Inorganica Chimica Acta, 46 (1980) L65–L66

X-Ray, EPR and Magnetic Susceptibility Studies of the Novel Copper Glycine Polymeric Complex: $\{[Cu_2^{2+}(NH_3^+CH_2COO^-)_4]\ [Cu_2^{1+}Cl_6]\}_n$

TADEUSZ GŁOWIAK and HENRYK KOZŁOWSKI

Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

Received February 16, 1980

Introduction

Recent X-ray studies of the metal–amino acid systems revealed quite interesting coordination mode of some amino acids [1–3]. Amino acid ligand coordinates to the metal ion *via* carboxyl group and 'cupric acetate' like dimeric species are created. This kind of coordination by amino acids is quite likely if the amine group is involved for example, in peptide linkage formation on a peptide C-terminal.

In this communication we report the X-ray and magnetic data of a new polymyric copper complex formed during the reaction between $CuCl_2$ and glycine.

Experimental

The title complex was obtained during the slow evaporation of a concentrated aqueous solution containing $CuCl_2 \cdot 2H_2O$ and glycine of 1:2 molar ratio with starting pH value of about 2. The excess of glycine which crystallized simultaneously with copper complex was washed out with cold water.

Crystal Data

The crystals of $\{[Cu_2^{2+}(NH_3^+CH_2COO^-)_4]\ [Cu_2^{1+}Cl_6]\}_n$ complex (M = 711.13) are triclinic. The space group is $P\bar{1}$ with a = 8.267(2), b = 8.408(2) and c = 8.535(2) Å; α = 84.89(1), β = 100.54(1) and γ = 114.97(1)°; V = 528.7 Å^3; D_m = 2.17 g cm^{-3}, Z = 1, D_c = 2.17 g cm^{-3}; μ = 49.1 cm^{-1}.

Intensities of 2780 independent reflections were measured on a Syntex $P2_1$ diffractometer with graphite monochromated Cu-K$_\alpha$ radiation.

The structure was solved by Patterson and Fourier methods and was refined by full-matrix least-squares procedure for 2383 reflections with $I > 1.96(I)$. The final values of R_1 = 0.052 and R_2 = 0.067 were found. The selected bond distances and angles are present in Fig. 1.

EPR and Magnetic Susceptibility Data

EPR spectra were recorded on a JEOL JES-ME-3X spectrometer at K band (25 GHz). The EPR spectrum of polycrystalline sample of the title complex (Fig. 2) is typical for the triplet state systems (S = 1). The simulation of this spectrum [4] yielded $g_\parallel$ = 2.380, $g_\perp$ = 2.060 and the zero-field splitting parameter D = 0.355 cm^{-1} and $E < 0.01$ cm^{-1}.

Magnetic susceptibility of the title complex was measured by Gouy's method from liquid nitrogen up to room temperature. The temperature dependence

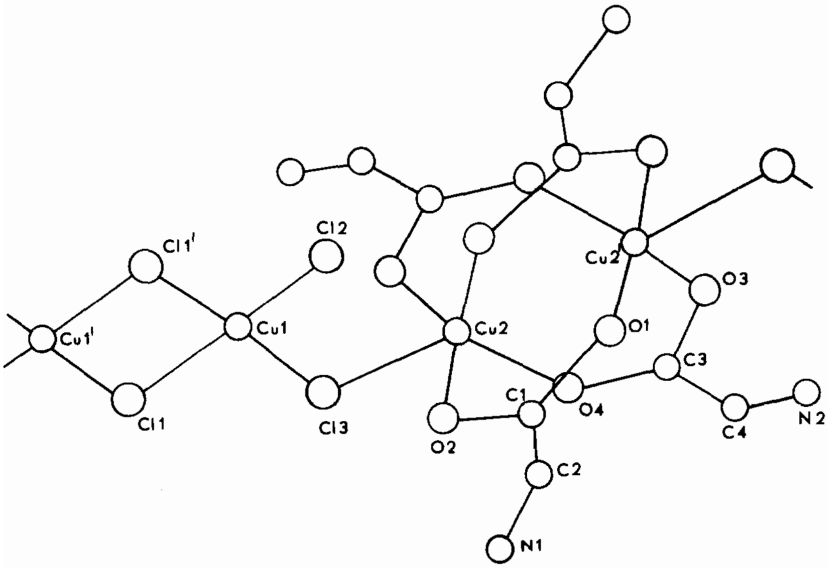

Fig. 1. The schematic representation of the structure of $\{[Cu_2^{2+}(NH_3^+CH_2COO^-)_4] \cdot [Cu_2^{1+}Cl_6]\}$ complex unit. The interatomic distances are: Cu(1)–Cu(1') 2.900(2), Cu(2)–Cu(2') 2.708(1), Cu(1)–Cl(1) 2.419(2), Cu(1)–Cl(1') 2.413(2), Cu(1)–Cl(3) 2.366(2), Cu(1)–Cl(3) 2.316(2), Cu(2)–Cl(3) 2.442(2), mean value for Cu(2)–O 1.978(4).

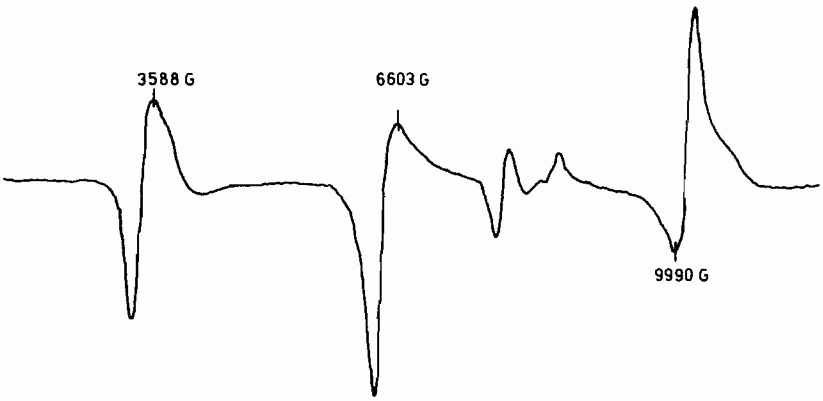

Fig. 2. EPR spectrum of the polymeric $\{[Cu_2^{2+}(NH_3^+CH_2COO^-)_4]\cdot[Cu_2^{1+}Cl_6]\}$ complex at 24.6 GHz and 295 K. Magnetic field was measured with MJ 110-R NMR marker and some points are given on the spectrum.

of the magnetic susceptibility showed that in the studied system there are antiferromagnetically coupled cupric ions in the dimeric species with the exchange integral $-2J = 385\ cm^{-1}$.

Discussion

X-ray, EPR and magnetic susceptibility data show that the title polymeric complex is composed of two centrosymmetric dimeric subunits containing the couple of the tetrahedral cuprous and the couple of the tetragonal cupric ions *i.e.* $[Cu_2^{1+}Cl_6]^{4-}$ and $[Cu_2^{2+}(Hgly)_4]^{4+}$, respectively. Both subunits are bound to each other through the chloride bridge (Fig. 1).

The cupric dimeric subunit contains four zwitterionic glycine molecules bound with the metal ion *via* carboxyl groups in the same mode as found in Cu^{2+} carboxylates [5]. The structural and the magnetic data are also analogous to those found in the dimeric carboxylates [5].

The Cu^{2+}–Cu^{2+} distance 2.708 Å, and the exchange integral $-2J = 385$ are both of larger values than those found for acetates (2.61–2.64 Å and 280–320 cm^{-1} [5]). These differences derive from the presence of an electrophylic NH_3^+ group in the bridging glycine molecules. The Cu^{2+}–Cu^{2+} distance of the title complex is also larger than that found in tetra-μ-N-acetyl-glycinatodiaquodicopper [3] (2.666 Å). These results clearly indicate the considerable sensitivity of the structural and magnetic features of a 'cupric acetate' like dimeric unit on the modification of a carboxylate bridge on the methyl group.

The quite unusual find in the studied system is the presence of the cuprous subunit. The formation of this tetragonal couple of Cu^{1+} ions is not clear and additional studies are now in progress.

Acknowledgements

Authors wish to thank Dr. J. Baranowski for help in the simulation of the EPR spectra and the Polish Academy of Sciences for financial support (the MR.I. 9 problem).

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