A three-dimensional copper(II) coordination polymer featuring the 2,3-dioxyquinoxalinate(-2) ligand: Preparation, structural characterization and magnetic study

Konstantis F. Konidaris [a], Giannis S. Papaefstathiou [b], Guillem Aromi [c], Simon J. Teat [d], Evy Manessi-Zoupa [a,*], Albert Escuer [c,*], Spyros P. Perlepes [a,*]

[a] Department of Chemistry, University of Patras, 265 04 Patras, Greece
[b] Inorganic Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis, Zografou 15771, Greece
[c] Departament De Quimica Inorganica, and Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain
[d] Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Mail Stop 2-400, Berkeley, CA 94720, USA

ARTICLE INFO

ABSTRACT

The synthesis, single-crystal X-ray structure and magnetic properties of $[Cu_3L_2Cl_2(DMF)_4]_n$ (**1**), where L^{2-} is the 2,3-dioxyquinoxalinate(-2) ligand, are reported. The complex was prepared by the reaction of $CuCl_2$ and 1,4-dihydro-2,3-quinoxalinedione (H_2L') under basic conditions using either solvothermal or normal laboratory techniques. Compound **1** is a 3D coordination polymer with an $(8^2.10)$-a, **lig** (LiGe) topology, containing the ligand in a novel 3.1111 (Harris notation) coordination mode. Variable-temperature and variable-field magnetic studies reveal that the ligand L^{2-} propagates weak antiferromagnetic exchange interactions through its "quinoxaline" part. IR data are discussed in terms of the structural features of **1** and the coordination mode of L^{2-}.

1. Introduction

There continues to be intense interest by many research groups around the world in the synthesis and characterization of molecular polymeric (also known as coordination polymers, metal-organic coordination networks, metal–organic frameworks or organic–inorganic hybrid coordination polymers) 3d metal complexes [1]. There are many reasons for this, not least of which is the aesthetic beauty of their structures and architectures [2]. Coordination polymers have also potential applications in catalysis, electrical conductivity, magnetism, luminescence, non-linear optics, molecular electronics, medicine, sensing and zeolitic behaviour [3]. The ultimate goal is the transformation of some coordination polymers to materials. Thus, there continues to be a need for new synthetic methods to such compounds.

The process of building a coordination polymer is principally directed by the coordination bond. The properties of coordination polymers originate either from the metal centers and/or the organic components. *The use of new organic ligands towards the synthesis of metal–organic coordination networks* is thus of great concern not only for the discovery of compounds with novel structures and interesting properties, but also as a means of building up families of related materials so that structure–property relations can be developed.

Inspired by the ideas of Chisholm [4], and Murillo and the late Cotton [5] on the linking of quadruply bonded Mo^{4+}_2 units, we have recognized that there is a special class of *cyclic diamidate* ligands which could bridge 3 or 4 metal ions leading to coordination polymers. One such ligand is 1,4-dihydro-2,3-quinoxalinedione (H_2L') which upon deprotonation can give the *diolate* dianion 2,3-dioxyquinoxalinate (L^{2-}). These two ligands, shown in the tautomeric forms established by crystallography, are illustrated in Scheme 1. We have recently started a project aim at the use of the ligands shown in Scheme 1 (and tautomers thereof) for the construction of coordination polymers. We report here the preparation, structural characterization and magnetic study of the 3D coordination polymer $[Cu_3L_2Cl_2(DMF)_4]_n$ (**1**), which is the first metal-containing polymeric compound featuring L^{2-} as ligand. Preliminary portions of this work have been communicated [6].

* Corresponding authors. Tel.: +30 2610 997147; fax: +30 2610 997118 (E. Manessi-Zoupa); tel.: +34 93 4021264; fax: +34 93 4907725 (A. Escuer); tel.: +30 2610 997146; fax: +30 2610 997118 (S.P. Perlepes).

E-mail addresses: emane@upatras.gr (E. Manessi-Zoupa), albert.escuer@qi.ub.es (A. Escuer), perlepes@patreas.upatras.gr (S.P. Perlepes).
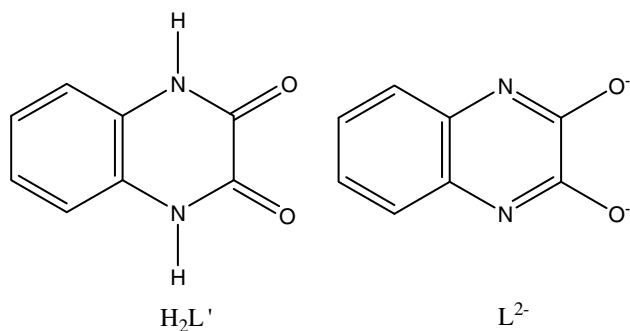
Scheme 1. The structural formulae of the ligands discussed in the text. The neutral ligand is written in the amide (ketoamine) tautomeric form, while the dianionic ligand in the hydroxylamine (or iminol) tautomeric form; these forms have been established by single-crystal X-ray crystallography (see text for details). Due to the different tautomeric forms involved, different abbreviations are used for the free neutral molecule and the dianionic ligand (H_2L' vs L^{2-}).

2. Experimental

2.1. General and spectroscopic measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer. IR spectra ($4000–450\ cm^{-1}$) were recorded on a Perkin-Elmer 16 PC FT-spectrometer with samples prepared as KBr pellets. Magnetic susceptibility measurements in the range 2–300 K were carried out on a polycrystalline sample of **1** using a Quantum Design SQUID magnetometer, under a magnetic field of 0.1 T, at the Magnetochemistry Service of the University of Barcelona. Diamagnetic corrections were estimated from Pascal tables.

2.2. Compound preparation

2.2.1. $[Cu_3L_2Cl_2\ (DMF)_4]_n$ (**1**)

Method A: A solution of $[Cu_2(O_2CMe)_4\ (H_2O)_2]$ (0.12 g, 0.30 mmol), $CuCl_2$ (0.013 g, 0.10 mmol) and H_2L' (0.049 g, 0.30 mmol) in DMF (8 ml) was heated at 130 °C in a sealed tube for 6 h, followed by slow cooling down to ambient temperature over a period of 2 days. X-ray quality dark green crystals of $[Cu_3L_2Cl_2\ (DMF)_4]_n$ (**1**) were obtained directly from the reaction solution. The crystals were collected by filtration under vacuum, washed with cold DMF (2 ml) and Et_2O (5 ml) and dried in air. Typical yields (based on the ligand) were in the 50–55% range. FT-IR (KBr pellet, cm^{-1}): 3421wb, 2924w, 1640vs, 1586m, 1560s, 1545vs, 1492s, 1473sh, 1419w, 1389m, 1375m, 1276m, 1156vw, 1118vw, 1104w, 1060vw, 955w, 754m, 693w, 642m. *Anal*. Calc. for $C_{28}H_{36}N_8O_8Cl_2Cu_3$ (874.26): C, 38.46; H, 4.16; N, 12.82. Found: C, 38.27; H, 4.18; N, 12.88%.

Method B: DMF (25 ml) was added to a mixture of $CuCl_2$ (0.061 g, 0.45 mmol), H_2L' (0.049 g, 0.30 mmol) and $LiOH \cdot H_2O$ (0.025 g, 0.60 mmol). The solids soon dissolved upon stirring. The resulting pale green solution was refluxed for 4 h and then layered with Et_2O (20 ml). Slow mixing gave a dark green microcrystalline solid which was isolated by filtration, washed with DMF (1 ml) and Et_2O (2 × 5 ml), and dried in air. Yield: 70%. The identity of the product was confirmed by elemental analyses and IR comparison with the authentic material prepared by Method A.

2.3. Single-crystal X-ray crystallography

The data were collected using a Bruker APEXII CCD diffractometer on station 16.2 of the Synchrotron Radiation Source at Dares-

Table 1
Crystallographic data for complex **1**.

Parameter	**1**
Chemical formula	$C_{28}H_{36}N_8Cu_3O_8Cl_2$
Formula weight	874.17
Crystal system, space group	tetragonal, $I4_1/a$
a (Å)	24.616(2)
b (Å)	24.616(2)
c (Å)	11.6525(10)
V (Å^3)	7060.8(10)
Z	4
T (K)	150(2)
Radiation, wavelength (Å)	synchrotron, 0.7848
ρ_{calc} (g cm^{-3})	1.645
μ (mm^{-1})	2.619
$R_1{}^a$	0.0453[b]
$wR_2{}^a$	0.1255[b]

[a] $w = 1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP]$ and $P = (\max\ F_o^2, 0) + 2F_c^2/3$, $R_1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
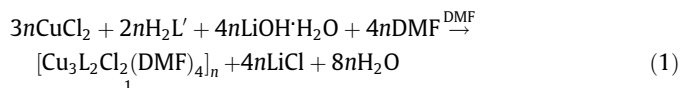[b] For 4234 reflections with $F^2 > 2\sigma(I)$.

bury Laboratory UK. Crystal data and selected parameters for data collection and processing are listed in Table 1. The data were integrated using SAINT v7.23a and the absorption correction was applied by SADABS. The SHELXTL suite of programs was used to solve the structure using direct methods and perform the least squares refinement. All non-hydrogen atoms were refined anisotropically, with displacement parameter restrains being used in the modeling of the ligands. Hydrogen atoms were placed geometrically where possible, the methyl hydrogen atoms were found in a rotational Fourier map; all were constrained and refined with a riding model.

3. Results and discussion

3.1. Brief synthetic comments and IR spectra

Complex **1** was initially obtained by solvothermal synthesis. Heating a solution of $[Cu_2(O_2CMe)_4\ (H_2O)_2]$, $CuCl_2$ and H_2L' in a 3:1:3 ratio in DMF at 130 °C in a sealed tube under autogenous pressure for 6 h, followed by slow cooling at room temperature, gave dark green crystals of the product. The $MeCO_2{}^-$ ions act as a base helping the deprotonation of the ligand. The usefulness of superheated fluids, i.e. solvothermal conditions, for preparing extended frameworks based on metal–ligand interactions has been demonstrated by several groups [7]. The temperature regime available in solvothermal techniques, intermediate between low-temperature solution chemistry and high-temperature solid-state chemistry, can favour the formation of metastable kinetic products rather than the thermodynamic products favoured at high temperature.

With the identity of **1** established by single-crystal, X-ray crystallography, we sought a convenient synthesis of the pure material under alternative, mild reaction conditions. It was logical to impose upon the knowledge of the chemical composition of **1** to select the starting materials and their ratios. Thus, the reaction of three equivalents of $CuCl_2$ with 2 equiv. of H_2L' and 4 equiv. of $LiOH \cdot H_2O$ in DMF gave, after convenient workup, the product in ~70% yield. The formation of the complex can be summarized by Eq. (1):

$$3nCuCl_2 + 2nH_2L' + 4nLiOH\cdot H_2O + 4nDMF \xrightarrow{DMF}$$
$$[Cu_3L_2Cl_2(DMF)_4]_n + 4nLiCl + 8nH_2O \tag{1}$$

Note that the ligand in the product is not the doubly deprotonated amide, i.e., L'^{2-}, but instead the di-iminolate (-2) [or diolate (-2)], i.e., L^{2-} (vide infra), see Scheme 1.

The IR spectrum of free H$_2$L′ shows the characteristic bands of the *cis* secondary amide groups with the bands at ∼3100, 1682, 1472 and 1392 cm^{-1} assigned to v(NH), v(C=O), v(CN)$_{amide}$ and δ(NH), respectively [8,9]. This spectral behaviour is consistent with the solid-state structure of the ligand (vide infra). The spectrum of **1** does not exhibit a band in the region for the amide carbonyl stretching, as expected from the absence of L′$^{2-}$ in the product. The v(C=O) and δ(OCN) vibrational modes of the coordinated DMF molecules appear at 1640 and 693 cm^{-1}, respectively [10]. Due to coordination, the v(C=O) and δ(OCN) bands are shifted to lower and higher wavenumbers, respectively, when compared with the corresponding bands in the spectrum of free DMF [11].

3.2. Description of structure

Various structural features of **1** are shown in Figs. 1–3. Selected interatomic distances and angles are listed in Table 2.

Complex **1** is a 3D coordination polymer built from centrosymmetric trinuclear [Cu$_3$L$_2$Cl$_2$(DMF)$_4$] units containing 2,3-dioxyquinoxalinate(-2) (L^{2-} in Scheme 1, vide infra) ligands that are responsible for the polymer formation. A perspective view of the trinuclear unit is shown in Fig. 1. Within the crystallographic asymmetric unit there are two, structurally different Cu^{II} sites, Cu(1) and Cu(2). The central Cu(1) ion sits on a crystallographically imposed inversion centre exhibiting *trans* coordination to two terminal chlorides and to two symmetry related L^{2-} ligands *via* the one of nitrogen atoms [N(1)] in each ligand. Each of the two "terminal" Cu^{II} ions [Cu(2), Cu(2′)] is bonded to two oxygen atoms of two terminal DMF molecules, both oxygen atoms from one L^{2-} ligand and to one nitrogen atom [N(2)] from an equivalent ligand in a different asymmetric unit.

The coordination geometry around Cu(1) is square planar. The Cu(1)–Cl(1) bond length of 2.277(1) Å is typical for square planar
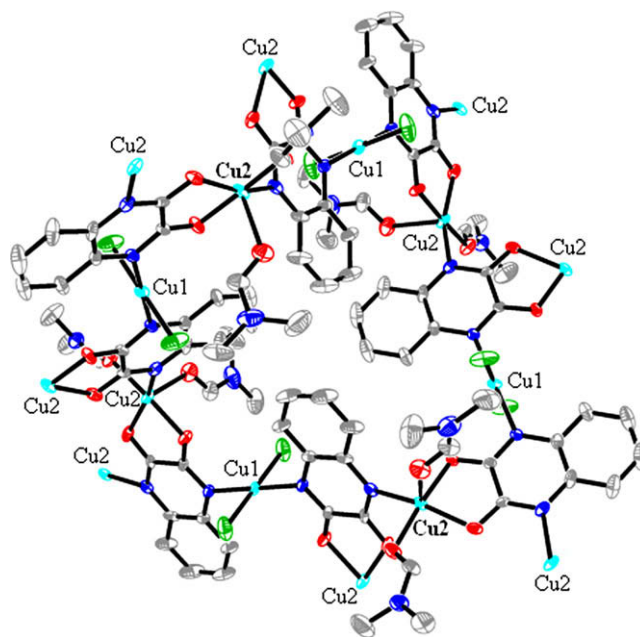

Fig. 2. The half folded square ring which makes up the substructure of **1**, with the fold along the Cu^{II} ions labeled in bold and the rest of the molecule being further away from the viewer. Displacement parameters are plotted at the 50% probability level.

copper(II) complexes involving chloro ligands [12]. The Cu(2) coordination geometry is well described as square pyramidal with the DMF oxygen O(3) occupying the apical position. Analysis of the shape-determining angles using the approach of Reedijk and Addison [13] yields a value for the trigonality indet τ of 0.26 for Cu(2)
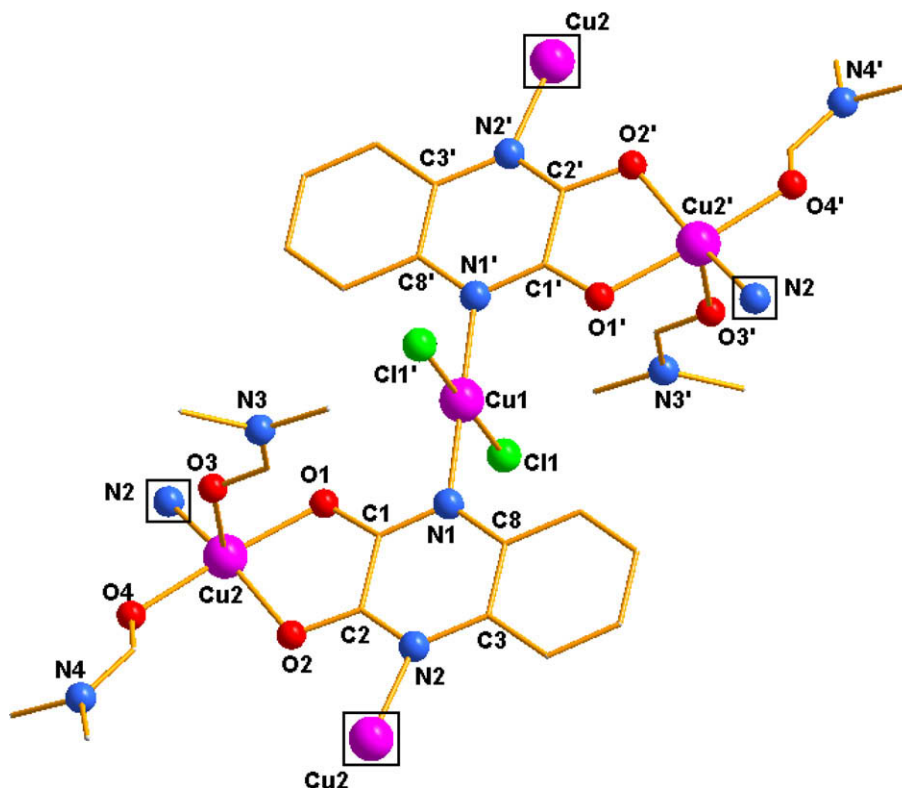

Fig. 1. The molecular structure of the repeat, centrosymmetric trinuclear unit present in the 3D network of **1**. The squared atoms belong to neighbouring units. The primed and unprimed atoms within the trinuclear unit are related by the symmetry operation $-x + 2, -y + 1, -z$.
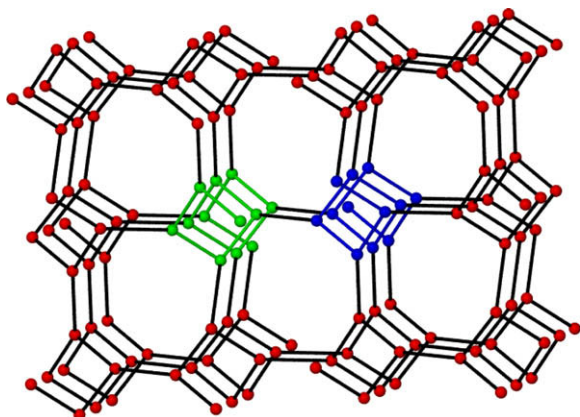
Fig. 3. Schematic representation of the $(8^2.10)$-a net of **1**, viewed along the c axis, containing 4-fold helices with opposite handedness (blue and green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 2**
Selected interatomic distances (Å) and angles (°).

Distances			
Cu(1)⋯Cu(2)	4.898(1)	Cu(2)–O(2)	1.972(2)
Cu(1)–Cl(1)	2.277(1)	Cu(2)–O(3)	2.336(2)
Cu(1)–N(1)	1.973(2)	Cu(2)–O(4)	1.988(2)
Cu(2)–O(1)	1.965(2)	Cu(2)–N(2″)	1.987(2)
Bond Angles			
Cl(1)–Cu(1)–Cl(1′)	180.0	O(1)–Cu(2)–N(2″)	93.8(1)
N(1)–Cu(1)–N(1′)	180.0	O(2)–Cu(2)–O(3)	91.1(1)
Cl(1)–Cu(1)–N(1)	89.8(1)	O(2)–Cu(2)–O(4)	89.9(1)
Cl(1)–Cu(1)–N(1′)	90.2(1)	O(2)–Cu(2)–N(2″)	158.9(1)
O(1)–Cu(2)–O(2)	89.5(1)	O(3)–Cu(2)–O(4)	87.0(1)
O(1)–Cu(2)–O(3)	90.5(1)	O(3)–Cu(2)–N(2″)	110.0(1)
O(1)–Cu(2)–O(4)	173.8(1)	O(4)–Cu(2)–N(2″)	92.4(1)

Symmetry operations used to generate equivalent atoms:
(′) $-x + 2, -y + 1, -z$; (″) $x - 1/4, -y + 5/4, z - 1/4$.

(τ = 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively) suggesting a distorted stereochemistry. As expected, the axial Cu(2)–O(3) bond is the longest [2.336(2) Å].

In solution, 1,4-dihydro-2,3-quinoxalinedione (H_2L', Scheme 1) is in equilibrium with the tautomers with one and two hydroxyl groups [14]. The question of which tautomer is predominant in the solid state was answered with the help of single-crystal X-ray crystallography some 30 years ago [14]; this technique revealed that the molecule is a dione (H_2L' in Scheme 1). A comparison of the structural data for the dianionic ligand in complex **1** with those of the free ligand H_2L' [14] shows that the excess electron density of the deprotonated nitrogen atom is partially delocalized over the oxygen atoms of the amido groups; this permits the formulation of the resonance structures **I** and **II** [15], see Scheme 2. In the case of **1**, the C–O bonds appear to be weaker than in H_2L' (1.278 and 1.284 versus 1.232 and 1.225 Å), whereas the C(1)-
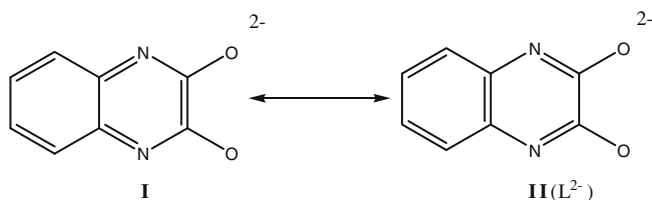
C(2) bond is stronger (1.484 versus 1.552 Å). This indicates less double-bond character in the CO bonds and more double-bond character in the CC bond for L^{2-}; this may suggest at first glance the dominance of the resonance form **I** (Scheme 2) in the real structure of the coordinated dianionic ligand. On the other hand, the CN bond lengths between the carbon atoms of the phenyl ring and nitrogen atoms in the heterocyclic ring for **1** (1.384 and 1.390 Å) are typical of those of a single C–N bond, as in the case of the free ligand (1.392 and 1.398 Å) [14]. Moreover, the C–N"amide" bond distances in **1** [(C(1)–N(1) = 1.316 Å, C(2)–N(2) = 1.318 Å)], which are less than the corresponding distances in the free ligand (1.337 and 1.345 Å), indicate the existence of double bonds. Thus, the CN bond distances of **1** are consistent with the dominance of the resonance form **II** (see Scheme 2) in the real structure of the coordinated dianionic ligand [15]; for this reason, the dianionic ligand is represented using the form **II** in Scheme 1 and Fig. 4 (vide infra).

The structural elements that are present in the repeat trinuclear unit of **1** arrange into a half folded square ring consisting of four Cu(1) and four Cu(2) ions and eight L^{2-} ligands (Fig. 2); each of these ligands is then coordinated through a square pyramidal copper [Cu(2)] via either nitrogen or both oxygens alternately to form a 3D coordination polymer. In this arrangement, the L^{2-} ligands serve as "T" shaped three-connected nodes while the Cu^{II} centres serve as linear bridges creating a rather uncommon three-connected $(8^2.10)$-a network, known also as **lig** (LiGe) (Fig. 3) [16,17]. This contains 4-fold helices with opposite handedness (Fig. 3). Although the $(8^2.10)$-a net has been predicted by Wells [18], it remains rare in coordination polymer chemistry. To the best of our knowledge, there are only five examples of coordination polymers adopting the **lig** topology [19], two of which are 2-fold interpenetrating [20]. Therefore, **1** represents the fourth example of a non-interpenatrating $(8^2.10)$-a topology and the sixth example of a $(8^2.10)$-a network. Given the relative roles of the ligands which serve as nodes and metal centres which serve as bridges within the $(8^2.10)$-a network, **1** can be characterized as an Inverted Metal–Organic Framework (IMOF) [21].

The ligand L^{2-} adopts the 3.1111 (using Harris notation [22]) coordination mode in **1** (Fig. 4). This is a novel coordination mode for this ligand. Complex **1** joins a handful of structurally character-
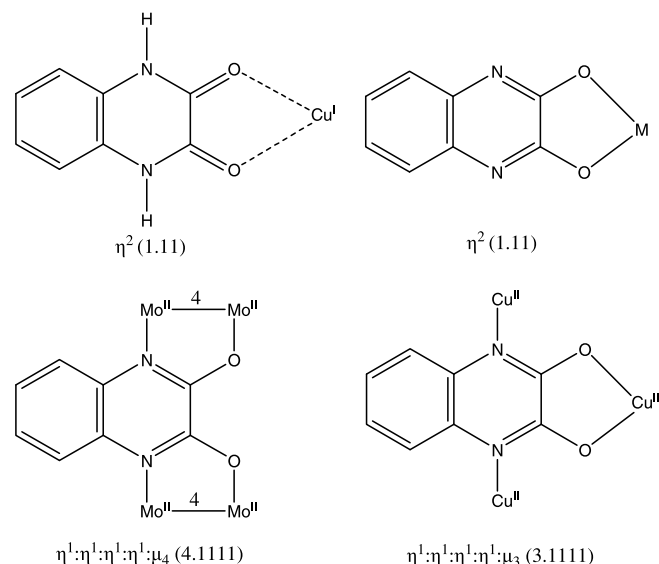

Fig. 4. The up-to-date crystallographically established coordination modes of 1,4-dihydro-2,3-quinoxalinedione (H_2L') and its 2,3-dioxyquinoxalinate(-2) dianionic ligand; the description of the modes by using the Harris notation [17] is shown in parentheses. The dashed lines represent weak interactions. M = Fe^{III}, Ru^{III}.

Scheme 2. Two resonance structures for the 2,3-dihydroxyquinoxalinate(-2) ion.

ized metal complexes containing H_2L' or L^{2-} as ligands [5,15,23,24]. The previously reported complexes are $[Mo^{II}_4 (DAniF)_6(L)]$ [5], $[Fe^{III}(L)_3]^{2-}$ [15], $[Cu^I(CN)(H_2L')]_n$ [23] and the organometallic compound $[(Cp^*)Ru(NO)(L)]$ [24], where $DAniF^-$ is the *N,N'*-di-*p*-anisylformamidinate(-1) ligand. The ligands H_2L' and L^{2-} have been observed in four ligation modes in these complexes (including **1**). The observed coordination modes are shown in Fig. 4. The metric parameters of L^{2-} in all the previous complexes support its formulation as shown in Scheme 1, i.e. the dominance of the resonance form **II** (see Scheme 2). Thus compound **1** is the first crystallographically characterized metal complex in which 2,3-dioxyquinoxalinate(-2) coordinates in the ene-1,2-diolate mode as a bridging ligand.

3.3. Magnetochemistry

Solid-state dc magnetic susceptibility data (Fig. 5) were collected on dried **1** under a constant field of 0.1 T in the temperature range 2.0-300 K. The product $\chi_M T$ at room temperature is 1.17 cm³ mol⁻¹ K per trinuclear unit, close to the value of 1.24 cm³ mol⁻¹ K expected for three non-interacting Cu^{II} ions with a *g* value of 2.1. The value of the $\chi_M T$ product decreases gradually upon cooling until ca. 60 K, and below this temperature it decreases rapidly down to a value of 0.62 cm³ K mol⁻¹ at 6 K, before increasing sharply at lower temperatures; the $\chi_M T$ value is 0.81 cm³ K mol⁻¹ at 2.0 K. Magnetization experiments performed at 2.0 K in the field range 0–5 T indicate a saturation value close to one electron per Cu^{II}_3 unit exhibiting a Brillouin shape for $S = 1/2$ and $g = 2.06(4)$, see inset of Fig. 5.

For a 3D compound in which all the superexchange pathways were operative and antiferromagnetic in nature, an $S = 0$ "ground state" would be expected in the absence of competitive interactions. The non-zero "ground" state of **1** can be explained by considering carefully the structural details of the complex. There are two different superexchange pathways, both provided by the ligand L^{2-}, and thus two different kinds of *J* values (Fig. 6; from now onwards the numbering scheme that will be used is the same with that used in the real structure of **1**, see Fig. 1). J_1 is associated with the *inter*trimer Cu(1)···Cu(2) interaction through the "pyrazine" portion of L^{2-} and J_2 is associated with two equivalent [one *intra*trimer Cu(1)···Cu(2) and one *inter*trimer Cu(2)···Cu(2)] interactions through the NCO^- and $NCCO^-$ moieties of L^{2-}. The magnetic data, which are indicative of the presence of one unpaired electron
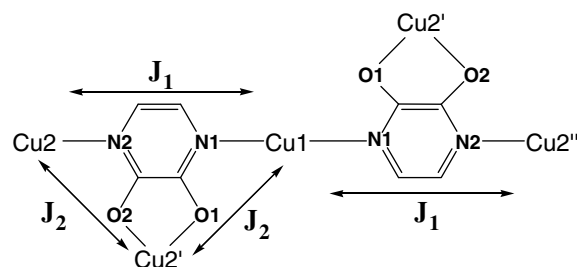
Fig. 6. The 2-*J* magnetic model initially considered for complex **1**; see the text for details. The benzene 'part' of the ligand L^{2-} has been omitted for clarity.

for each Cu^{II} triad, suggest that one of the pathways is not magnetically operative. Taking into account that (i) J_2 propagates the antiferromagnetic interaction in the three dimensions, and (ii) the quinoxaline bridge is a weak to moderate, but effective mediator of magnetic exchange interactions [25], we decided to fit the data assuming a negligible value of J_2. Since the J_1 interaction creates *pseudo*isolated Cu(2)···Cu(1)···Cu(2) subunits of the type shown in Fig. 6 (see also Fig. 1), we used the Hamiltonian of Eq. (2), including a Θ term in an attempt to adjust the low temperature data. Best-fit parameters are $J_1 = -10.4(3)$ cm⁻¹, $g = 2.057(6)$ and $\Theta = +1.1(1)$ K.

$$H = -J_1(S_2 \cdot S_1 + S_1 \cdot S_{2''}) \tag{2}$$

The obtained *J* value is in good agreement with reported values involving the exchange interaction between Cu^{II} ions through the quinoxaline bridging ligand, which is always weakly to moderately antiferromagnetic [25]. The minimum in the $\chi_M T$ versus T plot at 6 K (Fig. 5) indicates that J_2 (see Fig. 6) is not strictly zero. It is not possible to calculate accurately the value of this coupling constant for a 3D system with the observed topology, but the positive sign and low value of the Θ term clearly indicate that a very weak ferromagnetic interaction is mediated by the NCO^-/$NCCO^-$ moieties of L^{2-}.

4. Concluding comments and perspectives

The commercially available compound 1,4-dihydro-2,3-quinoxalinedione (H_2L') has fulfilled its promise as a good ligand for the preparation of coordination polymers with interesting structures and properties. The ligand has been transformed to the 2,3-dioxyquinoxalinate (L^{2-}) form upon complexation with copper(II). The obtained 3D coordination polymer **1** is novel in multiple ways, as described, but it also provides a rare example of a complicated structural type where the main magnetic exchange interaction is propagated through only one pathway. We also believe that the 'catecholate'-type deprotonated oxygen atoms of L^{2-} can each bridge two Cu^{II} ions, thus increasing its coordination potential to μ_4 or μ_5, a fact that may favour new structural types. Complexes of L^{2-} with Mn^{II}, Fe^{II}, Co^{II} and Ni^{II} are not known to date, and it is currently not evident whether the chemical identity and structure of such compounds are dependent on the particular nature of the metal ion; based on the unique nature of Cu^{II} among the divalent 3d-metals, we predict that the Mn^{II}, Fe^{II}, Co^{II} and Ni^{II}/L^{2-} polymers will have different structures and magnetic properties. Efforts to test the above expectations are currently in progress.

Supplementary data

CCDC 663054 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
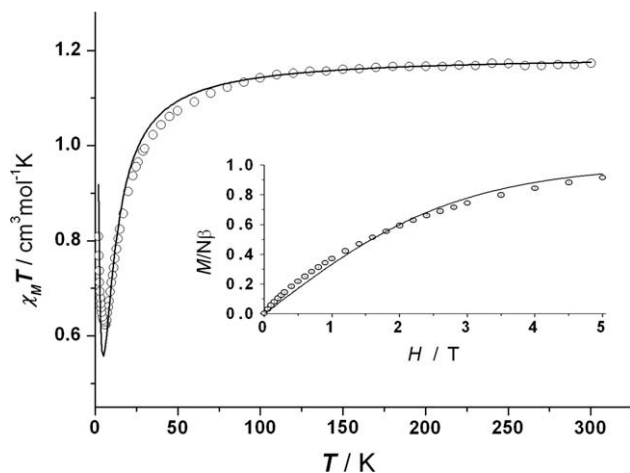

Fig. 5. $\chi_M T$ vs *T* for **1**; the solid line represents the best fit of the experimental data (see the text for the fit parameters). The inset shows magnetization data for the Cu^{II}_3 subunit; the solid line represents the Brillouin curve for the $S = 1/2$ state.

Acknowledgements

References

[1] (a) For selected reviews see: A.Y. Robin, K.M. Fromm, Coord. Chem. Rev. 250 (2006) 2127;
(b) A. Erxleben, Coord. Chem. Rev. 246 (2003) 203;
(c) S.R. Batten, Curr. Opin. Solid State Mater. Sci. 5 (2001) 107;
(d) D.-K. Bučar, G.S. Papaefstathiou, T.D. Hamilton, Q.L. Chu, I.G. Georgiev, L.R. MacGillivray, Eur. J. Inorg. Chem. (2007) 4559;
(e) C. Coulon, H. Miyasaka, R. Clérac, Struct. Bond. 122 (2006) 163;
(f) Y. Zhou, M. Hong, X. Wu, Chem. Commun. (2006) 135;
(g) M.L. Rosseinsky, Micropor. Mesopor. Mater. 73 (2004) 15.
[2] For an excellent review, see: S.R. Batten, R. Robson, Angew. Chem., Int. Ed. 37 (1998) 1460.
[3] For a review, see: C. Janiak, Dalton Trans. (2003) 2781.
[4] For example, see R.H. Cayton, M.H. Chisholm, J.C. Huffman, E.B. Lobkovsky, J. Am. Chem. Soc. 113 (1991) 8709.
[5] For example see F.A. Cotton, J.P. Donahue, C.A. Murillo, L.M. Perez, R. Yu, J. Am. Chem. Soc. 125 (2003) 8900.
[6] K.F. Konidaris, S.P. Perlepes, G. Aromi, S.J. Teat, A. Escuer, E. Manessi-Zoupa, Inorg. Chem. Commun. 11 (2008) 186.
[7] (a) For example, see L. Cheng, W.-X. Zhang, B.H. Ye, J.B. Lin, X.–M. Chen, Eur. J. Inorg. Chem. (2007) 2668;
(b) M.B. Doran, A.J. Norquist, D. O' Hare, Inorg. Chem. 42 (2003) 6968;
(c) S.O.H. Gutschke, D.J. Price, A.K. Powell, P.T. Wood, Angew. Chem., Int. Ed. 40 (2001) 1920.
[8] H.O. Desseyn, in: S. Patai (Ed.), The Chemistry of Acid Derivatives, vol. 2, Wiley, New York, pp. 291–293
[9] A.T.H. Lenstra, B. Bracke, B. Van Dijk, S. Maes, C. Van Alsenoy, H.O. Desseyen, S.P. Perlepes, Acta Crystallogr., Sect. B 54 (1998) 859.
[10] Th.C. Stamatatos, G.S. Papaefstathiou, L.R. MacGillivray, A. Escuer, R. Vicente, E. Ruiz, S.P. Perlepes, Inorg. Chem. 46 (2007) 8843.
[11] C. Airoldi, Inorg. Chem. 20 (1981) 998.
[12] K. Skorda, Th.C. Stamatatos, A.P. Vafiadis, A.T. Lithoxoidou, A. Terzis, S.P. Perlepes, J. Mrozinski, C.P. Raptopoulou, J.C. Plakatouras, E.G. Bakalbassis, Inorg. Chim. Acta 358 (2005) 565.
[13] A.W. Addison, T.N. Rao, J. Reedijk, T. Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[14] C. Svensson, Acta Chem. Scand. B 30 (1976) 581.
[15] M.C. Muñoz, R. Ruiz, M. Traianidis, A. Aukauloo, J. Cano, Y. Journaux, I. Fernández, J.R. Pedro, Angew. Chem., Int. Ed. 37 (1998) 1833.
[16] V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, CrystEngCommun 6 (2004) 377.
[17] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 127 (2005) 1504.
[18] A.F. Wells, Three-dimensional Nets and Polyhedra, Wiley, New York, 1977.
[19] (a) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang, X.-M. Chen, Dalton Trans. (2005) 3681;
(b) T. Wu, B.-H. Yi, D. Li, Inorg. Chem. 44 (2005) 4130;
(c) K. Li, Z. Xu, H. Xu, P.J. Carroll, J.C. Fettinger, Inorg. Chem. 45 (2006) 1032.
[20] (a) J.-C. Dai, X.-T. Wu, Z.-Y. Fu, S.-M. Hu, W.-X. Du, C.-P. Cui, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, Chem. Commun. (2002) 12;
(b) J.-C. Dai, X.-T. Wu, Z.-Y. Fu, S.-M. Hu, W.-X. Du, C.-P. Cui, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, Chem. Commun. (2008) 1296.
[21] (a) G.S. Papaefstathiou, L.R. MacGillivray, Angew. Chem., Int. Ed. 41 (2002) 2070;
(b) G.S. Papaefstathiou, L.R. MacGillivray, Coord. Chem. Rev. 246 (2003) 169.
[22] R.A. Coxall, S.G. Harris, D.K. Henderson, S. Parsons, P.A. Tasker, R.E.P. Winpenny, J. Chem. Soc., Dalton Trans. (2000) 2349.
[23] M. Heller, W.S. Sheldrick, Z. Anorg. Allg. Chem. 627 (2001) 569.
[24] K. Yang, S.G. Bott, M.G. Richmond, J. Chem. Crystallogr. 25 (1995) 283.
[25] (a) W.W. Richardson, W.E. Hatfield, J. Am. Chem. Soc. 98 (1976) 835;
(b) C.P. Landee, A. Delcheva, C. Galerium, G. Pena, M.M. Turnbull, R.D. Willett, Polyhedron 22 (2003) 2235.