by solvent ligation, eq. (1):

$$[(TAAP)CuX_2]_2 \cdot nH_2O + S \rightarrow 2[(TAAP)CuX_2S]S \qquad (1)$$

where $S = CHCl_3$, H_2O or DMSO. The observed color change in chloroform supports the dispro-

Table 4. Electronic and EPR spectral data for copper(II) complexes

		ν(kK)		
Complex	State	*d–d*	CT	EPR data
[(TAAP)CuCl$_2$]·2H$_2$O	Solid	16.4, 11.8	22.6	$g = 2.13$
	CHCl$_3$	16.9	26.2	
	DMSO	17.8	26.0, 24.6	
[(TAAP)CuBr$_2$]·H$_2$O	Solid	16.1, 11.6	25.0	$g = 2.14$
	CHCl$_3$	16.7	26.7	
	DMSO	17.2	25.0, 24.9	
[(TAAP)Cu](ClO$_4$)$_2$	Solid		22.7, 23.8	$g = 2.07$
	EtOH	15.2, 9.5	32.3	
	DMSO	12.7	28.8	
[(TAAP)$_2$Cu(NO$_3$)$_2$]	Solid	12.4	22.7	$g_{\parallel} = 2.22, g_{\perp} = 2.06$
[(FAAP)Cu(OH)Br]	Solid	16.1	32.6, 26.3	$g_1 = 2.01, g_2 = 2.08, g_3 = 2.15$
	CHCl$_3$	16.4, 10.5	23.8	
	DMSO	17.9	27.8	
[(FAAP)$_2$Cu](ClO$_4$)$_2$	Solid	16.8, 15.4	22.1	$g_{\parallel} = 2.53, g_{\perp} = 2.09$
	CHCl$_3$	16.1	23.8	
[(FAAP)Cu(NO$_3$)$_2$]	Solid	12.3	26.3, 21.7	$g_{\parallel} = 2.25, g_{\perp} = 2.07$

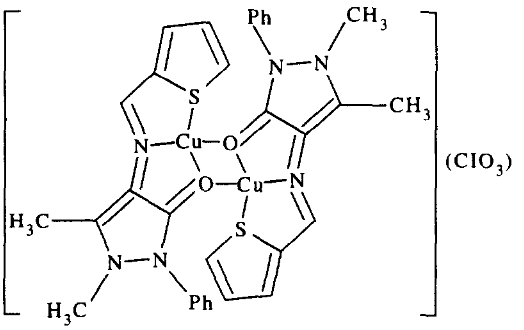
portionation. Trials to isolate the solid complex from the chloroform solution failed due to its decomposition during filtration.

The solution spectrum of [(FAAP)Cu(OH)Br] in chloroform exhibits two absorption bands at 16.4 and 10.5 kK indicating the structural stability of the complex in chloroform. The existence of the two absorption bands along with the blue shift of the higher energy band could be taken as evidence for solvation with chloroform without disproportionation.

In DMSO, the electronic spectra of the three complexes, [(TAAP)CuX$_2$], X = Cl or Br and [(FAAP)Cu(OH)Br] display only one absorption band at 17.2–17.9 kK, characteristic of square pyramidal copper(II) complexes. The blue shift of the spectral band could be taken as evidence for the involvement of DMSO, which have a strong ligand field, in coordination to copper (eq. 1).

The electronic absorption spectrum of [(TAAP)Cu](ClO$_4$)$_2$ displays an intense absorption band at 22.7 kK with a shoulder at 23.8 kK. No bands are located in the lower energy side of the visible region. Such spectral features are characteristic of diamagnetic copper(II) complexes. Based on both magnetic and spectral data, we tentatively propose the complex to have the following dimeric structure [23] (structure II).

On the other hand, the solution spectrum of the complex in ethanol, Table 4, displays a broad band at 14.4 kK with a shoulder at 9.5 kK characteristic of tetrahedral copper(II) environment [27]. Tentatively, this structure change in solution may proceed according to eq. (2) or Eq. (3).



(II)

$$[(\mathrm{TAAP})\mathrm{Cu}]_2(\mathrm{ClO}_4)_4 + \mathrm{EtOH} \leftrightarrow [(\mathrm{TAAP})_2\mathrm{Cu}](\mathrm{ClO}_4)_2 + \mathrm{Cu}(\mathrm{ClO}_4)_2 \quad (2)$$

$$[(\mathrm{TAAP})\mathrm{Cu}]_2(\mathrm{ClO}_4)_2 + \mathrm{EtOH} \leftrightarrow 2[(\mathrm{TAAP})\mathrm{Cu}(\mathrm{EtOH})_2](\mathrm{ClO}_4)_2 \quad (3)$$

In equation (2), a tetrahedral bis-chelate is formed through a breakdown of one of the ligand–metal bonds, maybe the Cu—S, and thus TAAP acts as a bidentate ligand. Equation (2), on the other hand, shows the second possibility in which the tetrahedral complex is achieved *via* solvent ligation. In DMSO, only one broad absorption band at 12.2 kK was obtained. Such spectra features are characteristic of distorted octahedral copper(II) complexes [27]. This arrangement can be achieved by the axial ligation of the dimeric form or the dissociation of the dimeric form followed by DMSO axial ligation.

The electronic spectrum of the corresponding FAAB complex, $[(FAAP)_2Cu](ClO_4)_2$, displays two broad absorption bands at 16.8 kK and 15.4 kK in addition to a strong charge transfer absorption band at 22.1 kK. The spectral data, Table 4, are consistent with that reported for square planar copper(II) complexes with a bidentate N_2O_2, ligand fields [27]. The lower energy bands are assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively, in D_{4h} symmetry. The absorption band due to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition could not be identified due to the asymmetric nature of the band at 15.4 kK. In chloroform, however, only one broad band at 16.1 kK was observed. This could be explained on the basis of structural change to square pyramidal copper(II) complex as a result of solvent ligation.

The Nujol mull electronic spectrum of $[L_2Cu(NO_3)_2]$, L = TAAP or FAAP, exhibit a broad absorption band at 12.4 kK and 12.3 kK, respectively. Such spectra are characteristic for tetragonally distorted copper(II) complexes [27].

Electron paramagnetic resonance

Room temperature X-band EPR spectra for the isolated polycrystalline copper complexes are listed in Table 4. Both $[(TAAP)CuX_2] \cdot nH_2O$, X = Cl or Br and $n = 2$ or 1, respectively, displayed only one broad signal with no appearance of hyperfine structure. The estimated g-values are 2.13 and 2.14, for X = Cl and Br, respectively. The broad unresolved spectral signal could be attributed to super exchange interaction between copper centers in the solid state. Furthermore, the inhomogeneity of the signals is due to the anisotropic exchange interaction. These spectral features are consistent with the magnetic data for these complexes.

A rhombic type EPR spectrum with three g-values $g_1 < g_2 < g_3$, Table 4, was recorded for (FAAP) Cu(OH)Br. The parameter $R = g_2 - g_1/g_3 - g_2 = 1$ is indicative of the admixing of the $d_{x^2-y^2}$ and d_{z^2} in the ground state. Furthermore, the low g_1-value which is little higher than the spin-only value of 2.00, could be taken as other evidence for the $d_{x^2-y^2}$ and d_{z^2} admixing and the low crystal field symmetry as well as the anisotropic exchange interaction in solid phase [29,30] which is in agreement with the room temperature magnetic moment of 1.18 B.M.

The EPR spectrum of $[(FAAP)_2Cu](ClO_4)_2$ at room temperature was found to be of axial type having $g_{\parallel} = 2.53$ and $g_{\perp} = 2.09$. The G-parameter, calculated from the relation $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, of 5.89, indicates the absence of interaction between the copper centers in the solid state; the local tetragonal axes have parallel alignment or are slightly misaligned.

The complexes $[L_2Cu(NO_3)_2]$, L = TAAP or FAAP, have X-band EPR spectra of axial type with $g_{\parallel} = 2.22$ and $g_{\perp} = 2.06$ for L = TAAP and $g_{\parallel} = 2.25$, $g_{\perp} = 2.07$ for L = FAAP.

The G-parameter values of the two complexes of 3.7 and 3.6, respectively, are in agreement with an orbitally non-degenerate ground state and the small interaction between the copper centers in the solid state [31,32].

The room temperature X-band EPR spectrum of $[(TAAP)Cu](ClO_4)_2$, Fig. 1, supports its stoichiometric analysis. The featureless spectrum, $g = 2.07$, is consistent with a polymeric structure for the complex.

Screening for antibacterial and antifungal activity

The antibacterial activity of the free ligands and their copper(II) complexes clearly illustrate that the organic compounds have no activity against any of the test organisms. Four copper complexes have both antibacterial and antifungal potency against eight of the thirteen test organisms, Table 5. The five organisms that showed complete resistance are *Staphylococcus aureus*, *Salmonella typhi*, *Proteus mirabilis*, *Aspergillus flavus* and *Penicillium chrysogenum*.

Table 6 summarizes the correlation matrix showing the correlation coefficients among the bioactive complexes. The data indicate that compounds $[(TAAP)CuCl_2] \cdot 2H_2O$ and $[(TAPP)CuBr_2] \cdot H_2O$ can exert similar positive effects against the sensitive test organisms. Also, these two complexes have positive correlation with [(FAAP)Cu(OH)Br]. This could be taken as evidence that the effective part in these complexes is the central copper ions but not the organic compounds. Furthermore this correlation could be attributed to the similar dimeric structure and stereochemistry for all the three complexes. The absence of such correlation with $[(TAPP)_2Cu](ClO_4)_2$ could be attributed to the different stereochemistry and nature of the latter (monomeric square planar) from the first three complexes, and the presence of ClO_4 as ionic group. Investigation of the data given in Tables 5 and 6 showed that:

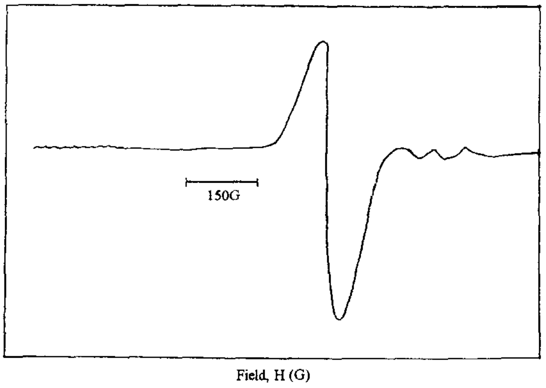


Fig. 1. Room temperature X-band EPR spectrum for polycrystalline $[(TAAP)Cu](ClO_4)_2$.

Table 5. Antimicrobial activities of some copper(II) complexes using disk diffusion method

Compound	Diameter of the inhibition zone (mm) against							
	Bacillus subtilis	*Sarcina lutea*	*Escherichia coli*	*Klebsiella pneumoniae*	*Pseudomonas aeruginosen*	*Serratia marcescens*	*Shigella sonnie*	*Candida albicans*
1. $[(TAAP)Cu](ClO_4)_2$	12	—	14	10	—	16	16	12
2. $[(TAAP)CuCl_2] \cdot H_2O$	14	14	20	20	10	24	22	16
3. $[(TAAP)CuBr_3] \cdot H_2O$	12	—	18	12	—	20	24	14
4. $[(FAAP)Cu](OH)Br]$	16	18	26	22	18	26	36	20

Table 6. Correlation matrix showing the correlation coefficients among the bioactive copper(II) complexes

Compound[a]	1	2	3	4
1	1.000	0.5508	0.6747	0.5123
2	0.5508	1.0000	0.9337	0.9900
3	0.6747	0.9337	1.0000	0.9126
4	0.5123	0.9900	0.9126	1.0000

[a] Compound number as given in Table 5.

(i) The presence of the dimeric structure as in compounds $[(TAAP)CuX_2] \cdot nH_2O$, $X = Cl$ or Br and $n = 2$ or 1 and [(FAAP)Cu(OH)Br] lead to an increase in their potential;

(ii) The presence of Cl^- as coordinated anion as in compound $[(TAAP)CuCl_2] \cdot 2H_2O$ caused a significant increase in its potential compared to compound $[(TAAP)CuBr_2] \cdot H_2O$ that contained coordinated Br^- ion in addition to the inactivity of the latter against *Pseudomonas* and *Sarcina*;

(iii) The existence of bridged O—H^- in addition to the Br^- in [(FAAD)Cu(OH)Br] caused a jump in the activity of this compound compared to the other two dimeric compounds $[(TAAP)CuCl_2] \cdot 2H_2O$ and $((TAAP)CuBr_2] \cdot H_2O$. Furthermore this compound could be considered as the most promising potent broad spectrum antimicrobial compound among the four complexes, where it was found to be superior to all other complexes against all the test organisms except *Pseudomonas aeruginosa*.

One can arrange the four complexes according to their biological activity in the order

$$[(FAAP)Cu(OH)Br] > [(TAAP)CuCl_2] \cdot 2H_2O > [(TAAP)CuBr] \cdot H_2O > [(TAAP)Cu](ClO_4)_2.$$

Acknowledgement—The authors would like to thank Professor Y. Gohar of the Department of Botany, Faculty of Science, Alexandria University for doing the biological screening of the prepared compounds.

REFERENCES

1. Reedijk, J. and ten Hoedt, R. W. M., *Recl. Trav. Chim.*, 1982, **101,** 49.
2. Trofimenko, S., *Prog. Inorg. Chem.*, 1986, **34,** 115.
3. Hergold-Brundic, A., Kaitner, B., Kamenar, B., Leovac, V. M., Iveges, E. Z. and Juranic, N., *Inorg. Chim. acta.*, 1991, **188,** 151.
4. Nair, M. K. M. and Radhakrishnan, P. K., *Polyhedron*, 1993, **12,** 1227.
5. Craciunescu, D. G., *An. R. Acad. Farm.*, 1977, **43,** 256.
6. Hosler, J., Tschanz, C., Hignite, C. E. and Azarnoff, D. L., *J. Invest. Dermatol.*, 1986, 74951.
7. Meffin, P. J., Williams, R., Blaschke, T. F. and Rowland, M., *J. Pharm. Sci.*, 1977, **66,** 135.
8. Olenovich, N. L. and Koval Chuk, L. I., *Zh. Anal. Kim.*, 1975, **28,** 2162.
9. Williams, D. R., *Chem. Revs.*, 1977, **72,** 203.
10. Furst, A. and Haro, R. T., *Prog. Exp. Tumor Res.*, 1969, **12,** 102.
11. Collee, J. G., Duguid, J. P., Fraser, A. G. and Marmion, B. P., *Practical Medical Microbiology*, 13th edn. Churchill Livingston, Edinburgh, London, Melbourne and New York, 1989.
12. Schwazenbach, G., *Complexometric Titration*, translated by H. Irving, Methuen Co., London, 1959.
13. Figgis, B. N. and Lewis, J., *Modern Coordination Chemistry*, eds R. Wilkins and J. Lewis. Interscience Publishers, New York, 1967, p. 245.
14. Radhakrishnan, P. K., *Polyhedron*, 1986, **5,** 995.
15. Al-kubaisi, A. H. and Ismail, K. Z., *Can. J. Chem.*, 1994, **72,** 1785.
16. El-Dissouky, A., *Spectrochim. Acta*, 1987, **43A,** 1182.
17. Iskander, M. F., El-sayed, L. and Ismail, K. Z., *Trans. Met. Chem.*, 1979, **4,** 225.
18. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
19. Hathaway, B. J., *Curr. Contents*, 1982, **45,** 20.
20. Gowda, N. M., Naikar, S. B. and Reddy, G. K., *Adv. Inorg. Chem. Radiochem.*, 1984, **28,** 255.
21. El-Dissouky, A., Fahmy, A. and Amer, A., *Inorg. Chim. Acta*, 1987, **133,** 311.
22. Hathaway, B. J., *Struct. Bonding* (*Berlin*), 1984, **57,** 55.
23. Hathaway, B. J., in *Comprehensive Coordination Chemistry*, vol. 5, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 5, p. 533.
24. Merz, L. and Haase, W., *J. Chem Soc. Dalton Trans*, 1980, 875.
25. El-Dissouky, A., Hindawey, A. M. and Abdelsalam, A., *Inorg. Chim. Acta*, 1986, **119,** 207.

26. El-Shazly, M. F., Salem, T and El-Sayed, M. A., *Inorg. Chim. Acta*, 1978, **29,** 155.
27. Lever, A. P., *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier Science Publishers, Amsterdam, 1984.
28. Nyholm, R. S. and Truter, M. R., *J. Chem. Soc. A*, 1971, 1577.
29. Hathaway, B. J. and Billing, D. E., *Coord. Chem. Rev.*, 1970, **5,** 143.
30. El-Dissouky, A., *Trans. Met. Chem.*, 1984, **9,** 112.
31. El-Shazly, M. F., El-Dissouky, A., Salem, T. M and Osman, M. M., *Inorg. Chim. Acta*, 1980, **40,** 1.
32. Wasson, J. R., *Spectrosc. Lett.*, 1976, **9,** 95.