

Dinuclear copper (II) and nickel (II) systems with planar $M_2N_2O_3$ bridge

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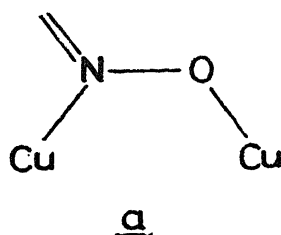
Abstract. The tridentate ligand system *b* (abbreviated as inkR_2) readily yield copper (II) and nickel (II) species of the formula $M_2(\text{inkR}_2)_2(\text{ClO}_4)_x \cdot 2x\text{H}_2\text{O}$ ($x = 0-1$). Dinuclear formulation is based on variable temperature magnetic susceptibility and conductivity data and on the known structure of some related systems. The $\text{Cu}_2(\text{inkR}_2)_4^{2+}$ species are strongly antiferromagnetic ($-2J = 600-800 \text{ cm}^{-1}$) while the $\text{Ni}_2(\text{inkR}_2)_4^{2+}$ species are diamagnetic. The major coordination sphere is planar around each metal (II). The metal ions in a dimer are linked by planar $M_2N_2O_3$ bridge. The copper (II) and nickel (II) species freely form solid solutions. In these statistical scrambling of copper and nickel occur among the metal ion sites of the dimeric structure. Powder epr spectra of such mixed crystals are indicative of axial geometry around copper (II) ion.

Keywords. Dinuclear copper (II) complexes; dinuclear nickel (II) complexes; magnetic properties.

I. Introduction

Many dinuclear systems in which two copper (II) atoms are linked by two monoatomic (oxygen, halogen, etc.) bridges are known (Kato *et al* 1964; Hodgson 1975; Crawford *et al* 1976; Andrew *et al* 1976; Sinn 1976; Bertand and Eller 1976; Estes and Hodgson 1976; Phelps *et al* 1976; Lintvedt *et al* 1976). The vast majority of these are antiferromagnetic. In general the strength and nature of the magnetic exchange interaction depends on the bridge angle, on the stereochemistry around copper (II) atoms and on the relative orientation of the copper (II) coordination spheres (the above refs; Hay *et al* 1975). Next to monoatomic bridges, the triatomic bridges are also widely investigated (Doedens 1976, Haris *et al* 1959). The diatomic bridge system is much less common. The $-\text{C}\equiv\text{N}-$ bridge is an example (Jungst and Stucky 1974; Anderson *et al* 1976). Our interest lies in the possible use of the oximato group as a diatomic bridge as in *a*. A very limited number of species having the structural feature *a* are known at present (Uhlig and Schneider 1964; Vaciano and Zambonelli 1970; Hatfield 1972; Singh and Sahoo 1974; Bertrand *et al* 1974; Ablov *et al* 1972; Frazer *et al* 1972; Beckett and Hoskins (1972);

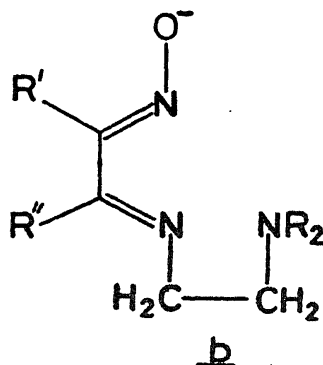
Beckett *et al* 1969; Chakravorty 1974; Mohanty *et al* 1974). We report in this work new systems containing *a* in which the antiferromagnetic interaction is strong.



2. Results and Discussion

2.1. Syntheses

The ligand system concerning us here is *b*. The general abbreviation for *b* is inkR_2 . The ligand *b* was not isolated as such, but it resulted in the *in situ* reaction involving



copper (II) perchlorate hexahydrate, isonitrosoketone and ethylenediamine or its *N,N*-disubstituted derivatives. The dark shining crystals of the complexes have the composition $\text{Cu}(\text{inkR}_2)\text{ClO}_4 \cdot x\text{H}_2\text{O}$ ($x = 1$, usually). These can be dehydrated by careful heating. The nickel (II) analogue $\text{Ni}(\text{inkR}_2)\text{ClO}_4$, obtained by a similar procedure is red to brown in colour and is anhydrous. The various compounds studied in this work are set out in table 1. In the succeeding discussion each compound will be identified by its code number as shown in table 1.

Table 1. $\text{M}_2(\text{inkR}_2)_2(\text{ClO}_4)_2 \cdot 2x\text{H}_2\text{O}$ systems and their electrical conductivities^{a,b,c} in nitromethane solution

Number	M	R	R'	R''	x	Λ ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
I	Cu	H	CH ₃	CH ₃	1	168
II	Cu	CH ₃	CH ₃	CH ₃	1	161
III	Cu	C ₂ H ₅	CH ₃	CH ₃	$\frac{1}{2}$	166
IV	Cu	C ₂ H ₅	H	CH ₃	1	154
V	Cu	C ₂ H ₅	C ₂ H ₅	CH ₃	1	178
VI	Cu	C ₂ H ₅	CH ₃	C ₂ H ₅	1	152
VII	Ni	C ₂ H ₅	CH ₃	CH ₃	0	166
VIII	Ni	C ₂ H ₅	C ₂ H ₅	CH ₃	0	171

- a. Λ is the molar conductivity in nitromethane solution calculated using dimer formula weight.
 b. Concentrations of the solutions are in the range $0.85\text{--}1.30 \times 10^{-3}$ mol per litre.
 c. Temperature range 20–25°C.

2.2. Binuclear formulation

The copper complexes reported here have subnormal magnetic moments showing that they are not mononuclear. Assuming a dimeric formulation, the electrical conductivity data in nitromethane solution (table 1) exhibit the expected 2:1 electrolytic behaviour ($\text{Cu}_2(\text{inkR}_2)_2^{+2}; 2\text{ClO}_4^-$). The conductivity of 2 : 1 electrolytes is known (Geary 1971) to lie in the range $150\text{--}180 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. This is an indication that the complexes are binuclear i.e., $\text{Cu}_2(\text{inkR}_2)_2(\text{ClO}_4)_2$ (water molecules not shown). The nickel (II) species are diamagnetic. Their conductivity data (table 1) taken in conjunction with the fact that they freely form mixed crystals (*vide infra*) with the corresponding copper (II) species support the dimeric formulation $\text{Ni}_2(\text{inkR}_2)_2(\text{ClO}_4)_2$.

2.3. Antiferromagnetic behaviour

The magnetic data for the copper(II) species are set out in table 2. The moments increase with increasing temperature and are independent of the external magnetic field. The Van Vleck equation for exchange coupled dimers ($S_1=S_2=1/2$) can be stated in the form, (Herring *et al* 1971).

$$-\frac{2J}{kT} = \ln(F-3) \quad (1)$$

where
$$F = \frac{Ng^2\beta^2}{kT} \chi^{-1} \quad (2)$$

Table 2. Magnetic data for the various $\text{Cu}_2(\text{inkR}_2)_2(\text{ClO}_4)_2 \cdot 2x\text{H}_2\text{O}$ systems

Compounds	Experimental data ^a	$-2J(\text{cm}^{-1})$
I	(304, 263, 0.80).	603
II	(273, 78, 0.41); (293, 94, 0.47); (328, 133, 0.59); (354, 153, 0.66); (373, 169, 0.71); (390, 178, 0.75).	815
III	(273, 216, 0.69); (302, 252, 0.78); (322, 266, 0.83); (340, 287, 0.88); (367, 316, 0.96).	614
III (anhydrous)	(273, 182, 0.63); (305, 206, 0.71); (326, 233, 0.78); (350, 258, 0.85); (369, 274, 0.90); (388, 297, 0.96).	653
IV	(296, 238, 0.75); (348, 295, 0.89).	617
V	(290, 118, 0.52); (301, 124, 0.55); (320, 160, 0.64); (348, 173, 0.69); (370, 193, 0.76).	765
VI	(301, 186, 0.76); (348, 176, 0.7) ^b .	682

a. The data are set out in the order ($T, \chi, \mu_{\text{eff}}$) where T is the absolute temperature, χ is the susceptibility in c.g.s. unit ($\times 10^6$) per g. atom of copper corrected for diamagnetism and T.I.P. (60×10^{-6} c.g.s. unit per g. atom of copper), μ_{eff} is the effective magnetic moment in Bohr Magneton calculated from Curie law.

b. Slight decomposition occurred at this temperature.

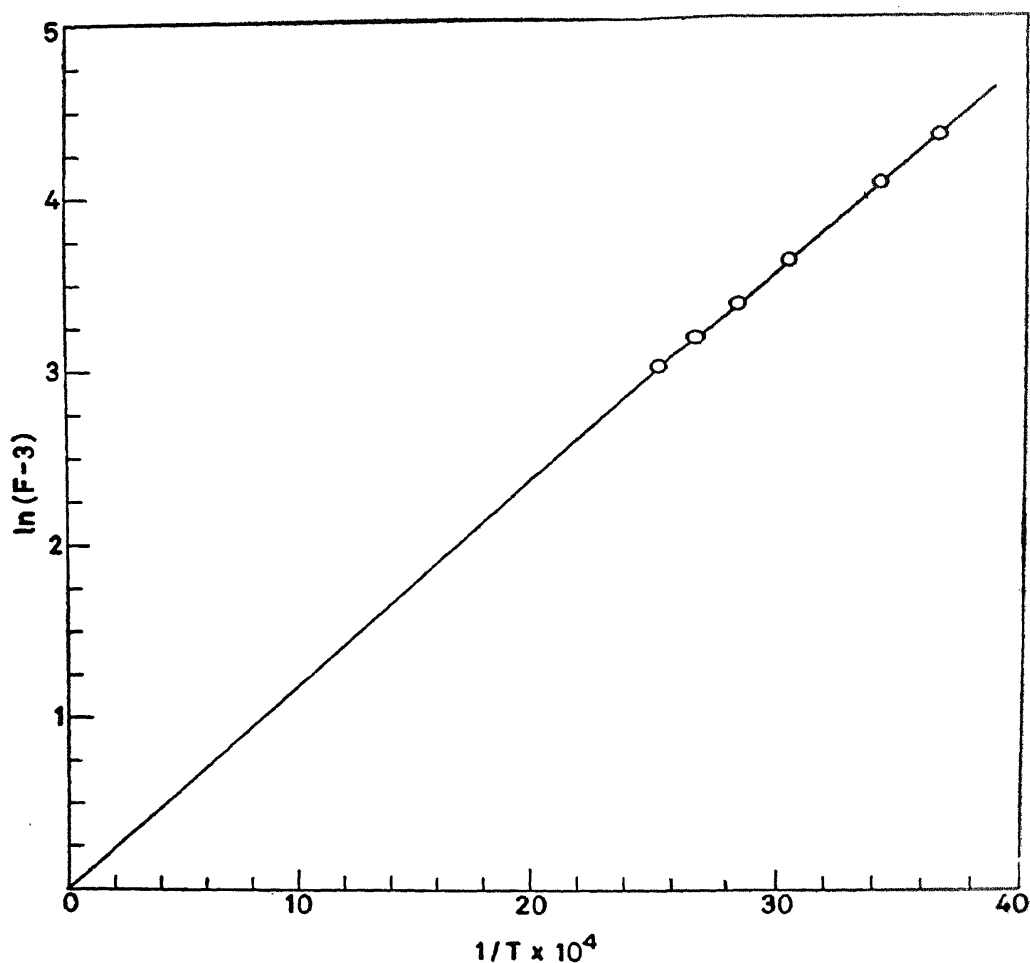


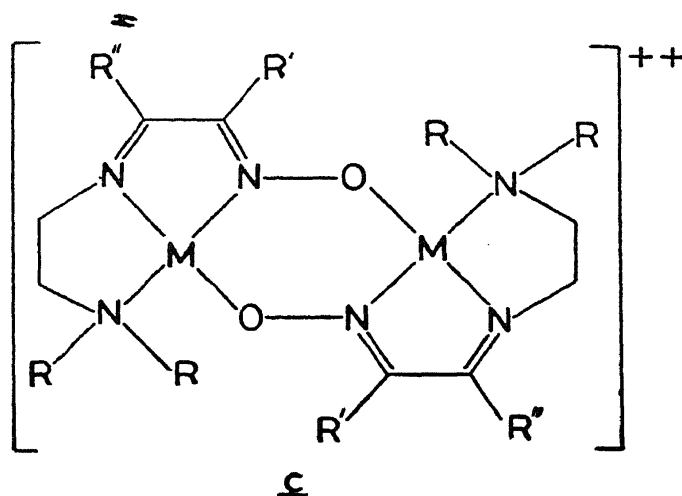
Figure 1. Fit of variable temperature magnetic data of complex II to dimer model.

In (1), $2J$ is the singlet-triplet separation. In (2), N is the Avogadro number, g is the g -factor, β is the Bohr Magneton, χ is the corrected susceptibility per g . atom of copper, k is the Boltzmann constant and T is the absolute temperature. According to (1) the plot of $\ln(F-3)$ against T^{-1} should be linear with a slope of $-2J/k$ and a zero intercept. The results of table 2 uniformly display this behaviour. One case is illustrated in figure 1. Values of $2J$, as obtained from the slope of the least square fit are included in table 2. The g -factor was taken as 2.09 (*vide infra*, epr data). Admittedly, the temperature range used by us is rather narrow. The systems tend to decompose (sometimes explosively) at higher temperatures. This precluded the observation of Néel point. Cooling to low temperature was not attempted since the susceptibilities become small leading to large experimental errors. In spite of these limitations, the data available at hand clearly demonstrate that dimeric species are involved. On the basis of the observed $2J$ values, the $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ system can be described as strongly antiferromagnetic.

2.4. Structural considerations

The $\text{Ni}_2(\text{inkR}_2)_2^{2+}$ species are diamagnetic. This means that the geometry of each nickel (II) is grossly planar. The alternative possibility, *viz.*, a very strongly exchange

coupled dimer with high spin nickel (II) is excluded on the basis of epr data (section 2.5). Since copper (II) can be grown freely in the nickel (II) lattice and *vice versa*, it is evident that each copper (II) has primarily a planar environment in $\text{Cu}_2(\text{inkR}_2)_2^{2+}$. In planar copper (II), the unpaired electron is invariably located on the coordination plane in the d_{xy} or $d_{x^2-y^2}$ orbital (depending on axes system). When the two copper (II) coordination planes are coplanar, a strong superexchange *via* bridging ligands is a common phenomenon (Hodgson 1975; Bertrand and Eller 1976; Lintvedt *et al* 1976; Hay *et al* 1975). Taking all factors into consideration we propose that the major* coordination in $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ occur as in *c*:



Accurate structural data from diffraction work are available (Bertrand *et al* 1974) on a dinuclear copper (II) species $\text{Cu}_2\text{L}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2$ in which the ligand *L* is closely related to *b* (NR_2 group is replaced by OH group; $\text{R}' = \text{R}'' = \text{CH}_3$). The observed structure is akin to *c* (NR_2 replaced by OH), in which all the coordinating atoms are strongly bound and are very nearly coplanar. In particular the six membered $\text{Cu}_2\text{N}_2\text{O}_2$ bridge is planar to within 0.03 \AA . There are weak axial coordination from perchlorate and water oxygen atoms. The magnetic susceptibility (50×10^{-6}) of this complex is lower than those of $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ species (table 2) showing that the antiferromagnetic coupling is stronger in the former complex. This may mean that the bridge is somewhat longer and/or slightly distorted from planarity. Distortion of the bridge from planarity** will also mean a distortion of each individual copper (II) coordination sphere from planarity. In planar or nearly planar *c* the exchange is expected to be strongly antiferromagnetic since the two symmetry adapted combinations of the metal spin bearing orbitals combine with

* Weak axial coordination by ClO_4^- and/or H_2O is not excluded; in fact this is likely to be present. However noting that compound III and its anhydrous analogue have very similar magnetic behaviours (table 2), one may conclude that, the binding of H_2O , if present, is not very significant magnetically.

** Dimeric copper (II) complexes with oxime ligands are known in which the $\text{Cu}_2\text{N}_2\text{O}_2$ bridge deviates severely from planarity leading to a chair (Vaciago and Zombonelli 1970) or a boat (Frazer *et al* 1972) configuration. In such complexes copper (II) is pentacoordinated (sp or tbp) and each N—O bridge connects an axial position of one copper (II) with an equatorial position of the other copper (II). In such out of plane dimers the exchange coupling is usually small due to near orthogonality of the spin bearing orbitals on the two halves.

energetically very different orbitals (constructed from $2s$ and $2p$ orbitals of nitrogen and oxygen atoms) of the N—O bridge, (Bertrand *et al* 1974; Baral and Chakravorty—unpublished).

It is also proposed that structure *c* applies for the nickel (II) species $\text{Ni}_2(\text{inkR}_2)_2^{2+}$. Tridentate amine-oxime ligands yield diamagnetic dinuclear nickel (II) complexes in which the existence of planar $\text{Ni}_2\text{N}_2\text{O}_2$ bridge and planar four coordinate stereochemistry for each nickel (II) have been proven by diffraction work. (Schlamper and Murmann 1974). In fact the coordination sphere (*i.e.*, two MN_3O units interconnected at oxygen atoms) in such complexes is essentially the same as in *c*.

2.5. Scrambling of Cu (II) and Ni (II) sites

The $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ and $\text{Ni}_2(\text{inkR}_2)_2^{2+}$ species freely form solid solutions. In such mixed crystals, scrambling of the copper (II) and nickel (II) among the metal sites of structure *c* occurs. The magnetic susceptibility of one system (V+VIII) has been studied at two different compositions (table 3). Assuming that there is a statistical distribution of copper (II) and nickel (II) among the metal ion sites of *c*, the mole-fractions of the Cu_2 , Ni_2 and CuNi dimers are f_{Cu}^2 , f_{Ni}^2 and $2f_{\text{Cu}}f_{\text{Ni}}$ respectively, where f_M is the mole fraction of the formula unit of the complex of *M* in the mixed crystal. The expected corrected susceptibility (χ_{mc}) per g. atom of copper (II) can then be written as

$$\chi_{mc} = n\left(\frac{1}{2} f_{\text{Cu}}^2 \chi_{\text{Cu}_2} + f_{\text{Cu}}f_{\text{Ni}} \chi_{\text{CuNi}}\right) \quad (3)$$

where n is the total number of g. atoms of copper (II) and nickel (II) for every g. atom of copper (II) in the mixed crystal, χ_{Cu_2} and χ_{CuNi} are respectively the corrected susceptibilities of the Cu_2 and CuNi dimers. The value of χ_{Cu_2} is taken from table 2 and of χ_{CuNi} is calculated using a g -factor obtained from epr spectra (see below). Results shown in table 3 demonstrate that the distribution is indeed statistical.

Pure $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ species give powder epr spectra (Baral and Chakravorty—unpublished) which are characteristic (Wasserman *et al* 1964) of the triplet state. Spectrum intensity decreases on cooling as expected. Dilute mixed crystals of $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ (0.5% of $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ + 95.5% of $\text{Ni}_2(\text{inkR}_2)_2^{2+}$) give rise to a powder epr spectrum characteristic of axially symmetric $S=1/2$ spectrum. In such dilute

Table 3. Magnetic susceptibility of the mixed crystal system (V+VIII) at 293°K

Weight percentage of copper	Mol ratio Cu:Ni	Contribution towards Calculated susceptibility ^a from		Total calculated susceptibility ^a	Observed susceptibility ^a
		Cu_2 dimer	CuNi dimer		
10.42%	1:0.586	122	540	662	679
8.37%	1:0.989	97	727	824	831

a. Susceptibility values are in c.g.s. unit $\times 10^6$.

crystals virtually all copper is present as CuNi dimer. The spectrum originates from these CuNi dimers. In X-band, the spectrum is complicated by the presence of an extra absorption (Kivelson and Neiman 1961; Gersman and Swalen 1961) in the perpendicular region. In the K band, the complication disappears. Computer simulations (Rollmann and Chan 1969) of the observed spectra were done (Baral and Chakravorty—unpublished). The best fit give the following spin hamiltonian parameters: III+VII, $g_{\parallel}=2.177$, $g_{\perp}=2.040$, $a_{\parallel}=195$ Gauss, $a_{\perp}=15$ Gauss; V+VIII, $g_{\parallel}=2.193$, $g_{\perp}=2.045$, $a_{\parallel}=195.5$ Gauss, $a_{\perp}=14$ Gauss. A parallel hyperfine coupling constant of 195 Gauss is strongly indicative (Kokoszka and Gordon 1965) of diamagnetic nickel (II) in CuNi dimers.

3. Experimental

3.1. Preparation of compounds

Isonitrosoketones were prepared following the procedures reported elsewhere (Semon and Damerell 1948; Hartung and Crossby 1948) $\text{Cu}_2(\text{inkR}_2)_2(\text{ClO}_4)_2 \cdot 2x\text{H}_2\text{O}$ species were prepared by the following general procedure. 0.01 mol of isonitrosoketone was dissolved in 20 ml of ethanol and to it 0.01 mol of ethylenediamine or its N, N-dialkyl derivative was added. This mixtures was boiled on a water bath for a few minutes. This was then added to an ethanolic solution of 0.01 mol (3.75g) of copper perchlorate hexahydrate with vigorous stirring. The mixture was allowed to stand for a few hours. Dark coloured crystals separated. These were recrystallised from ethanol and were dried in air (yield 60%). The anhydrous species was obtained by heating the hydrated complex at 120°C in vacuum oven phosphorous pentoxide for about 8 hrs. $\text{Ni}_2(\text{inkR}_2)_2(\text{ClO}_4)_2$ species were prepared from nickel perchlorate hexahydrate, following the same general procedure as above (yield 70%). All $\text{Cu}_2(\text{inkR}_2)_2(\text{ClO}_4)_2 \cdot 2x\text{H}_2\text{O}$ and $\text{Ni}_2(\text{inkR}_2)_2(\text{ClO}_4)_2$ systems gave satisfactory elements and/or group analysis (C, H, N, ClO_4^- , metal). Mixed crystals were prepared by crystallising $\text{Cu}_2(\text{inkR}_2)_2^{2+}$ and $\text{Ni}_2(\text{inkR}_2)_2^{2+}$ species together from ethanol and drying in air.

3.2. Physical measurements

Magnetic susceptibilities were determined using a sensitive Gouy balance described elsewhere (Kannan and Chakravorty 1970). Solution electrical conductivities of samples were determined with the help of a Systronics (India) conductivity meter of type 302. Epr spectra were recorded using a Varian V4502 epr spectrometer.

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