Title	A pyrazolate-bridged cyclic tetranuclear copper(II) complex : synthesis, crystal structure and magnetic properties
Author(s)	Zhang, Hua; Fu, Degang; Ji, Feng; Wang, Guoxiong; Yu, Kaibe; Yao, Tianyang
Citation	Zhang, H., Fu, D., Ji, F., Wang, G., Yu, K., & Yao, T. (1996). A Pyrazolate-bridged Cyclic Tetranuclear Copper(II) Complex : Synthesis, Crystal Structure and Magnetic Properties. Journal of the Chemical Society, Dalton Transactions, (19), 3799-3803.
Date	1996
URL	http://hdl.handle.net/10220/8334
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A Pyrazolate-bridged cyclic tetranuclear copper(II) complex: synthesis, crystal structure and magnetic properties†

Hua Zhang, [a] Degang Fu, [b] Feng Ji, [a] Guoxiong Wang,*[a] Kaibe Yu[c] and Tianyang Yao[a]

[a] Department of Chemistry, Nanjing University, Nanyang, 210008, P.R. China

[b] National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing, 210096, P.R. China

[c] Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu, 610016, P.R. China

† Non-SI unit employed: eV $\approx 1.60 \times 10^{-19}$ J

A new pyrazolate-bridged tetranuclear copper(II) complex [{CuL(H$_2$O)}$_4$]· 12 H$_2$O(H$_2$L = 5-methoxy-carbonylpyrazole-3-carboxylic acid) was synthesized and its crystal structure determined. The molecule has C_2 symmetry and consists of four copper atoms bridged by four planar L ligands through the nitrogen atoms of the pyrazole groups to form a (-Cu-N-N-)$_4$ 12-membered ring. The co-ordination of each copper is distorted square planar. The basal plane of each copper atom is nearly parallel to a neighbouring pyrazole plane and perpendicular to another neighbouring pyrazole plane. In the crystal there is a hydrogen-bond network between water molecules and carboxylate groups which may control the packing. The magnetic properties of the complex have also been investigated down to 5 K. the fitting of the experimental data using a Heisenberg Hamiltonian shows that the exchange interaction between the copper atoms propagated through the monopyrazolate bridge is antiferromagnetic with J = -12.34 cm^{-1}. The reason for this small value relative to those in di-μ-pyrazolato-dicopper(II) complexes is discussed.

The chemistry of pyrazole and its derivatives has attracted interest for many years.[1] It acts as a bridging group through its two nitrogen atoms in polynuclear complexes.[2] Most of these are dicopper complexes which have been designed for model studies on the active site of type III copper proteins and usually have another bridging group, such as alcoholate, phenolate, thiolate, acetate or azide.[3,4] The purely pyrazolate-bridged polynuclear complexes are relatively few and most are di-μ-pyrazolates. These include some chain-like complexes [5] and some discrete dicopper complexes.[6] Studies on the magnetic peoperties of these di-μ-pyrazolates show that pyrazole may transmit exchange interaction between metal ions, J ranging from -50 to -200 cm^{-1}. However, purely mono-μ-pyrazolate-bridged complexes, to our knowledge, have not been reported until now. In previous study we synthesized a di-μ-pyrazolato-dicopper complex using HL^1 which acted as a tetradentate ligand through two nitrogen atoms of pyrazole and two oxygen atoms of amides.[6b] Continuing our interest in pyrazole complexes, we used HL^2 in synthesis, which was expected to act as a bidentate ligand to form a one-dimensional

polymer with copper atoms in chain-like complexes,[5] or as a tetradentate ligand to form a dicopper complex. However, instead we obtained a novel monopyrazole-bridged tetranuclear complex having a 12-membered ring comprised of four copper atoms and eight nitrogen atoms from pyrazole groups. Cyclic tetra- and tri-nuclear copper complexes with similar imidazolate bridges have been reported.[7] However, for pyrazolate-bridged copper complexes only a cyclic trinuclear complex with a μ_3-OH group has been reported.[2e] Here we report the synthesis, structure and magnetic properties of the new complex.

Experimental

Preparation

3,5-Bis(methoxycarbonyl)pyrazole (HL^2) was synthesized by the literature procedure.[8] A 95% methanol solution (20 cm^3) containing $Cu(O_2CMe)\cdot H_2O$(0.401 g, 2 mmol) was added to a 95% methanol solution (20 cm^3) containing HL^2 (0.367 g, 2 mmol). The mixture was heated to boiling, refluxed and stirred for 2 h. After filtration and cooling to room temperature, a blue crystal was collected after several days and dried in vacuum (Found: C, 25.15; H, 3.50; N, 9.65. Calc. for $C_6H_{10}CuN_2O_7$: C, 25.2; H, 3.50; N, 9.80%).
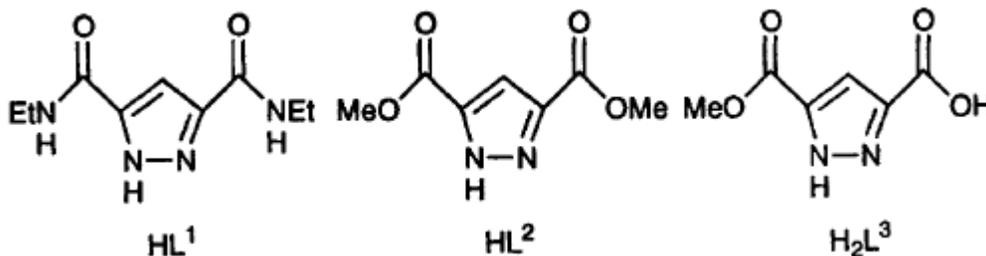
X-Ray crystallography

A suitable crystal was mounted on a R3M/E four-circle diffractometer and unit-cell parameters were refined for 25 reflections (2θ = 6.82-23.84 °). The reflection intensities were measured in the ω-2θ scan mode with graphite-monochromated Mo-K$_\alpha$ radiation. All diffraction intensities were corrected for Lorentz-polarization factors but not for absorption. The coordinates of two copper atoms were obtained by the direct method. The other coordinates of the non-hydrogen atoms were determined by several Fourier syntheses. The structure was refined by the block-diagonal-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms and partial hydrogen atoms. The positions of hydrogen atoms attached to O(10),C(3), and C(9) were located on a Fourier-difference map and the others by theoretical calculation. Their positions were fixed in the last refinement. All calculations were performed using SHELXTL.[9] A summary of the crystal data and structure refinement (based on F) is presented in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for

Physical measurements

Variable-temperature magnetic susceptibility measurements of a powder sample were made by using a SQUID magnetometer. All data points at 5-300 K were collected at 5000G (0.5 T). Diamagnetic contributions were calculated from Pascal's constants.[10]

Results and Discussion

Synthesis

Although compound HL^2 was used as a starting material, it was found that it is partially hydrolysed in 95% methanol solution containing $Cu(O_2CMe)_2$. The partial hydrolysis product having a single carboxylate group reacts with Cu^{2+} ions to form a cyclic tetranuclear species $[\{CuL^3(H_2O)\}_4] \cdot 12H_2O$ **1**.

   It has long been known that in transition-metal complexes the metal ions can catalyse the reactions of ligands.[11] In the synthesis of complex **1** the occurrence of copper ions may improve the hydrolysis of HL^2. It is considered that the pyrazolate nitrogen atom first anchors the Cu^{2+} ion, then coordination of a carboxyl oxygen atom to the Cu^{2+} reduces the electron density at the carbon atom of the carboxyl group, which benefits nucleophilic substitution of H_2O to form the tridentate ligand L^3 and consequently the tetranuclear copper(II) complex.

Structure

The molecular structure of complex **1** is shown in Fig. 1, selected bond lengths and angles in Table 2. The molecule has C_2 symmetry. The four copper atoms and eight nitrogen atoms of four pyrazole groups form a $(-Cu-N-N-)_4$ 12-membered ring with the bridge structures between copper atoms being almost identical. The distances between adjacent copper atoms are also near equal, Cu(1) $\cdots$ Cu(2) 4.098, Cu(1) $\cdots$ Cu(2a) 4.115 Å, while those between diagonal copper atoms Cu(1) $\cdots$ Cu(1a) and Cu(2) $\cdots$ Cu(2a) are 4.658, 4.715 Å, respectively. The four copper atoms are not coplanar, angles Cu(1)-Cu(2)-Cu(1a), Cu(2)-Cu(1)-Cu(2a), Cu(1)-Cu(2)-Cu(2a) and Cu(2)-Cu(1a)-Cu(2a) all being close to 70 °, and so they form a distorted tetrahedron.

   The ligand L^3 has reasonable planarity, the five atoms of the pyrazole ring being coplanar and the other atoms of the ligand deviating less than 0.1 Å except for O(3)(0.12) and C(6)(0.24Å). The four copper atoms all have a distorted square-planar co-ordination from one oxygen atom of water, one oxygen atom of carboxylate and two nitrogen pyrazole atoms. Together these atoms form a basal plane with the copper atom located in this plane, for example in the case of Cu(1), the sum of the four angles N(1)-Cu(1)-O(1), O(1)-Cu(1)-O(5), O(5)-Cu(1)-N(4a) and N(4a)-Cu(1)-N(1) is equal to 360 ° and Cu(1) deviates from the basal plane by only 0.0609Å. The dihedral angles between the basal plane of Cu(1) and the planes of the two pyrazole groups which co-ordinate to it through

N(1) and N(4a) are 5.1 and 89.4 ° respectively. The corresponding values for Cu(2) are 3.4 and 91.5 °. These values show that the basal plane of the copper atom is nearly parallel to a neighbouring pyrazole plane which has the shortest bond($ca.$ 1.95Å) to the copper atom in the inner sphere, and perpendicular to another neighbouring pyrazole plane which has the longest bond($ca.$ 1.98Å) to the copper atom. All of the bond lengths and angles are in the normal range.

The pyrazole planes of the four ligands can be divided into two sets. In each two pyrazole planes are linked by a two-fold axis and opposite to each other. The angles between this axis (in direction b) and the planes of the two sets are 2.36, 2.08 ° respectively, so the dihedral angles between the two pyrazole planes linked by the two-fold axis are $2 \times 2.08 = 4.16$ ° for the two sets. That is, in each set, the two planes are nearly parallel. The distance between the copper atom and the opposite pyrazolate plane is nearly 3Å. However, the pyrazole planes which belong to different sets have dihedral angles of 92.9 ° and are nearly perpendicular to each other.

The unit-cell packing is shown in Fig. 2. Table 3 lists the oxygen-oxygen distances which are within the hydrogen-bonding range [12] in the crystal. Hydrogen bonding is one of the main factors in the construction of supermolecular systems. It can ben seen that there are a variety of such linkages among the oxygen atoms of the carboxylate, co-ordinated and crystal water molecules. The packing is such that while the co-ordinated water molecules forms a hydrogen bond with the carboxylate oxygen atom in an adjacent molecule, the methoxycarbonyl group near the same copper atom extends toward the methoxycarbonyl group in another adjacent molecule. So in the crystal there exist two networks, one involving hydrogen bonding between co-ordinated H_2O and carboxylate oxygen atoms and one involving packing of methoxycarbonyl groups, which run through each other. However, in the stacking domains of the methoxycarbonyl groups the shortest inter-group distance is 2.93 Å for O(3) ⋯O(9); this value is a little smaller than 3.04Å, the sum of twice the van der Waals radius of oxygen(1.52Å).[13]

Magnetic properties

The magnetic exchange interaction for this tetranuclear complex can be described as in Scheme 1. The exchange interactions between the pyrazole-bridged copper atoms are considered to be identical as demonstrated by the molecular structure, that is the identity of the bridging units and near equal Cu ⋯ Cu distances, and are denoted as J_1. The exchange interactions between non-bridging copper atoms Cu(1) ⋯ Cu(1a) and Cu(2) ⋯ Cu(2a) are characterized with parameter J_2. So the Heisenberg Hamiltonian can be written as in equation (1). The magnetic susceptibility can then be expressed as in equations (2)-(4) where ρ is the percentage of

$$H = -2J_1(S_1S_2 + S_1S_{2a} + S_2S_{1a} + S_{2a}S_{1a}) - 2J_2(S_1S_{1a} + S_2S_{2a})$$

(1)

$$\chi = \frac{2Ng^2\beta^2}{kT} \cdot \frac{A}{B}(1 - \rho) + \frac{Ng^2\beta^2}{kT}\rho$$

(2)

$$A = 2\exp(2J_2/kT) + \exp[(4J_2 - 2J_1)/kT] +$$
$$5\exp[(4J_2 + 2J_1)/kT] \tag{3}$$

$$B = 1 + 6\exp(2J_2/kT) + \exp[(4J_2 - 4J_1)/kT] +$$
$$3\exp[(4J_2 - 2J_1)/kT] + 5\exp[(4J_2 + 2J_1)/kT] \tag{4}$$

Mononuclear copper(II) ions, the other symbols having their usual meanings. Since there are hydrogen bonds between the molecules, the intermolecular exchange interaction zJ' must be considered and we use equation (5) to express the magnetic

$$\chi'_m = \frac{\chi_m}{1 - (2zJ'\chi_m/Ng^2\beta^2)} \tag{5}$$

susceptibility of complex **1** with molecular field correction.[4]

Using equations (2) and (5), the experimental data can be fitted as in Fig. 3 with $J_1 = -12.34$ cm^{-1}, $J_2 = 0.57$ cm^{-1}, g= 2.17, $zJ' = -0.76$ cm^{-1}, $\rho = 0.031$, and $R = 3.1 \times 10^{-6}$ where $R = \sum_{(\chi exptl-\chi calc)}{}^2/\sum_{(\chi exptl)}{}^2$. These results show that the coupling in complex **1** through the pyrazole groups is antiferromagnetic. The $|J_1|$ value is smaller than those found in other purely dipyrazolate-bridged complexes.[6,7] In these complexes, the $|J|$ value is large when the co-ordination of the copper atoms is square planar or square pyramidal ($\approx$ 120-210 cm^{-1}) and relatively small when tetrahedral or trigonal bipyramidal ($\approx$ 50-100 cm^{-1}). This can be explained by the difference between di- and mono-pyrazolate bridging.

Complete neglect of differential overlap (CNDO/2) calculations on pyrazole have shown that two high-energy occupied σ orbitals have σ$_S$ or σ$_A$ symmetry with respect to the mirror plane perpendicular to the N-N vector with an energy gap of 0.17eV where the level of σ$_S$ is higher.[14] In dipyrazole-bridged copper complexes combination of the σ$_S$ orbitals of the two bridging pyrazole groups given φ$_S$ and φ$_A$ orbirals with respect to the inversion centre in the middle of the Cu-Cu vector as shown in Scheme 2. The two degenerate orbitals d$_S$ and d$_A$ which are a combinration of two singly occupied d$_{xy}$ orbitals of copper also with respect to the inversion centre mainly interact with φ$_S$ and φ$_A$. However, φ$_S$ and φ$_A$ are anticomplementary,[4,15] the overall overlap of d$_S$ and φ$_S$ is zero, so the evergy of the non-bonding orbital ψ$_S$ remains unchanged while d$_A$ and φ$_A$ have a strong overlap and the resulting antibonding molecular orbital ψ$_A$ is raised in energy to give a large gap ΔE between ψ$_S$ and ψ$_A$. In a monopyrazolate-bridged copper complex the combination of two copper d$_{xy}$ orbitals gives d$_S$' and d$_A$' with respect to the mirror plane perpendicular to the N-N vector, d$_S$' will interact with the σ$_S$ orbital of pyrazole and d$_A$' will interact with σ$_A$; the energies of the two resulting antibonding MOs ψ$_S$' and ψ$_A$' are all raised and give a smaller energy gap $\Delta E'$ than ΔE for the doubly bridged complex. According to Hoffmann's theory,[16] a weaker-exchange interaction should be expected in mono-pyrazolate-bridged complexes than in dipyrazolate-bridged ones.

In Scheme 2 we consider the case where the pyrazolate planes and basal planes of the copper atoms are coplanar. It has been found that in dipyrazolate-bridged complexes the grater the coplanarity between the bridging pyrazolate plane and the copper basal plane

the stronger is the exchange interaction.[17] We also performed CNDO/2 calculations on a model of monopyrazolate-bridged dicopper complexes in which the bond lengths and angles of the pyrazole group take the mean values of those in **1**and Cu-N and Cu-F are fixed at 1.95 and 1.93Å respectively (Scheme 3). The CNDO/2 parameters are listed in Table 4. The calculations were performed on two different geometric structures. One was a planar geometry where all the atoms are in the xy plane. In this case the angles F(10)-Cu(15)-F(9) and F(8)-Cu(16)-F(7) are optimized at 77.3 ° and the F(8)···F(9) distance is 2.031Å, so the angles F(9)-Cu(15)-F(5) and F(8)-Cu(16)-F(4) are 102.7 °. The other angles in the basal planes of the copper atoms such as F(10)-Cu(15)-F(11) and F(11)-Cu(15)-N(5) are set at 90 °. In the second geometry atoms F(6), Cu(16) and F(8) are located in the same line perpendicular to the xy plane [F(8)-Cu(16)-F(7) 90 °], while the arrangement of the other atoms is not changed but F(9) was moved to make F(9)-Cu(15)-F(10) 90 °. We found that the energy difference between two singly occupied molecular orbitals (HOMO) is smaller in the second case (0.071 eV) than in the first where all atoms are in the xy plane(0.767 eV). In other words, compared with the case in Scheme 2(*b*), the exchange interactions in complex **1** are further decreased due to the partial coplanarity between the bridging pyrazole plane and the basal planes of the copper atoms where the bridging pyrazole plane is parallel to one neighbouring copper basal plane but perpendicular to another. Though the exchange interaction between copper atoms through the single pyrazolate group in **1** is relatively small compared with those in dipyrazolate-bridged dicopper complexes, it could be concluded that pyrazole is an effective ligand to propagate exchange interaction between metal ions as are other heterocyclic ligands such as imidazole. [7a,19]

The interaction between the diagonal copper atoms Cu(1)···Cu(1a) or Cu(2)···Cu(2a) is ferromagnetic as seen from the small positive value of J_2. This may arise from the spin frustration in the polynuclear complex, especially in cyclic polynuclear complexes.[2e,20] In fact, if J_2 is neglected in the fitting of the experimental data and almost identical result is obtained.

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Scheme 1.

Scheme 2.   Orbital interaction in di- (*a*) and mono- (*b*) pyrazolate-bridged dicopper complexes

Scheme 3.   Model complex used for CNDO/2 calculation in the planar geometry.

Formula	$C_{24}H_{48}Cu_4N_8O_{32}$
M	1214
Crystal symmetry	Monoclinic
Space group	$C2/c$
$a/Å$	20.591(3)
$b/Å$	19.416(3)
$c/Å$	15.174(3)
$\beta/°$	133.39(1)
$U/Å^3$	4408(1)
Z	4
$F(000)$	2480
$D_c/g\ cm^{-3}$	1.83
$T/°C$	21 ± 1.5
Crystal size/mm	$0.24 \times 0.44 \times 0.50$
Monochromated radiation ($\lambda/Å$)	Mo-Kα (0.710 73)
μ(Mo-Kα)/cm^{-1}	21.0
Scan type and rate	ω–2θ, 7.32° min^{-1}
Data collection range, $2\theta/°$	2–45
Number of unique data, total	3105
with $I \geqslant 1.5\sigma(I)$	2509
R^a	0.0449
R'^b	0.0404
Largest shift/e.s.d.	0.092

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|.$ $^b R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{4}}$ where
$w = [1 - \exp(-5\sin\theta^2/\lambda^2)]/[\sigma^2(F) + 0.00014F^2].$

Table 1.

Cu(1)–N(1)	1.951(6)	N(1)–N(2)	1.328(8)
Cu(1)–O(1)	1.953(3)	N(1)–C(2)	1.358(6)
Cu(1)–O(5)	1.974(6)	N(2)–C(4)	1.356(9)
Cu(1)–N(4a)	1.989(3)	O(2)–C(1)	1.247(6)
Cu(2)–N(2)	1.984(4)	O(3)–C(5)	1.203(6)
Cu(2)–N(3)	1.953(3)	O(1)–C(1)	1.270(10)
Cu(2)–O(6)	1.961(3)	O(4)–C(5)	1.320(9)
Cu(2)–O(10)	1.958(3)	O(4)–C(6)	1.443(16)
C(1)–C(2)	1.469(10)	C(2)–C(3)	1.385(12)
C(3)–C(4)	1.387(7)		
N(1)–Cu(1)–O(1)	82.3(2)	N(1)–Cu(1)–O(5)	170.4(1)
O(1)–Cu(1)–O(5)	88.1(2)	N(1)–Cu(1)–N(4a)	96.8(2)
O(1)–Cu(1)–N(4a)	173.6(1)	O(5)–Cu(1)–N(4a)	92.7(2)
N(2)–Cu(2)–N(3)	96.9(1)	N(2)–Cu(2)–O(6)	175.5(3)
N(3)–Cu(2)–O(6)	82.1(1)	N(2)–Cu(2)–O(10)	92.7(1)
N(3)–Cu(2)–O(10)	168.9(2)	O(6)–Cu(2)–O(10)	87.9(1)
Cu(1)–N(1)–N(2)	137.8(3)	Cu(1)–N(1)–C(2)	112.9(5)
N(2)–N(1)–C(2)	109.2(6)	Cu(2)–N(2)–N(1)	131.7(4)
Cu(2)–N(2)–C(4)	120.6(5)	N(1)–N(2)–C(4)	107.5(4)
Cu(2)–N(3)–N(4)	137.6(3)	Cu(2)–N(3)–C(8)	113.4(2)
Cu(1)–O(1)–C(1)	115.3(4)	C(5)–O(4)–C(6)	116.1(6)
Cu(2)–O(6)–C(7)	115.3(3)	O(1)–C(1)–O(2)	123.6(7)
O(1)–C(1)–C(2)	115.6(4)	O(2)–C(1)–C(2)	120.7(7)
N(1)–C(2)–C(1)	113.8(6)	N(1)–C(2)–C(3)	109.1(5)
C(1)–C(2)–C(3)	137.1(5)	C(2)–C(3)–C(4)	104.0(5)
N(2)–C(3)–C(4)	110.2(7)	N(2)–C(4)–C(5)	116.0(4)
C(3)–C(4)–C(5)	133.8(6)	O(3)–C(5)–O(4)	124.9(8)
O(3)–C(5)–C(4)	122.3(7)	O(4)–C(5)–C(4)	112.7(5)

Table 2.

$O(9) \cdots O(3^{I})$	2.928	$O(3) \cdots O(9^{I})$	2.928
$O(5a) \cdots O(7^{I})$	2.742	$O(7) \cdots O(5^{II})$	2.742
$O(7a) \cdots O(5^{III})$	2.742	$O(5) \cdots O(7^{IV})$	2.742
$O(9a) \cdots O(3^{IV})$	2.928	$O(3a) \cdots O(9^{IV})$	2.928
$O(10) \cdots O(2^{V})$	2.667	$O(2) \cdots O(10^{V})$	2.667
$O(10a) \cdots O(2^{VI})$	2.667	$O(2a) \cdots O(10^{VI})$	2.667
$O(w4) \cdots O(w3^{III})$	2.811	$O(w2) \cdots O(10^{VII})$	2.744

Superscripts refer to symmetry operations: I $-x$, $1 - y$, $-z$; II x, $1 - y$, $-\frac{1}{2} + z$; III $-x$, $1 - y$, $1 - z$; IV x, $1 - y$, $\frac{1}{2} + z$; V $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$; VI $-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$; VII $\frac{1}{2} - x$, $\frac{3}{2} - y$, $1 - z$.

Table 3.

	H	C	N	F	Cu*
ζ (orbital exponential)	1.20	1.625	1.95	2.60	1.540 for 4s
					0.462 for 4p
					3.084 for 3d
$(I_s + A_s)/2$	7.176	14.051	19.316	32.2724	4.567
$(I_p + A_p)/2$		5.572	7.275	11.080	1.347
$(I_d + A_d)/2$					6.520
β	-9.00	-21.00	-25.00	-39.00	-25.4 for 4s
					-19.0 for 4p
					-31.0 for 3d

* Parameters for Cu were selected from ref. 18: I and A represent the ionization energy and electron affinity for orbitals in eV; β is the parameter for each atom in the relation $H_{rs} = S_{rs}(\beta_A + \beta_B)/2$ where rs represents the number of non-atomic orbitals.

Table 4.

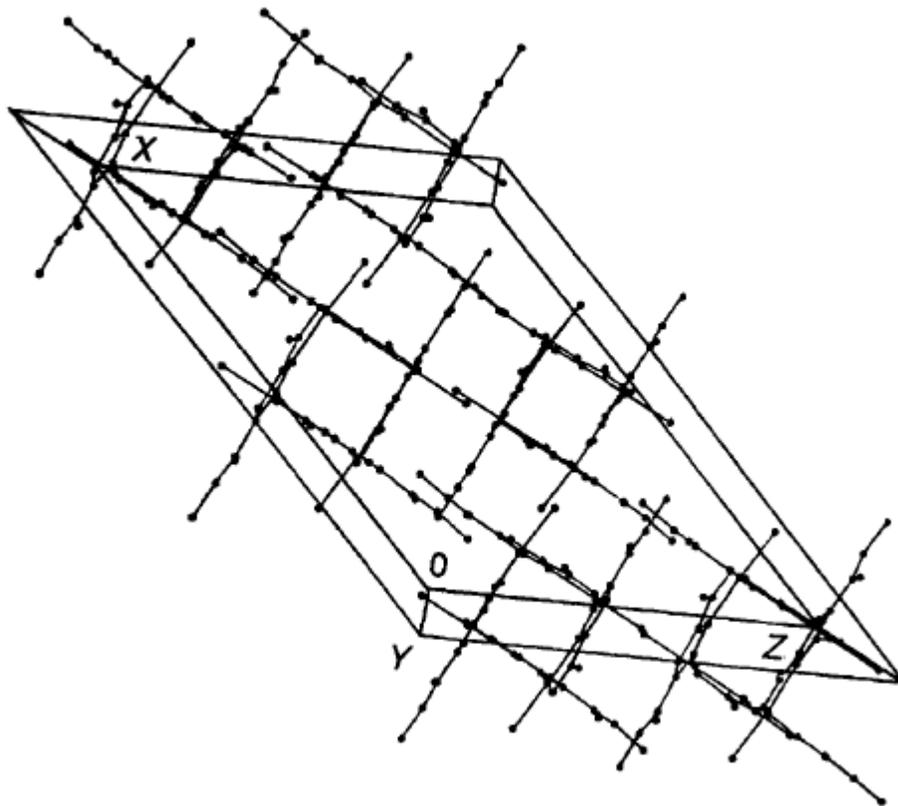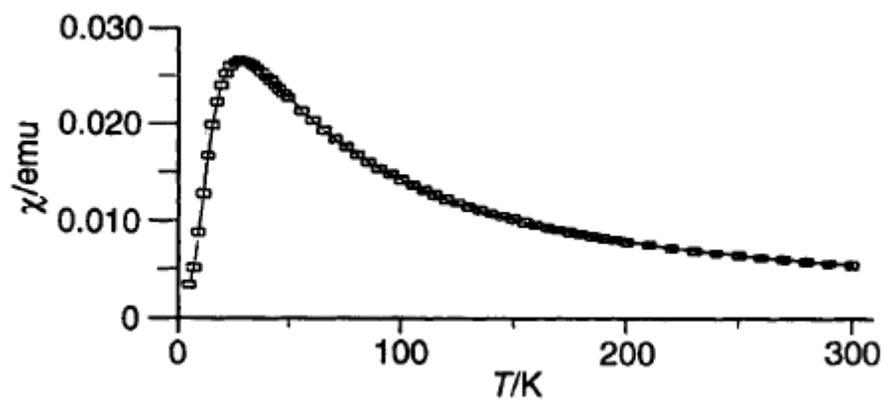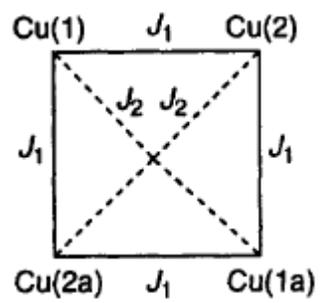**Fig. 1.**

Fig. 2.

Fig. 3.

Scheme 1.

(a)

ϕ_S ϕ_A ψ_A ΔE $d_A d_S$ ψ_S ϕ_A ϕ_S

(b)

σ_S σ_A ψ_S ΔE $d_A d_S$ ψ_A σ_S σ_A

Scheme 2.

Scheme 3.