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Crystal Structure and Magnetic Properties of $Cu_2(fsa)_2en$, CH_3OH, with $H_4(fsa)_2en$ = N, N'-bis(2-hydroxy, 3-carboxybenzilidene)-1,2-Diaminoethane

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The title compound $Cu_2(fsa)_2en$, CH_3OH was synthesized and its crystal structure solved at room temperature from 3830 independent reflections. It crystallizes in the monoclinic system, space group $P2_1/n$. The lattice constants are a = *11.456(5)* Å, b = *11.425(3)* Å, c = *14.357(4)* Å *and* β = *104.15(3)°* *with Z = 4. Least squares refinement of the structure led to a conventional weighted R factor of 0.043. The structure is made of non-symmetrical binuclear units in which a copper atom is five-fold coordinated to two nitrogens, two phenolic oxygens and an oxygen of the methanol molecule, the other copper atom being coordinated to two phenolic oxygens and two carboxylic oxygens in a plannar manner. The temperature dependence of the magnetic susceptibility, studied in the range 10–312 K, showed a strong antiferromagnetic coupling with a J singlet–triplet separation of -650 cm^{-1}. This magnetic behaviour was compared to those of the other binuclear complexes with the same Cu_2O_2 network and an explanation for such a strong coupling was proposed.*

Introduction

The bichelating ligand $(fsa)_2en^{4-}$ derived from the Schiff base N,N'-bis (2-hydroxy, 3-carboxybenzilidene)-1,2-diaminoethane and, to our knowledge, used for the first time by Okawa *et al.* [1] has already attained a large number of non-symmetrical homobinuclear complexes and heterobinuclear complexes [2–12]. The magnetic behaviour of several of these complexes was studied in detail and, in the case where both transition ions were paramagnetic, the parameters characterizing the exchange interaction were determined [5, 8–10]. In other respects, an orbital model for interpreting these results, based on the concept of semi-localized magnetic orbitals, was proposed [5]. So far, the most important result is probably the strict orthogonality of the magnetic orbitals centred on the one and the other metallic ions, which was realized in $CuVO(fsa)_2en$, CH_3OH [8] and in $CoCu(fsa)_2en$, $3H_2O$ [10]. In the former complex, this orthogonality was evidenced by the X-ray study of the crystal structure. This would show, if it was still necessary, the importance of the structural data to interpret the magnetic properties of a polynuclear complex.

After having obtained $CuVO(fsa)_2en$, CH_3OH, we attempted to synthesize, from the same ligand, the VO(II) Cu(II) complex in which the Cu(II) and VO(II) ions would be reverted regarding to their positions in $CuVO(fsa)_2en$, CH_3OH. Such a synthesis seemed feasible, especially as the mononuclear complex $VO(fsa)_2en$, $2H_2O$ in which the VO(II) ion occupies the N_2O_2 site was easy to prepare. In fact the action of the lithium salt of $VOH_2(fsa)_2en$, $2H_2O$ in methanolic solution does not give the expected VO(II) Cu(II) heterobinuclear complex, but, among other compounds, $Cu_2(fsa)_2en$, CH_3OH in the form of very well formed single crystals, suitable for X-ray study. Of course, the Cu(II) Cu(II) complex can be obtained in a more direct manner by action of $2CuCl_2$, $2H_2O$ on the Schiff base $H_4(fsa)_2en$ [3] or of $CuCl_2$, $2H_2O$ on the lithium salt of $CuH_2(fsa)_2en$, $\frac{1}{2}H_2O$; however, in all our attempts carried out according to the one or the other procedure, the Cu(II) Cu(II) complex formed as a polycrystalline powder, proved unsuitable for a complete structural study.

In this paper, we describe the crystal structure of $Cu_2(fsa)_2en$, CH_3OH and its magnetic behaviour. The very strong intramolecular antiferromagnetic coupling emphasized by this magnetic study is discussed in comparison with the situation encountered in other copper(II) binuclear systems containing the same Cu_2O_2 network.

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TABLE I. Crystallographic and Physical Data for $Cu_2(fsa)_2en, CH_3OH$.

1. *Physical and crystallographic data*

formula: $Cu_2O_7N_2C_{19}H_{18}$
crystal system: Monoclinic
$a = 11.456(5)$ A
$b = 11.425(3)$ A $\beta = 104.15(3)^\circ$
$c = 14.357(4)$ A
$\rho_{exp} = 1.89(2)$ g/cm^3 $\rho_X = 1.87$ g/cm^3
absorption factor: $\mu_{(\lambda)} = 24.36$ cm^{-1}
morphology: (0.28 × 0.26 × 0.22) mm

molecular weight: 513.30
space group: $P2_1/n$
$V = 1822$ A^3
$Z = 4$
$F(000) = 1040$

2. *Data collection*

temperature: 20 °C
radiation: Mo(Kα) $\lambda K\bar{\alpha} = 0.71069$
monochromatisation: Monochromator graphite
crystal-detector distance: 207 mm
detector window: height* = 4 mm width* = $(1.8 + 3.5\ \mathrm{tg}\theta)$mm
take-off angle*: 4.25
scan mode: $\theta/2\theta$
maximum Bragg angle: 30°
scan angle: $(0.85 + 0.35\ \mathrm{tg})^\circ$ for omega angle
values determining the scan speed:
SIGPRE* = 400 SIGMA* = 0.018 VPRE* = -10°/mm TMAX* = 90 s
controls: – intensity – orientation
reflections: $\bar{4}42, \bar{3}05, 600$ $\bar{4}52, 413, \bar{6}00$
periodicity: 3600 s after 100 reflections

3. *Conditions for refinement*

reflections for the refinement of the cell dimensions: 25
recorded reflections: 4541 (249 intensity controls)
independent reflections: 3830
utilized reflections: $2958 > 3\sigma$
refined parameters: 272
reliability factors: $R = \Sigma |k|F_O| - |F_C|| / \Sigma k|F_O| = 0.043$
$R_w = [\Sigma w(k|F_O| - |F_C|)^2 / \Sigma w\, k^2 F_O^2]^{1/2} = 0.052$

Experimental

Synthesis

As noticed in the introduction, well formed single crystals of $CuCu(fsa)_2en, CH_3OH$ were obtained in a quite peculiar way, the bichelating ligand being introduced under the form of the mononuclear complex $VOH_2(fsa)_2en, 2H_2O$. The preparation of $VOH_2(fsa)_2en, 2H_2O$ has been described elsewhere [10]. The lithium salt of this complex was prepared by stirring together 0.5×10^{-3} mol of $VOH_2(fsa)_2en, 2H_2O$ and 10^{-3} mol of $LiOH, H_2O$ in 50 cm^3 of methanol. To this solution was slowly added a solution of 10^{-3} mole of $CuCl_2, 2H_2O$ in 40 cm^3 of methanol. The mixture was then filtered and the resulting green-blue solution kept in a closed flask. Well formed, blue-black single crystals appeared in about a week. *Anal.* Calcd for $C_{19}H_{16}N_2O_7Cu_2$: C, 44.62; H, 3.15; N, 5.48; Cu, 24.85. Found: C, 44.71; H, 3.19, N, 5.39; Cu, 24.54.

Crystal Structure and Refinement

Blue-black crystal of approximate dimensions 0.28 mm × 0.26 mm × 0.22 mm of the title compound was selected and studied using precession camera.

The cell is monoclinic and the space group $P2_1/n$. The crystal attached on a glass fiber was mounted on a CAD 4-Enraf-Nonius automatic diffractometer. Twenty-five reflections have then been accurately centred using $\lambda K\alpha$ molybdenum radiation. Least-squares analysis yielded accurate cell dimensions, the values of which are given in Table I with other crystallographic and physical data. Intensity data were collected following the scheme indicated in Table I. Periodic checks of three standard reflections showed a continuous linear decrease of 7% in intensity and the whole set of data was corrected. The intensity of selected reflections ($I > 2.5\sigma(I)$) were corrected for Lorentz and polarization factors. In spite of the small μR value, 0.32, a spherical absorp-

TABLE II. Atomic Coordinates and Thermal Factors of All Atoms.

Atom	X	Y	Z	B11 or B(A^2)	B22	B33	B12	B13	B23
Cu(1)	0.464888(50)	0.047681(56)	0.264428(42)	44.12(48)	60.86(59)	30.72(33)	−8.99(45)	12.71(30)	−11.89(37)
Cu(2)	0.682123(51)	0.131561(56)	0.403138(42)	45.92(49)	64.43(62)	30.52(34)	−9.75(47)	12.51(31)	−6.68(37)
O(1)	0.51199(26)	0.11832(29)	0.38967(22)	41.3(25)	60.7(32)	31.7(18)	−13.3(24)	13.8(17)	−14.4(20)
O(2)	0.63244(26)	0.06898(29)	0.27491(21)	42.4(27)	60.0(33)	32.0(18)	−2.3(24)	12.1(18)	−12.5(20)
O(3)	0.70513(28)	0.19277(30)	0.52807(22)	50.5(29)	69.1(35)	28.9(19)	−17.9(26)	9.3(19)	−8.9(21)
O(4)	0.84296(28)	0.14384(32)	0.39686(24)	48.2(30)	89.5(41)	38.9(21)	−13.1(28)	14.0(20)	−17.8(24)
O	0.41413(33)	0.21897(38)	0.18517(32)	51.1(36)	111.5(48)	97.8(33)	4.7(34)	16.4(27)	48.5(33)
O(31)	0.66054(31)	0.27365(35)	0.65213(24)	79.6(37)	89.2(42)	37.7(21)	−28.4(32)	18.0(22)	−23.8(24)
O(41)	0.99830(29)	0.14575(34)	0.33278(26)	45.4(30)	102.9(43)	56.8(25)	−14.1(29)	22.7(22)	−18.1(26)
N(5)	0.30633(32)	0.01066(35)	0.27285(27)	39.5(32)	48.3(38)	32.6(23)	−0.8(27)	4.4(21)	−5.6(23)
N(6)	0.44203(33)	−0.05916(36)	0.15917(27)	50.6(34)	51.1(40)	29.7(22)	−2.3(30)	4.5(22)	−2.9(24)
C(11)	0.44577(38)	0.13188(40)	0.45354(31)	46.3(37)	29.2(39)	31.0(25)	5.5(32)	12.9(25)	1.4(26)
C(12)	0.49782(40)	0.18248(41)	0.54337(33)	50.2(39)	39.2(41)	28.2(26)	2.5(33)	11.1(25)	3.7(26)
C(13)	0.42647(44)	0.19931(45)	0.60894(34)	69.2(47)	55.5(51)	31.4(27)	9.3(38)	18.7(29)	−3.3(30)
C(14)	0.30569(45)	0.16716(48)	0.58637(37)	62.2(47)	67.9(53)	38.4(31)	10.3(40)	23.9(31)	−1.7(32)
C(15)	0.25539(40)	0.11601(45)	0.49933(36)	46.3(40)	57.2(50)	40.2(29)	0.9(36)	15.7(28)	4.3(31)
C(16)	0.32283(40)	0.09715(41)	0.43105(32)	43.8(39)	40.6(42)	31.1(26)	5.5(32)	11.2(28)	−0.1(26)
C(21)	0.69961(41)	0.02983(40)	0.21752(32)	54.4(41)	34.6(42)	28.5(25)	6.1(33)	12.3(28)	3.2(25)
C(22)	0.82395(39)	0.05574(43)	0.23843(33)	50.7(39)	41.8(43)	32.1(26)	7.6(34)	14.6(28)	9.1(28)
C(23)	0.88989(45)	0.01909(46)	0.17334(38)	60.4(45)	62.1(52)	46.5(33)	5.2(38)	26.3(31)	2.3(32)
C(24)	0.83778(49)	−0.04594(51)	0.09335(39)	77.8(53)	71.7(54)	46.2(33)	4.9(46)	34.9(35)	−0.2(37)
C(25)	0.71853(49)	−0.07676(46)	0.07566(36)	79.7(52)	64.7(53)	35.1(30)	13.6(42)	23.4(32)	−1.2(31)
C(26)	0.64685(42)	−0.04017(45)	0.13694(33)	60.8(43)	50.9(46)	28.4(25)	10.8(37)	12.1(26)	2.9(29)
C(31)	0.62763(43)	0.21999(42)	0.57657(33)	61.9(44)	39.8(42)	28.2(26)	−7.3(35)	10.5(27)	1.1(27)
C(41)	0.89310(40)	0.12054(45)	0.32762(35)	43.1(38)	50.4(47)	40.5(29)	3.8(35)	13.7(27)	4.4(30)
C(51)	0.26055(41)	0.03841(42)	0.34261(36)	41.0(40)	41.2(41)	43.3(31)	4.6(33)	11.2(28)	3.9(29)
C(52)	0.23879(41)	−0.04784(47)	0.18415(35)	45.1(41)	66.4(50)	37.4(28)	−8.2(38)	2.1(27)	−9.1(32)
C(61)	0.52337(46)	−0.08604(43)	0.11503(34)	69.3(49)	48.6(45)	27.9(27)	3.6(37)	9.1(29)	−8.7(27)
C(62)	0.32722(43)	−0.12202(46)	0.14386(35)	60.6(44)	60.3(50)	35.8(28)	−7.1(39)	8.5(28)	−14.5(31)
C	0.48713(53)	0.28693(56)	0.13981(45)	130.2(68)	137.5(74)	97.3(49)	9.7(58)	26.3(48)	5.8(49)
H(115)	0.171	0.095	0.484	3.0					
H(114)	0.251	0.179	0.632	3.6					
H(113)	0.462	0.233	0.671	3.4					
H(124)	0.889	−0.072	0.052	3.8					
H(125)	0.680	−0.124	0.019	3.1					
H(123)	0.976	0.040	0.188	3.4					
H(151)	0.177	0.018	0.336	2.9					
H(161)	0.501	−0.142	0.063	3.0					
H(182)	0.297	−0.132	0.075	3.5					
H(282)	0.340	−0.196	0.173	3.5					
H(152)	0.178	−0.098	0.198	3.4					
H(252)	0.199	0.009	0.138	3.4					
H(1)O	0.337	0.235	0.170	4.5					
H(2)C	0.528	0.347	0.182	6.0					
H(2)O	0.438	0.327	0.080	6.0					
H(3)C	0.551	0.234	0.121	6.0					

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(B11H^2 + B22K^2 + B33L^2 + 2B12HK + 2B13HL + 2B23KL)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

TABLE III. Selected Bond Lengths and Bond Angles.

Bond Lengths (A)

Cu(1)–O(1)	1.924(3)	Cu(1)–O(2)	1.902(3)
Cu(1)–O	2.266(4)	Cu(1)–N(5)	1.895(4)
Cu(1)–N(6)	1.907(4)	Cu(2)–O(1)	1.919(3)
Cu(2)–O(2)	1.929(3)	Cu(2)–O(3)	1.884(3)
Cu(2)–O(4)	1.873(3)	O(1)–O(2)	2.461(4)
O(1)–O(3)	2.725(4)	O(1)–N(5)	2.818(5)
O(1)–C(11)	1.332(5)	O(2)–O(4)	2.751(5)
O(2)–N(6)	2.806(5)	O(2)–C(21)	1.335(5)
O(3)–O(4)	2.796(5)	N(5)–N(6)	2.630(6)
C(11)–C(12)	1.406(6)	C(12)–C(13)	1.403(6)
C(13)–C(14)	1.396(7)	C(14)–C(15)	1.372(7)
C(15)–C(16)	1.407(7)	C(16)–C(11)	1.417(6)
C(21)–C(22)	1.418(6)	C(22)–C(23)	1.402(7)
C(23)–C(24)	1.376(8)	C(24)–C(25)	1.370(7)
C(25)–C(26)	1.403(7)	C(26)–C(21)	1.413(7)
O(3)–C(31)	1.294(6)	C(12)–C(31)	1.509(7)
C(31)–O(31)	1.220(6)	O(4)–C(41)	1.291(6)
C(22)–C(41)	1.522(7)	C(41)–O(41)	1.219(5)
C(16)–C(51)	1.464(7)	C(26)–C(61)	1.471(7)
C(51)–N(5)	1.280(6)	C(61)–N(6)	1.287(6)
C(5)–C(52)	1.478(6)	N(6)–C(62)	1.465(6)
N(52)–C(62)	1.537(7)	O–C	1.414(7)

Bond Angles (°)

N(5)–Cu(1)–O(2)	170.4(2)
N(5)–Cu(1)–N(6)	87.5(2)
N(5)–Cu(1)–O(1)	95.1(2)
N(5)–Cu(1)–O	95.2(2)
O(2)–Cu(1)–N(6)	94.9(2)
O(2)–Cu(1)–O(1)	80.0(1)
O(2)–Cu(1)–O	93.4(2)
N(6)–Cu(1)–O(1)	163.9(2)
N(6)–Cu(1)–O	100.6(2)
O(1)–Cu(1)–O	94.9(2)
O(4)–Cu(2)–O(3)	96.2(2)
O(4)–Cu(2)–O(1)	171.7(2)
O(4)–Cu(2)–O(2)	92.7(2)
O(3)–Cu(2)–O(1)	91.5(2)
O(3)–Cu(2)–O(2)	171.1(1)
O(1)–Cu(2)–O(2)	79.5(1)
Cu(2)–O(1)–Cu(1)	99.9(1)
Cu(1)–O(2)–Cu(2)	100.3(1)

tion correction was performed (average R = 0.013 mm).

Atomic scattering factors of Cromer and Waber [13] for the non-hydrogen atoms and those of Steward, Davidson and Simpson [14] for the spherical hydrogen atoms were used. Real and imaginary dispersion corrections given by Cromer were used for copper.

The structure was solved using direct methods (MULTAN program) and by successive refinements and Fourier synthesis.

The expected structure of the complex was recognized and also the presence of a methanol molecule in the unit cell. After a few cycles of full matrix least-squares refinement in which the coordinates and isotropic thermal parameters of the non-hydrogen atoms were varied, the R value brought down to 0.12.

Two cycles of full matrix least squares refined the coordinates and anisotropic thermal parameters of the non-hydrogen atoms and R fell to 0.06. A difference Fourier synthesis showed peaks at all expected positions for the hydrogen atoms. After attribution of the isotropic thermal parameter B_{iH} = 1,2 B_{iC} (B_{iC} is the equivalent isotropic temperature factor of the carbon to which the hydrogen is bonded) to the hydrogen atoms the R value dropped to R = 0.043.

A difference Fourier map showed then no peak greater than 0.2 e/Å^3. The final atomic parameters are given in the Table II with their standard deviations calculated by a least-squares refinement program.

A listing of the bond distances and main bond angles is given in Table III.

Magnetic Measurements

The magnetic measurements were carried out on two powder samples in the temperature range 10–312 K with a Faraday type magnetometer, equipped with a continuous flow cryostat designed by Oxford Instruments. The temperature is given by a gold–iron/chromel thermocouple. A magnetic induction of about 12 kG was used. The independence of the susceptibility from the magnetic induction was checked at room temperature; this gives evidence of the absence of ferromagnetic impurities in the sample. Mercuritetrathiocyanatocobaltate(II) was used as a susceptibility standard. The absolute accuracy on temperature is estimated at ±0.1 K and the relative accuracy on the apparent increase of the weight of the sample when the magnetic field is applied is about 1%. The correction for diamagnetism is estimated at -238 cm^3 mol^{-1}, this value being the one of the magnetic susceptibility of the complex NiCd(fsa)$_2$en, 3.5H$_2$O in which both metallic centres are diamagnetic.

Results and Discussion

Crystal Structure

The structure consists of discrete units of the non-symmetrical binuclear complex Cu$_2$(fsa)$_2$en, CH$_3$OH. A perspective view of the whole molecule without the hydrogen atoms is shown in Fig. 1. In Fig. 2, the detailed picture around the two copper atoms is given. The closest packing of two molecular units which occurs around a symmetry centre is shown in

TABLE IV. Mean Planes of Copper Surrounding.

Mean Planes

1	O(1)–O(2)–N(5)–N(6)	−0.14734 x	+0.83397 y	−0.53177 z	+2.35533 = 0
2	O(1)–O(2)–O(3)–O(4)	−0.06350 x	+0.92556 y	−0.37325 z	+1.07890 = 0
3	Cu(1)–O–Cu(2)	−0.73144 x	+0.24014 y	0.63594 z	+0.74164 = 0
4	Cu(1)–O–C	−0.14404 x	−0.50366 y	−0.85181 z	+4.04366 = 0

Angles between Mean Planes (°)

(1)–(2)	191.6
(1)–(3)	91.4
(1)–(4)	86.9
(2)–(3)	98.0
(3)–(4)	124.1

Deviations of the Atoms from Mean Planes (Å)

	1	2	3	4
Cu(1)	0.204	−0.070	0	0
Cu(2)	−0.318	−0.030	0	−2.416
O(1)	−0.061	0.023	1.237	−1.906
O(2)	0.054	−0.018	−1.225	−0.515
O(3)	−0.632	−0.019	1.407	−4.223
O(4)	−0.427	0.015	−1.388	−2.681
O	2.468	2.173	0	0
N(5)	0.062	−0.387	1.318	0.379
N(6)	−0.049	−0.658	−1.309	1.846

The Orientation of the Referential Axis is:

y // b; z // c* and x ⊥ y o z

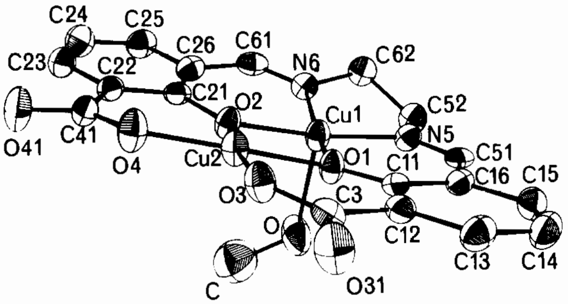


Fig. 1. ORTEP drawing of $Cu_2(fsa)_2en$, CH_3OH, with 50% probability thermal ellipsoids.

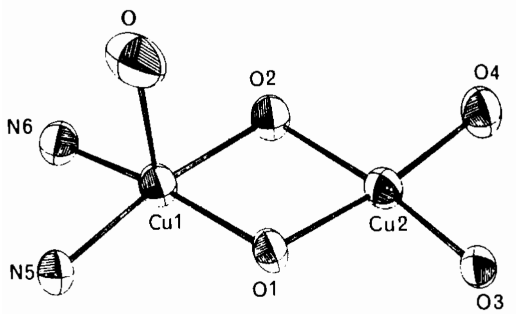


Fig. 2. ORTEP drawing of the $Cu_2N_2O_2O_2O$ (methanol) skeleton, with 50% probability thermal ellipsoids.

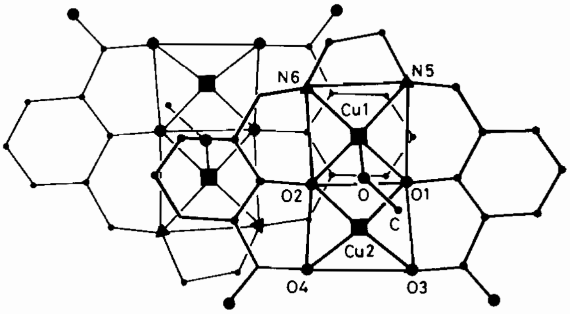


Fig. 3. Closest packing of two molecular units around a symmetry centre.

Fig. 3. The Cu(1) atom is five-fold coordinated in a square pyramid to two nitrogens, two phenolic oxygens and the oxygen of the methanol molecule occupying the apex of the pyramid. The length of the Cu(1)–O (methanol) bond, 2.266 Å, shows that the interaction Cu(1)–methanol is strong enough to pull the Cu(1) atom out of the mean plane O(1)O(2)N(5)-N(6) by 0.20 Å (see Table IV). The Cu(1)–O(1) and Cu(1)–O(2) distances are 1.924 Å and 1.902 Å respectively. These values are similar to the ones found in most copper(II) binuclear complexes with the Cu_2O_2 network [15]. The Cu(2) is coordinated

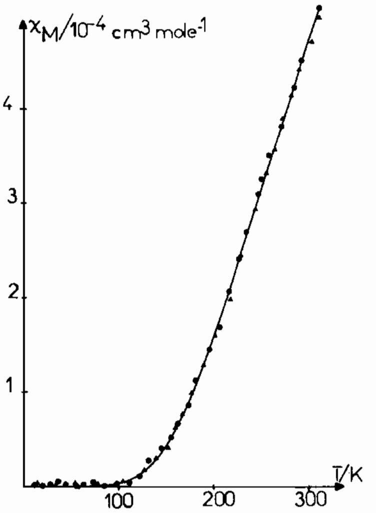


Fig. 4. Temperature dependence of the molar magnetic susceptibilities corrected for the non coupled Cu(II) impurity for samples A (●) and B (▲) and theoretical curve (continuous line).

to two phenolic oxygens and two carboxylic oxygens. In contrast with Cu(1), Cu(2) is located in an essentially planar environment. The deviation of Cu(2) from the mean plane O(1)O(2)O(3)O(4) is only 0.030 Å (see Table IV). The two mean planes O(1)O(2)-N(5)N(6) and O(1)O(2)O(3)O(4) make a dihedral angle of 191.6°. On the other hand the Cu(1)O(1)-Cu(2)O(2) network is close to the planarity, the dihedral angle between the Cu(1)O(1)O(2) and Cu(2)-O(1)O(2) planes being 184.5°. The terminal Cu(2)–O(3) and Cu(2)–O(4) bonds (average 1.879 Å) are slightly but significantly smaller than the bridging Cu(2)–O(1) and Cu(2)–O(2) bonds (average 1.919 Å). The average values of the bridging Cu(1)–O and Cu(2)–O bonds are identical.

The Cu(1)–Cu(2) distance is 2.942 Å and the bridging angles Cu(1)O(1)Cu(2) and Cu(1)O(2)Cu(2) are 99.9° and 100.3° respectively. These values are in the range found with other copper(II) complexes with oxygen bridging atoms. The Cu(1), Cu(2) and O (methanol) atoms make out a plane which is very close to a mirror-plane for the whole molecule (see Table IV). Finally, this structure is very similar to the one of CuVO(fsa)$_2$en, CH$_3$OH [8] in which a vanadyl group is substituted to the Cu(2) atom.

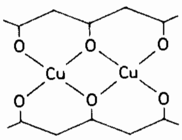
Magnetic Susceptibility

The temperature dependence of the molar magnetic susceptibilities for two samples coming from two different preparations is shown in Fig. 4. The experimental points are corrected for a very weak amount of monomeric impurity according to a previously described procedure [16]. The magnetic behaviour is characteristic of pairs of strongly antiferromagnetically coupled Cu(II). The susceptibilities continuously decrease upon cooling down from 312 K and become essentially negligible below 120 K. The experimental data closely follow the equation giving the temperature dependence of the molar magnetic susceptibility for a Cu(II) dimer:

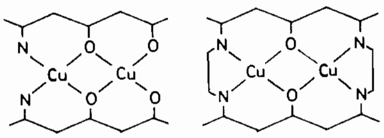
$$\chi_M = \frac{2N\beta^2 g^2}{kT}\left[3 + \exp\left(-\frac{J}{kT}\right)\right]^{-1} + 2\,N\alpha$$

where the symbols have their usual meaning, J being the singlet–triplet separation. A least squares fit leads to J = –650 cm^{-1}, g = 2.197 and Nα negligible. The J value in Cu$_2$(fsa)$_2$en, CH$_3$OH is very close to the one obtained by Tanaka *et al.* in Cu$_2$(fsa)$_2$en, ½H$_2$O from more limited magnetic data [3]. Most likely, both complexes have analogous structures.

A large number of copper(II) dimers with the Cu$_2$O$_2$ network are known and the magnetic properties of several of them were interpreted in the light of structural data. In this way, the work of Hatfield *et al.* concerning the hydroxo-bridged copper(II) dimers is now classical [15]. These authors established a linear correlation between the values of the J singlet–triplet separation and of the Cu$\widehat{O}$Cu bridging angle. From this correlation, the expected J value in a planar hydroxo-bridged copper(II) dimer with bridging angles of 100.1 degrees is about –190 cm^{-1}. In other words, in Cu$_2$(fsa)$_2$en, CH$_3$OH, the coupling is much more antiferromagnetic than in a complex of the OH-bridged series having the same Cu$\widehat{O}$Cu bridging angle. In fact, very strong antiferromagnetic coupling was found in all the known copper(II) binuclear systems with the triketonato ligands of type I [17] or with the Schiff base bichelating ligands of type II [18, 19]. In the bis(1,3,5-trikenato)dicopper(II) complexes, the antiferromagnetic coupling is so large that they appear diamagnetic at room temperature without EPR signal [17].



Type I



Type II

This behaviour may be interpreted as follows: it has been established that in the Cu(II) binuclear complexes, the magnitude of the antiferromagnetic

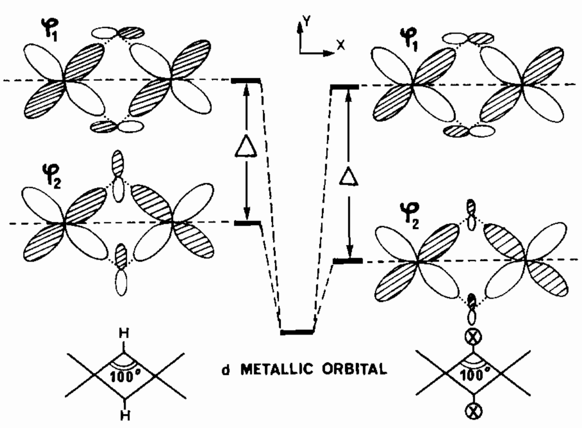
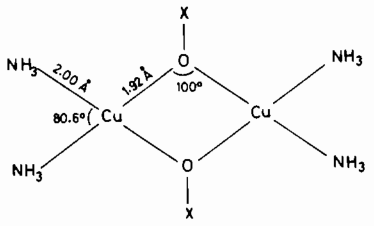


Fig. 5. Schematic comparison of the ϕ_1 and ϕ_2 molecular orbitals in the Cu_2O_2 network of a OH-bridged complex and of a OX-bridged complex with X more electronegative than H.

coupling was governed by $(\Delta^2 - \delta^2)^{1/2}$ where Δ is the energy gap between the two singly occupied molecular orbitals in the triplet state and δ the energy gap between the two magnetic orbitals centred on the one and the other Cu(II) ions [5]. When the binuclear complex is symmetric, δ vanishes and the dominant factor for the antiferromagnetic coupling simply becomes Δ [20]. The ϕ_1 and ϕ_2 singly occupied molecular orbitals in the triplet state for our complex are sketched in Fig. 5. They are constructed from the $3d_{xy}$ metallic orbitals pointing towards the bridging and terminal ligands and are antibonding with regard to these d metallic orbitals. The bridging oxygen orbitals involved in ϕ_1 are essentially the $2p_x$ and in ϕ_2 the $2p_y$. When, as in the studied compound, the environments of the Cu(II) ions are not equivalent, there are some weak contributions of $2p_x$ in ϕ_2 and $2p_y$ in ϕ_1. In the qualitative discussion which follows, these contributions may be neglected. The more important in absolute value the metal–ligand overlaps, the more destabilized the molecular orbitals. In $Cu_2(fsa)_2en, CH_3OH$, as in the other Cu(II) binuclear complexes of type I or II, the crystal structures of which are known, the $Cu\widehat{O}Cu$ bridging angle values are higher than 90°, hence $|\langle 3d_{xy}|2p_x\rangle|$ is larger than $|\langle 3d_{xy}|2p_y\rangle|$ and ϕ_1 more destabilized than ϕ_2 [16–20]. In complexes of type I or II, the bridging oxygen atoms are σ-bonded to more electronegative organic groups than hydrogen and the electronic density around these oxygens is weaker than in the complexes of the OH-bridged series. More precisely, the weakening of the electronic density when the hydrogen of the hydroxo-bridge is replaced by a more electronegative group mainly affects the $2p_y$ orbital pointing towards this group. Thus, the contribution of the $2p_y$ oxygen orbitals in ϕ_2 diminishes much more than the one of the $2p_x$ orbital in ϕ_1. ϕ_2 is therefore less antibonding with regard to the d metallic orbitals, thus the Δ energy gap between ϕ_2 and ϕ_1 increases and the coupling is more antiferromagnetic. This process is schematized in Fig. 5. To obtain a semiquantitative interpretation of this effect, we used the Forticon 8 Extended Hückel program [21] with the parametrization of reference [16] and calculated the Δ energy gap for the complex model shown below, as the electronegativity of X varied.



X was chosen as a hydrogen atom whose orbital energy varied from −13.6 to −20 eV. It results from this calculation that Δ increases from 0.173 eV to 0.270 eV as X is made more electronegative. It should be noted here that this result is the opposite of the one obtained by Hoffmann and coworkers in their investigation of the influence of the X substituents for the model complex $Cl_2Cu(\mu\text{-}OCX_3)_2CuCl_2$ with a $Cu\widehat{O}Cu$ bridging angle of 90° [20].

In conclusion, we would like to emphasize that, in the last few years, progress in the understanding of the mechanism of the antiferromagnetic coupling has been important. This work, which is intended to be an experimental and theoretical contribution to this problem, confirms this situation.

Listings of the structure factor amplitudes and of the magnetic data may be obtained on request from the authors.

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