Direct X-ray confirmation of the possible use of magnetochemical criteria for binuclear structural isomers of copper(II) complexes based on acylhydrazones of salicylic aldehyde-substituted derivatives

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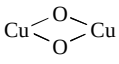
X-Ray structural investigations and magnetic measurements of binuclear copper(II) complexes with salicylic aldehyde acylhydrazone have demonstrated the possible use of magnetochemical criteria for the identification of structural isomers in the given class of compounds.

It was shown earlier[1–3] that complex formation between acylhydrazones of salicylic aldehyde-substituted derivatives and copper(II) acetate leads to two possible isomeric structures **1a** or **1b** whereas copper(II) perchlorate gives a binuclear analogue of the type **1b′**.

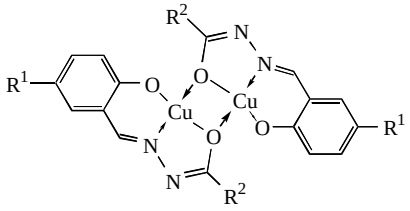
The difference between these structures lies in the different electronic nature of the bridging oxygen atoms. In fact the bridging atom in **1a** is the α-oxyazinic atom of the hydrazide moiety while in **1b** and **1b′** it is the phenoxide oxygen atom of the salicylic moiety. We believe that the types of hybridization of these two oxygen atoms are quite different, so as a consequence the bond angles Cu–O–Cu in the exchange fragment



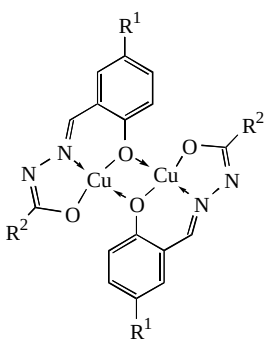
A

are different too.

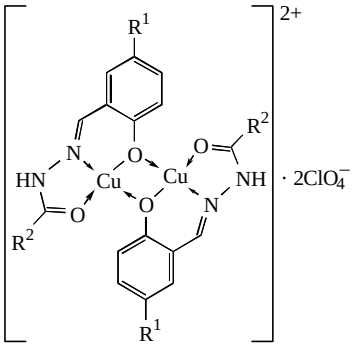
The systematic magnetochemical study carried out by us revealed that the antiferromagnetic exchange interaction for the complexes **1b** and **1b′** is always much stronger (the exchange parameters $2J$ lie in the range –300–500 cm^{-1}) than for the binuclear complexes **1a** ($2J$ lie in the range –20–130 cm^{-1}).[3,4] This can be explained by the greater degree of planarity of the exchange fragment including the phenoxide oxygen atom (types **1b**, **1b′**). A geometrical model which explains these differences has been developed earlier,[5] and the experimental data in this field were also systematized. These data point to a possible use of magnetochemical criterion in the identification of given structural isomers. The present paper is devoted to the first confirmation of the above hypothesis using X-ray diffraction data.† The type **1b′** binuclear copper(II) complex (R^1 = H, R^2 = $C_{12}H_{25}$) has been used as an object of investigation; its magnetic properties have been compared with the properties of the type **1a** complex (R^1 = H, R^2 = $C_{12}H_{25}$) which has been especially synthesized for the first time.



1a



1b



1b′

Table 1 Magnetic properties of type **1a** and **1b′** binuclear complexes.

T/K	μ_{eff}/B.M. (exp.)	μ_{eff}/B.M. (calc.)
1a: $2J$ = –118 cm^{-1}, g = 2.02, r = 0.66%,[a] f = 0[b]		
85.4	1.12	1.11
102	1.24	1.24
119	1.33	1.33
137	1.40	1.40
150	1.44	1.44
171	1.50	1.49
230	1.59	1.59
242	1.60	1.60
263	1.62	1.62
293	1.65	1.64
1b′: $2J$ = –349 cm^{-1}, g = 2.00, r = 1.47%,[a] f = 0.03[b]		
77.4	0.38	0.38
101	0.46	0.47
136	0.66	0.66
160	0.78	0.78
190	0.93	0.93
216	1.04	1.04
232	1.10	1.10
254	1.17	1.16
271	1.22	1.21
299	1.27	1.28

[a]Mean square error. [b]Mole part of paramagnetic impurity. [c]The value of μ_{eff} is calculated per one copper ion in the binuclear molecule.

It can easily be seen that in this particular case the exchange parameters $2J$ (calculated in terms of the HDVV model[6]) for the **1a** type complex are much lower (in absolute value) than for **1b′**. This can be explained[3] by the geometrical differences between the exchange fragments. Indeed, the structure of the

† *Crystal data for* **1b′**: $C_{42}H_{70}N_4O_6Cu_2^{2+} \cdot 2ClO_4^-$, monoclinic, space group $P2_1/c$, a = 17.528(5) Å, b = 18.087(7) Å, c = 7.812(2) Å, β = = 94.54(2)°, V = 2469(1) Å^3, $F(000)$ = 1108, D_c = 1.416 g cm^{-3}, Z = 2. Data were measured using a Syntex $P2_1$/PC diffractometer (T = 193 K, graphite-monochromated MoKα radiation, λ = 0.71073 Å, $\theta/2\theta$ scan, $2\theta_{max}$ = 50°). The structure was solved by direct methods using the SHELXTL PLUS program package. Refinement against F^2 in an anisotropic approximation (the hydrogen atoms isotropic in the riding model) by a full matrix least-squares method for 2888 reflections was carried out to R_1 = 0.077 [for 1754 reflections with $F > 4\sigma(F)$, wR_2 = 0.244, S = 1.02]. Atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1135/28.

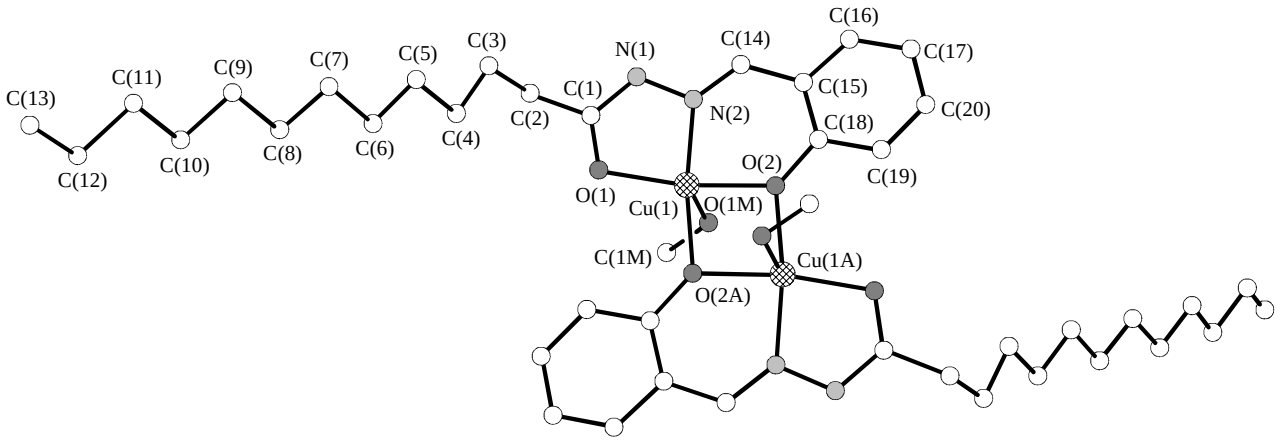


Figure 1 Structure of complex **1b′** (R^1 = H, $R^2 = C_{12}H_{25}$), ClO_4^- anions are not shown. Selected bond lengths (Å) and bond angles (°): Cu(1)–N(2) 1.918(7), Cu(1)–O(2) 1.971(5), Cu(1)–O(2A) 1.974(5), Cu(1)–O(l) 2.011(5), O(2)–Cu(1A) 1.974(5), Cu(1)–O(1M) 2.320(6), Cu(1)–Cu(1A) 2.885(8); N(2)–Cu(1)–O(2) 90.5(3), N(2)–Cu(1)–O(2A) 170.2(2), O(2)–Cu(1)–O(2A) 80.5(2), N(2)–Cu(1)–O(1) 81.1(3), O(2)–Cu(1)–O(1) 171.2(2), O(2A)–Cu(1)–O(1) 107.6(2), Cu(1)–O(2)–Cu(1A) 99.5(2).

complex (Figure 1) has confirmed this assumption; the exchange fragment **A** is strictly planar. The small displacement (0.06 Å) of the copper atom from the plane O(2), O(2A), O(1), N(2) to the O(1M) atom is possibly caused by the small differences in the Cu(1)–O (perchlorate-ion) [2.600(6) Å] and Cu(1)–O (methanol) [2.320(6) Å] bond lengths. As shown earlier the type **1b′** complexes are ionic in organic solvents so Cu(1)–O (perchlorate) coordinative bonds are not strong and the anions are out of the coordination sphere in solution. Nevertheless in contrast to other types of complexes[7] the type **1b′** complexes, according to magnetochemical data, remain dimeric in solution. All these results confirm the high stability of the complex molecules due to their high symmetry. The following brief description of complex structure confirms this.

In the crystal the molecule **1b′** (R^1 = H, $R^2 = C_{12}H_{25}$) is arranged in the centre of symmetry which is situated at the intersection of the Cu(1)–Cu(1A) and O(2)–O(2A) lines. The copper atom is six-coordinate (taking into account weak coordination of the metal with ClO_4^-). The organic ligand is almost planar. The atom deviations from the mean plane are less than 0.04 Å. The bond length values in the O=C–NH–N=C–C_{ar} fragment indicate considerable delocalization of electron density. The five-membered metallocycle is planar. The atomic deviations from the mean plane are less than 0.05 Å. The six-membered metallocycle has a flattened sofa conformation. The deviation of the Cu(1) atom from the N(2), C(14), C(15), C(18), O(2) plane is 0.18 Å. The alkyl substituent has a *trans*-conformation with regard to all C(sp^3)–C(sp^3) bonds, excluding the C(2)–C(3) bond. This substituent is directed almost orthogonally to the plane of the organic ligand. The angle between their mean planes is 110.4°. The methanol molecule is turned, with respect to the Cu(1)–O(1) bond, by –30.0(7)° [the O(1)–Cu(1)–O(1M)–C(1M) torsion angle]. Unfortunately, the position of the hydroxy group hydrogen could not be determined.

In the crystal complex molecules form infinite chains due to H-bonding H(1N)···O(25)ʃ (1 – *x*, 0.5 + *y*, 1.5 - *z*) (O···H 2.06 Å, O···H–N 163.9°).

Thus, the X-ray confirmation discussed in this paper allows one to use with great confidence the magnetic exchange parameters for binuclear copper(II) complexes based on acylhydrazones as the magnetochemical criterion of structural isomerism.

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