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Crystal and Molecular Structure, Magnetic and Spectral Properties of Triaquabis(quinoxaline)copper(II) Perchlorate

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Abstract

The crystal and molecular structure of triaquabis(quinoxaline)copper(II) perchlorate, $[Cu(C_8N_2H_6)_2(H_2O_3)](ClO_4)_2$, was determined by direct and Fourier methods. The compound crystallized in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 8.263(2)$, $b = 17.259(7)$, $c = 15.307(5)$ Å, $\beta = 90.07(2)°$ and $Z = 4$. The densities were $D_m = 1.763(3)$ and $D_x = 1.76$ g cm^{-3}. The molecular structure of the title compound consists of a cation $[Cu(C_8N_2H_6)_2(H_2O)_3]^{2+}$, where the copper atom is coordinated to two nitrogen atoms of the quinoxaline molecules and to three oxygen atoms of the water molecules. The coordination polyhedron about the copper atom is a trigonal bipyramid, the oxygen atoms forming the basal plane and the nitrogen atoms occupying the apical positions. The water molecules are involved in hydrogen bonding to perchlorate anions and to two uncoordinated nitrogen atoms of the quinoxaline ligands. The magnetic, infrared and reflectance spectral data are compared with those found for other copper quinoxaline complexes.

Introduction

Quinoxaline is a heterocyclic amine with chemical and physical properties near pyrazine and therefore forms complexes with many transition metals [1]; the complexes with copper being especially numerous [2]. The copper complexes of quinoxaline are normally of the type $Cu(Q)X_2$, where Q = quinoxaline and X = anion (halide, nitrate, sulphate etc.). The molecular structures of these compounds have not so far been determined, but it has been proposed that in many cases these complexes would be polymeric corresponding to pyrazine copper complexes. Recently [2e, f] we determined the crystal structure of *catena*-μ-perchlorato(O,O')-tris-μ-quinoxaline(N,N')dicopper(I) perchlorate, which is polymeric. In this paper we report the crystal and molecular structure of triaquabis(quinoxaline)copper(II) perchlorate, $[Cu(C_8N_2H_6)_2(H_2O)_3](ClO_4)_2$, with some magnetic and spectral properties compared with previously published data.

Experimental

Preparation and Analyses of the Compound

Triaquabis(quinoxaline)copper(II) perchlorate was prepared by adding an ethylacetate solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith Chem. Co.) to an ethylacetate solution of quinoxaline (Fluka, purum) in a 1:2 molar ratio. After stirring for 2 h the mixture was allowed to stand for several days. The separated dark green crystals were filtered and washed with ethylacetate. Recrystallization of the complex was unsuccessful because of the easy reduction of copper to oxidation state I. The other reagents used in this synthesis were of analytical grade. Copper and perchlorate contents were determined by conventional methods. *Anal.* Found: Cu, 11.01; ClO_4^-, 33.64. Calc. for $C_{16}N_4H_{18}O_{11}Cl_2Cu$: Cu, 11.02; ClO_4^-, 34.48%.

Crystal and Molecular Structure Determination

The crystal and intensity data were collected using a crystal of dimensions 0.2 × 0.2 × 0.3 mm on a Nicolet P3F diffractometer with monochromated Mo Kα radiation. Unit cell parameters were determined from 24 centered reflections and the space group $P2_1/c$ (No. 14) on the basis of systematic absences ($h0l$:$l = 2n + 1$, $0k0$:$k = 2n + 1$, $00l$:$l = 2n + 1$). Crystal data of the compound are presented in Table I. The intensity measurements were carried out at room temperature with the ω/θ scan technique; the scan rate varied from 2 to 29.3° min^{-1} depending on the number of counts measured in a fast preliminary scan through the peak. Data were corrected for Lorentz and polarization effects and also for absorption through the φ scan technique. Corrections for extinction effects were considered unnecessary. The intensities of three standard reflections (−1, −1, 3; −1, 4 − 3; −2, −3, 4) monitored after every 50th measurement showed no significant variation. Altogether 5536 reflexes were

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TABLE I. Crystal Data of the Complex $[Cu(C_8N_2H_6)_2(H_2O)_3](ClO_4)_2$

Monoclinic	$M = 576.79$
Space group $P2_1/c$ (No. 14)	$Z = 4$
$a = 8.263(2)$ Å	$D_m = 1.763(3)$ g cm^{-3}
$b = 17.259(7)$ Å	$D_x = 1.76$
$c = 15.307(5)$ Å	$V = 2183(1)$ Å^3
$\beta = 90.07(2)°$	$F(000) = 1172$
λ(Mo Kα) = 0.71069 Å	$T = 295$ K
μ(Mo Kα) = 13.5 cm^{-1}	

collected from $2\theta = 3.0$ to $55°$ ($0 \leqslant h \leqslant 11$; $0 \leqslant k \leqslant 23$; $-20 \leqslant l \leqslant 20$). From these 5013 were considered as unique and 3207 as observed ($F_o \geqslant 3\sigma(F_o)$), and from which 3182 were used in full-matrix refinement.

The structure was solved by direct and Fourier methods using the programs MULTAN 80 [3] and XTAL 83 [4]. Full-matrix least-squares refinement with non-hydrogen atoms as unisotropic and H atoms with fixed temperature factor $U = 0.05$ Å^2 (361 variables) converged to $R = \Sigma||F_o| - |F_c||/|F_o| = 0.069$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.073$, where $w = 1$. After the last cycle the average shift/e.s.d. was 0.02241 and the maximum shift/e.s.d. 0.4277 (H(2), z). Further cycles with H atom coordinates fixed (307 variables) gave the same R values, but the average Δ/σ was 0.0009859 and maximum $\Delta/\sigma = 0.01443$. The maximum and minimum peaks in the final difference Fourier map were 0.70 (near Cu) and -0.67 e Å^{-3} (near Cl(2)), respectively. Scattering factors were from Cromer and Mann [5] and the anomalous dispersion corrections from International Tables for X-ray Crystallography [6]. The most important planes were calculated by the program MPLN [7]. All calculations were carried out on UNIVAC 1100/61 E1 and VAX 8600 computers.

Physical Measurements

The infrared spectrum of the complex was recorded on a Perkin-Elmer Grating Infrared Spectrophotometer Model 577 using KBr disks (c. 10:200 mg).

The reflectance spectra were recorded on a Beckman DK-2A spectrophotometer using paraffin oil paste of the complex on a filter paper.

The magnetic susceptibilities of the title compound were measured in the temperature range 93.2–303.2 K on a Newport variable temperature Gouy balance. Copper(II) sulphate pentahydrate was used for calibration [8]. The calculated diamagnetic correction was -278.76×10^{-6} e.m.u. [9]. The results are mean values from measurements at four magnetic field strengths.

Density of the crystals was determined by the flotation method in CH_3I–toluene.

Results and Discussion

Description of the Structure

The atomic coordinates and the equivalent values of the isotropic temperature factors for non-hydrogen atoms are listed in Table II. The bond lengths and angles of the asymmetric unit (molecule) are listed in Table III. An ORTEP drawing [10] of the complex cation is presented in Fig. 1. Packing of the molecules in the unit cell and possible hydrogen bonding are seen in a stereoscopic PLUTO drawing [11] in Fig. 2.

The asymmetric unit of the title complex consists of a discrete cation $[Cu(C_8N_2H_6)_2(H_2O)_3]^{2+}$ and two uncoordinated perchlorate anions (Figs. 1 and 2). The copper atom is pentacoordinated to two quinoxaline molecules at N(1) and N(3) and to three water

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Values of the Isotropic Temperature Factor Coefficients ($\times 10^4$) of Non-hydrogen Atoms[a]

Atom	x	y	z	U_{eq} (Å^2)[b]
Cu	5749(1)	9193(1)	2337(1)	293(2)
Cl(1)	7355(3)	5944(2)	252(2)	623(6)
Cl(2)	5452(2)	1659(1)	1385(1)	444(4)
O(1)	4528(5)	9715(3)	1408(3)	401(12)
O(2)	6959(6)	8364(3)	2910(4)	503(15)
O(3)	5661(7)	10125(4)	3311(4)	585(16)
O(4)	5746(10)	5856(6)	6(6)	1165(32)
O(5)	8156(10)	6525(5)	−177(5)	934(24)
O(6)	7408(18)	5954(10)	1117(6)	2008(63)
O(7)	8052(21)	5265(9)	−18(14)	2572(84)
O(8)	6975(9)	1613(6)	1802(5)	1020(26)
O(9)	5378(7)	1094(3)	687(3)	460(13)
O(10)	5114(11)	2388(4)	1053(5)	909(27)
O(11)	4228(9)	1476(5)	2010(5)	896(24)
N(1)	3624(7)	8683(3)	2686(4)	335(13)
N(2)	378(7)	8267(4)	2982(4)	432(16)
N(3)	7923(6)	9601(3)	1875(4)	320(13)
N(4)	11193(6)	9874(4)	1524(4)	393(15)
C(1)	2798(9)	8953(4)	3359(5)	403(17)
C(2)	1174(9)	8733(5)	3502(5)	453(19)
C(3)	1231(8)	7930(4)	2320(5)	405(17)
C(4)	499(9)	7364(5)	1768(6)	542(22)
C(5)	1373(11)	7025(6)	1137(6)	581(23)
C(6)	2981(11)	7216(5)	986(5)	538(21)
C(7)	3748(9)	7761(5)	1495(5)	454(18)
C(8)	2885(8)	8130(4)	2171(5)	348(15)
C(9)	8792(8)	10079(5)	2345(5)	407(17)
C(10)	10448(9)	10218(5)	2160(6)	445(20)
C(11)	10306(8)	9407(4)	984(5)	343(15)
C(12)	11049(9)	9034(5)	277(5)	478(19)
C(13)	10152(11)	8571(6)	−251(6)	564(22)
C(14)	8501(10)	8450(5)	−91(5)	488(20)
C(15)	7759(8)	8792(5)	588(5)	395(17)
C(16)	8625(7)	9277(4)	1155(4)	301(14)

[a] e.s.d.s given in parentheses. [b] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$ [15].

TABLE III. Bond Distances (Å) and Angles (°)[a]

(a) The coordination sphere of copper			
Cu–N(1)	2.036(6)	N(1)–Cu–O(3)	96.3(3)
Cu–N(3)	2.055(5)	N(3)–Cu–O(1)	92.4(2)
Cu–O(1)	1.961(5)	N(3)–Cu–O(2)	87.6(2)
Cu–O(2)	1.954(6)	N(3)–Cu–O(3)	90.7(2)
Cu–O(3)	2.194(6)	O(1)–Cu–O(2)	157.6(2)
N(1)–Cu–N(3)	173.0(2)	O(1)–Cu–O(3)	98.0(2)
N(1)–Cu–O(1)	86.9(2)	O(2)–Cu–O(3)	104.4(2)
N(1)–Cu–O(2)	90.3(2)		
(b) The quinoxaline molecules			
N(1)–C(1)	1.321(10)	C(1)–C(2)–N(2)	123.3(7)
C(1)–C(2)	1.411(10)	C(2)–N(2)–C(3)	117.0(6)
C(2)–N(2)	1.308(10)	N(2)–C(3)–C(4)	120.8(6)
N(2)–C(3)	1.365(10)	N(2)–C(3)–C(8)	120.7(7)
C(3)–C(4)	1.426(12)	C(8)–C(3)–C(4)	118.5(7)
C(3)–C(8)	1.428(10)	C(3)–C(4)–C(5)	119.8(7)
C(4)–C(5)	1.340(13)	C(4)–C(5)–C(6)	122.2(9)
C(5)–C(6)	1.389(13)	C(5)–C(6)–C(7)	120.6(8)
C(6)–C(7)	1.375(12)	C(6)–C(7)–C(8)	119.4(7)
C(7)–C(8)	1.409(11)	C(7)–C(8)–N(1)	120.6(6)
C(8)–N(1)	1.381(9)	C(7)–C(8)–C(3)	119.5(7)
C(1)–N(1)–C(8)	117.4(6)	C(3)–C(8)–N(1)	119.9(6)
N(1)–C(1)–C(2)	121.2(7)		
N(3)–C(9)	1.309(9)	C(9)–C(10)–N(4)	122.1(7)
C(9)–C(10)	1.418(10)	C(10)–N(4)–C(11)	118.0(6)
C(10)–N(4)	1.297(10)	N(4)–C(11)–C(12)	120.2(6)
N(4)–C(11)	1.367(9)	N(4)–C(11)–C(16)	120.1(6)
C(11)–C(12)	1.401(11)	C(16)–C(11)–C(12)	119.7(6)
C(11)–C(16)	1.432(9)	C(11)–C(12)–C(13)	119.4(7)
C(12)–C(13)	1.356(12)	C(12)–C(13)–C(14)	121.0(8)
C(13)–C(14)	1.402(13)	C(13)–C(14)–C(15)	121.0(8)
C(14)–C(15)	1.344(11)	C(14)–C(15)–C(16)	120.5(7)
C(15)–C(16)	1.402(10)	C(15)–C(16)–N(3)	121.8(6)
C(16)–N(3)	1.365(9)	C(15)–C(16)–C(11)	118.4(6)
C(9)–N(3)–C(16)	117.9(6)	C(11)–C(16)–N(3)	119.8(6)
N(3)–C(9)–C(10)	121.7(7)		
(c) The perchlorate ions			
Cl(1)–O(4)	1.389(8)	O(4)–Cl(1)–O(6)	107.7(8)
Cl(1)–O(5)	1.370(9)	O(4)–Cl(1)–O(7)	103.1(9)
Cl(1)–O(6)	1.325(10)	O(5)–Cl(1)–O(6)	117.0(8)
Cl(1)–O(7)	1.369(16)	O(5)–Cl(1)–O(7)	106.1(8)
O(4)–Cl(1)–O(5)	114.4(6)	O(6)–Cl(1)–O(7)	107(1)
Cl(2)–O(8)	1.412(8)	O(8)–Cl(2)–O(10)	113.3(5)
Cl(2)–O(9)	1.447(6)	O(8)–Cl(2)–O(11)	108.5(5)
Cl(2)–O(10)	1.386(8)	O(9)–Cl(2)–O(10)	109.4(4)
Cl(2)–O(11)	1.428(8)	O(9)–Cl(2)–O(11)	108.4(4)
O(8)–Cl(2)–O(9)	109.4(4)	O(10)–Cl(2)–O(11)	107.7(5)

[a] e.s.d.s given in parentheses.

molecules at O(1), O(2) and O(3) (Table III). The coordination sphere around the central copper atom is a slightly distorted trigonal bipyramid, where the three oxygen atoms form the basal plane within experimental errors (Table IV). The two nitrogen atoms form the tops of the bipyramid. The Cu–N(1) and Cu–N(3) distances are 2.036(6) and 2.055(5) Å, respectively. The angle N(1)–Cu–N(3) is 173.0(2)° and the angles O–Cu–N are all near 90°. However, the basal triangle is not equiangular, because the angles O–Cu–O are 98.0(2), 104.4(2) and 157.6(2)° (Table III). This deviation is due to steric hindrance caused by the quinoxaline molecules, which are in *cis* conformation to each other (Fig. 1). The axial and equatorial bond lengths are in the region commonly reported for these dimensions. Two water molecules are strongly hydrogen bonded to the oxygen atoms of perchlorate ions (O(1)...O(9) = 2.717(7) and O(2)...O(10^i) = 2.880(10) Å) and to the uncoordinated nitrogen atoms of the quinoxaline ligands ((O(1)...N(4) = 2.775(7) and O(2)...N(2) = 2.832(7) Å) (Table V.) The third water molecule is more weakly bonded to other perchlorate ions (O(3^i)...O(4^{ii}) = 3.098(12) and O(3)...O(6^i) = 3.042(16) Å) (Fig. 2).

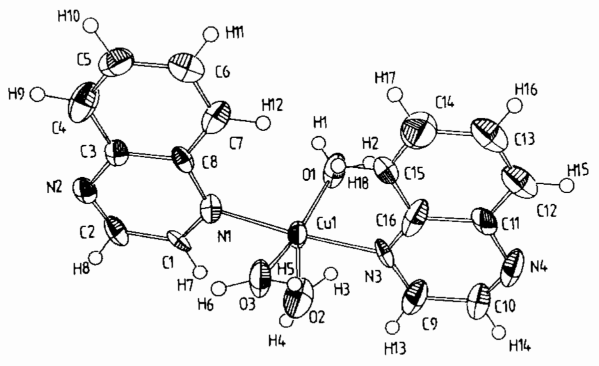

Fig. 1. An ORTEP drawing showing the environment of the central metal atom. Thermal ellipsoids with 50% probability.

The quinoxaline molecules are nearly planar, since the maximum deviations of the atoms within the planes are −0.061(8) and 0.057(6) Å (Table IV). The two quinoxaline ligands are also nearly coplanar, because the angle between the planes ((1) and (2)) is 5(1)° and the angles with the basal plane ((3)) are 75.6(2) and 72.5(2)°, respectively. The bond lengths and angles of the quinoxaline rings are comparable with the earlier calculations [12] and measurements [13].

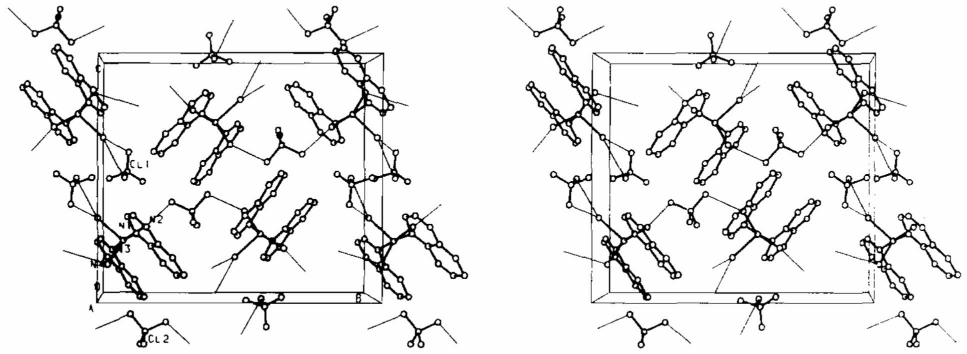

Fig. 2. Stereoscopic PLUTO drawing showing molecular packing and possible hydrogen bonding.

TABLE IV. Analyses of the most Significant Planes with Displacements of each Atom[a]

Plane (1): $0.8528(9)x + 0.375(2)y - 0.364(2)z = 8.69(4)$
Cu 0.003(1), O(1) −0.001(5), O(2) −0.001(6), O(3) −0.000(6)
Plane (2): $-0.292(2)x + 0.730(1)y - 0.618(1)z = 7.47(2)$
N(1) 0.057(6), N(2) 0.036(7), C(1) −0.041(8), C(2) −0.061(8), C(3) 0.032(7), C(4) 0.016(9), C(5) −0.025(9), C(6) −0.030(9), C(7) −0.009(8), C(8) 0.026(7)
Plane (3): $-0.237(2)x + 0.782(1)y - 0.576(1)z = 9.81(2)$
N(3) −0.052(6), N(4) −0.014(7), C(9) 0.009(8), C(10) 0.036(8), C(11) 0.005(7), C(12) −0.020(8), C(13) −0.005(9), C(14) 0.014(8), C(15) 0.022(8), C(16) 0.007(6)

[a] x, y, z are the fractional coordinates in direct space. e.s.d.s given in parentheses.

TABLE V. Distances (Å) and Angles (°) in Interactions of the Type D–H...A

D	H	A	D–H	D...A	H...A	D–H...A
O(1)	H(1)	N(4)	0.871(5)	2.775(7)	1.989(5)	149.6(4)
O(1)	H(2)	O(9)	0.580(5)	2.717(7)	2.155(5)	163.5(5)
O(2)	H(3)	N(2)	0.938(5)	2.832(7)	1.914(6)	165.8(4)
O(2)	H(4)	O(10^i)	0.651(5)	2.880(10)	2.239(8)	168.9(6)
O(3^i)	H(5^i)	O(4^{ii})	0.714(6)	3.098(12)	2.395(10)	168.4(6)
O(3)	H(6)	O(6^i)	0.675(6)	3.042(16)	2.426(14)	152.7(6)

i: $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; ii: $-x, -y, -z$.

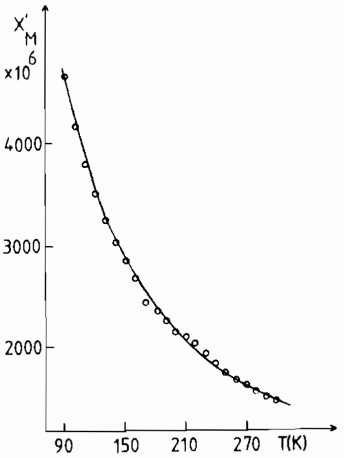

Fig. 3. Temperature dependence of the molar magnetic susceptibility of the complex. The solid curve represents susceptibilities calculated from the Curie–Weiss equation.

The average bond distances and angles of the two perchlorate anions are Cl(1)–O = 1.363, Cl(2)–O = 1.418 Å, O–Cl(1)–O = 109.2 and O–Cl(2)–O = 109.5° (Table III). The differences between bond lengths and angles are due to packing and hydrogen bonding.

Magnetic and Spectral Properties

The paramagnetic susceptibilities of the complex in the temperature interval 93.2–303.2 K are shown in Fig. 3. The least-squares calculations based on the experimental susceptibility values gave for the Curie–Weiss law the equation $\chi'_M = 0.4066/(T - 2.57) + 1.362 \times 10^{-4}$. The magnetic moment μ_{eff} of the complex is 1.89(2) BM at 20 °C ($\mu_{eff} = 2.828(\chi'_M \times T)^{1/2}$). This value lies in the region 1.74–1.99 BM found for other copper(II) quinoxaline complexes [2a]. The spin-only value of μ_{eff} is 1.73 BM for Cu^{2+}, therefore the value 1.89 BM implies a certain amount of orbital contribution.

The reflectance spectrum of the title complex has a broad band at 14815 cm^{-1} (675 nm) due to d–d transition (e' or $e'' \rightarrow a'_1$ of Cu(II)) and a sharp rise of the intensity of absorption above 20000 cm^{-1} (500 nm). The reflectance spectrum of this complex resembles that of dichlorobis(methylquinoxaline)-copper(II), where methylquinoxaline ligands were also proposed to be unidentate [2c]. The bands of quinoxaline are shown at 31545 cm^{-1} (317 nm) and 42918 cm^{-1} (233 nm).

The IR spectrum of triaquabis(quinoxaline)-copper(II) perchlorate shows the following main bands: 1505m, 1465w, 1355m, 1210m, 1140–1060vs,br, 970w, 940w, 873s, 780w, 750vs, 630vs, 540w, 460w, 430m, 420m, and 400sh. The strong, broad band at 1140–1060 cm^{-1} (1140, 1110, 1090 cm^{-1}) is due to ionic perchlorate and is assigned to ν(Cl–O stretching vibrations. The other bands correspond to those of quinoxaline, but appear as shifted and weakened. The very sharp single peaks at 940 and 750 cm^{-1} may characterize monodentate quinoxaline [14]. The two quinoxaline peaks at 604 cm^{-1} (in plane deformation) and at 405 cm^{-1} (out of plane deformation) are shifted to higher frequencies, the former to 630 cm^{-1} and the latter as splitted to 430 and 420 cm^{-1}.

Supplementary Material

Lists of the anisotropic temperature factors; fractional atomic coordinates, bond lengths and angles of H atoms; observed and calculated structure factors, and magnetic data are available from the authors on request.

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