

## New Trinuclear Copper(II) Species

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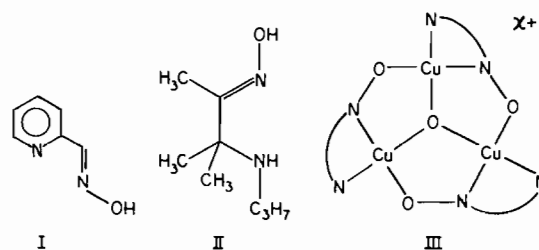
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*Bidentate isonitrosoketimine ligands containing the functions  $-C(=NOH)-C(=NR)-$  (abbreviated as HinkR) and  $-C(=NOH)-C(=NAr)-$  (HinkAr) readily yield trinuclear copper(II) species  $[Cu_3O(inkR)_3]ClO_4$  and  $[Cu_3OH(inkAr)_3](ClO_4)_2$  which have been characterised using solution electrical conductivity, electronic and infrared spectra and variable temperature magnetic susceptibility. The complexes uniformly have magnetic moments of  $\sim 1.8$  BM per molecule ( $\sim 1$  BM per copper) over the temperature range 80-380 K. The species are thus strongly anti-ferromagnetic in nature and only doublet states are populated. The lower limit of the exchange integral  $|J|$  is set at  $\sim 350$  cm<sup>-1</sup>. Structures containing a central  $Cu_3O$  or  $Cu_3OH$  core held by peripheral oximato bridge is strongly indicated by the experimental data taken collectively with some known structural information. The superexchange mechanism has been investigated. Results of EHT calculation on the  $Cu_3O^{4+}$  core is presented. It is shown that the O bridge can bring about considerable anti-ferromagnetic interaction. However on the basis of experimental and theoretical results concerning the role of oximato bridge in bringing about exchange, it is suggested that the peripheral oxime bridge plays a dominant role. A new system which is most probably trinuclear and contains the  $Cu_3$  core held only by oximato group (no central oxygen) also has  $S = 1/2$ , thus showing the pivotal importance of the oximato bridges in relation to the strong magnetic coupling.*

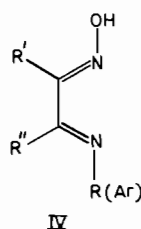
### Introduction

The existence of  $M_3O$  core (M = metal ion) held by peripheral bridging organic ligands is well known in the chemistry of e.g., iron(III) and chromium(III) [1]. In the case of copper(II) [2, 3] only two well-characterised systems having the  $Cu_3O$  (or  $Cu_3OH$ ) core have been described so far. These are based on the ligands 2-pyridine aldoxime(I), Hpao and 2-propylamino-2-methyl-3-butanoneoxime(II), Hprao:

$[Cu_3OH(pao)_3]SO_4 \cdot 10.5H_2O$  [4, 5] and  $Cu_3-(Prao)_3(H_2O)_3OH_{0.5}(ClO_4)_{1.5} \cdot 4H_2O$  [6, 7]. In each case, the central  $Cu_3O(H)$  core is held by peripheral oximato bridges as shown schematically in (III) [5, 7]. A common structural feature of ligands (I) and (II) is the presence of an oximato group two carbon



atoms away from a potentially donor nitrogen atom. We suspected that the formation of (III) could be general to ligand systems with this particular structural feature. In this paper new trinuclear species derived from the N-alkyl or N-aryl isonitrosoketimine ligand system (IV) are described [8].



IVa	R = C <sub>2</sub> H <sub>5</sub>	R' = CH <sub>3</sub>	R'' = CH <sub>3</sub>
IVb	R = n-C <sub>3</sub> H <sub>7</sub>	R' = CH <sub>3</sub>	R'' = CH <sub>3</sub>
IVc	R = n-C <sub>4</sub> H <sub>9</sub>	R' = CH <sub>3</sub>	R'' = CH <sub>3</sub>
IVd	Ar = C <sub>6</sub> H <sub>5</sub>	R' = CH <sub>3</sub>	R'' = CH <sub>3</sub>
IVe	Ar = o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	R' = CH <sub>3</sub>	R'' = CH <sub>3</sub>
IVf	Ar = C <sub>6</sub> H <sub>5</sub>	R' = CH <sub>3</sub>	R'' = C <sub>2</sub> H <sub>5</sub>
IVg	Ar = C <sub>6</sub> H <sub>5</sub>	R' = C <sub>2</sub> H <sub>5</sub>	R'' = CH <sub>3</sub>

The specific ligands concerning us are (IVa) to (IVg). Except for the last two cases, all other ligands have  $R' = R'' = CH_3$ . The ligands are abbreviated as HinkR or HinkAr depending on whether R is alkyl or aryl (H refers to the dissociable oxime proton).

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## Experimental

3-oximinobutane-2-one, 3-oximinopentane-2-one and 2-oximinopentane-3-one were prepared by the nitrosation of ethylmethylketone, methylpropylketone and diethylketone respectively [9]. Ethylamine (anhydrous) and n-propylamine were obtained from Eastman Organic Chemicals, U.S.A., n-butylamine, aniline, *o*-toluidine, N,N-diethyl-1,3-propanediamine and N,N-dibutyl-1,3-propanediamine were obtained from Aldrich Chemical Co., U.S.A.

### Synthesis of Schiff Bases (*HinkAr*)

0.1 mol of the isonitrosoketone was taken in a 100 ml round bottom flask and was dissolved in 20 ml of absolute ethanol. To it 0.1 mol of freshly distilled amine was added and the mixture was heated to reflux on a water bath for 24 hr. At the end of this period, the hot contents of the flask was poured in a beaker containing 400 ml of ice cold water with stirring. The Schiff base separated out as a white solid. This was filtered, dried and then recrystallised from dry toluene. The yield was 20%.

### Synthesis of $[Cu_3O(inkR)_3]ClO_4$

1 g (0.01 mol) of biacetylmonoxime was dissolved in 20 ml of ethanol. To this, a solution of 3.7 g (0.01 mol) of copper(II) perchlorate hexahydrate in 25 ml of ethanol was added with stirring. The resulting mixture was deep green in colour. Freshly distilled amine was added dropwise with constant stirring to this deep green solution. Initially, a green precipitate was formed. This dissolved with further addition of amine. About 2.5–2.8 mol of amine was required. The mixture was then heated to reflux for 0.5 hr and filtered hot. The filtrate was evaporated to 20 ml in volume and kept at 0 °C for 5 hr. The crystals separated were filtered, recrystallised from ethanol and then dried over phosphorus pentoxide. The yield was 50%.

### Synthesis of $[Cu_3OH(inkAr)_3](ClO_4)_2$

3.7 g (0.01 mol) of copper(II) perchlorate hexahydrate was dissolved in 20 ml of 95% ethanol and to it an ethanolic solution of 0.01 mol of isonitrosoketone was added. The resulting green solution was heated to reflux on a water bath and then 1.25 mol of freshly distilled amine was added dropwise with stirring. After the addition was complete, the mixture was boiled for a few minutes and then cooled to room temperature. Large shining crystals separated. These were filtered, washed with ethanol and then dried over phosphorus pentoxide in vacuum. The yield was 70%.

The complexes can also be synthesised from preformed Schiff base: 3.7 g (0.01 mol) of copper(II) perchlorate hexahydrate was dissolved in 20 ml of 95% ethanol and to it an ethanolic solution of 0.01 mol of the preformed Schiff base was added. The

resulting dark green solution was heated to reflux on a water bath for a few minutes and then cooled. The deposited crystals were collected by filtration and washed with ethanol. These were then dried over phosphorus pentoxide. The yield was 60%.

### Synthesis of $[Cu_3(inkpnR_2)_3](ClO_4)_3 \cdot 3qH_2O$ ( $q = 3$ , $R = C_2H_5$ ; $q = 2$ , $R = n-C_4H_9$ )

1 g (0.01 mol) of biacetylmonoxime was dissolved in 10 ml of absolute ethanol and to it 0.01 mol of freshly distilled amine was added with stirring. The mixture was then heated to reflux for 5 min on a water bath and then a solution of 3.7 g (0.01 mol) of copper(II) perchlorate hexahydrate in 10 ml of absolute ethanol was added to it with vigorous stirring. The resulting deep green solution was heated to reflux for a further 10 min and was then kept overnight in a refrigerator. The black shining crystals were collected by filtration, washed with absolute ethanol and then dried in vacuum over phosphorus pentoxide. The yield was 30%.

### Analysis

Copper was estimated gravimetrically by precipitating as CuSCN. Perchlorate was also estimated gravimetrically with nitron reagent. The analytical data for all complexes described here are set out in Table I.

### Physical Measurements

Electronic spectra were taken on a Cary-14 recording spectrophotometer. The solution electrical conductivity was measured at room temperature using a Systronic (India) conductivity bridge in nitromethane which has twice been distilled over phosphorus pentoxide. The concentrations of the experimental solutions were in the range  $0.92\text{--}1.02 \times 10^{-3} M$ . The infrared spectra were recorded on a Perkin-Elmer 521 recording spectrophotometer with the sample in KBr disc as well as in nujol mull. The bulk magnetic susceptibilities were measured using a highly sensitive Gouy balance described elsewhere [10]. The measurements at lower temperatures were carried out by surrounding the Gouy tube with a Dewar system containing a suitable coolant (liquid nitrogen for 80 K and ice water for 273 K). Dry N<sub>2</sub> gas was passed around the Gouy tube to prevent the condensation of moisture. For measurements above room temperature, the Dewar system is replaced by a jacket with an asbestos heating coil wound over it non-inductively. This is fed with a controlled current. After an initial heating period of about half an hour, a fairly steady temperature ( $\pm 0.2$  K) was attained, in spite of the simplicity of the arrangement. In all measurements, the actual temperature of the sample was measured accurately from a chromel–alumel (at higher temperature) or copper–constantan (at lower temperature) thermocouple junction placed very close to the Gouy tube.

TABLE I. Characterisation Data of the Trinuclear Complexes.

Serial No.	Complex Type	Ligand System <sup>a</sup>	% C		% H		% N		% Cu		% ClO <sub>4</sub>	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	[Cu <sub>3</sub> O(inkR) <sub>3</sub> ]ClO <sub>4</sub>	IVa	31.44	31.50	4.84	4.47	12.22	12.50	27.72	27.54	14.46	14.35
2	[Cu <sub>3</sub> O(inkR) <sub>3</sub> ]ClO <sub>4</sub>	IVb	34.57	34.60	5.39	5.42	11.52	11.39	26.12	26.30	13.63	13.42
3	[Cu <sub>3</sub> O(inkR) <sub>3</sub> ]ClO <sub>4</sub>	IVc	37.35	37.57	5.88	5.70	10.89	10.50	24.70	24.57	12.89	12.89
4	[Cu <sub>3</sub> OH(inkAr) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	IVd	38.65	38.47	3.68	3.67	9.02	9.15	20.45	19.98	21.34	20.97
5	[Cu <sub>3</sub> OH(inkAr) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	IVe	40.68	40.72	4.14	4.08	8.63	8.59	19.57	19.62	20.42	20.27
6	[Cu <sub>3</sub> OH(inkAr) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	IVf	40.68	40.78	4.14	4.25	8.63	8.48	19.57	19.48	20.42	20.46
7	[Cu <sub>3</sub> OH(inkAr) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	IVg	40.68	40.82	4.14	4.19	8.63	8.68	19.57	19.69	20.42	20.38
8	[Cu <sub>3</sub> (inkpnR <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	VIIa	30.77	30.92	6.57	6.48	9.79	9.72	14.80	14.78	23.16	23.01
9	[Cu <sub>3</sub> (inkpnR <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	VIIb	38.54	38.38	7.33	7.15	8.99	8.83	13.59	13.62	21.27	21.14

<sup>a</sup> For the ligand code numbers, see text.

### Molecular Orbital Computation

Slater orbitals [11] are used for oxygen while Richardson's double  $\zeta$  wave functions [12] are used for the  $3d_{x^2-y^2}$  orbitals on copper atoms. The overlap integrals in the local coordinate systems were evaluated by the usual methods [13] *i.e.* the computation of diatomic overlaps followed by their transformations. The  $H_{ii}$  for copper  $3d_{x^2-y^2}$  orbitals were computed [14] from the relationship  $H_{ii} = (Aq^2 + Bq + C) \text{ cm}^{-1}$  where  $A = 32,917$ ,  $B = 45,422$ ,  $C = 86,003$  and  $q$  is the charge on copper taken as +0.8 unit. The  $H_{ij}$  of the oxygen orbitals were taken as the orbital ionisation energies [13]. The off-diagonal elements  $H_{ij}$  were obtained [14] by using the Mulliken formula  $H_{ij} = 0.5kS_{ij}(H_{ii} + H_{jj})$  with  $k = 1.75$ . The secular equation was then solved to obtain the eigenfunctions and eigenvalues of the  $\text{Cu}_3\text{O}^{4+}$  core.

### Results and Discussion

#### Ligands and Complexes

The HinkAr ligands could be isolated in the crystalline state by reacting the isonitrosoketones with aromatic amines. The HinkR ligands are liquids or low melting solids and no attempts were made to isolate them in pure state. The majority of trinuclear complexes of interest in this paper could be obtained by *in situ* reactions in which prior isolation of the ligand is not obligatory. It is noted that under different experimental conditions HinkAr yields [15] mononuclear and binuclear copper(II) complexes in addition to the trinuclear species described below.

The reaction of copper(II) perchlorate with isonitrosoketone and  $\text{ArNH}_2$  in hot ethanolic medium readily yields black crystals of composition  $[\text{Cu}_3\text{OH}(\text{inkAr})_3](\text{ClO}_4)_2$ . The same species is also obtained by the reaction between stoichiometric quantities of copper(II) perchlorate and HinkAr in hot ethanol. When  $\text{ArNH}_2$  is replaced by  $\text{RNH}_2$  in the synthesis described earlier black crystals are again obtained but these have the composition  $[\text{Cu}_3\text{O}(\text{inkR})_3]\text{ClO}_4$ . In spite of various attempts it has not been possible to link the  $\text{Cu}_3\text{O}$  unit with inkAr and the  $\text{Cu}_3\text{OH}$  unit with inkR. All complexes described here form dark shining needles which appear dark green in powdered form. They have limited solubility in polar solvents (water, alcohols, acetone, nitromethane). Green solutions thus obtained are stable as such but decompose in presence of dilute acids or alkalis.

The molar electrical conductivities of these complexes in nitromethane solution are set out in Table II. The ideal ranges prescribed for 1:1 and 1:2 electrolytes in nitromethane [16] are 80–90 and 150–180  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively. Thus in nitromethane, the  $[\text{Cu}_3\text{O}(\text{inkR})_3]\text{ClO}_4$  and  $[\text{Cu}_3\text{OH}(\text{inkAr})_3](\text{ClO}_4)_2$  complexes show the expected 1:1 and 1:2 electrolytic behaviour.

TABLE II Solution Electrical Conductivity and Electronic Spectral Data of the Trinuclear Complexes

Serial No <sup>a</sup>	Molar Electrical Conductivity <sup>b</sup>	Medium	Electronic Spectral Data <sup>c</sup> $\lambda_{\max}$ ( $\epsilon$ )
1	84	Nujol	650, 415, 390 <sup>d</sup>
		Methanol	640(190), 410 <sup>d</sup> (770), 350(2250)
2	87	Methanol	656(170), 408 <sup>d</sup> (780), 348(2210)
3	79	Methanol	652(220), 412 <sup>d</sup> (750), 350(2350)
4	166	Nujol	618, 410, 345 <sup>d</sup>
		Methanol	620(230), 410 <sup>d</sup> (770), 340(2290)
5	158	Methanol	625(190), 410 <sup>d</sup> (740), 340(2200)
6	156	Methanol	620(210), 410 <sup>d</sup> (770), 340(2250)
7	169	Methanol	620(220), 410 <sup>d</sup> (750), 340(2170)
8	238	Nujol	640, 410, 330
		Methanol	620(450), 425(1680), 315(2290)
9	225	Methanol	618(480), 425(1820), 315(2480)

<sup>a</sup>The serial numbers are the same as in Table I <sup>b</sup>In  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , Solvent Nitromethane, Concentration  $\sim 10^{-3} M$ , Room temperature <sup>c</sup> Band maximum in nm,  $\epsilon$  in  $\text{litre mol}^{-1} \text{cm}^{-1}$  (per g atom of copper) <sup>d</sup>Shoulder

TABLE III Selected Infrared Spectral Data <sup>a</sup> of the Trinuclear Complexes

Serial No *	$\nu_{\text{O-H}}$	$\nu_{\alpha\text{-dumine}}$	$\nu_{\text{N-O}}$	$\text{ClO}_4$ vibrations
1	—	1620, 1520	1205	1130(b), 1100(b), 940(w), 635, 630
2	—	1620, 1520	1200	1130(b), 1110(b), 940(w), 635, 630
3	—	1620, 1520	1200	1140(b), 1100(b), 940(w), 635, 630
4	3400(b)	1620, 1520	1190	1135(b), 1100(b), 940(w), 635, 630
5	3440(b)	1620, 1520	1200	1135(b), 1110(b), 935(w), 635, 630
6	3420(b)	1620, 1520	1200	1130(b), 1100(b), 935(w), 635, 630
7	3440(b)	1620, 1520	1195	1125(b), 1105(b), 935(w), 635, 630
8	3500(b)	1630, 1520	1210	1130(b), 1100(b), 935(w), 635, 630
9	3500(b)	1630, 1525	1215	1130(b), 1100(b), 930(w), 635, 630

<sup>a</sup>The spectra were run both in KBr phase as well as in nujol mull, the peak positions are in  $\text{cm}^{-1}$  All bands are sharp and medium to strong in intensity unless otherwise stated, b - broad, w - weak

\*Serial numbers are the same as in Table I

The electronic spectral data are summarised in Table II. A characteristic feature both in the solid state (nujol mull) as well as in methanolic solution is a broad ligand field band near 650 nm. In general the band for  $[\text{Cu}_3\text{O}(\text{inkR})_3]\text{ClO}_4$  is at lower energy than that of  $[\text{Cu}_3\text{OH}(\text{inkAr})_3](\text{ClO}_4)_2$ .

Selected vibration frequencies are collected in Table III. The  $\text{Cu}_3\text{OH}$  systems show a broad  $\nu_{\text{O-H}}$  absorption near  $3400 \text{ cm}^{-1}$ . This band is absent in  $\text{Cu}_3\text{O}$  systems. A pair of sharp bands of medium intensity at  $1620 \text{ cm}^{-1}$  and  $1520 \text{ cm}^{-1}$  appear uniformly in all the complexes. These were assigned to stretching modes of the  $\alpha$ -dumine fragment. The  $\text{ClO}_4^-$  ion gives rise to a broad feature at  $1100 \text{ cm}^{-1}$  ( $\nu_3$ ) which has two overlapping components. The forbidden  $\nu_1$  (in  $T_d$  symmetry) band appears as a weak absorption at  $\sim 930 \text{ cm}^{-1}$ . The  $\nu_4$  band around  $630 \text{ cm}^{-1}$  is slightly split ( $\sim 5 \text{ cm}^{-1}$ ) into a doublet.

These data indicate that the  $\text{ClO}_4$  group is weakly bound [17] in a mono or tridentate fashion ( $C_{3v}$  symmetry).

#### Magnetic Data and Structure

Magnetic susceptibilities were measured in the temperature interval 80–370 K (Table IV). Measurements could not be conducted at higher temperatures because of the explosive nature of these compounds. The susceptibility values uniformly follow Curie law with  $\mu_{\text{eff}} \sim 1.80 \text{ BM}$  per mol ( $\sim 1.00 \text{ BM}$  per copper) over the range of temperature studied. Thus there is only one unpaired electron ( $S = 1/2$ ) per  $\text{Cu}_3$  unit. There is thus a strong antiferromagnetic interaction among the three copper(II) ions. Assuming that the three atoms are equivalent (*vide infra*) the  $S = 1/2$  ground state is lower than the  $S = 3/2$  state by  $|3J|$  where  $2J$  is the pair exchange integral [4].

TABLE IV. Variable Temperature Magnetic Susceptibility Data<sup>a</sup> of the Trinuclear Complexes.

Serial No. <sup>b</sup>	Temperature (K)	$\chi_M \times 10^6$ (c.g.s.)	$\mu_{\text{eff}}$ per mol (BM)	$\mu_{\text{eff}}$ per copper (BM)
1	80	4527	1.70	0.98
	273	1484	1.80	1.04
	296	1430	1.84	1.06
	320	1323	1.84	1.06
	347	1206	1.83	1.06
	369	1147	1.84	1.06
2	80	4731	1.74	1.00
	273	1517	1.82	1.05
	296	1445	1.85	1.07
	319	1356	1.86	1.07
	347	1246	1.86	1.07
	370	1156	1.85	1.07
3	80	4569	1.71	0.99
	273	1500	1.81	1.05
	296	1430	1.84	1.06
	319	1327	1.84	1.06
	347	1220	1.84	1.06
	370	1144	1.84	1.06
4	80	4569	1.71	0.99
	273	1434	1.77	1.02
	300.5	1274	1.75	1.01
	358	1106	1.78	1.03
	383	1034	1.78	1.03
	5	80	4254	1.65
273		1292	1.68	0.97
300.5		1274	1.75	1.01
358		1094	1.77	1.02
383		1034	1.78	1.03
6		80	4410	1.68
	273	1323	1.70	0.98
	300.5	1274	1.75	1.01
	358	1069	1.75	1.01
	383	1022	1.77	1.02
	7	80	4785	1.75
273		1434	1.77	1.02
300.5		1216	1.71	0.99
358		1094	1.77	1.02
383		1034	1.78	1.03
8		80	4623	1.72
	273	1402	1.75	1.01
	291	1346	1.77	1.02
	307	1276	1.77	1.02
	337	1175	1.78	1.03
	368	1162	1.77	1.02
	383	1057	1.80	1.04
	9	80	4785	1.75
273		1451	1.78	1.03
291		1361	1.78	1.03

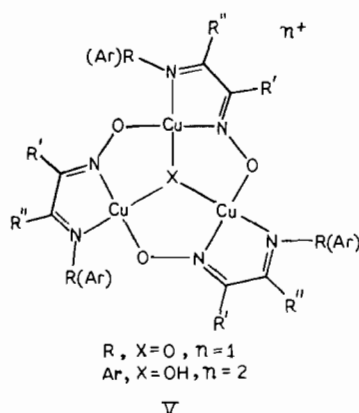
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TABLE IV. (Continued)

307	1276	1.77	1.02
337	1162	1.77	1.02
368	1076	1.78	1.03
383	1057	1.80	1.04

<sup>a</sup> $\chi_M$  is the molar magnetic susceptibility of the complexes corrected for the diamagnetism of the ligand (computed from Pascal's constants) and T.I.P. of  $\text{Cu}^{2+}$  ( $60 \times 10^{-6}$  c.g.s. unit per g. atom of copper).  $\mu_{\text{eff}}$  per mol is the effective magnetic moment of the trimeric unit calculated from Curie law.  $\mu_{\text{eff}}$  per copper is the effective magnetic moment per copper. <sup>b</sup>Serial numbers are the same as in Table I.

The magnetic properties of the present system are strikingly analogous [4, 6] to the trinuclear species  $[\text{Cu}_3\text{OH}(\text{pao})_3]\text{SO}_4 \cdot 10.5\text{H}_2\text{O}$  and  $\text{Cu}_3(\text{prao})_3(\text{H}_2\text{O})_3 \cdot \text{OH}_{0.5}(\text{ClO}_4)_{1.5}$  which also have magnetic moments of  $\sim 1.00$  BM per copper. It is very logical to suggest that the present systems also belong to the structural type (III). A more specific description is shown in (V). In view of the infrared data, it is likely that the per-

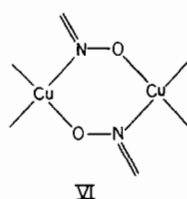


chlorate ion is tridentate and completes the gross square pyramidal geometry around each copper. This happens if the  $C_3$  axis of bound  $\text{ClO}_4$  is coincident with the  $C_3$  axis of the  $\text{Cu}_3$  unit. The anions in the trinuclear complexes of Hpao and Hprao play a very similar role [5, 7]. In  $\text{Cu}_3(\text{prao})_3(\text{H}_2\text{O})_3\text{OH}_{0.5}(\text{ClO}_4)_{1.5} \cdot 4\text{H}_2\text{O}$ , half the molecules have  $\text{Cu}_3\text{OH}$  core, the remaining half having  $\text{Cu}_3\text{O}$  core. The  $[\text{Cu}_3\text{O}(\text{inkR})_3]\text{ClO}_4$  species are the first example of trinuclear complex having solely the  $\text{Cu}_3\text{O}$  core.

#### Superexchange Pathway

The observed copper-copper distances in the two accurately known structures [5, 7] are too large ( $>3.2$  Å) for any appreciable direct metal-metal interaction. The strong antiferromagnetism observed in these trimers therefore arises from superexchange through bridging ligands. The weakly bonded perchlorato group is unlikely [18] to make large contributions to such exchange. The central oxygen atom and the peripheral planar oximato groups are then the potential exchange pathways.

The oximato group is known to give rise to strong antiferromagnetism ( $-2J = 700\text{--}900\text{ cm}^{-1}$ ) in several [15, 19, 20] copper(II) dimers containing the planar bridge system (VI). The orbital pathway of this superexchange interaction has been investigated [21] by the SCCC-EHT method. The major results are briefly stated here. The  $d_{x^2-y^2}$  orbitals on the two copper(II) atoms and appropriate ligand orbitals combine to



form antibonding  $B_u$  and  $A_g$  (idealised  $C_{2h}$  symmetry) levels in which the interactions within the N-O frame are bonding and antibonding respectively (Fig. 1). The exchange pathway is mainly provided by the  $2p_x$  and  $2p_y$  orbitals of the nitrogen and oxygen atoms of the bridging N-O fragments. The  $B_u$  orbital is more stable than the  $A_g$  orbital ( $\Delta E = 2030\text{ cm}^{-1}$ ).

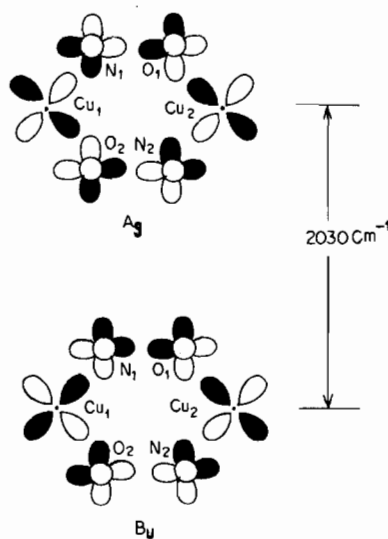


Fig. 1. The combinations of  $3d_{x^2-y^2}$  (Cu) and bridge orbitals in VI.

The electronic configuration of the singlet and triplet states are  $B_{2g}^1 A_g^0$  and  $B_{1g}^1 A_g^1$  respectively. The magnetic exchange parameter  $2J$  is approximately proportional to  $(\Delta E)^2$  [14]. If the proportionality constant is assumed to be of similar magnitude as that of copper(II) acetate monohydrate [14],  $-2J$  for (VI) is computed to be  $\sim 1000 \text{ cm}^{-1}$  which is not far from the observed value.

Although in the trinuclear complexes, the two N-O bridges attached to a given copper ion are connected to two different copper ions, the qualitative effect of the bridge towards magnetic exchange is likely to be similar to that in (VI). Interestingly, it can be readily computed from the appropriate population formulae [22] that the limiting value of  $|J|$  required to depopulate the  $S = 3/2$  state, to the extent that its presence will not be reflected in the magnetic susceptibility observed at 400 K, is  $\sim 350 \text{ cm}^{-1}$ . In fact  $|J|$  values of this order are usually observed with planar oximato bridged dimers. The superexchange through the oximato bridges alone can possibly give rise to the observed magnetic properties of these complexes.

To explore the possibility of any magnetic interaction through the central oxygen atom, an EHT calculation was done on the  $\text{Cu}_3\text{O}^{4+}$  part of the trinuclear moiety. The effect of the remaining part of

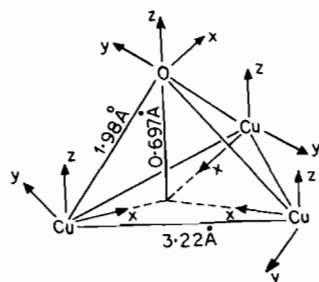


Fig. 2. The molecular parameters and local coordinates of  $\text{Cu}_3\text{O}^{4+}$  unit.

the molecule was considered in an indirect manner. The degeneracy of the d orbitals of the individual copper(II) ions was taken as lifted due to the crystal field of the imino-oxime, central oxygen and bound anion (if any). The charge on the individual copper(II) ion was taken as +0.8 unit. Very similar charges on copper were obtained from M.O. calculation [23] for several copper(II) complexes. In the coordinate system chosen (Fig. 2) the  $3d_{x^2-y^2}$  orbitals on each copper(II) will be the energetically highest 3d orbital, and it was assumed that the highest occupied and the lowest unoccupied orbitals of the trinuclear moiety will be predominantly made up of these  $3d_{x^2-y^2}$  orbitals. With this in mind, only the  $3d_{x^2-y^2}$  orbitals on each copper were included in the basis set. Other orbitals in the basis set are the 2s and the 2p orbitals on central oxygen atom. The molecular parameters for the  $\text{Cu}_3\text{O}^{4+}$  unit were taken to be those [5] of  $[\text{Cu}_3\text{OH}(\text{pao})_3]\text{SO}_4 \cdot 10.5\text{H}_2\text{O}$ . In  $C_{3v}$  symmetry, the  $3d_{x^2-y^2}$  orbitals span the representations  $A_1$  and E. The 2s and  $2p_z$  orbitals on central oxygen atom span  $A_1$  representation while the  $2p_x$  and  $2p_y$  orbitals span the E representation. The energies and atomic orbital coefficients of the resulting molecular orbitals are shown in Table V.

The following observations can be made from Table V. The two degenerate  $S = 1/2$  ground states arise from the  $E_{(2)}^3$  configuration and the excited  $S = 3/2$  state arises from the  $E_{(2)}^2 A_{1(3)}^1$  configuration. The energy separation between the  $E_{(2)}$  and  $A_{1(3)}$  molecular orbitals is sufficiently large as to give rise to a considerable antiferromagnetism. This separation is due to the fact that the  $A_1$  group orbital on copper interacts strongly with the  $sp_z$  hybrid orbital (directed towards the  $\text{Cu}_3$  plane) on the oxygen while the E group orbital on copper interacts only weakly with the  $p_x$  and  $p_y$  oxygen orbitals which are parallel.

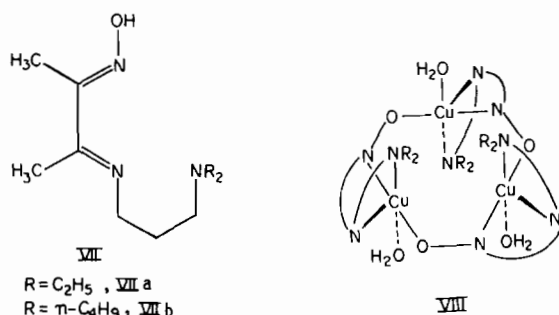
Earlier, in a qualitative discussion [4] the observed antiferromagnetism in  $[\text{Cu}_3\text{OH}(\text{pao})_3]\text{SO}_4 \cdot 10.5\text{H}_2\text{O}$  was attributed solely to the central hydroxo bridge. The possible role of oximato bridge was not recognised at that time. The present computation indeed shows that considerable interaction can occur

TABLE V. Molecular Orbitals and Their Energies.

Atomic Orbitals	Molecular Orbitals						
	$A_1(1)$	$E(1)$	$E(1)$	$A_1(2)$	$E(2)$	$E(2)$	$A_1(3)$
O2s	0.935	0	0	0.200	0	0	-0.307
O2p <sub>x</sub>	0	0.850	0	0	0	-0.531	0
O2p <sub>y</sub>	0	0	0.850	0	-0.531	0	0
O2p <sub>z</sub>	-0.053	0	0	0.897	0	0	0.443
Cu <sub>1</sub> ( $3d_{x^2-y^2}$ )	0.155	-0.193	0.335	-0.205	0.626	-0.361	0.519
Cu <sub>2</sub> ( $3d_{x^2-y^2}$ )	0.155	-0.193	-0.335	-0.205	-0.626	-0.361	0.519
Cu <sub>3</sub> ( $3d_{x^2-y^2}$ )	0.155	0.387	0	-0.205	0	0.722	0.519
Energy ( $\text{cm}^{-1}$ )	-150207	-131219	-131219	-130253	-116767	-116767	-114379

through the central oxygen atom. Nevertheless, we believe that while the oxo or hydroxo bridge does play a role, the oximate bridge is likely to be of much importance in bringing about the strong antiferromagnetic interaction in  $\text{Cu}_3\text{O}(\text{H})$  systems.

In this connection the following observations are significant. Reaction of the ligand system (VII, abbreviated as  $\text{HinkpnR}_2$ ) prepared *in situ* with copper(II) perchlorate hexahydrate in ethanolic solution yields complexes of empirical composition  $\text{Cu}(\text{inkpnR}_2)\text{ClO}_4\text{XH}_2\text{O}$  which have been characterised



with the help of analytical, spectral and solution conductivity data (Table I, II and III). The complexes uniformly show a magnetic moment of 1 BM per copper over the temperature range 80–380 K (Table IV). We strongly suspect that these species are trinuclear, a probable structure for the cation being (VIII) in which each copper(II) ion is tetragonal pyramidal – the flexibility of the  $-(\text{CH}_2)_3$ - chain in (VII) permitting this stereochemistry. Interestingly, when this chain is substituted by  $-(\text{CH}_2)_2$ -chain, only binuclear species are obtained [20]. In (VIII) there is no central oxygen atom to bridge the copper(II) atoms which are interconnected solely through oximate bridges. The exchange interaction even in this situation is sufficiently strong to populate only the ground  $S = 1/2$  states thereby suggesting the predominant role of oximate bridges in bringing about the strong antiferromagnetism in (V).

## Conclusion

The present study establishes that trinuclear complexes with  $\text{Cu}_3\text{O}$  or  $\text{Cu}_3\text{OH}$  core are of general occurrence for iminoxime ligands of type (IV) and thus increases the scope for structural type (III). It has also been observed that the isoelectronic aryl-azooxime ligand  $\text{R}-\text{C}(=\text{NOH})-\text{N}=\text{N}-\text{Ar}$  behaves similarly [24]. The fascinating electron transfer properties of these trinuclear systems will be published shortly [25].

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