Isomeric forms of Cu(quinoline-2-carboxylate)$_2$·H$_2$O
Spectroscopic and magnetic properties

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Spectroscopic and magnetic data for the compound Cu(2-qic)$_2$·H$_2$O (1), where 2-qic is quinoline-2-carboxylate, were studied in the light of its known X-ray structure. The geometry of the CuN$_2$O$_3$ chromophore shows a very distorted five-coordinated structure, intermediate between tetragonal pyramid and trigonal bipyramid, resulting from the didentate N,O-bonded two chelate ligands and one water molecule. The crystal structure is stabilized by an extended hydrogen-bonding network. Magnetic data reflect the molecular character of the compound with a very weak exchange interaction ($zJ' = -0.23$ cm$^{-1}$) transmitted through H-bonds. The physico-chemical properties of 1 are compared with those of recently reported isomeric forms of identical stoichiometries, namely Cu(quinoline-2-carboxylate)$_2$·H$_2$O, obtained in an unusual oxidative P-dealkylation reaction. The compound 1 was prepared directly from quinaldinic acid.

Key words: copper(II) complexes; quinolinecarboxylate; isomerism; magnetism

1. Introduction

The coordination chemistry of transition-metal complexes containing carboxylates is interesting from the structural and magnetic point of view. Copper(II) carboxylates have been the subject of numerous investigations, especially with nitrogen donor ligands [1, 2]. The literature on complexes of metal(II) with quinoline-2-carboxylate is rather scarce, in fact only some X-ray structures have been reported [3–8]. Their crystal structure shows an N,O-chelating behaviour of the quinoline-2-carboxylate ion. In a recent publication [9], the spectroscopic and magnetic properties of two differently synthesized forms – green (2) and blue-green (3) quinoline-2-carboxylates with the same formula Cu(2-qca)$_2$·H$_2$O (ligand abbreviated as 2-qca) were presented. Both of these complexes are five-coordinated, involve the same CuN$_2$O$_3$ chromophore, and are examples of distortion isomers. It is interesting from the synthetic and

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structural point of view that both forms of Cu(2-qca)$_2$·H$_2$O (2 and 3) have been obtained in an unusual oxidative P-dealkylation reaction [9]. Figure 1 shows the conversion of the starting 2-qmpe to the 2-qca ligand, where 2-qmpe is diethyl 2-quinolylmethylphosphonate ligand.

Fig. 1. A schematic drawing of the starting 2-qmpe converted to 2-qca ligand in oxidative P-dealkylation reaction of the 2-qmpe [9]

Unfortunately, we have not succeeded in preparing crystals suitable for X-ray studies for neither compound 2 nor 3. Therefore, here we describe the results of spectroscopic and magnetic measurements of Cu(quinoline-2-carboxylate)$_2$·H$_2$O (1), obtained directly from quinaldinic acid of known X-ray structure [3]. The crystal structure of 1, on the basis of the known structural data, is presented in relation to the spectral and magnetic properties. The physico-chemical properties of the 1, 2, and 3 forms of Cu(quinoline-2-carboxylate)$_2$·H$_2$O are compared.

2. Experimental

Synthesis of the complex(1): The starting materials and solvents for synthesis were obtained commercially and used as received. Cu(2-qic)$_2$·H$_2$O was prepared according to the procedure described earlier [3]. Note that, although no problem was encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care. Elemental analysis calculated for [C$_{20}$H$_{14}$CuN$_2$O$_5$]: C, 56.40; H, 3.32; N, 6.58; Cu, 14.92, Found: C, 56.85; H, 3.30; N, 6.34; Cu, 14.53 wt. %.

Physical techniques. Metal content was determined using a Carl Zeiss Jena atomic absorption spectrophotometer, elemental analyses were carried out using a Perkin-Elmer elemental analyser 2400CHN, and solid-state electronic spectra (28 000–4000 cm$^{-1}$) on a Cary 500 spectrophotometer. Solid-state EPR spectra were recorded at room temperature and at 77K on a Bruker ESP 300E spectrometer operating at X-band, equipped with a Bruker NMR gauss meter ER 0.35 M and a Hewlett Packard microwave frequency counter HP 5350B. Magnetic susceptibility measurements were carried out with a Quantum Design SQUID magnetometer (type MPMSXL-5). Measurements were recorded at a magnetic field of 0.5 T in the temperature range
Isomeric forms of Cu(quinoline-2-carboxylate)$_2$⋅H$_2$O

1.8–300 K. Corrections are based on subtracting the sample holder signal and estimating the contribution $\chi_0$ from the Pascal constants [10]. The effective magnetic moment was calculated from $\mu_{\text{eff}} = 2.83(\chi M T)^{1/2}$ using a temperature-independent paramagnetism of $60 \times 10^{-6}$ cm$^3$·mol$^{-1}$ for Cu(II) ions [11].

3. Results and discussion

The molecular structure of Cu(2-qic)$_2$⋅H$_2$O (1), described elsewhere [3], is shown in Fig. 2. The quinaldinate ion acts as a didentate ligand bonded through a pyridyl nitrogen and carboxylate oxygen atoms to form a complex involving a five-member stable chelating ring. Water molecule occupies the fifth position. This compound is mononuclear with its coordination geometry around the copper(II) ion five-coordinated, with a configuration intermediate between a trigonal bipyramid and a square-based pyramid. This is consistent with calculations of the degree of distortion for coordination polyhedra, which give a structural index $\tau = 0.44$ ($\tau$ distinguishes between square-pyramidal and trigonal-bipyramidal geometries, defined as $\tau = (\beta - \alpha)/60$, where $\alpha = 140.3(1)0$: O(1)–Cu(1)–O(2) and $\beta = 168.2(1)0$: N(1)–Cu(1)–N(2) are the largest coordination angles [12]).

Fig. 2. Molecular structure of Cu(2-qic)$_2$⋅H$_2$O (1) with the atomic numbering [3]

An interesting feature of the crystal structure, not presented earlier, results from the fact that water molecules appear to be involved in two particularly short intermolecular hydrogen bonds with two non-coordinated carboxylic oxygen atoms of a neighbouring molecule (O–H...O: 1.60(5) and 1.80(5) Å), which enhances the crystal-packing stability (Table 1). This gives rise to a two-dimensional (2D) polymer sheet hydrogen-bonded lattice (Fig. 3) with two different Cu...Cu distances: 7.628(3) [x, y – 1, z] and 7.756(2) Å [x – 1, y, z] (Fig. 2). Additionally, the crystal lattice is stabilized by inter- and intramolecular (C–H...O) hydrogen bonds (Table 1).
### Table 1. Hydrogen bonds for Cu(2-qic)$_2$.H$_2$O (1)

<table>
<thead>
<tr>
<th>D–H...A</th>
<th>d [Å]</th>
<th>Angle DHA [deg]</th>
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<tr>
<td>D–H</td>
<td>H...A</td>
<td>D...A</td>
</tr>
<tr>
<td>1 O(5)–H(1)...O(4)$^i$</td>
<td>1.05(5)</td>
<td>1.60(5)</td>
</tr>
<tr>
<td>2 O(5)–H(2)...O(3)$^{ii}$</td>
<td>0.93(5)</td>
<td>1.80(6)</td>
</tr>
<tr>
<td>3 C(4)–H(4)...O(3)$^{iii}$</td>
<td>1.00(6)</td>
<td>2.48(6)</td>
</tr>
<tr>
<td>4 Intra C(9)–H(8)...O(2)</td>
<td>0.99(6)</td>
<td>2.57(5)</td>
</tr>
<tr>
<td>5 Intra C(19)–H(14)...O(1)</td>
<td>1.00(5)</td>
<td>2.45(6)</td>
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Symmetry transformations used to generate equivalent atoms: $[i] = 1 – x, –1/2 + y, 1/2 – z; [ii] = –1 + x, y, z; [iii] = x, 1 + y, z.$

The infrared spectrum of 1 shows strong carboxylate stretching frequencies, $\nu_\text{as}(\text{COO})$ at 1635 and $\nu_\text{s}(\text{COO})$ at 1377 cm$^{-1}$, in the range characteristic of copper(II) carboxylate compounds. Separation values ($\Delta \nu$) of 260 cm$^{-1}$ for $\nu(\text{COO}^-)$ bands indicate that the coordination of the carboxylate group is monodentate [13, 14].

The distortion of the CuN$_2$O$_3$ chromophore causes the appearance of an asymmetric band in d-d reflectance spectra, with a maximum at 13 890 cm$^{-1}$. There is also evidence of a weak, poorly resolved shoulder on the low-frequency side with almost comparable intensity at about 10 200 cm$^{-1}$, which is consistent with the stereochemistries between the tetragonal pyramid and trigonal bipyramid. This splitting indicates a very distorted structure, and these bands can be assigned to the $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{y^2} \rightarrow d_{x^2-y^2}$ transitions on the basis of the information reported by Hathaway et al. [15]. A strong bonding of the $\nu(\text{OH})$ stretching region, observed at 3294 cm$^{-1}$, is in good agreement with polymeric intermolecular O–H...O association [16], confirmed by the X-ray crystal structure.

The X-band EPR spectra of polycrystalline solids at room temperature and at 77 K exhibit only one isotropic line, with a small deformation for the $g$ value of approximately 2.10. This phenomenon may be due to the exchange coupling and a misalignment of the molecular axes of different molecules in the unit cell [15], and does not allow for conclusions about the geometry.

In view of the structural data, one should expect that exchange interactions occur between copper ions through a strong hydrogen bond system. Therefore, here we describe the results of magnetic measurements on this compound in the temperature range of 1.8–300 K and analyse the data in order to obtain the precise magnitude of the exchange interaction energy between copper(II) ions from susceptibility measurements at low temperatures.

Magnetic susceptibility results for the polycrystalline sample show that the magnetic moment is close to the normal value for an uncoupled copper(II) system, which may suggest the absence of spin exchange, however the values of $\chi_{\text{Cu}}T$ (Fig. 4) slightly decrease with temperature. They are 0.413 cm$^3$-K·mol$^{-1}$ ($\mu_{\text{eff}} = 1.82 \mu_B$) at 300 K and 0.384 cm$^3$-K·mol$^{-1}$ ($\mu_{\text{eff}} = 1.75 \mu_B$) at 4.2 K. The magnetic susceptibility data obey the Curie
Isomeric forms of Cu(quinoline-2-carboxylate)$_2$·H$_2$O

- Weiss law within the measured temperature region, with $C = 0.42$ cm$^3$·K·mol$^{-1}$ and $\theta = -0.25$ K. A small negative value of $\theta$ may suggest the existence of a very weak intermolecular antiferromagnetic exchange between copper ions within the crystal lattice via the hydrogen bond system. Keeping with the crystal structure, the experimental susceptibility was fitted to the expression for the magnetic susceptibility of a magnetic centre of Cu(II) (1), in a molecular-field correction, namely Eq. (2) [17]:

$$\chi_{\text{Cu}} = \frac{N\beta^2g^2}{4kT} \tag{1}$$

$$\chi_{\text{Cu}}^{\text{corr}} = \frac{\chi_{\text{Cu}}}{1 - \frac{2\chi''}{N\beta^2g^2}\chi_{\text{Cu}}} \tag{2}$$

where $\chi_{\text{Cu}}$ is the magnetic susceptibility of a paramagnetic centre, $\chi_{\text{Cu}}^{\text{corr}}$ is the measured experimental susceptibility, $\chi''$ is the intermolecular exchange parameter, and $z$ is the number of nearest neighbours. Least squares fitting of the experimental susceptibility data to this equation gives $\chi'' = -0.23$ cm$^{-1}$ and $g = 2.06$ ($R = 5.52 \times 10^{-5}$).

Fig. 3. Projection of the layer of Cu(2-qic)$_2$·H$_2$O (1) along $z$ axis. Hydrogen bonds are represented as dashed lines.
Table 2. Ligand-field infrared spectral data and magnetic parameters (cm⁻¹)

| Compound                                | Colour     | Reaction                                      | ν(COO)⁻⁻⁻| ν(COO)⁻ | Δν | δ(C≡N) | ν(OH) | ν(Cu–N) | ν(Cu–O)⁻⁻⁻| d-d | Parameters
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<tr>
<td>Cu(2-qic)_2·H_2O (1)</td>
<td>Green</td>
<td>Cu(CH_3COO)_2·H_2O + 2-Hqic</td>
<td>1630 vs</td>
<td>1370 vs</td>
<td>260</td>
<td>406</td>
<td>3294 vs</td>
<td>270 m</td>
<td>351 s, 323 vs</td>
<td>13900 s, 10200 s</td>
<td>ΔJ' = -0.25 cm⁻¹, g = 2.08</td>
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<tr>
<td>Cu(2-qca)_2·H_2O (2)</td>
<td>Blue-green</td>
<td>CuCl_2 + 2-qmpe</td>
<td>1635 vs</td>
<td>1377 vs, 1347 vs, sh</td>
<td>258</td>
<td>406</td>
<td>3292 vs</td>
<td>262 m</td>
<td>320 m, 285 vs</td>
<td>13950 s, 9550 s</td>
<td>ΔJ' = -0.21 cm⁻¹, g = 2.10</td>
</tr>
<tr>
<td>Cu(2-qca)_2·H_2O (3)</td>
<td>Green</td>
<td>Cu(ClO_4)_2 + 2-qmpe</td>
<td>1636 vs</td>
<td>1377 vs, 1346 vs, sh</td>
<td>259</td>
<td>405</td>
<td>3294 vs</td>
<td>263 m</td>
<td>320 m, 284 vs</td>
<td>14000 s, sh 11950 s</td>
<td>ΔJ' = -0.23 cm⁻¹, g = 2.06</td>
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For complexes 2 and 3, experimental magnetic data, presented earlier [9], were analysed using the same model function (2). The fit gives ΔJ' = -0.21 cm⁻¹, g = 2.10, (R = 5.39·10⁻⁵) for 2, and ΔJ' = -0.22 cm⁻¹, g = 2.08, (R = 5.42·10⁻⁵) for 3.
A small negative value of $zJ'$ for 1, 2, and 3 reveals very weak antiferromagnetic interactions between copper(II) ions through a hydrogen bond system in the crystal lattice, which has been confirmed by X-ray data for 1. The same fitting agreement factor $R$

$$
R = \sqrt{\frac{\sum \frac{1}{\chi_i^{\exp}}(\chi_i^{\exp} - \chi_i^{\text{calc}})^2}{\sum \frac{1}{\chi_i^{\exp}}}}
$$

was used throughout the paper.

In this paper, we compare (Table 2) the properties of three forms of Cu(quinoline-2-carboxylate)_2·H_2O (1), presented here with a known crystal structure [3], and differently prepared forms 2 and 3, which have been recently published [9].

4. Summary

In conjunction with crystal structure and spectral studies, the magnetic properties of a hydrogen bond network polymer of Cu(quinoline-2-carboxylate)_2·H_2O was investigated. The hydrogen bonds generate an extensive network, which is likely to contribute to the stability of the crystal lattice. Structural analysis of the network structure of Cu(2-qic)_2·H_2O (1) demonstrates that water molecules and geometric disposition of the organic ligand plays an important role in the construction of network polymers. In general, it is significant to note that the intermolecular hydrogen bonding interactions are very important, since they enhance the stability of the complexes and are responsible for creating distinct structural features in the crystal structure and realizing the dimensionality of the system [18, 19]. It is also worth noting that the exchange interactions between magnetic centres are a general phenomenon for coordination in bio-inorganic chemistry.

Finally, the study presented here suggests that the compound 1 of known crystal structure and compound 2 have stereochemistries between those of the tetragonal pyramid and trigonal bipyramid. Compound 3 has a trigonal-bipyramidal stereochemistry. This may be considered as an example of distortion isomers differing by the degree of distortion of their CuN_2O_3 chromophore.

References


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