PHYSICAL METHODS
OF INVESTIGATION

Structure Copper(II) Complexes with *N*-Methylacetohydroxamic Acid in Crystal and Solution

A. V. Rotov, E. A. Ugolkova, N. N. Efimov, E. Kh. Lermontova, and V. V. Minin

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia
e-mail: rotov@igic.ras.ru
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Abstract—The structure of the dimeric complex $[CuL_2]_2$ (HL is *N*-methylacetohydroxamic acid) formed by two square-planar CuL_2 moieties with the *trans* coordination of the ligands has been studied by X-ray crystallography. In methylene chloride at 297 K, the complex exists as two species, which are monomeric as probed by electron paramagnetic resonance. At 80 K, the dimeric and monomeric forms are identified. The relative concentrations of paramagnetic forms and their magnetic resonance parameters have been determined from simulation of EPR spectra.

Hydroxamic acids are widely used in biology, medicine, analytical chemistry, and metallurgy. Both hydroxamic acids as such and their metal complexes can exist as different isomers and polymolecular structures [1−4]. According to X-ray diffraction, all of the known copper(II) hydroxamates CuL_2 (HL is N-substituted hydroxamic acid) in crystal are mononuclear complexes with the *trans* coordination of the ligands [5]. The structure of copper hydroxamates in solution is more diverse. EPR demonstrates that, in frozen toluene, the copper(II) complex with *N*-methylbenzoylhydroxamic acid exists as dimeric and monomeric species [6]. A combination of these two physical methods offers the opportunity to study changes in the complex structure upon dissolution of a crystalline sample. The present work is aimed at studying the structure of the copper(II) complex with *N*-methylacetohydroxamic acid in crystal and in methylene chloride by X-ray diffraction and EPR.

EXPERIMENTAL

The CuL_2 complex (**I**) (HL is *N*-methylacetohydroxamic acid) was synthesized as described in [7] with the use of the ^{63}Cu isotope. Single crystals obtained by crystallization from methylene chloride were studied on a Bruker Smart APEX II automated diffractometer at 150 K (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) using the ω scan mode. Corrections for absorption were applied from measuring the intensities of equivalent reflections [8]. The structures were solved by direct methods and refined by full-matrix anisotropic least squares calculation on F^2 for all non-hydrogen atoms (SHELXTL-Plus [9]).

All hydrogen atoms were introduced in geometrically calculated positions and refined using the riding model. Crystal data, experimental details, and refine-

Table 1. Crystal data and experimental details for compound **I**

| Empirical formula	$C_{12}H_{24}Cu_2N_4O_8$
FW	479.43
Crystal system	Monoclinic
Space group	$P2/n$
Crystal size, mm	$0.20 \times 0.10 \times 0.05$
Unit cell parameters:	
a, Å	7.715(3)
b, Å	10.670(5)
c, Å	10.833(5)
α, deg	90
β, deg	96.922(7)
γ, deg	90
V, Å^3	885.2(7)
Z	2
ρ_{calc}, g/cm^3	1.799
$\mu(MoK_\alpha)$, mm^{-1}	2.452
$F(000)$	492
θ range, deg	1.91−26.00
hkl ranges	$-9 \le h \le 9$
	$-13 \le k \le 13$
	$-13 \le l \le 13$
All reflections	5378
Unique reflections	1750
	($R_{int} = 0.0622$)
Number of variables	122
$R1$ on $I > 2\sigma(I)$	0.0417
$wR2$ (all data)	0.1143
Goodness-of-fit on F^2	1.098
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	−0.565/0.694
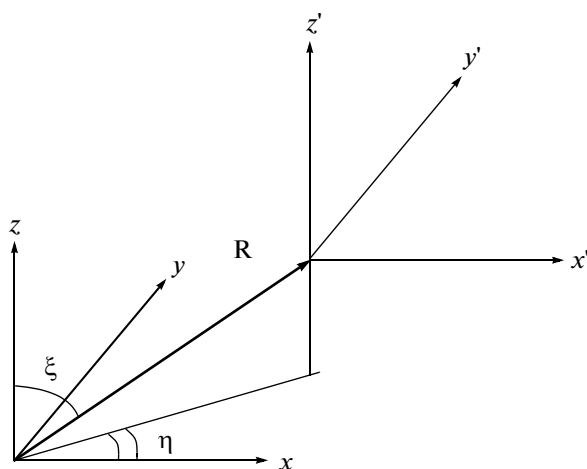
Fig. 1. Principal axes of mononuclear moieties and their mutual orientation in the dimer.

ment parameters are listed in Table 1. Selected bond lengths and angles are listed in Table 2. Structure **I** was deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1010671).

The EPR spectra were recorded on a Bruker Elexsys E680X spectrometer at a working frequency of 9.8 GHz. A solution of complex **I** in methylene chloride was cooled to $T = 80$ K with an Oxford Instrument Direct Cryospares temperature controller. The analytical form of spin Hamiltonians (SH) describing EPR spectra in solutions was reported in [3, 4, 6].

The SH parameters were determined by finding the best fit between the experimental and theoretical spectra through minimization og the error functional

$$F = \sum_i (Y_i^T - Y_i^E)^2 / N,$$

where Y_i^E is the experimental array of EPR intensity values with a constant step along field H, Y_i^T is the theoretical values at the same field H values, and N is the number of points.

Theoretical spectra were constructed as described in [10]. A sum of the Lorentzian and Gaussian functions was used as a line shape function [11].

According to the relaxation theory [12], the line width was defined as

$$\Delta H = \alpha + \beta m_I + \gamma m_I^2,$$

where m_I is the nuclear spin projection onto the magnetic field direction α, β, and γ are parameters. In the course of minimization, the following parameters were varied: relative concentrations of paramagnetic complexes, g factors, HFC constant, and line width and shape parameters for each complex. For a dimer, the following parameters were additionally varied: zero-field splitting (D) and rhombic distortion (E) parameters, the distance between point dipoles (R), the angle ξ between the radius vector connecting the metal atoms and the z axis of the local environment of the metal, and the angle η between the x axis and the projection of the radius vector connecting the metal atoms onto the xy plane (Fig. 1). The SH parameters for the monomeric complex and monomers forming a

Table 2. Selected bond lengths (d) and bond angles (ω) in structure **I**

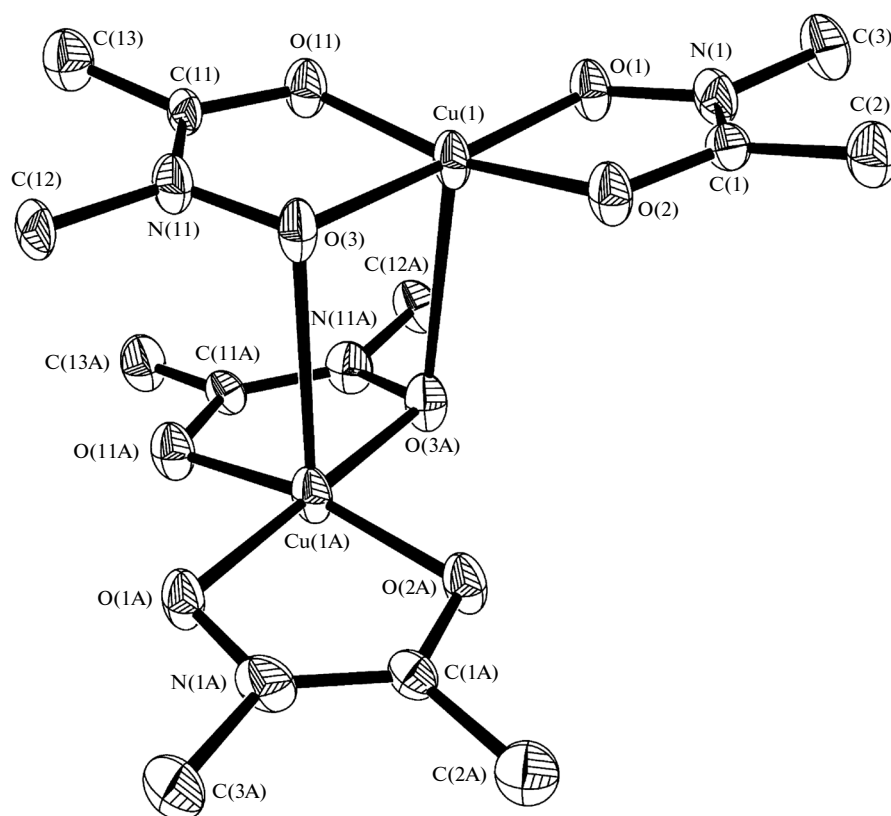| Bond	d, Å	Angle	ω, deg
Cu(1)−O(1)	1.917(3)	O(2)Cu(1)O(1)	84.23(10)
Cu(1)−O(2)	1.917(3)	O(1)Cu(1)O(11)	94.88(10)
Cu(1)−O(11)	1.918(3)	O(2)Cu(1)O(11)	166.76(13)
Cu(1)−O(3)	1.923(3)	O(1)Cu(1)O(3)	178.30(12)
Cu(1)−O(3a)	2.668(3)	Cu(1)O(3)Cu(1a)	96.412(10)
O(3)−N(11)	1.361(5)	O(11)Cu(1)O(3)	83.84(10)
O(1)−N(1)	1.349(4)	Cu(1)O(1)N(1)	108.2(4)
N(1)−C(1)	1.295(5)	Cu(1)O(11)C(11)	110.9(2)
N(11)−C(11)	1.303(5)		

Fig. 2. Molecular structure of the copper(II) dimer with *N*-methylacetohydroxamic acid.

dimer are listed in Table 3. The SH parameters corresponding to the interaction of monomeric moieties in the dimer are presented in Table 4.

RESULTS AND DISCUSSION

X-ray crystallography data demonstrate that compound **I** in crystal is a binuclear complex located on the twofold crystallographic axis (Fig. 2). The coordination polyhedron of the copper atom is a distorted tetragonal pyramid (TP). The base of this pyramid consists of by the oxygen atoms of ligands forming a planar square around the copper atom. The Cu–O

distances are roughly the same and vary within 1.917(3)−1.923(3) Å, and the OCuO angles are 88.81°−90.69°. The double oxygen bridge in the binuclear molecules of the complex is formed by the O(3) and O(3A) atoms of the ligands: in the TP of one copper atom. The O(3) atom is in the equatorial position at the base vertex with the Cu(1)−O(3) distance 1.923(3) Å, while in the TP of the inverted Cu(1A) atom, the O(3) atom is in the axial position with a substantially longer Cu(1A)−O(3) bond (2.668 Å). The copper atom is 0.221 Å out of the plane formed by three oxygen atoms (O(1), O(2), and O(11)) toward the apical oxygen. The Cu···Cu distance in the dimers

Table 3. SH parameters of the EPR spectrum of complex **I** in methylene chloride at $T = 80$ K

Complex	g_z	g_x	g_y	A	B	C	Concentration*, %
				$\times 10^{-4}$ cm^{-1}			
I, form C	2.245	2.035	2.042	187.8	11.2	41.7	35
I, form B	2.245	2.069	2.058	195.0	23.4	9.8	65

* In calculation of the concentration of complexes, it was taken into account that the dimer comprises two monomeric moieties.
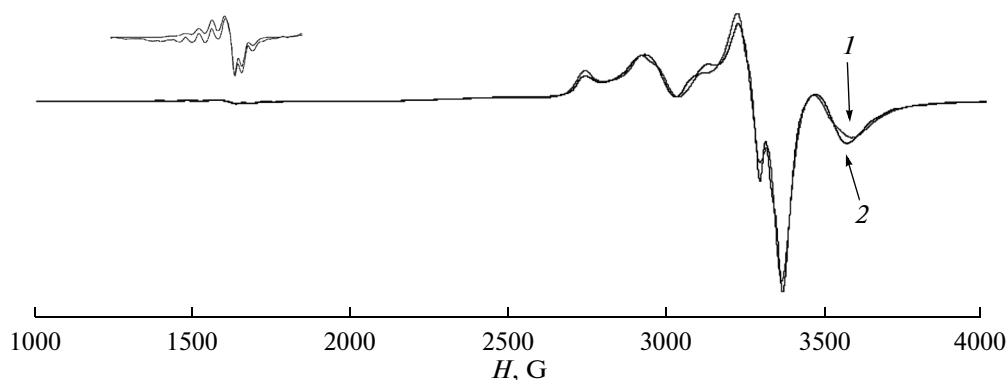
Fig. 3. EPR spectra of complex **I** at 80 K: (1) experimental spectrum and (2) theoretical spectrum with parameters reported in this work.

is 3.458 Å. It is worth noting that, according to Cambridge Crystal Database [13], most of the binuclear copper(II) complexes of the $(O)_3Cu(\mu_2\text{-}O)_2Cu(O)_3$ type are centrosymmetric, unlike compound **I**.

The EPR spectrum of compound **I** in methylene chloride at 297 K (Fig. 3) looks like a spectrum of one mononuclear copper(II) complex (a 1 : 1 : 1 : 1 quartet). Mathematical processing of experimental data showed that the spectrum is a superposition of the spectra of two mononuclear copper(II) compounds (**A** and **B**). The SH parameters for both monomeric copper(II) complexes are similar. For compound **A**, $g_A = 2.115$ and $a_A = 81.8 \times 10^{-4}$ cm^{-1}; for compound **B**, $g_B = 2.116$ and $a_B = 75.1 \times 10^{-4}$ cm^{-1}. The concentrations of compounds **A** and **B** are roughly the same. The other copper(II) complexes with N-substituted hydroxamic acids in solutions at room temperatures also exist as two species which are monomeric, according to EPR [3, 4].

The EPR spectrum of a frozen solution of compound **I** is a superposition of two copper(II) complexes (Fig. 3). The spectrum of one of them is typical of a monomeric copper(II) complex located in a diamagnetic solid matrix. The EPR spectrum of the second compound is typical of dimeric copper(II) complexes. In the low-field range of the spectrum, there is

a forbidden transition $m_s = \pm 2$ with a well-resolved seven-component hyperfine structure (FHS) due to two equivalent copper atoms. In the g range ~2, the spectrum shows two lines of a fine structure (transitions of the "perpendicular" orientation). The EPR theory for dimeric complexes with spin $S = 1$ has been well developed [14]. The spin Hamiltonian that describe the EPR spectrum of a frozen solution is a sum of Hamiltonians of two individual spectra, those of the monomer and dimer. The calculated isotropic parameters of the SH of the monomeric complex in a frozen solution $\langle g \rangle = 2.124$ and $\langle a \rangle = 76.1 \times 10^{-4}$ cm^{-1} are close to the parameters of compound **B** in a solution at room temperature. The EPR data enable the conclusion that compound **B** in a frozen solution remains monomeric, whereas compound **A** dimerizes when frozen to form species **C**. The structural parameters of this species are close to those of the dimer of copper(II) with N-methylbenzoylhydroxamic acid [6] (Table 4).

Thus, as probed by EPR, dissolution of crystalline [CuL$_2$] in methylene chloride leads to formation of two complex species. At 297 K, both complex species are monomeric. On cooling the solution to 80 K, one species remain monomeric, while the other dimerizes.

Table 4. SH parameters of EPR spectra of dimeric complexes [CuL$_2$]$_2$ (L = R$_1$N(O)−(O)CR$_2$) in frozen solutions

Complex	Solvent	R, Å	ξ, deg	η, deg	D, $\times 10^{-4}$ cm^{-1}	E, $\times 10^{-4}$ cm^{-1}	T, K
I, form C	Methylene chloride	3.50	23.0	1.7	132.0	23.1	80
[Cu(MeN(O)(O)CPh)$_2$]$_2$ [6]	Toluene	3.50	29.8	2.8	122.0	19.3	100

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