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SYNTHESIS AND CHARACTERIZATION OF TETRANUCLEAR COPPER(II) COMPLEXES BY CONTINUED COMPLEXATION OF A NEW CLASS OF BINUCLEATING LIGAND 3,3′-DIMETHOXY-4,4′-BIS(1-ALKYL(R)TRIAZENE-1-OXIDE)BIPHENYL

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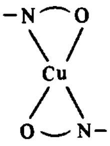
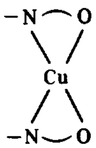
Abstract—A new class of binuclear copper(II) complexes, Cu_2L_2, yielded a series of tetranuclear copper(II) complexes, $Cu_2L_2(CuA_2)_2$, when mixed with CuA_2 in a 1 : 2 molar ratio (where LH_2 = 3,3′-dimethoxy-4,4′-bis(1-alkyl(R)triazene-1-oxide)biphenyl denoted as R-triaz-bp-OCH_3 and A = Cl, Br). No appreciable antiferromagnetic interaction was observed between any two sets of copper(II) centres as suggested by magnetochemical or ESR studies. The optical spectra suggest that the two sets of copper(II) centres have different geometries, the Cu_2L_2 based coppers are near square-planar while the CuA_2 based ones are near tetrahedral. The reason for the absence of magnetic interaction between any two copper(II) centres is discussed in the light of the structure of the complexes.

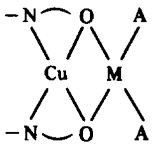
The unusual properties observed in the polynuclear metal complexes have maintained their interest over three decades. Recently, we reported the synthesis and studies of two novel series of binuclear copper(II) complexes, viz. bis-[3,3′-di(X)-substituted-4,4′-bis(3-alkyl(R)triazene-3-oxide)-diphenyl]dicopper(II) denoted as [Cu_2(R-triaz-bp-X)$_2$] (**1a**);[1,2] [3,3′-di(X)-substituted-4,4′-bis(salicylidinimino)diphenyl]dicopper(II) denoted as [Cu_2(Sal-bp-X)$_2$] (**1b**).[3] Unlike the mononuclear analogues of these two series, which possess



type *trans* chelate groups,[4–6] the binuclear complexes, [Cu_2(R-triaz-bp-X)$_2$] and [Cu_2(Sal-bp-X)$_2$] contain *cis* chelation to give



type chromophores. This *cis* positioning of the oxygen ligating atoms may facilitate further coordination to another metal centre so as to give



type centres (**1c**), where A can be any end ligand atom or group such as halide or thiocyanate, respec-

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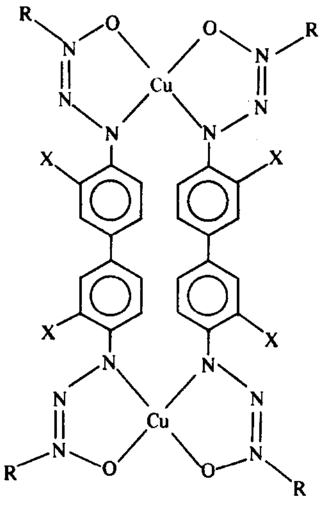
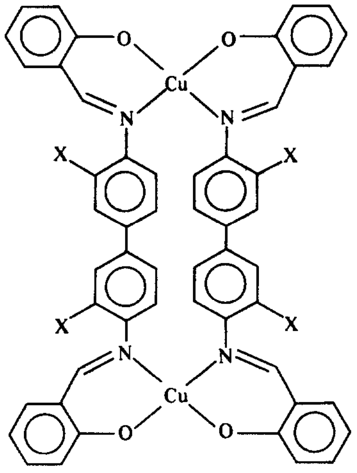


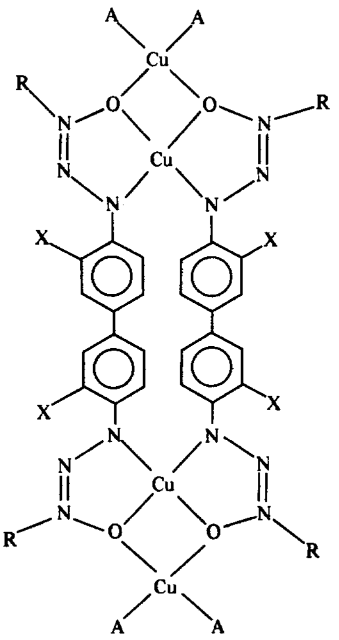
1a

Cu_2(R - triaz - bp - X)$_2$



1b

Cu_2(Sal - bp - X)$_2$



1c

Cu_2(R - triaz - bp - X)$_2$(CuA_2)$_2$

tively. This type of continued bridging is not unusual.[7–11] Here we report the synthesis and characterization of the complexes, [Cu_2(R-triaz-bp-OCH_3)$_2$(CuA_2)$_2$] (**1c**) generated from **1a**.

EXPERIMENTAL

The details of the synthesis of the binuclear complexes which act as ligands for the present tetranuclear complexes were previously reported.[1–3] Mixing ethanolic solutions of the anhydrous cupric halides with the concentrated solutions of the binuclear complexes in chloroform immediately yields the tetranuclear complexes. The green, shiny precipitates obtained from triazene-1-oxide-based complexes were filtered and air-dried.

In a typical experiment, 422 mg (~ 0.5 mM) of the binuclear complex, Cu_2(CH_3-triaz-bp-OCH_3)$_2$, were dissolved in 25 cm^3 of chloroform to which were added 130 mg (~ 1.0 mM) of anhydrous cupric chloride dissolved in 10 cm^3 of absolute ethanol. A shiny, green and silky precipitate, obtained immediately, was filtered and dried under nitrogen. The filtrate was nearly colourless indicating a quantitative reaction between the dark brown solution of the binuclear complex and the green solution of the cupric halide (yield ~ 98%).

The microanalytical data were obtained on a Hewlett–Packard CHN analyser and the metal content from either the thiocyanate method[12] or atomic absorption spectrophotometry.

The room and variable temperature susceptibility measurements, using Pascal constants[13] for diamagnetic correction, were obtained on a Sartorius microbalance with a liquid helium cryostat using Faraday's method. Cupric sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) was used as the reference.

IR spectra from 4000 to 200 cm^{-1} were recorded on a Perkin–Elmer Model 283 spectrophotometer. The solution electronic spectra were obtained on a Cary 17D spectrophotometer and the solid-state spectra on a PARC Photoacoustic spectrometer. The X-band ESR spectra were recorded on a JEOL FE 3X spectrometer.

RESULTS AND DISCUSSION

Infrared spectra

The C, H, N and metal analysis data are collected in Table 1 and are consistent with structure **1c**. The metal–halogen stretching frequencies and $\nu(M—Cl)/\nu(M—Br)$ ratios are collected in Table 2. It is well known[14] that terminal metal–chloride stretches appear around 350 cm^{-1} and metal–bromide ones at 250 cm^{-1}, and also that the ratio $\nu(M—Cl)/\nu(M—Br)$ (where $M = Cu^{2+}$, Zn^{2+}, Ni^{2+}, Co^{2+}) is in the order 1.30–1.35 for terminal metal–halogen bonds. The frequency ratios for the present complexes (~ 1.32) suggest that the halogen atoms are in terminal positions and not bridging.

Electronic spectra

The PAS spectra recorded for the tetranuclear copper(II) complexes exhibit well-resolved absorption bands at ~ 8000 and ~ 17,000 cm^{-1}. The solid-state electronic spectral data of the complexes are collected in Table 2, with that of the parent binuclear complexes given in parentheses. Representative spectra are given in Fig. 1.

In the case of the complexes shown in structure **2**, it is established that the square planarity of the chelated inner coppers in the parent complex is enhanced upon further complexation with copper halides,[9,10,15] resulting in a hypsochromic (blue)

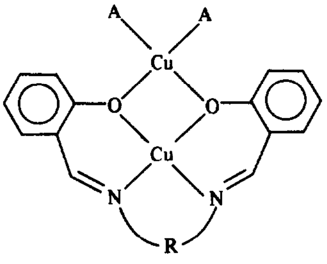


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Table 1. Elemental analysis of tetranuclear copper(II) complexes, $Cu_2L_2(CuA_2)_2$[a]

Compound	Colour	% Cu	% C	% H	% N
$Cu_2(CH_3\text{-triaz-bp-OCH}_3)_2(CuCl_2)_2$	Olive green	23.1	34.6	3.5	15.2
		(22.7)	(34.5)	(3.3)	(15.1)
$Cu_2(CH_3\text{-triaz-bp-OCH}_3)_2(CuBr_2)_2$	Pale green	19.8	29.6	2.8	13.0
		(19.5)	(29.9)	(2.8)	(13.0)
$Cu_2(C_2H_5\text{-triaz-bp-OCH}_3)_2(CuCl_2)_2$	Green	22.0	36.8	3.8	14.4
		(21.6)	(37.0)	(3.8)	(14.4)
$Cu_2(C_2H_5\text{-triaz-bp-OCH}_3)_2(CuBr_2)_2$	Pale green	19.1	32.2	3.3	12.5
		(18.7)	(32.1)	(3.3)	(12.5)
$Cu_2(n\text{-}C_3H_7\text{-triaz-bp-OCH}_3)_2(CuCl_2)_2$	Green	21.2	32.2	4.2	13.7
		(20.6)	(32.2)	(4.3)	(13.7)
$Cu_2(n\text{-}C_3H_7\text{-triaz-bp-OCH}_3)_2(CuBr_2)_2$	Green	18.2	34.2	3.7	11.8
		(18.0)	(34.3)	(3.7)	(12.0)
$Cu_2(t\text{-}C_4H_9\text{-triaz-bp-OCH}_3)_2(CuCl_2)_2$	Green	17.8	47.2	4.2	11.9
		(17.8)	(47.2)	(4.3)	(11.8)
$Cu_2(t\text{-}C_4H_9\text{-triaz-bp-OCH}_3)_2(CuBr_2)_2$	Pale green	15.7	41.9	3.7	10.4
		(15.9)	(42.0)	(3.8)	(10.5)

[a] Calculated values are given in parentheses.

Table 2. Magnetic, IR and electronic spectral data of tetranuclear copper(II) complexes, $Cu_2L_2(CuA_2)_2$

Compound	μ_{eff} (BM)[a]	ν(Cu—A)[b]	ν(Cu—Cl)/ν(Cu—Br)	ν_{max}[c]
$Cu_2(CH_3$-triaz-bp-$OCH_3)_2(CuCl_2)_2$	1.78	325	1.300	7930 17,240 (10,200)
$Cu_2(CH_3$-triaz-bp-$OCH_3)_2(CuBr_2)_2$	1.82	250		7810 17.850
$Cu_2(C_2H_5$-triaz-bp-$OCH_3)_2(CuCl_2)_2$	1.80	330	1.320	7690 16,600 (9009)
$Cu_2(C_2H_5$-triaz-bp-$OCH_3)_2(CuBr_2)_2$	1.84	250		7690 17,240
$Cu_2(n\text{-}C_3H_7$-triaz-bp-$OCH_3)_2(CuCl_2)_2$	1.81	332	1.296	7140 16,700 (10,400)
$Cu_2(n\text{-}C_3H_7$-triaz-bp-$OCH_3)_2(CuBr_2)_2$	1.85	256		6250 16,700
$Cu_2(t\text{-}C_4H_9$-triaz-bp-$OCH_3)_2(CuCl_2)_2$	1.79	338	1.305	7570 17,500 (9700)
$Cu_2(t\text{-}C_4H_9$-triaz-bp-$OCH_3)_2(CuBr_2)_2$	1.83	259		6675 17,460

[a] Per copper centre.

[b] Stretching frequency in cm^{-1}.

[c] Recorded on a Photoacoustic spectrometer. The values in parentheses are the solid-state λ_{max} of the parent Cu_2(R-triaz-bp)$_2$ complexes (values in cm^{-1}).

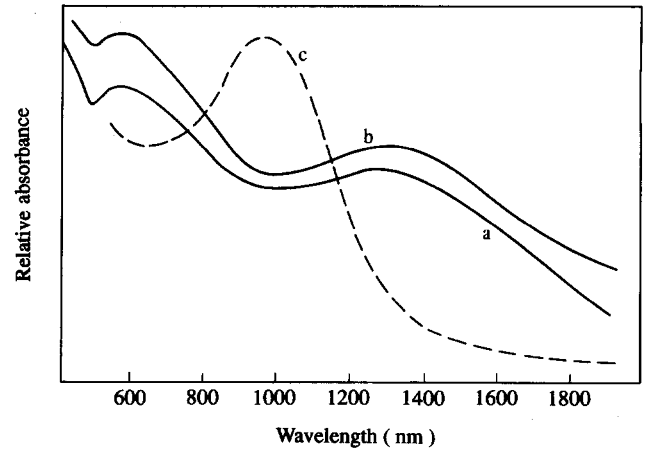

Fig. 1. Solid-state photoacoustic electronic spectra of (a) Cu_2(R-triaz-bp-$OCH_3)_2(CuCl_2)_2$, (b) Cu_2(R-triaz-bp-$OCH_3)_2(CuBr_2)_2$ and (c) Cu_2(R-triaz-bp-$OCH_3)_2$ in the near-IR and visible range.

shift, with respect to the parent complex. The low energy transition is attributed to the lower symmetric (C_2) outer copper.

It is also observed that the heavier the halogens on the outer coppers are, the greater is the tetrahedral nature for the outer coppers.[16] Tetrahedral coppers generally possess their crystal-field absorption in the range 14,000–7000 cm^{-1}, whereas the square-planar ones possess theirs in the range 19,000–14,000 cm^{-1}. The appearance of two λ_{max}

values for the present complexes indicates the presence of two structurally distinct copper pairs, one outer pair in near tetrahedral geometry absorbing at ~ 8000 cm^{-1}, and the other at near square planarity absorbing at ~ 17,000 cm^{-1}. The parent binuclear complexes, from which the inner coppers of the present tetranuclear complexes originate, have been observed to absorb at ~ 11,000 cm^{-1} and a distorted square-planar geometry was assigned to them.[2] The shift of this band to higher energy upon extended complexation in obtaining the present complexes means that planarity is enhanced at the inner coppers. The higher energy band at ~ 17,000 cm^{-1} is assigned to the $d_{z^2} \leftarrow d_{x^2-y^2}$ transition of the inner copper, and the lower one at ~ 8000 cm^{-1} is assigned to the $B_1 \leftarrow A_1$ transition of the outer copper.

Magnetic and ESR spectral data

The magnetic system in the present complex can be represented as

$$\mathrm{Cu(1)} \overset{J}{\text{---}} \mathrm{Cu(2)} \overset{J'}{\text{---}} \mathrm{Cu(3)} \overset{J}{\text{---}} \mathrm{Cu(4)},$$

with J' as the interaction energy between the two inner copper centres, and J being the interaction energy between one outer copper and one inner copper. The other possible interaction between Cu(1) and C(3) or Cu(2) and Cu(4) is negligible. The magnetic moment data of all the complexes, collected in Table 2, are normal. It was already reported that the magnetic interaction between the two coppers in the parent binuclear complexes is negligibly small.[2] The observation of normal magnetic moment data for the present tetranuclear complexes is interesting, since there are copper centres bridged only by oxygen atoms. Even cryomagnetic studies from 4.2 K did not give any indication of the presence of measurable antiferromagnetic interaction.

In a planar $\mathrm{CuO_2Cu}$ type magnetosphere, the extent of magnetic interaction depends on the Cu—O—Cu bridging angle, ϕ. For hydroxo-bridged systems the interaction energy, $2J$, is given by[6,17]

$$2J = -74.53\phi + 7270\ \mathrm{cm}^{-1}.$$

It is implied that the angle ϕ where J is nearly zero is around 98°. For bulky substitution on oxygen atoms, this angle comes close to 90°. X-ray crystallographic studies could not be undertaken on the present complexes as it was difficult to grow single crystals of them. However, the Cu—O—Cu angle was tentatively calculated from the X-ray crystallographic data available on their parent representative binuclear complex, $\mathrm{Cu_2(CH_3\text{-triax-bp-}OCH_3)_2}$ and that on comparable complexes having a site, $\mathrm{CuO_2CuA_2}$, as in the present complexes assuming planarity to the $\mathrm{CuO_2Cu}$ core.[18–20] The angle thus calculated was ~ 87°, close to 90°, resulting in a negligible magnetic interaction.

The absence of magnetic interaction is further proved from the X-band ESR spectral analysis. All the copper complexes exhibit well-resolved parallel and perpendicular ESR transitions. The peak profiles are invariant throughout the temperature range 77–340 K. No solution ESR studies could be carried out as the complexes are highly insoluble in most of the solvents. The resolution of the parallel and perpendicular absorptions may be due to the negligible presence of dipolar interactions. A representative room-temperature polycrystalline ESR spectrum is provided in Fig. 2, and the relevant data in Table 3. The $\Delta M_s = \pm 2$ half-field transition was not observed even with improved instrumental parameters. The relative intensity of the $\Delta M_s = \pm 2$ transition with respect to that of the normal $\Delta M_s = \pm 1$ transition is given by

$$\text{relative intensity} = \frac{C}{r^6}\left(\frac{9.1}{\nu}\right)^2$$

for interacting binuclear systems[21] and is independent of the value of J. Here C is a constant (approximately 22 for bivalent copper systems), ν is the operating ESR frequency in GHz and r the interacting Cu—Cu distance. In the present tetra-

Table 3. ESR spectral data of tetranuclear copper(II) complexes, $\mathrm{Cu_2L_2(CuA_2)_2}$

Compound	$g_\parallel$		$g_\perp$		g_0[a]	
	A = Cl	A = Br	A = Cl	A = Br	A = Cl	A = Br
$\mathrm{Cu_2(CH_3\text{-triaz-bp-}OCH_3)_2(CuA_2)_2}$	2.259	2.252	2.095	2.1165	2.15	2.161
$\mathrm{Cu_2(C_2H_5\text{-triaz-bp-}OCH_3)_2(CuA_2)_2}$	2.259	2.250	2.107	2.0815	2.158	2.14
$\mathrm{Cu_2(}n\mathrm{\text{-}C_3H_7\text{-triaz-bp-}OCH_3)_2(CuA_2)_2}$	2.259	2.250	2.1285	2.097	2.172	2.148
$\mathrm{Cu_2(}i\mathrm{\text{-}C_3H_7\text{-triaz-bp-}OCH_3)_2(CuA_2)_2}$	2.214	2.210	2.106	2.118	2.142	2.148

[a] $g_0 = 1/3[g_\parallel + 2g_\perp]$.

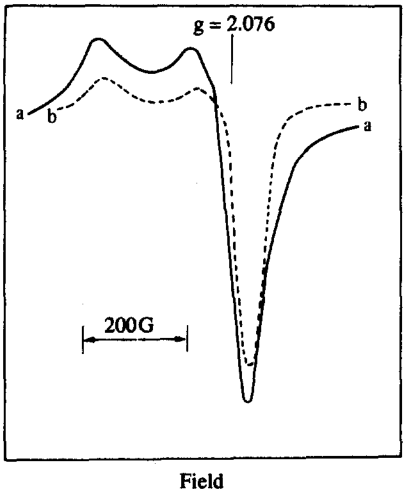

Fig. 2. *X*-band ESR spectra of (a) $Cu_2(R\text{-triaz-bp-OCH}_3)_2(CuCl_2)_2$ and (b) $Cu_2(R\text{-triaz-bp-OCH}_3)_2(CuBr_2)_2$ at room temperature.

nuclear complexes the distance between the closest copper atoms is *ca* 3 Å which gives $\sim 3.0\times10^{-2}$ as the relative intensity of the $\Delta M_s = \pm 2$ transition for an operating frequency of $\sim$ 9.5 GHz. This very intense peak, could readily be observed by our instrument, but no $\Delta M_s = \pm 2$ transition was observed either at room temperature or 77 K implying the absence of antiferromagnetic interaction in the complexes.

Other indirect evidence for the absence of the magnetic interaction stems from the evident absence of zero-field splitting, D, given for the interacting binuclear complexes, by

$$D = \frac{1.39\times10^4\times g}{r^3},$$

where g is the average g factor and r is the interacting Cu—Cu separation.[22,23] For $r = \sim 3$ Å and $g = \sim 2.15$, the value of D is calculated as $\sim$ 1130 G implying the splitting of the normal $\Delta M_s = \pm 1$ transition separated by $\sim$ 2260 G. No such split peaks were observed.

X-ray crystallographic molecular structure determinations would have provided interesting information but could not be undertaken due to the difficulty of generating a single crystal because of their insolubility in various solvents and thermal instability above 150°C.

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