Structure and magnetic properties of copper(II) carboxylate with pyridyl-substituted nitronyl nitroxides

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Abstract

The synthesis, crystal structure and magnetic properties of four new copper(II) carboxylate complexes with pyridyl-substituted nitronyl nitroxides, \([\text{Cu}_2(\mu-\text{ClCH}_2\text{CO}_2)_{4}(\text{ClCH}_2\text{CO}_2)_{4}\text{(NITpPy)}_{4}(\text{H}_2\text{O})_{4}]\text{CH}_3\text{OH} (1), [\text{CuCl}_2\text{CHCO}_2]_2(\text{NITpPy})_2(\text{H}_2\text{O})] (2), [\text{Cu}(\text{Cl}_2\text{CO}_2)_{4}(\text{NITpPy})_2(\text{H}_2\text{O})] (3) and [\text{Cu}(\text{Cl}_2\text{CHCO}_2)_{4}(\text{NITmPy})_2(\text{H}_2\text{O})_2] (4) (NITpPy = 4,4,5,5-tetramethyl-2-(4-pyridyl)-2-imidazoline-N₁-oxyN₃-oxide, NITmPy = 4,4,5,5-tetramethyl-2-(3-pyridyl)-2-imidazoline-N₁-oxyN₃-oxide) are reported. Complex 1 has a dimeric structure where two copper ions are doubly bridged by four oxygen atoms from two \(-\text{ClCH}_2\text{CO}_2^−\) ions. Complexes 2 and 3 are mononuclear, the copper(II) ion has five coordination with square-pyramidal symmetry. In complex 4, the copper(II) ion has distorted-octahedral six coordination. Temperature dependence studies of the \(\chi_mT\) values of complexes 1–4 revealed that 1 exhibits a strong intramolecular metal–metal antiferromagnetic interaction and a weak intramolecular metal–nitroxide antiferromagnetic coupling, 2 and 3 exhibit a weak intramolecular metal–nitroxide antiferromagnetic coupling, while 4 possesses weak ferromagnetic exchange interactions between metal and NITmPy. A simple spin polarization model has been used to justify the observed magnetic exchange interactions between Cu(II) and radical ligands. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Copper(II) carboxylate complexes; Pyridyl-substituted nitronyl nitroxides; Antiferromagnetic coupling; Spin polarization

1. Introduction

The magnetic properties of a large number of stable organic \(\text{N-oxyl N’-oxides} (\text{nitronyl nitroxides})\) and their metal complexes have been studied, especially in order to understand the factors that influence the magnetic exchange interactions between the metal ion and the radical centers [1–8]. The magnetic metal complexes with pyridyl-substituted nitronyl nitroxides have been intensively studied [1,2,4–19] in the past decade. These radicals are especially attractive due to their donor atoms and their ability to assemble extended coordination geometries with changing magnetic coupling. The heterospin systems consisting of organic free radicals and paramagnetic metal ions constitute one of the most promising design strategies for high Curie-temperature molecular-based magnets [1,20]. The observed magnetic properties of the metal–radical complexes were clearly explained in terms of the spin polarization mechanism of \(\pi\)-electrons [16,21].

In magnetic copper(II)–nitronyl nitroxide radical heterospin systems, the sign and magnitude of the spin coupling between the two components depends not only on the periodicity of the radical ligand \(\pi\) orbital, but also strongly on the orbital occupied by the unpaired \(\pi\)-electrons of the copper ion. The copper(II) ion has one unpaired electron in the \(d_{x^2−y^2}\) orbital that has \(\sigma\) magnetic orbital character, its complexes are expected to display quite different magnetic behavior.

Along this line, we wish to report here the structural and magnetic characterization of \([\text{Cu}_2(\mu-\text{ClCH}_2\text{CO}_2)_2(\text{ClCH}_2\text{CO}_2)_2(\text{NITpPy})_2(\text{H}_2\text{O})_2]_2\text{CH}_3\text{OH} (1), [\text{CuCl}_2\text{CHCO}_2]_2(\text{NITpPy})_2(\text{H}_2\text{O})] (2), [\text{Cu}(\text{Cl}_2\text{CO}_2)_2(\text{NITpPy})_2(\text{H}_2\text{O})_2] (3) and [\text{Cu}(\text{Cl}_2\text{CHCO}_2)_2(\text{NITmPy})_2(\text{H}_2\text{O})_2] (4) (Scheme 1).
Table 1
Crystal data and structure refinement parameters for complexes 1–4

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<th>1</th>
<th>2</th>
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X-ray crystal data for complexes 1, 4 and 2, 3 were collected in a Siemens P4 and in an Enraf–Nonius CAD4 diffractometer, respectively, equipped with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) and 2θ–θ scan mode. The unit-cell parameters were determined from 2.2 < θ < 25.0° for 1, 1.64 < θ < 22.47° for 2, 1.61 < θ < 22.49° for 3 and 2.08 < θ < 24.99° for 4. N independent reflections and Nw with I > 2σ(I) were observed. The details of data at 25 °C for several days, and then dark-blue well-shaped crystals suitable for X-ray diffraction were collected. Satisfactory microanalyses for complexes 1–4 were obtained. Anal. Found: C, 38.1; H, 4.6; N, 8.2. Calc. for C₃₃H₄₈Cl₂Cu₂N₆O₁₅ (1): C, 38.2; H, 4.6; N, 8.1%. Anal. Found: C, 41.6; H, 4.5; N, 10.5. Calc. for C₂₉H₂₆Cl₄CuN₆O₈ (2): C, 41.6; H, 4.5; N, 10.4%. Anal. Found: C, 38.4; H, 3.9; N, 9.6. Calc. for C₂₉H₃₈Cl₂CuN₆O₁₀ (3): C, 38.5; H, 3.9; N, 9.6%. Anal. Found: C, 40.9; H, 4.5; N, 10.0. Calc. for C₂₉H₃₈Cl₂CuN₆O₁₀ (4): C, 40.8; H, 4.6; N, 10.0%.

2.2. Physical measurements

X-band EPR spectra at 300 K for the complexes in the form of powder and in CH₃Cl₂ solutions were recorded in a Bruker ESC-106 spectrometer. The magnetic susceptibilities were carried out on polycrystalline samples with a fully automated MPMS superconducting quantum interference device (SQUID) magnetometer working in the range 4–300 K under a magnetic field of 1 T. Diamagnetic corrections were estimated from Pascal’s constants [24].

2.3. Crystallography

2.1. Preparation of the ligands and the copper(II) carboxylates

The pyridyl-substituted radicals NITpPy (4,4,5,5-tetramethyl-2-(4-pyridyl)-2-imidazoline-N¹-oxyl N¹-oxide) and NITmPy (4,4,5,5-tetramethyl-2-(3-pyridyl)-2-imidazoline-N¹-oxyl N¹-oxide) were prepared and purified according to literature methods [22]. Copper(II) carboxylates, [Cu(RCO₂)₂(H₂O)₂], where R = ClCH₂–, ClCH– and ClC–, were prepared as described previously [23]. Copper(II) nitrate trihydrate (6 mmol) and the carboxylic acid (12 mmol) were dissolved in approximately 100 cm³ of water at pH 5–6. The solution was allowed to stand at 25 °C for several days, giving precipitated products that were filtered.

2.1.1. [Cu₂(μ-CICH₂CO₂)₂(CICH₂CO₂)₂(NITpPy)₂- (H₂O)₂]CH₂OH (1), [Cu(ClCHCO₂)₂(NITpPy)₂(H₂O)] (2), [Cu(ClC₂CO₂)₂(NITpPy)₂(H₂O)] (3) and [Cu(ClC₂CHCO₂)₂(NITmPy)₂(H₂O)] (4)

Copper(II) carboxylates (3 mmol) and NITpPy or NITmPy (6 mmol) were dissolved in 20 cm³ of methanol (CH₃OH) at 25 °C. The mixtures were stored

\[ \text{NITpPy} \]

\[ \text{NITmPy} \]

Scheme 1.
Table 2
Selected bond lengths (Å) and bond angles (°) for complexes 1 and 2

\[
\text{[Cu(II)-CICH}_{2}\text{CO}_{3})_{2}(\text{CICH}_{2}\text{CO}_{3})_{2}((\text{NITpPy})_{2})_{2}\text{H}_{2}\text{O}_{2}\text{I}] (1)
\]

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<th>Cu(1)-O(1)</th>
<th>Cu(1)-O(3)</th>
<th>Cu(1)-N(3)</th>
<th>Cu(1)-Cu(2)</th>
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<td>1.933(4)</td>
<td>2.008(4)</td>
<td>2.394(4)</td>
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<td>Cu(1)-O(3)</td>
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<td>2.008(4)</td>
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<td>Cu(1)-N(3)</td>
<td>2.008(4)</td>
<td>1.975(4)</td>
<td>2.394(4)</td>
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Table 3
Selected bond lengths (Å) and bond angles (°) for complexes 3 and 4

\[
\text{[CuCl}_{2}\text{COCO}_{3})_{2}((\text{NITpPy})_{2})_{2}\text{H}_{2}\text{O}_{2}\text{I}] (2)
\]

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<th>Cu(1)-N(3)</th>
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<tr>
<td>Cu(1)-O(1)</td>
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<td>1.956(4)</td>
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<td>Cu(1)-O(3)</td>
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<td>Cu(1)-N(3)</td>
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\[
\text{[CuCl}_{2}\text{COCO}_{3})_{2}((\text{NITpPy})_{2})_{2}\text{H}_{2}\text{O}_{2}\text{I}] (3)
\]

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<td>1.963(5)</td>
<td>2.006(3)</td>
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<td>Cu(1)-O(3)</td>
<td>1.963(5)</td>
<td>1.999(5)</td>
<td>2.394(4)</td>
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<td>Cu(1)-N(3)</td>
<td>2.006(3)</td>
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\[
\text{[CuCl}_{2}\text{COCO}_{3})_{2}((\text{NITpPy})_{2})_{2}\text{H}_{2}\text{O}_{2}\text{I}] (4)
\]

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<td>1.999(3)</td>
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</tbody>
</table>

3. Results and discussion

3.1. Structures of complexes 1-4

The crystal structure of \([\text{Cu}_{2}(\mu-\text{CICH}_{2}\text{CO}_{3})_{2}(\text{CICH}_{2}\text{CO}_{3})_{2}((\text{NITpPy})_{2})_{2}\text{H}_{2}\text{O}_{2}\text{I}] (1)\) is illustrated in Fig. 1. In this dinuclear compound, the four oxygen atoms and one nitrogen atom bound to the copper ion are located at the apices of a distorted square pyramid. The basal coordination sites are occupied by two oxygen atoms of \(\text{CICH}_{2}\text{CO}_{3}^{-}\), one oxygen atom of \(\text{H}_{2}\text{O}_{2}\), and one nitrogen atom of NITpPy groups, while the axial position is occupied by the bridging oxygen atom of a \(\mu-\text{CICH}_{2}\text{CO}_{3}^{-}\) group. The Cu(II) ion is not coplanar with the basal plane, with a displacement of 0.35 Å out of the basal plane. The copper–oxygen distance (Å) of Cu(1)–O(1A) (axial bridging acetate) 2.394(4) Å is larger than that of Cu(1)–O(3) (acetate) 1.933(4), Cu(1)–O(1) (basal bridging acetate) 1.965(3), or Cu(1)–O(7) (water) 1.975(4). The Cu-O2 core is planar and the Cu–Cu separation is 3.429(4) Å. The fragment O(5)–N(3)–C(6)–N(2)–O(6) [N(3)–O(5) 1.296(5) and N(2)–O(6) 1.274(6) Å] is nearly planar but forms a dihedral angle of 34.4° with the plane of the pyridyl ring.

Complexes 1 and 2 consist of two crystallographically independent mononuclear Cu(1) and Cu(2) complexes with the same five coordination core of \(\text{N}_{2}\text{O}_{4}\) and square-pyramidal coordination geometry. Due to their structural isomorphism, the corresponding bond distances and angles of Cu(1) and Cu(2) complexes are not significantly different, here only the structures around the Cu(1) coordination sphere in 2 (Fig. 2) and 3 (Fig. 3) are discussed. The mean Cu–O (monodentate acetate) bond distances [Cu(1)–O(1) and Cu(1)–O(3)] for 2 and 3 are 1.963(5) and 1.961(5) Å, respectively, and these are shorter than the mean bond distances of Cu(1)–N (pyridyl) 2.023(5) Å for 2 and 2.026(6) Å for 3. The O(5)–N(2)–C(6)–N(3)–O(6) and O(7)–N(5)–C(18)–N(6)–O(8) moieties in 2 and 3 are as expected coplanar, but form mean dihedral angles of 11.08° for 2 and 20.65° for 3 with the plane of pyridyl ring.
The structure of complex 4 is shown in Fig. 4, two pyridyl nitrogen atoms are coordinated to the copper(II) ion in the trans configuration. The coordination sphere of the Cu(1) ion is a distorted octahedron in which the bond lengths are Cu(1)–O(3) = 1.961(6) Å, Cu(1)–O(3A) = 1.963(6) Å, Cu(1)–N(1) = 1.962(9) Å, Cu(1)–N(1A) = 2.013(7) Å, Cu(1)–O(5)(H2O) = 2.567(7) Å and Cu(1)–O(10)(H2O) = 2.585(8) Å, and the bond angles between Cu(1)–O(3) and the other ligands are nearly 90° (Table 3). As the elongation axis is through O(5)–Cu(1)–O(10) (178.9(4)°), this indicates that the lobes of the magnetic orbital $d_{x^2-y^2}$, which is orthogonal to the $d_{z^2}$ orbital of Cu(II) ion, are directed toward the carboxylate oxygen atoms and the pyridyl nitrogen atoms. It is worthy of note that the distances of O(5)···O(4) (carboxylate) and O(10)···O(4) (carboxylate) are 2.697(2) and 2.673(2) Å, indicative of a hydrogen bond within. The fragments O(1)–N(2)–C(6)–N(3)–O(2) and O(1A)–N(2A)–C(6a)–N(3A)–O(2A) are as expected coplanar, but form dihedral angles 24.91° and 25.26°, respectively, with the plane of the pyridyl ring.

3.2. Magnetic properties of complexes 1–4

The $\chi_mT$ value at 300 K of 1, 1.17 cm$^3$ K mol$^{-1}$, is slightly lower than the value expected for four non-coupled spins $S = 1/2$, two for the dicopper(II) ions and two for the NITpPy radicals in 1. In Fig. 5, the variation of $\chi_mT$ with $T$ is shown over the temperature range 300–2 K. The plot reveals three domains: (i) from 300 K to about 100 K, $\chi_mT$ rapidly decreases...
from a value of 1.17 cm$^3$ K mol$^{-1}$ (3.06 \( \mu_B \)) to a value of about 0.80 cm$^3$ K mol$^{-1}$, larger than that for two coupled \( S = 1/2 \) spin states; (ii) between approximately 100 and 25 K, the value of \( \chi_m T \) gradually decreases with decreasing temperature, and (iii) below 25 K, \( \chi_m T \) decreases to 0.46 cm$^3$ K mol$^{-1}$ (1.92 \( \mu_B \)) as the temperature approaches 2 K. In addition, for the plot of \( \chi_m T \) versus temperature, the range 100–2 K essentially follows the Curie–Weiss law with values for the Curie constant \( C = 0.39 \) cm$^3$ mol$^{-1}$ and Weiss constant \( \theta = -1.63 \) K.

The crystal structure of complex 1 consists of a carboxy-bridged dinuclear Cu(II) and copper–nitroxyl units, in which strong intramolecular Cu(1)–Cu(1a) magnetic interactions and weak intramolecular copper–nitroxy magnetic couplings are expected to occur in the complex. Therefore, we assumed that the organic free radicals behave as isolated \( S = 1/2 \) spins. Accordingly, the variation of the \( \chi_m T \) product was attributed, to a large extent, to the pair of exchange-coupled copper(II) ions and to the two isolated NITpPy radicals. Finally, an approximate fit is performed by using Eq. (1) for complex 1:

\[
\chi_m = \chi_1 + 2\chi_2 + N_s
\]

\[
\chi_1 = (2Ng^2\mu_B^2/kT)[3 + \exp(-2J/kT)]^{-1}
\]

\[
\chi_2 = C/T
\]

The best fit with \( J = -170 \) cm$^{-1}$, \( g = 2.0 \), \( C = 0.39 \) cm$^3$ mol$^{-1}$ and \( N_s = 5.6 \times 10^{-5} \) cm$^3$ mol$^{-1}$ for 1 is obtained as the solid line in Fig. 5. This result again shows a very weak antiferromagnetic interaction through the NITpPy–Cu moieties. In this regard, it is noteworthy that the nitroxide moiety forms a large dihedral angle of 34.4° with the plane of the pyridyl...
ring in the NITpPy radical, resulting in difficult spin-polarization of π* of the NO group in the radical.

As shown in Fig. 6, The values of $\chi_mT$ at 300 K for complexes 2 and 3 are 1.02 and 1.00 cm$^3$ K mol$^{-1}$, respectively, which are slightly lower than the sum of the Curie constants (1.11 cm$^3$ K mol$^{-1}$) of the three isolated $S = 1/2$ spins. When the systems are cooled down from 300 to approximately 100 K, the values of $\chi_mT$ for complexes 2 and 3 are slightly decreased, and below approximately 100 K, $\chi_mT$ decreases rapidly reaching values of 0.26 and 0.19 cm$^3$ K mol$^{-1}$, respectively, indicating the presence of weak antiferromagnetic exchange interactions between the magnetic sites.

Based on the results of structural studies, the nitroxide moiety in complexes 2 and 3 forms low dihedral angles of 10.08 and 20.65°, respectively, with the plane of the pyridyl ring in the NITpPy radical, resulting in an easy π* spin-polarization of the NO group in the radical. Therefore, the magnetic data for complexes 2 and 3 were fitted by considering a central symmetric linear of three $S = 1/2$ spins, $S_1 - S_2 - S_3$, where $S_1$ and $S_3$ refer to the nitroxide sites and $S_2$ refers to the copper(II) ion. Eq. (2) [16] for this linear three $S = 1/2$ spins system was applied and fitted to the observed $\chi_mT$–$T$ plots for complexes 2 and 3 by means of a least-squares method. All the symbols have their usual meaning:

$$\chi_mT = (N\mu_B^2 g^2/3k(T - \theta))(A/B)$$

$$A = 60 \exp(3J/T) + 6 \exp(2J/T) + 6$$

$$B = 4(\exp(3J/T) + 2 \exp(2J/T) + 2)$$

The best-fitted values of the parameters are: $J = -11.5$ cm$^{-1}$, $\theta = -0.66$ K, and $g = 1.98$ for complex 2; $J = -13$ cm$^{-1}$, $\theta = -0.79$ K and $g = 1.97$. A solid line in Fig. 6 represents the theoretical curve.

We have performed room temperature EPR spectra (at 9.75 GHz) for complexes 2 and 3 in CH$_2$Cl$_2$ solutions and these show major lines in the ratio 1:2:3:2:1 with $g = 2.01$, and nitrogen hyperfine coupling constants $a_N = 7.72$ and 7.70 G ($G = 10^{-4}$ T), respectively, as expected for coupling with two identical nitrogens of the NO groups of NITpPy; no signal from the copper(II) ions was observed. Here we used the formula of $g = (8/15)g_\text{Cu} + (7/15)g_\text{NO}$, and we obtained the same $g_\text{Cu}$ value of 1.97 for complexes 2 and 3.

A plot of $\chi_mT$–$T$ for complex 4 is shown in Fig. 6. When the temperature was decreased from 300 to 2 K, the $\chi_mT$ values (1.10 cm$^3$ K mol$^{-1}$ at 300 K) increased gradually, reached a maximum (1.28 cm$^3$ K mol$^{-1}$ at 15 K), characteristic of intramolecular magnetic exchange interactions, and then decreased.

The structural study of complex 4 shows the low mean dihedral angle of 25.17° between the nitroxide moiety and pyridyl ring, so that easy spin-polarization can take place in the NITmPy radical. The theoretical expression for the magnetic susceptibility of the system also uses Eq. (2), leading to the following parameters: $g = (g_\text{Cu} + g_\text{NO})/2 = 2.0$, $J = 12.0$ cm$^{-1}$ and $\theta = -1.6$ K.

Since the fitted magnetic data of complex 4 provide evidence for a weak intramolecular ferromagnetic interaction, one must consider a possible mechanism for the exchange interaction between the radical NITmPy and Cu(II) ion. An acceptable mechanism is suggested by McConnell [26] for the interpretation of the ferromagnetic behavior of the $N$-oxyl $N$-oxides [27] and $N$-terabutylaminoxyl radical [28]. According to this model a spin distribution arising from intramolecular spin polarization of the adjacent atoms leads to alternating
positive and negative spin density on the carbon backbone of the radical ligands. A schematic representation of the alternating spin densities for 4 is given in Scheme 2. The magnetic orbital $d_{x^2-y^2}$, orthogonal to the elongated axis of octahedral Cu(II), is directed to the two nitrogen atoms of the pyridine groups. The positive spin density on the NO site of one NITmPy moiety induces negative spin density on the neighboring carbon atom due to a spin polarization, which in turn induces positive spin density on the Cu(II) ion and on the NO site of the other adjacent NITmPy moiety.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 161298, 161308, 161309 and 161299 for compounds 1–4, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: de-posit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References