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Antiferromagnetism tuned by the topology of the intervening bridging ligand. Crystal structure and magnetic properties of the (μ-phthalato){[bis(piperidine)]Cu(II)} chain complex

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Abstract

The crystal structure of the chain complex $[(\mu\text{-phth})(\text{pip})_2\text{Cu}]_n$, where phth is the dianion of phthalic acid and pip is piperidine, has been determined by single crystal X-ray methods. The complex crystallizes in the monoclinic space group $I2/a$ with $\alpha=15.853(2)$, $b=10.785(1)$, $c=11.629(1)$ Å, $\beta=111.321(3)°$, $Z=4$ and $V=1852.11$ Å^3. Solution of the structure led to final values of $R=0.0298$ and $R_w=0.0330$ with 167 least-squares parameters for 1578 unique reflections with $F_o>6.5\sigma(F_o)$. The compound is a chain copper(II) complex, $[(\text{pip})_2\text{Cu}(\mu\text{-phth})]_n$ being the polymeric entity. Within the chain the copper(II) ions are bridged by the phth ligand in an anisobidentate fashion, the coordination geometry about each Cu(II) ion is distorted octahedral; two nitrogen atoms belonging to two piperidine molecules along with two carboxylato oxygen atoms of two different phthalato bridges occupy the equatorial positions, whereas the two remaining oxygen atoms of the same carboxylato groups occupy the axial positions. Thus, chains along the c direction are formed. The intrachain metal–metal separation is 5.814 Å. The variable-temperature (4.2–290 K) magnetic susceptibility data of the complex showed a perfect Curie law. The role of the topology of the intervening bridge on the strength of the antiferromagnetic coupling of the complex is discussed.

Key words: Crystal structures; Antiferromagnetism; Copper complexes; Phthalato complexes; Piperidine complexes

Introduction

The study of superexchange interactions between magnetic ions in a variety of magnetic systems has been a vital field in inorganic chemistry in the last decades [1]. Owing to its fundamental importance, the study of long-range magnetic interactions has also been an active field of research. Within this framework, for instance, through the exciting synthetic chemistry of the μ-terephthalato–Cu(II) magnetic partners — exhibiting a variety of magnetic systems ranging from pure dinuclear [2] to 1-D [3], 2-D [4] and to molecular-based magnetic systems exhibiting a spontaneous magnetization below a critical temperature T_c [5] — it is now well established that an intradimer separation of *c.* 11 Å is not the distance limit for the smallest $|J|$ value (*c.* 0.1 cm^{-1}), detectable by the usual magnetic techniques [6]. Furthermore, the *ortho* derivative of terephthalato, the phthalate dianion, appeared to be a promising candidate for supporting long-range ferromagnetic exchange interactions [7]. In particular, from an orbital interpretation of the coupling of a μ-phthalato Cu(II) complex, a new situation arose leading to ferromagnetic interaction between magnetic centers separated by multiatom bridging units based on the topology of the intervening bridge. It was shown that the variations in ω, being the angle between the planes of the two carboxylato groups of each phthalato intervening bridge, could play a significant role on the antiferromagnetic coupling of the complex. In order to verify that further, we initiated a systematic experimental approach in an attempt to design μ-phthalato–Cu(II) magnetic systems, with a variety of ω values. To accomplish this, contrary to the previously used [7] diethylenetriamine, dien, as

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the nitrogen donor molecule, two bulky piperidine molecules per Cu(II) were used as a further testing ground to force the two carboxylato groups of each terephthalato dianion to adopt a smaller dihedral angle than before. We were pleased to realize that this systematic experimental approach does work. Consequently, we report herein on the synthesis, crystal structure and the interpretation of the magnetic behavior – in correlation with the structural data and EHMO calculations – of the one-dimensional, polymeric {(μ-phthalato)[bis(piperidine)]Cu(II)} complex. The key point here is that, despite the closer proximity between the magnetic centers of the complex under study than before [7], it does not exhibit any sign of exchange interaction.

Experimental

Synthesis

A methanolic solution (50 ml) of piperidinium phthalate (1 mmol) was added to a methanolic one (100 ml) of copper(II) acetate (1 mmol) at room temperature. To the blue–green limpid solution derived, 2 mmol of piperidine were added and the colour of the solution turned to medium blue. The final solution remained limpid upon overnight standing in a fridge, whereupon the solvent was eliminated in a rotaevaporator to one third of its original volume. The final solution gave purple single crystals, suitable for the structure and the magnetic determination upon standing in the fridge for 12 days.

Anal. Calc. for $CuC_{18}H_{27}N_2O_{4.5}$: Cu, 15.61; C, 53.12; H, 6.69; N, 6.88; O, 17.69. Found: Cu, 15.73; C, 53.52; H, 6.71; N, 6.87; O, 17.17%.

X-ray data collection and structure determination

Slow crystallization from methanol yielded purple prismatic crystals. One of them was mounted in air on a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic using Nb-filtered Mo radiation. Unit cell dimensions were determined and refined, by using the angular settings of 21 automatically centered reflections, in the range $11 < 2\theta < 24°$; they appear in Table 1. Intensity data were recorded using the θ–2θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization but no absorption correction were applied using Crystal Logic software.

The structure was solved by direct method using SHELXS-86 [8] and refined by full-matrix least-squares techniques with SHELX-76 [9]. All hydrogen atoms were located by difference maps and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically, see 'Supplementary material'.

The final values for R, R_w and GOF, for all data are 0.0610, 0.0624 and 2.41, respectively. The equivalent values for the observed data are given in Table 1. The maximum and minimum residual peaks in the final difference map were 0.356 and -0.33 e/Å^{-3}. The largest shift/e.s.d. in the final cycle was 0.009. Positional and U_{eq} thermal parameters are given in Table 2 and selected bond distances and angles in Table 3.

Magnetic and EPR measurements

Magnetic measurements were carried out on a Faraday type magnetometer with a He continuous-flow cryostat in the 4.2–300 K temperature range. Mercuric tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. Correction for diamagnetism was estimated as -217×10^{-6} cm^3 mol^{-1}. The EPR spectrum was recorded at room temperature with a Bruker X-band ER 200D spectrometer equipped with a Hall probe and a Hewlett-Packard frequency meter.

Results and discussion

Description of the structure

Each unit cell contains four formula units. The crystal structure of the complex is built up by polymeric $_\infty|(\mu$-phth)Cu(pip)$_2|$ entities. Each polymeric unit consists of Cu(II) ions, occupying crystallographic inversion centers, each coordinated to two piperidines, bridged by phth dianions, coordinated in an anisobidentate fashion through the O(1) and O(2) atoms (Cu–O(1) = 1.981(2), Cu–O(2) = 2.632(2) Å) of their carboxylate groups. Thus, infinite chains along the c axis are derived. An ORTEP perspective view of three symmetry-related units is shown in Fig. 1. The copper environment is 4 + 2 distorted octahedral. The equatorial plane includes the two O(1) atoms, belonging to two different phth bridges and the two N atoms of two different piperidine molecules (Cu–N = 2.026(2) Å). Moreover, the second oxygen atom, O(2), of each carboxylato group occupies the axial positions. Due to the small carboxylate bite (O(1)–Cu–O(2) = 55.1(1)°) (see Table 3), the octahedron is very distorted. The equatorial planes of each octahedral environment, being the magnetic orbitals of the complex (*vide infra*), are parallel to those of their next nearest neighbors (see Fig. 2), whereas the dihedral angle between the two nearest neighbors is only 12.14°.

The Cu–N bond distances of 2.026(2) Å are comparable with those found in other analogous μ-phthalato and/or μ-terephthalato Cu(II) amine complexes [3, 4, 7]; this is also the case with both the Cu–O 'short' and 'long' distances, being 1.981(2) and 2.632(2) Å, respectively.

The two nearest-neighbor Cu(II) ions, connected by the same phth dianion in the c direction, are separated

TABLE 1. Summary of crystal and intensity collection data of the complex

Molecular formula	$CuC_{18}H_{26}N_2O_4$
Formula weight	397.96
Crystal dimensions (mm)	0 17×0.11×0 30
Temperature (K)	296
Space group	*I*2/*a*
a (Å)	15.853(2)
b (Å)	10.785(1)
c (Å)	11.629(1)
β (°)	111 321(1)
V (Å^3)	1852.11
Z	4
D_{calc} (g cm^{-3})	1.427
D_{meas} (g cm^{-3})	1.40
F(000)	836
λ (Å)	0.7107
μ (cm^{-1})	12.10
Radiation	Mo/Nb 0.71073
Max. absorption correction factor	–
Scan speed (° min^{-1})	3.0
Scan range (°)	$2.4+\alpha_1\alpha_2$ separation
2θ limit (°)	57
hkl Range	$-21\leqslant h\leqslant 21$, $0\leqslant k\leqslant 14$, $0\leqslant l\leqslant 15$
Data collected	2450
Data unique	2345
Data used	1578
F_o	$>6.5\sigma(F_o)$
R_{int}	0.0373
Parameters refined	167
GOF[a]	1.55
R^b (obs.) (%)	2.98
R^b (all data) (%)	6.10
R_w^c (obs.) (%)	3.30
R_w^c (all data) (%)	6.24

[a] $GOF=[\Sigma w(|F_o|-|F_c|)^2/(N-P)]^{1/2}$, P = no. of parameters, N = no. of observed reflections. [b] $R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [c] $R_w=\{\Sigma[w(|F_o|-|F_c|)^2]/\Sigma w|F_o|^2\}^{1/2}$.

TABLE 2. Positional and thermal parameters for the non-hydrogen atoms (standard deviations in parentheses) ($\times 10^4$)

Atom	*x*	*y*	*z*	U_{eq}[a]
Cu	2500	2500(0)	2500(0)	255
O(1)	2644(1)	721(2)	2190(2)	333
O(2)	1700(2)	1368(2)	375(2)	400
N	3552(2)	2828(2)	1947(2)	294
C(1)	4424(2)	2387(4)	2862(3)	437
C(2)	5178(3)	2447(5)	2351(5)	620
C(3)	5285(3)	3745(4)	1930(5)	622
C(4)	4393(3)	4199(4)	1009(4)	485
C(5)	3657(2)	4105(3)	1546(3)	373
C(6)	2206(2)	573(2)	1039(3)	296
C(7)	2354(2)	−640(2)	498(2)	247
C(8)	2201(2)	−1764(3)	976(3)	322
C(9)	2344(2)	−2871(3)	482(3)	344

[a] $U_{eq}=(U_{11}+U_{22}+U_{33})/3$.

by 5.814 Å; the shortest Cu–Cu interchain separation being 9.587 Å.

The six carbon atoms of the benzene ring of the phth ligand do not deviate less than the standard deviations of their atomic positions from their respective mean plane. The dihedral angles between the carboxylate planes and the benzene ring are 55.78°, whereas that between the two carboxylate planes of the same phth bridge is 44.85°.

The piperidine ring takes a chair conformation: N and C(3), deviate by 0.66 and 0.66 Å, respectively, from the plane through C(1), C(2), C(4) and C(5). Moreover, each piperidine molecule is further linked with O(2) by N–H···O hydrogen bonds (H(N)···O = 2.23(3) Å, ∠N–H···O = 170(3)°) (see Fig. 2). All C–C and C–N bond distances, ranging from 1.483(3) to 1.518(5) Å, are comparable with those found in the literature [10], and, this is also the case with the C–C–C and C–N–C angles.

Magnetic data and their interpretation

Variable-temperature (4.2–295 K) magnetic susceptibility data were collected for a solid sample of the complex.

The molar magnetic susceptibility per copper(II), χ_M of the complex follows the Curie law $\chi_M T = 0.44$ cm^3

TABLE 3. Bond distances (Å) and angles (°) (e.s.d.s in parentheses)

Bond distances			
Cu···Cu[a]	5.814	Cu·Cu[b]	9.587
Cu–N	2.026(2)	C2–C3	1.512(6)
Cu–O1	1.981(2)	C3–C4	1.512(6)
Cu–O2	2.632(2)	C4–C5	1.513(4)
C6–O1	1.274(3)	C6–C7	1.507(3)
C6–O2	1.234(3)	C7–C8	1.391(3)
C1–N	1.483(4)	C7–C7	1.395(5)
C5–N	1.483(4)	C8–C9	1.378(4)
C1–C2	1.518(5)	C9–C9	1.380(6)
Bond angles			
N–Cu–O1	87.0(1)	C7–C8–C9	120.6(3)
O2–Cu–O1	55.1(1)	C2–C3–C4	110.1(3)
N–Cu–O2	87.6(1)	C3–C4–C5	110.4(3)
Cu–O1–C6	104.9(2)	N–C5–C4	112.5(3)
Cu–N–C1	112.1(2)	O1–C6–O2	123.6(2)
Cu–N–C5	117.5(2)	O1–C6–C7	116.0(2)
C1–N–C5	110.0(3)	O2–C6–C7	120.4(2)
C1–C2–C3	111.3(3)	C6–C7–C8	120.9(2)
N–C1–C2	111.5(3)		

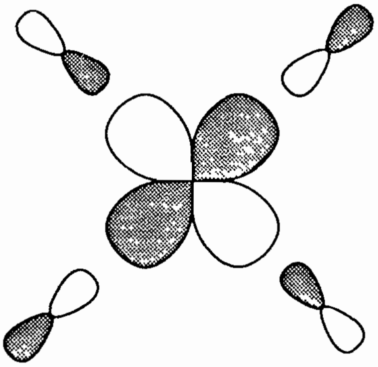
[a] Closest intrachain [b] Closest interchain

K mol^{-1} down to liquid-helium temperature. This behavior is characteristic of non-coupled copper(II) ions.

Moreover, the room-temperature X-band powder EPR spectrum of the complex is axial with $g_{\parallel} = 2.25$ and $g_{\perp} = 2.046$. This is in line with copper(II) in a distorted-tetragonal elongated environment; still a $G = (g_{\parallel}{}^{-2})/(g_{\perp}{}^{-2})$ value of 5.44 could be deduced [11] accounting well for the absence of any exchange interaction for the complex [12].

In an attempt to probe deeper into the magnetic superexchange interactions, the magnetic behavior of the complex is closely combined with its molecular and crystal structure.

As it was shown in the previous section, the complex has a very interesting crystal structure, built from magnetic planes almost parallel to each other, which are coupled through the bridging phthalato dianions, the Cu–Cu separation being *c.* 5.814 Å. Moreover, the copper(II) ions are in distorted octahedral surroundings. This, along with the long Cu–O2 distances, suggests that the unpaired electron around each Cu(II) magnetic center is described by a x^2–y^2-type magnetic orbital pointing from the metal towards the four nearest-neighbor atoms, N1, N1, O1 and O1, in the equatorial plane:



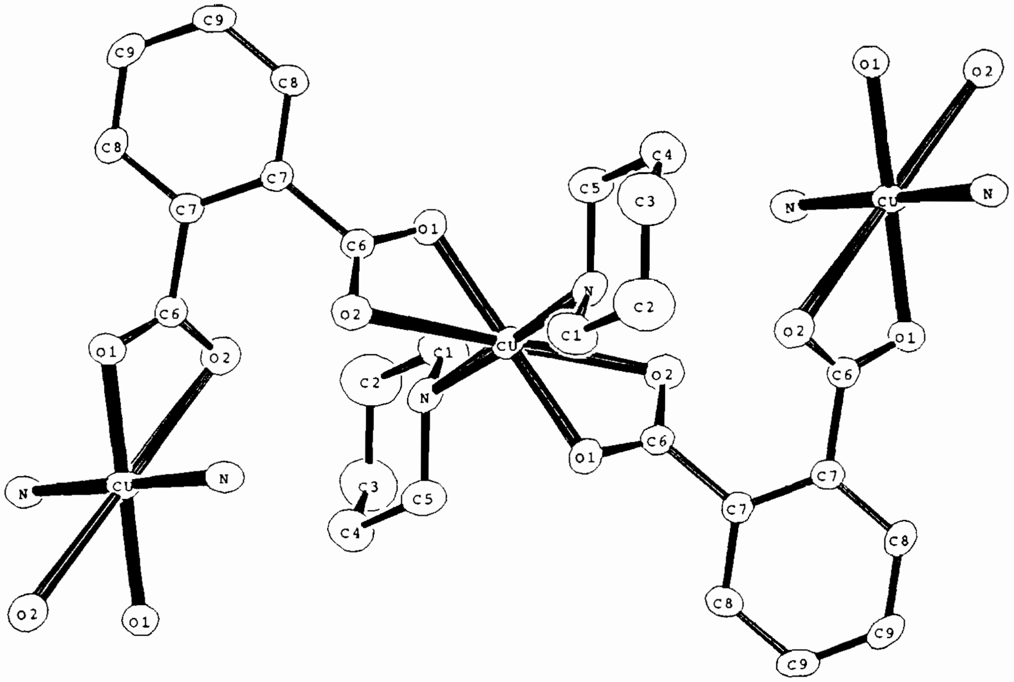


Fig 1 ORTEP perspective view, along with the atom labelling, of three symmetry-related units of the complex (50% probability ellipsoids)

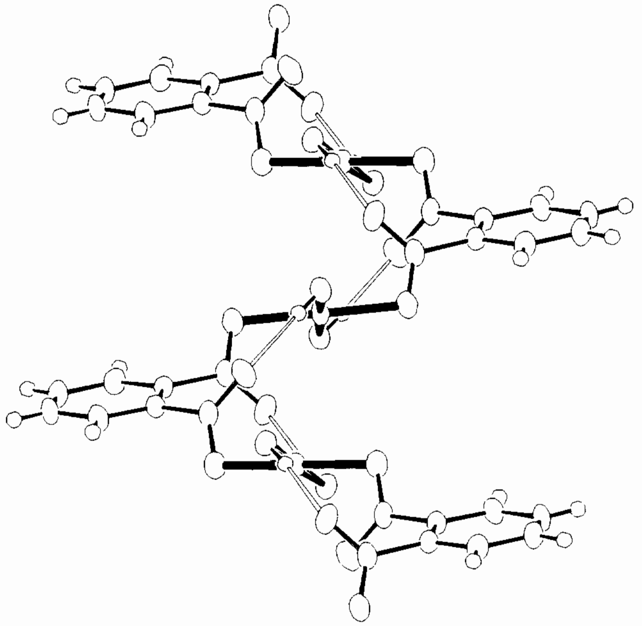


Fig. 2. ORTEP perspective view of three symmetry-related units of the complex (50% probability ellipsoids), showing both its almost parallel magnetic planes and the H bonds Each piperidine molecule has been omitted for clarity, represented only by its coordinated N atom

Along the chain structure, the magnitude of the antiferromagnetic interaction is governed [13] by the overlap of the magnetic orbitals of the complex centered on the nearest-neighboring Cu ions. However, the magnetic orbitals of the complex are almost parallel to each other (see Fig. 2), hence they are unfavorably oriented to give a strong overlap. Consequently, the absence of any significant interaction for the present complex could be well understood. Moreover, even the hydrogen bonds, linking the N atom of each piperidine molecule of a magnetic orbital with the O2 of a nearest-neighboring magnetic orbital (see Fig. 2), could propagate a very weak interaction [14].

Further support for the absence of any significant interaction for the complex could also be given by the topology of the phthalato intervening bridging ligand. Actually, as was shown in our previous paper [7], δ, being the energy difference between the symmetric and antisymmetric MOs of the phthalato bridging ligand, symmetry-adapted to interact with the degenerate single-occupied in- and out-of-phase combinations of the metal d orbitals, is decreased as ω, being the crystallographic dihedral angle between the two carboxylato groups of the phthalato bridge, increases (see Fig. 6 of ref. 7). The minimum of δ, i.e. the minimization of the antiferromagnetic contribution in the exchange coupling, corresponded to an ω value of 80°. Our previous μ-phthalato Cu(II) complex exhibited an ω value of 80° and due to that the antiferromagnetic contribution in the complex was lowered to such an extent that the ferromagnetic one became predominant (S–T energy gap of *c.* 80 cm^{-1}). However, the complex under study presents an ω value of *c.* 45°, hence, the antiferromagnetic contribution in the exchange coupling of the complex is differentiated from being minimum. It is very likely then that the antiferromagnetic contribution in the exchange coupling of the complex could equally compensate the ferromagnetic one, accounting well for the experimental zero J value of the complex.

The conclusion that can be drawn from the two μ-phthalato Cu(II) complexes studied by us so far [7], is that a new situation arises which leads to ferromagnetic interaction through extended bridging ligands, based mainly on the topology of the bridge, by tuning the antiferromagnetic contribution in the exchange interaction. As a matter of fact, the previously studied complex [7], owing to the minimization of the antiferromagnetic contribution in the exchange coupling, exhibited a ferromagnetic interaction, whereas the present complex, due to both its almost parallel magnetic orbitals and the equal compensation between the antiferromagnetic and the ferromagnetic terms of the exchange, exhibited a zero experimental J value. What is left now is to try to synthesize another μ-phthalato Cu(II) complex with an ω bite smaller than 45°, which, according to our predictions, should exhibit a pure antiferromagnetic interaction. Further work along this line is under way in our laboratory.

Supplementary material

Positional and isotropic thermal parameters of hydrogen atoms (Table S1), anisotropic thermal parameters (Table S2), and a listing of calculated and observed structure factors (10 pages) are available from the authors on request.

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