

## Crystal Structure and Magnetic Properties of Di- $\mu$ -[2-(*N*-(2-hydroxyethyl)-2-aminoethyl)imino-3-butanone oximato]dicopper(II) Perchlorate

MATTI NÄSÄKKÄLÄ, HEIKKI SAARINEN, JORMA KORVENRANTA and ELINA NÄSÄKKÄLÄ

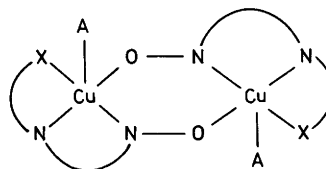
Department of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

The crystal structure of the title compound,  $[\text{Cu}_2(\text{C}_8\text{H}_{16}\text{N}_3\text{O}_2)_2](\text{ClO}_4)_2$ , has been determined from X-ray diffraction data and refined to an  $R$  value of 0.050 for 1681 observed reflections. The compound crystallizes in the monoclinic space group  $P2_1/c$  with two dimeric units in a cell of dimensions  $a=7.678(2)$ ,  $b=10.647(5)$ ,  $c=16.568(10)$  Å, and  $\beta=91.28(4)^\circ$ . The structure consists of binuclear complex cations and perchlorate anions. The coordination about copper is square pyramidal in which the tetradentate ligand is bound to copper through its oxime, imine and amine nitrogen atoms at the base of the pyramid, and through the alcohol oxygen atom occupying the axial position. The basal plane is completed by the oxime oxygen of the second ligand of the dimer. The central six-membered ring in the structure formed by two copper atoms and two oxime NO bridges is non-planar and adopts a chair conformation. The magnetic susceptibility of a powdered sample of the complex has been studied in the temperature range 93–303 K and the complex found to exhibit a relatively large antiferromagnetic coupling,  $-2J=545(8)\text{ cm}^{-1}$ .

A pair of oxime N–O bridges between two copper(II) atoms is found to be responsible for magnetic-exchange interactions of very variable nature. The coupling, which may be weakly ferromagnetic, weakly antiferromagnetic, or strongly antiferromagnetic, seems to be related to the type of bonding in the central six-membered  $(\text{CuNO})_2$  ring in the structure. Thus weak ferro- or antiferromagnetic interactions result from the out-of-plane bridging between the copper atoms,<sup>1–3</sup> and strong antiferromagnetic coupling occurs if the complexes

contain only basal donor atoms in the  $(\text{CuNO})_2$  ring.<sup>1,4–7</sup>

X-Ray analyses of the latter type of compounds<sup>1,4–7</sup> have all dealt with complexes of different tridentate ligands, and in each case a distorted square pyramidal coordination about copper atoms with the following schematic structure has been established (the axial groups may be *cis* or *trans* relative to the central plane):



In these structures there are naturally some differences in the conformation of the basal planes and consequently in the strength of the magnetic interaction. However, the reported values of the room-temperature magnetic moment, which vary from *ca.* 0.4 (the compound shows only temperature independent paramagnetism) to 0.67 BM, are all indicative of very marked antiferromagnetic coupling. The ligand chosen for the present study contains one more donor atom than do the ligands of the previously studied compounds. Although a dimeric structure comparable to the above scheme was expected, our preliminary measurements showed the magnetic moment of the complex to be considerably higher [ $\mu_{\text{eff}}(293\text{ K})=1.07\text{ BM}$ ] than in the previous compounds. It seemed worthwhile therefore to find out if the additional geometrical constraint in the ligand brings about any distinct

conformational differences to account for the altered magnetic behaviour.

## EXPERIMENTAL

**Crystal preparation.** The complex was prepared by the *in situ* reaction of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1 mol equiv.) with 2,3-diacetylmonoxime (1 mol equiv.) and *N*-(2-hydroxyethyl)ethylenediamine (1 mol equiv.) in boiling methanol. The black crystals submitted for analysis were obtained by recrystallization from water.

**Magnetic measurements.** Magnetic susceptibilities were measured with a Newport Variable-Temperature Gouy Balance from liquid nitrogen temperature to room temperature, the apparatus being calibrated with copper(II) sulfate pentahydrate. Diamagnetic corrections were made to all data.<sup>8</sup> Fitting the Bleaney-Bowers equation<sup>9</sup> to the magnetic susceptibilities gave  $g = 2.25(4)$ ,  $-2J = 545(8) \text{ cm}^{-1}$  and  $N\alpha = 98(4) \times 10^{-6} \text{ cgsu/Cu(II) atom}$ . The temperature dependence of the paramagnetic susceptibilities is shown in Fig. 1. The effective magnetic moment at 293 K calculated from the equation  $\mu_{\text{eff}} = 2.828 \times \sqrt{\chi_M \times T}$  is 1.07 BM.

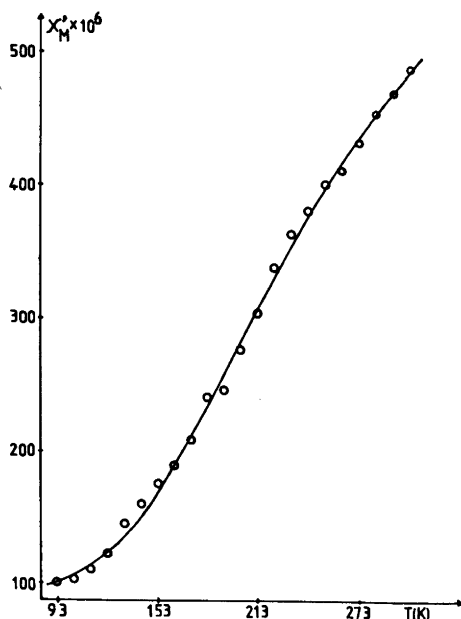


Fig. 1. Experimental temperature dependence of the molar magnetic susceptibility for the complex. The solid curve represents susceptibilities calculated from the Bleaney-Bowers equation with  $g = 2.25$ ,  $-2J = 545 \text{ cm}^{-1}$  and  $N\alpha = 98 \times 10^{-6}$  (cgs units).

**Crystal and intensity data.** Weissenberg photographs showed the crystals to be monoclinic and the space group from systematic absences, was identified as  $P2_1/c$ . A crystal with approximate dimensions  $0.3 \times 0.25 \times 0.25 \text{ mm}$  was used for the data collection. The cell dimensions were obtained by a least-squares fit to the automatically centred settings for 14 reflections on a Syntex  $P2_1$  diffractometer equipped with a graphite monochromator. The crystal data for  $[\text{Cu}_2(\text{C}_8\text{H}_{16}\text{N}_3\text{O}_2)_2](\text{ClO}_4)_2$  are:  $a = 7.678(2)$ ,  $b = 10.647(5)$ ,  $c = 16.568(10) \text{ \AA}$ ,  $\beta = 91.28(4)^\circ$ ,  $Z = 2$ , space group  $P2_1/c$ ,  $D_x = 1.713 \text{ g cm}^{-3}$ ,  $D_m = 1.72 \text{ g cm}^{-3}$  (by flotation),  $V = 1354.0 \text{ \AA}^3$ ,  $\mu = 18.4 \text{ cm}^{-1} (\text{MoK}\alpha)$ ,  $\lambda(\text{MoK}\alpha) = 0.7107 \text{ \AA}$ .

X-Ray intensities were measured by the  $\omega$ -scan technique ( $3^\circ < 2\theta < 57^\circ$ ) with  $\text{MoK}\alpha$  radiation. The scan rate varied from  $2.20$  to  $20^\circ \text{ min}^{-1}$ , depending on the intensity of the reflection. The intensity of the test reflection remeasured after every 60 reflections showed no significant change during the data collection. The intensities were corrected for Lorentz and polarization effects, but no correction for absorption was made. Of the 3691 recorded reflections 1685 with  $F_o > 6\sigma(F_o)$  were used in the calculations.

**Determination and refinement of the structure.** The structure was solved by direct methods with the MULTAN program.<sup>10</sup> The copper, oxime oxygen, three nitrogen atoms and three of the carbon atoms were located in the initial  $E$  map, and subsequent Fourier syntheses gave the positions of the other non-hydrogen atoms. The refinement was carried out by block-diagonal least-squares calculations (X-RAY SYSTEM)<sup>11</sup> with the non-hydrogen atoms refined anisotropically. All hydrogen atoms were located on a difference Fourier map. The refinement was then continued with the fixed temperature factor  $U = 0.09 \text{ \AA}^2$  for the hydrogen atoms. The atomic scattering factors were those used by the programme.<sup>11</sup> Anomalous dispersion corrections ( $\Delta f'$ ,  $\Delta f''$ ) were included for Cu and Cl.<sup>12</sup> The weighting scheme used in the calculations was  $w = 1/(25.0 + |F_o| + 0.02|F_o|^2)$ . The final  $R$  value was 0.050 for the 1685 observed reflections.

The atomic coordinates for the non-hydrogen and hydrogen atoms are given in Tables 1 and 2, respectively. A list of the observed and calculated structure factors as well as the temperature factors is obtainable from the authors.

**The perchlorate group.** The perchlorate group is disordered and the difference Fourier map showed two separate positions for the perchlorate oxygen O3 atom. In the refinement of the structure neither one of the alternative sites led alone to a satisfactory result and it proved necessary to share the perchlorate oxygen O3 between these two positions (O31 and O32), each with an occupancy of 0.5. The perchlorate group is thus strongly irregular and the

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for the non-hydrogen atoms.

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu	1739(1)	-776(1)	571(1)	N2	2439(7)	-655(6)	1702(3)
Cl	3142(2)	2888(2)	1216(1)	N3	3963(7)	-1824(6)	511(3)
O1	-1661(5)	625(5)	575(3)	C1	-193(8)	396(6)	1757(3)
O2	530(7)	-2819(6)	495(3)	C2	1433(9)	-89(7)	2163(4)
O31	1568(26)	3363(23)	997(19)	C3	4140(9)	-1170(8)	1944(4)
O32	2529(17)	2457(20)	484(8)	C4	5143(9)	-1355(8)	1158(5)
O4	4215(14)	3928(9)	1149(5)	C5	-1564(11)	1072(8)	2206(5)
O5	2318(24)	2753(15)	1903(8)	C6	1714(11)	124(10)	3036(4)
O6	4062(26)	1882(12)	1155(15)	C7	3550(11)	-3179(8)	596(5)
N1	-263(7)	200(5)	984(3)	C8	1916(13)	-3490(8)	132(6)

Table 2. Fractional atomic coordinates ( $\times 10^3$ ) and bond distances for the hydrogen atoms.

Atom	X/a	Y/b	Z/c	Bond length
H(O2)	-79(12)	-282(10)	27(6)	1.00(9)
H(N3)	431(12)	-172(9)	-1(6)	0.90(10)
H1(C3)	488(13)	-54(9)	234(6)	1.08(10)
H2(C3)	386(12)	-196(9)	210(6)	0.91(10)
H1(C4)	602(13)	-198(9)	128(6)	0.96(10)
H2(C4)	573(12)	-46(9)	97(6)	1.10(10)
H1(C5)	-221(12)	147(9)	188(6)	0.84(10)
H2(C5)	-246(12)	47(9)	257(6)	1.12(10)
H3(C5)	-130(12)	189(9)	237(6)	0.94(10)
H1(C6)	139(13)	92(9)	327(6)	0.97(10)
H2(C6)	56(12)	-1(10)	338(6)	1.08(9)
H3(C6)	265(12)	-5(10)	337(6)	0.92(9)
H1(C7)	447(12)	-368(9)	42(6)	0.94(10)
H2(C7)	347(12)	-340(9)	118(6)	1.00(9)
H1(C8)	195(12)	-315(9)	-49(6)	1.09(10)
H2(C8)	180(12)	-437(9)	14(6)	0.94(10)

O—Cl—O bond angles ( $80-140^\circ$ ) deviate considerably from the tetrahedral values. Evidently the description of the perchlorate ion is not very successful but we considered this point not to be of great importance for the study, and no other modes of refinement were tried.

## RESULTS AND DISCUSSION

The structure consists of binuclear centrosymmetric copper(II) complex cations and discrete perchlorate anions. A stereoscopic view of the unit cell contents is shown in Fig. 2, the complex ion with the bond lengths is illustrated in Fig. 3 and the bond angles are given in Table 3. The crystal structure is apparently stabilized by a weak hydrogen bond between the perchlorate oxygen O3

and the alcohol oxygen O2 atoms. Since it was just this O3 perchlorate oxygen that was refined with two positions, there are also two possible schemes for the hydrogen bonding:  $O2 \cdots O31(-x, -y, -z) = 2.85(1) \text{ \AA}$ ,  $O2-H \cdots O31 = 156(8)^\circ$  or  $O2 \cdots O32(-x, -y, -z) = 2.97(3) \text{ \AA}$ ,  $O2-H \cdots O32 = 126(7)^\circ$ .

As displayed in Figs. 2 and 3, the copper atom has a distorted square pyramidal coordination. The tetradentate ligand is bound to copper to form five-membered chelate rings through its oxime, imine and amine nitrogen atoms at the base of the pyramid, and through its alcohol oxygen atom occupying the axial position. The basal plane is completed by the oxime oxygen atom of the ligand from the other half of the dimer, resulting in a central six-membered ring with two oxime N—O bridges between the copper atoms. Excluding the

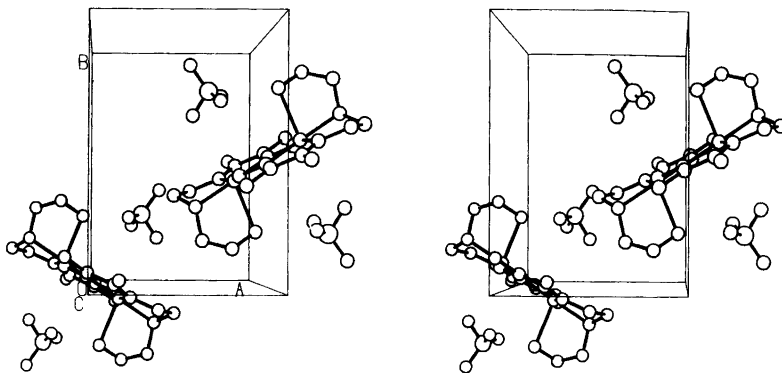


Fig. 2. A stereoscopic view of the unit cell contents.

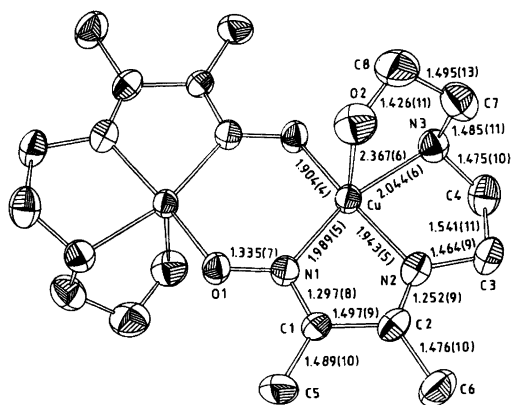


Fig. 3. A perspective view of the dimeric complex ion showing bond lengths (Å).

presence of the hydroxyethyl link, the basic structure of the complex is fully consistent with the coordination scheme of the tridentate ligands referred to above. This is not unexpected given the  $sp^2$ -hybridization of the oxime and imine nitrogen atoms, and the limited length of the aminoethyl

chain emanating from the imine nitrogen, which constrains the tetradentate ligand to dispose of all of its three nitrogens essentially in the same plane. With this arrangement of nitrogen atoms the axial position for the coordinated alcohol oxygen is less constrained than the basal one.

The varied strength of the magnetic interaction of the compounds with only in-plane bridging between the copper atoms has previously been related to differences in the planarity of the six-membered  $(\text{CuNO})_2$  ring.<sup>5</sup> This relation does indeed emerge from a consideration of the known structures of the series (Table 4); in the two complexes reported to be diamagnetic (ultimate limit of antiferromagnetism) the  $(\text{CuNO})_2$  ring has been very nearly planar, whereas in the other three compounds exhibiting somewhat less strong antiferromagnetic coupling (room-temperature magnetic moments between 0.6 and 0.67 BM), the  $(\text{CuNO})_2$  ring has been noticeably less planar in nature.

Arguing in the same manner, the relatively high magnetic moment  $\mu_{\text{eff}}(293 \text{ K}) = 1.07 \text{ BM}$  ( $-2J = 545(8) \text{ cm}^{-1}$ ) of the present complex should indicate a markedly nonplanar  $(\text{CuNO})_2$  ring. Owing to the

Table 3. Bond angles ( $^\circ$ ) in the complex ion.

N1—Cu—N2	80.4(2)	O1'—Cu—O2	91.2(2)	C7—C8—O2	107.3(7)
N1—Cu—N3	162.7(2)	C2—C1—N1	113.8(5)	C1—N1—O1	117.5(5)
N1—Cu—O2	101.1(2)	C2—C1—C5	122.3(6)	C1—N1—Cu	114.1(4)
N2—Cu—N3	82.5(2)	C1—C2—N2	114.3(5)	C2—N2—Cu	117.3(5)
N2—Cu—O1'	163.3(2)	C1—C2—C6	119.3(6)	C4—N3—Cu	106.3(4)
N2—Cu—O2	102.3(2)	C4—C3—N2	106.0(6)	C7—N3—Cu	110.2(5)
N3—Cu—O1'	90.3(2)	C3—C4—N3	110.3(6)	C8—O2—Cu	100.8(5)
N3—Cu—O2	79.8(2)	C8—C7—N3	110.2(7)	C3—N2—Cu	117.7(4)

centre of inversion in the middle of the  $(\text{CuNO})_2$  ring the four oxime atoms in the structure are coplanar, but the copper atoms deviate 0.245 Å from this plane giving a chair conformation to the six-membered ring and a dihedral angle of 12.2° between the  $\text{N1O1N1'O1'}$  and  $\text{CuN1O1'}$  planes (the primed quantities indicate atoms related by the symmetry). This conformation differs from that of the other in-plane nonplanar cases, where only boat conformations for the  $(\text{CuNO})_2$  ring have been found. This conformational difference is, however, slight since in all these structures the deviations from planarity are in fact relatively small. It cannot, therefore, be of primary importance for the magnitude of the magnetic interaction. Generally it is very difficult to compare the "goodness" of planarity of different planes with each other. In a situation like this when differences are only minor and especially when there may or may not be symmetry imposing on this ring, any strict comparison in this respect is impossible. Thus there is no precise parameter which would describe the planarity of the  $(\text{CuNO})_2$  ring in these compounds, and thereby also the strength of their antiferromagnetic coupling.

The dimensions of structures like the title compound are collected in Table 4. The corresponding bond lengths and bond angles are found to be nearly constant with only one exception: the  $\text{O}-\text{Cu}-\text{N}$  angle of 95.0° for di- $\mu$ -{2-[2-( $\alpha$ -pyridyl)ethyl]imino-3-butanone oximate}dicopper(II)<sup>1</sup> is significantly smaller than this angle in the other structures (103.2–108.7°). The difference evidently follows from the fact that the complex in question contains six-membered chelate rings opposite to the  $(\text{CuNO})_2$  ring in contrast to the five-membered chelate rings in the other complexes. These do not, however, bring about any apparent changes in the magnetic properties of the compound. In general the data in Table 4 do not exhibit any obvious trend that could be related to the magnitude of the magnetic coupling.

It is possible that the structural differences affecting magnetic properties of these complexes are better revealed if the environment of the copper atom is considered in its entirety. In this connection the influence of the apical group on the geometry of the pyramid base is of importance. The length of the apical  $\text{Cu}-\text{O}$  bond in the present structure is 2.367(6) Å, and the axial-copper-basal angles vary from 79.8(2) to 102.3(2)°, with the smallest angle occurring in the five-membered chelate ring. This results in a basal plane which is only approximate,

Table 4. Comparison of geometries of the planar and in-plane nonplanar  $(\text{CuNO})_2$  cores in different complexes.

Complex species	Bond angles (°)			Bond lengths (Å)			Magnetic moment		Ref.
	Cu-N-O	O-Cu-O	Cu-O-N	Cu-N	Cu-O	N-O	$\mu_{\text{eff}}$ (~295 K)	diamagn.	
$[\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_2]^a$	129.4(3)	108.3(3)	121.9(3)	1.987(5)	1.870(4)	1.325(6)		diamagn.	4
$[\text{Cu}_2\text{L}_2(\text{ClO}_2)]^{b,*}$	127.7(3)	108.2(1)	127.7(1)	1.983(2)	1.887(2)	1.311(3)		diamagn.	5
$[\text{Cu}_2\text{L}_2(\text{CH}_3\text{OH})_2]^{b,*}$	129.5(2)	105.0(1)	124.1(1)	2.008(2)	1.886(2)	1.327(3)			5
$[\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_2]^c$	127.7(3)	108.7(1)	120.7(3)	2.023(4)	1.876(4)	1.326(5)	0.6		6
	127.9(3)	107.9(1)	121.2(3)	2.029(4)	1.875(3)	1.338(5)			6
$[\text{Cu}_2\text{L}_2(\text{CH}_3\text{CN})_2]^d$	128.4(2)	95.0(1)	120.3(2)	2.014(3)	1.928(2)	1.329(4)	0.66		1
$[\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_2]^e$	127.5(10)	104.6(5)	123.8(8)	2.046(13)	1.882(11)	1.315(18)	0.67		7
	128.5(9)	103.2(5)	123.9(9)	2.040(11)	1.890(12)	1.323(16)			7
$[\text{Cu}_2\text{L}_2]^f$	128.4(4)	106.9(2)	122.8(4)	1.989(5)	1.904(4)	1.335(7)	1.07		This work

Ligand acids. <sup>a</sup> 2-(2-Hydroxyethyl)imino-3-butanone oxime. <sup>b</sup> 1-(*N,N*-Dimethyl-2-aminoethyl)-1-phenyl-2-propanone oxime. <sup>c</sup> 2,6-Diacetylpyridine dioxime. <sup>d</sup> 2-[2-( $\alpha$ -pyridyl)ethyl]imino-3-butanone oxime. <sup>e</sup> 2-(*N,N*-Dimethyl-2-aminoethyl)imino-3-butanone oxime. <sup>f</sup> 2-(*N*-(2-Hydroxyethyl)-2-aminoethyl)imino-3-butanone oxime. The species marked with an asterisk are present in the same structure.

the maximum deviation being 0.148 Å for the amine nitrogen atom; the displacement of the copper atom from the mean plane toward the apical group is 0.123 Å. Compared with the other structures of the series (Table 4) this deviation from planarity is large. It is found that in complexes with the strongest antiferromagnetic coupling the four basal donor atoms are very closely coplanar and in the other structures, too, the deviation is considerably less than in the present compound. This suggests that the magnitude of the magnetic coupling is also influenced by the deviation from coplanarity of the basal ligand atoms, and that it is possibly more sensitive to such changes than to changes in planarity occurring in the six-membered  $(\text{CuNO})_2$  ring.

The distortions in the pyramid base evidently arise from the geometry of the ligand as well as from the nature of the apical group; the large deviation from planarity in the present structure undoubtedly originates in the steric requirements of the hydroxyethyl link of the tetradentate ligand. It is clear that the coordination geometry at the copper atom and the conformation of the  $(\text{CuNO})_2$  ring are closely related to each other. In both cases the dependence of the magnitude of the magnetic exchange interaction on the "goodness" of planarity can be understood to follow from the variations in the degree of overlap between copper and ligand orbitals. For the present the available data are too limited to allow an examination of the relationship between these structural features and the parameter that dominates the magnetic exchange.

The copper-copper separations in the complexes in Table 4 are all very near to the value of 3.6 Å. This large separation indicates that any direct metal-metal exchange must be insignificant in comparison with the superexchange through the bridging oxime atoms. The mechanism of the magnetic coupling in these dimers is still uncertain and possibly dependent on the structural type. Thus a simple  $\sigma$ -bonded pathway has usually been proposed for the in-plane nonplanar complexes, whereas the additional stabilization of the antiferromagnetic coupling in the planar cases has been explained by  $\pi$ -overlap throughout the exchange pathway.<sup>3-5</sup> Participation of a  $\pi$ -system in the bonding geometry can, however, be questioned since in the magnitude of the antiferromagnetic coupling of the complexes there is no sharp boundary between the "planar" and in-plane nonplanar cases. From this study it is apparent that suitable

choice of ligand and axial group can give a series of complexes which in spite of very slight conformational differences in the  $(\text{CuNO})_2$  ring may exhibit large variations in the strength of the magnetic coupling.

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