Inorganica Chimica Acta 396 (2013) 66-71

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Synthesis and structure of mono-, di- and tri-nuclear copper(II) benzoate complexes with a tridentate N_2O donor Schiff base ligand

Pallab Bhowmik^{a,b,c}, Shouvik Chattopadhyay^{a,*}, Ashutosh Ghosh^{c,*}

^a Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata 700 032, India

^b Department of Chemistry, Sundarban Mahavidyalaya, Kakdwip, West Bengal, India

^c Department of Chemistry, University College of Science, University of Calcutta, 92, A.P.C. Road, Kolkata 700 009, India

ARTICLE INFO

Article history: Received 26 April 2012 Received in revised form 22 September 2012 Accepted 9 October 2012 Available online 17 October 2012

Keywords: Crystal structure Copper(II) Schiff base Benzoates Centrosymmetric dimer Trimer

ABSTRACT

Three copper(II) complexes [CuL(PhCOOH)(ClO₄)] (1), [Cu₂L₂(PhCOO)](ClO₄) (2) and [Cu₃L₂((o-NO₂)-PhCOO)₂](ClO₄) (3), where HL = 2-[1-(2-dimethylamino-ethylimino)-ethyl]-phenol, a well known Schiff base ligand, have been prepared and characterized by elemental analysis, IR and UV–Vis spectroscopy and single crystal X-ray diffraction studies. Complex 1 crystallizes in triclinic space group P - 1, complex 2 in monoclinic C_2 and complex 3 in monoclinic $P2_1/c$. The co-ordination polyhedron around each copper atom is best described as an elongated (4 + 1) square pyramid. Complex 1 is monouclear with a terminal benzoate, complex 2 is dinuclear containing a $\mu_{1,3}$ benzoate whereas complex 3 is trinuclear having a rare $\mu_{1,1,3}$ benzoate binding three copper centers simultaneously.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The design and synthesis of coordination polymers, based on transition-metal ions bridged by benzoate groups, to fabricate low-dimensional molecule-based magnetic materials are currently under intense research [1–8]. Among them, the coordination chemistry of polynuclear copper(II) complexes with bridging N₂O-donor ligands continues to be actively investigated because of their relevance to a number of areas of importance, including bioinorganic modeling chemistry [9], magnetic properties of polynuclear species [10], catalysis [11] and coordination polymers chemistry [12]. The dynamic character of the metal-ligand bonds, nature and coordinating topologies of the ligands used, metal-ligand ratio, different coordination geometries of the metal centers; nature of the counter ions and a variety of experimental conditions (such as the temperature, solvents and methods of crystallization) control the ultimate supra-molecular assemblies formed. The rising attention in this field is justified by the logical challenge in controlling and manipulating the self-assembly process [13-16]. To build up the coordination networks containing metal ions with magnetic anisotropy is also interesting because of the magnetic properties [17-22].

Polynuclear complexes containing bridging benzoate groups are also of current interest due to their biological relevance in many biochemical systems involving mono- and poly-metallic active sites [23,24]. In addition, polynuclear metal benzoates are good candidates for the investigation of exchange-coupling interaction between adjacent metal ions [25-28]. In these complexes, a benzoate group can assume many types of bridging conformations, the most important being triatomic syn-syn, anti-anti, and syn-anti and monatomic [27,28] (Scheme 1). These bridging modes usually bind two metal atoms, but a third $\mu_{1,1,3}$ bridging mode is also possible with which a carboxylate group binds three metal atoms, but such bridging modes are relatively rare [29]. A CSD search provides only two examples with copper(II), one with anthracene-9-carboxylato-0,0,0' and another with 2,6-bis(trifluoromethyl)benzoato-0,0,0', where three copper(II) are bridged by a benzoate group [30,31]. In the present paper, we report the facile syntheses, characterisations and X-ray structures of three copper(II) complexes with a tridentate N₂O donor Schiff base. Of these three complexes, one contains a rare $\mu_{1,1,3}$ benzoate bridge which binds three copper(II) centers simultaneously.

2. Experimental

All chemicals were of reagent grade and used without further purification.

^{*} Corresponding authors. Tel.: +91 9007777373.

E-mail addresses: shouvik.chem@gmail.com (S. Chattopadhyay), ghosh_59@ yahoo.com (A. Ghosh).

^{0020-1693/\$ -} see front matter \circledcirc 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ica.2012.10.003



Scheme 1. Syn–Syn, Syn–Anti and Anti–Anti bridging mode of benzoate group.

3. Materials

The reagents and solvents used were of commercially available reagent quality, unless otherwise stated.

3.1. Preparations

3.1.1. Synthesis of the ligand 2-[1-(2-dimethylamino-ethylimino)ethyl]-phenol (HL)

The ligand (HL) was synthesized by refluxing the *N*,*N*-dimethylethelenediamine (10 mmol) with 2-hydroxy acetophenone (10 mmol) in methanol solution (20 ml) for ca. 3 h. The ligand was not isolated. The methanolic solution was used for the synthesis of the complexes.

3.1.2. Synthesis of complex $[CuL(PhCOOH)(ClO_4)]$ (1)

A methanol solution (5 ml) of copper(II) perchlorate hexahydrate (0.74 g, 2 mmol) was added to the methanol solution of HL (2 mmol) with constant stirring. A solution of PhCOOH (0.245 g, 2 mmol) in methanol (5 ml) was then added to it and stirring was continued for 30 min. An immediate separation of a small amount of precipitate was filtered off. The filtrates were left to stand overnight in open atmosphere when crystalline complexes started to separate and were collected by filtration. Black single crystals suitable for X-ray diffraction were also obtained at that time.

Yield: 0.59 g (60%). Anal. Calc. for $C_{19}H_{23}ClCuN_2O_7$ (489.39): C, 46.53; H, 4.73; N, 5.71. Found C, 46.7; H, 4.5; N, 5.7%. IR (KBr, cm⁻¹): 1598 ($\gamma_{C=N}$), {1672.8 ($\gamma_{asC=O}$), 1374.5 ($\gamma_{sC=O}$)} for carboxyalate, 1113.7 1056.9 (γ_{ClO4}), UV–VIS, λ_{max} (nm), (ϵ_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 603, 371, 300, 271.

3.1.3. Synthesis of complexes $[Cu_2L_2(PhCOO)](ClO_4)$ (2)

It was prepared in a similar method to that of complex **1** except that trimethyl amine (2 mmol) was added after the addition of PhCOOH. Brown single crystals suitable for X-ray diffraction were obtained from the filtrate by slow evaporation in open atmosphere.

Yield: 1.117 g. (75%). Anal. Calc. for $C_{31}H_{39}Cu_2N_4O_8Cl: C, 49.11$; H, 5.18; N, 7.39. Found: C, 49.1; H, 5.2; N, 7.4%. IR (KBr, cm⁻¹): 1599.8 ($\gamma_{C=N}$), {1550.5 ($\gamma_{asC=0}$), 1434.2($\gamma_{sC=0}$), } for carboxyalate, 1094.4 (γ_{ClO4}), UV–VIS, λ_{max} (nm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 602, 368, 297, 269.

3.1.4. Synthesis of complex $[Cu_3L_2\{(o-NO_2)PhCOO\}_2](ClO_4)$ (3)

It was prepared in a similar method to that of complex **2** except o-nitrobenzoic acid was used instead of benzoic acid. Deep blue parallelepiped- shaped single crystals of 3 suitable for X-ray diffraction were obtained from the methanol of the complex by slow evaporation in air.

Yield: 1.68 g. (75%). Anal. Calc. for C₄₅H₄₁Cu₃N₇O₁₈Cl (FW 1193.95): C, 45.27; H, 3.46; N, 8.21. Found: C, 45.1; H, 3.58; N, 8.2%. IR (KBr, cm⁻¹): 1605.4 (γ_{C=N}), {1534.7 (γ_{asC=O}), 1396.2(γ_{sC=O})} for carboxyalate, 1091.7 (γ_{CIO4}), UV–VIS, λ_{max} (nm), (ϵ_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 594, 365, 298, 273.

3.2. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm⁻¹) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1200– 350 nm) were recorded in a Hitachi U-3501 spectrophotometer.

3.3. X-ray crystallography

Crystal data for the three crystals are given in Table 1. Single crystals having suitable dimensions for complexess **1**, **2** and **3** were used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The molecular structures were solved by direct methods and refinement by full-matrix least squares on F^2 using the SHELX-97 package [32]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Empirical absorption corrections were carried out with the ABSPACK program [33]. Data collection and structure refinement parameters and crystallographic data for the three complexes are given in Table 1.

4. Results and discussion

4.1. Syntheses

The ligand (HL) was prepared by the 1:1 condensation of the *N*,*N*-dimethylethelenediamine and 2-hydroxyacetophenone in methanol following the literature method [21]. The complexes were synthesized simply by allowing the Schiff base to react with

 Table 1

 Crystal data and structure refinement of complexes 1–3.

		•	
	1	2	3
Formula	$\mathrm{C_{19}H_{23}ClCuN_2O_7}$	$C_{31}H_{39}Cu_2N_4O_8Cl$	C45H41Cu3N7O18Cl
Μ	490.39	758.21	1193.95
Crystal system	triclinic	monoclinic	monoclinic
Space group	P1 (No. 2)	C ₂ (No. 5)	<i>P</i> 2 ₁ /c (No. 14)
a (Å)	8.8242(17)	13.452(2)	14.0418(4)
b (Å)	10.931(2)	17.648(3)	25.1942(6)
c (Å)	12.043(2)	7.421(2)	13.8830(3)
α (°)	66.977(2)	90	90
β (°)	83.821(2)	108.580(5)	95.696(1)
γ (°)	77.396(2)	90	90
$V(Å^3)$	1043.0(3)	1669.9(5)	4887.2(2)
Z	2	2	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.561	1.508	1.623
μ (mm ⁻¹)	1.219	1.408	1.431
F(000)	506	784	2432
R _{int}	0.026	0.101	0.051
Total reflections	8155	8174	73411
Unique reflections	4793	2450	9362
$I > 2\sigma(I)$	3313	2107	7043
R_1 , wR_2 $(I > 2\sigma(I))$	0.0404, 0.1140	0.0993, 0.3028	0.0388, 0.1064
T (K)	293	293	293

a methanol solution of $Cu(ClO_4)_2$ ·6H₂O and benzoic acid (for **1** and 2) or o-nitrobenzoic acid (for 3) in 1:1:1 M ratio. Equimolar amount of triethylamine was added for deprotonation of the respective benzoic acid for the synthesis of complexes 2 and 3 (see Section 2). The mononegative tridentate Schiff base ligand along with a benzoate or o-nitrobenzoate anion (in presence of trimethylamine) and perchlorate balance the charge of the complex species (2 and 3) but the metal ion remains coordinately unsaturated. In such a situation, the benzoate group can exploit their well known bridging properties to complete the coordination sphere in copper(II) to result in dinuclear (2) and trinuclear (3) complexes. The benzoic acid remains in the protonated form in complex **1**, as triethylamine is not used during its synthesis. The coordination polyhedron around copper(II) is completed by the coordination of a perchlorate oxygen atom as evident from the X-ray crystal structure. It is worth mentioning that in absence of the benzoic acid, a water bridged dinuclear complex is formed, the structure of which is reported elsewhere [34]. Use of copper fluoroborate produced the same hydroxo bridged dimeric cation [35]. Use of copper acetate instead of copper perchlorate produces $[CuL(OAc)(H_2O)]$ in which copper(II) assumes a distorted square pyramidal geometry [36]. The details of the synthesis are shown in Scheme 2.

4.2. Structural description of complexes 1, 2 and 3

4.2.1. Complex 1

The structure of **1** together with the atomic numbering scheme is shown in Fig. 1. The co-ordination polyhedron around the copper(II) is best described as an elongated (4 + 1) square pyramid. Two nitrogen atoms, N(1) and N(2), and one oxygen atom, O(1), from the deprotonated Schiff base ligand L and one oxygen atom O(2) from a coordinated benzoic acid define the equatorial plane. One oxygen atom, O(7) of a perchlorate group is semi-coordinated to the copper(II) in the axial position at distances of 2.423(0) Å. There is a slight distortion to the square plane and the deviations of the coordinating atoms N(1), N(2), O(1), O(2) from the leastsquare mean plane through them are 0.089, -0.086, 0.088 and -0.085 Å, respectively, and that of the copper(II) from the same



Scheme 2. Synthesis of complexes 1, 2 and 3 and some related complexes.

plane is 0.124 Å. This deviation from planarity of the equatorial plane also manifests itself in the trans angles [O(1)-Cu(1)-N(2), N(1)-Cu(1)-O(2)], which are 167.59 and 176.95.

The puckering analysis [37,38] of Cu(1)–N(1)–C(10)–C(11)–N(2) ring with q3 = 0.060(4) Å, q2 = Q = 0.777(4) Å indicates the fivemembered chelate ring assumes a gauche conformation. The N(1)–Cu(1)–N(2) angle is 92.4(2).

4.2.2. Complex 2

The structure determination reveals that complex 2 consists of a discrete, centrosymmetric dinuclear complex cation [(CuL)₂ (PhCOO)]⁺ and one non-coordinated perchlorate anion. A view of the complex is given in Fig. 2. In the dimer, two distorted square-pyramidal copper(II) centers are bridged by a centrosymmetrically related benzoate anion in $\mu_{1,3}$ fashion leading to relatively small Cu…Cu distance (3.136 Å). Within the dimeric unit, each of the two trigonally distorted square-pyramidal copper(II) centers is coordinated equatorially by N(1), N(2) and O(1) of the deprotonated tridentate Schiff base ligand (L) and an oxygen atom, O(2), of the bridging $\mu_{1,3}$ benzoate ion, comprising the basal plane. A second oxygen atom, O(1)*, from the centrosymmetrically related bridging phenoxo of other Schiff base coordinates axially at a rather long distance (Cu1...O1, 2.574(11) Å) furnishing an elongated square-pyramidal (4 + 1) geometry for each copper(II) center in the dimeric complex (Symmetry element * = 1 - x, y, -z). The basal bond lengths are 1.924(15), 2.012(18), 1.949(13) and 1.872(13) Å for Cu1...N1, Cu1...N2, Cu1...O2, and Cu1...O1, respectively, for both of two copper(II) centers as they are centrosymmetrically related to each others. The deviation of the coordinating atoms, N1, N2, O1, and O2, from the mean plane passing



Fig. 1. The structure of **1** with ellipsoids at 30% probability. The H atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): Cu(1)-O(1) 1.892(2), Cu(1)-O(2) 1.997(2), Cu(1)-N(1) 1.941(3), Cu(1)-N(2) 2.017(3), Cu(1)-O(7) 2.422(3), O(1)-Cu(1)-N(1) 91.90(13), O(1)-Cu(1)-O(2) 90.06(10), O(2)-Cu(1)-N(2) 90.75(11), N(1)-Cu(1)-N(2) 86.83(13), O(1)-Cu(1)-N(2) 167.57(12), O(2)-Cu(1)-N(1) 176.90(12).



Fig. 2. The structure of **2** with ellipsoids at 20% probability. The H atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): Cu(1)-O(1) 1.872(13); Cu(1)-O(2) 1.949(13), Cu(1)-N(1) 1.924(15), Cu(1)-N(2) 2.012(18); $Cu(1)-O(1^*)$ 2.574(11), O(1)-Cu(1)-N(1) 93.0(6), O(1)-Cu(1)-N(2) 91.1(5), O(2)-Cu(1)-N(2) 87.7(6), N(1)-Cu(1)-N(2) 87.4(7), O(1)-Cu(1)-N(2) 169.8(5), O(2)-Cu(1)-N(1) 173.9(6), $O(1)-Cu(1)-O(1^*)$ 84.1(4), $O(1^*)-Cu(1)-O(2)$ 96.1(4), $O(2)-C(13)-O(2^*)$ 129(2). Symmetry element * = 1 – x, y, –z.

through them are not more than 0.061 Å, and that of the Copper(II) atom from the same plane is 0.101 Å.

4.2.3. Complex 3

The structure of **3** together with the atom numbering scheme is shown in Fig. 3. The asymmetric unit consists of a tri-nuclear species and a perchlorate ion. In the trinuclear structure, there are three bridging o-nitrobenzoate moieties; out of which two are in $\mu_{1,3}$ syn-syn bridging modes and the third one is in a very rare $\mu_{1,1,3}$ mode binding three copper(II) center. Each $\mu_{1,3}$ syn-syn bridging benzoate binds to two Copper(II) centers; Cu(1) and Cu(2) are bridged by O(2) and O(3), whereas Cu(2) and Cu(3) by O(6) and O(5), respectively with syn-syn bridging fashion. O(8) of $\mu_{1,1,3}$ benzoate moiety binds Cu(1) and O(7) binds to Cu(2,3) in the same syn-syn fashion. It is here worth mentioning that this type of $\mu_{1,1,3}$ benzoate bridge, binding three copper(II) units at a time is very rare in the literature. Only two complexes have been reported till date [30,31].

The co-ordination polyhedron around the each copper(II) is best described as an elongated (4 + 1) square pyramid. The square pyramidal geometry of central Cu(2) is formed by five oxygen atoms; two phenoxo oxygen atoms, O(1) and O(4), from two Schiff base units, three oxygen atoms O(3), O(6) and O(7) from three o-nitrobenzoate units. The square pyramidal environment of each the two terminal copper(II) is formed by N(1), N(2), O(1) or N(3), N(4), O(4) of the Schiff base ligand and O(2), O(8) or O(5), O(7) of two different o-nitrobenzoates.

Cu···Cu distances in the complex **3** are Cu(1)–Cu(2) 3.143(5) Å, Cu(2)–Cu(3) 3.127(5) Å and Cu(1)–Cu(3) 5.931 Å. The coordinating atoms around central copper(II), Cu(2), in the basal plane (i.e. O(1), O(3), O(4), and O(6)) deviate from the mean square plane passing



Fig. 3. The structure of **1** with ellipsoids at 10% probability. The H atoms are not shown for clarity. Selected bond lengths (Å): Cu(1)–O(1) 1.907(2), Cu(1)–O(2) 1.978(2), Cu(1)–O(8) 2.329(3), Cu(1)–N(1) 1.947(3), Cu(1)–N(2) 2.018(3), Cu(2)–O(1) 1.987(2), Cu(2)–O(3) 1.913(2), Cu(2)–O(4) 2.092(19), Cu(2)–O(6) 1.917(2), Cu(2)–O(7) 2.203(2), Cu(2)–O(8) 2.848(3), Cu(3)–O(4) 1.908(2), Cu(3)–O(5) 1.990(2), Cu(3)–O(7) 2.484(2), Cu(3)–N(3) 1.952(3), Cu(3)–N(4) 2.006(3).

through them are -0.175, 0.166, -0.159 and 0.168 Å, respectively and the deviation of the Cu(2) from the same plane is 0.318 Å. The deviation of the coordinating atoms in the basal plane around terminal Cu(1) (i.e. N(1), N(2), O(1), O(2)) from the mean plane passing through them are -0.12, 0.114, -0.117, and 0.112 Å, respectively and that of copper(II), Cu(1), from the same plane is 0.144 Å. Similar is the case for another terminal copper(II), Cu(3), which deviates from the mean plane passing through N(3), N(4), O(5), and O(4) is 0.116 Å and the deviations of the coordinating atoms from the same plane are -0.118, 0.116, -0.114, and 0.116 Å, respectively. The angles between mean square planes, containing terminal Cu(1) and central Cu(2), terminal Cu(3) and central Cu(2), terminal Cu(1) and terminal Cu(3) are 49.95, 55.37 and 74.86°, respectively.

Bond distances between benzoate oxygen and copper(II) for $\mu_{1,3}$ and $\mu_{1,1,3}$ bridging modes differ significantly. Longer bond distances of $\mu_{1,1,3}$ bridging o-nitrobenzoates with different copper(II) centers, 2.203(2) {Cu(2)–O(7)}, 2.484(2) {Cu(3)–O(7)} and 2.329(3) Å {Cu(1)–O(8)}, indicate the coordination in the axial positions, whereas smaller bond distances of $\mu_{1,3}$ bridging o-nitrobenzoates, 1.978(2) {Cu(1)–O(2)}, 1.913(2) {Cu(2)–O(3)}, 1.917(2) {Cu(2)–O(6)} and 1.990(2) Å {Cu(3)–O(5)} imply coordination in equatorial plane. The bridging angles are 127.10(3)° (O2–C13– O3), 126.60(3)° (O5–C32–O6) and 126.20(3)° (O7–C39–O8) for two $\mu_{1,3}$ and one $\mu_{1,1,3}$ benzoate respectively.

4.3. IR and electronic spectra and magnetic moments

In the IR spectra of all the complexes 1, 2 and 3 strong and sharp bands due to azomethine $\gamma(c=N)$ appear at 1598, 1599.8 and 1605.4 cm⁻¹, respectively. The other IR spectral bands in the 1300–1650 cm^{-1} region are difficult to assign due to the appearance of several absorption bands both from the Schiff base and from benzoate ligands. Nevertheless, by comparing the IR spectra of the Ni(II) complexes of the same ligand but with other anions (azide and halides), the strong bands at 1672.8, 1550.5 and 1534.7 cm⁻¹ may be assigned to the antisymmetric stretching mode of the benzoate group, whereas the bands at 1374.5, 1434.2 and 1396.2 \mbox{cm}^{-1} may be attributed to the symmetric stretching modes of the benzoate ligands in the complexes 1, 2 and 3, respectively. A strong and sharp band due to perchlorate appears at 1113.7, 1094.4, and 1091.7 cm⁻¹ for complexes 1, 2 and 3, respectively [39]. The splitting of the band at1056.9 cm⁻¹ in the IR spectrum of 1 is indicative of the presence of coordinated perchlorate ions.

The electronic spectra of **1**, **2** and **3** in acetonitrile solution display d–d absorption band at 603, 602 and 594 nm, respectively. The positions of these bands are consistent with the observed square-pyramidal geometry around the copper(II) centers [40,41]. The UV absorption bands at 371, 300 nm for complex **1**, 368, 297 nm for complex **2** and 365, 298 nm for complex **3** nm

may be assigned to the charge transfer transition. The bands at 271, 269 and 273 for complexes **1**, **2** and **3**, respectively are due to the π - π ^{*} transition of aromatic ring.

Room temperature magnetic susceptibility measurements show that complexes **1**, **2** and **3** have magnetic moments close to 1.73 BM as expected for discrete magnetically non-coupled spin-only value for copper(II), as was observed in similar systems [42–43].

5. Summary

The facile synthesis and characterization of three copper(II) complexes with a Schiff base ligand have been described in this paper. The first one is mononuclear, the second one is dinuclear and the last one is trinuclear. A $\mu_{1,1,3}$ bridging benzoate is present in trinuclear complex. The mononuclear complex can be converted to the dinuclear one by using a base which helps to deprotonate the benzoic acid, thereby facilitating the dimerization. However, trinuclear complex is formed when o-nitrobenzoic acid is used. The –I effect of nitro group increases the acidity of benzoate group, allowing it to bind simultaneously three metal atoms in presence of triethylamine. The facile synthesis of complex **3** may afford a convenient synthetic route for this type of trinuclear species.

Acknowledgments

Crystallographic data were performed at the DST-FIST, Indiafunded Single Crystal Diffractometer Facility at the Department of Chemistry, Jadavpur University.

Appendix A. Supplementary data

CCDC Nos. 842621 (complex **1**), 842622 (complex **2**) and 842623 (complex **3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.a-c.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.ica.2012.10.003.

References

- [1] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.
- [2] S. Hazra, B. Sarkar, S. Naiya, M.G.B. Drew, J. Ribas, C. Diaz, A. Ghosh, Inorg. Chem. Commun. 14 (2011) 1860.
- [3] R. Biswas, P. Kar, Y. Song, A. Ghosh, Dalton Trans. 40 (2011) 5324.

- [4] M. Verdaguer, Polyhedron 20 (2001) 1115.
- [5] D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268.
- [6] H. Oshio, M. Nakano, Chem. Eur. J. 11 (2005) 5178.
- [7] J.S. Miller, Dalton Trans. (2006) 2742.
- [8] A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, G. Christou, Angew. Chem., Int. Ed. 43 (2004) 2117.
- [9] E.I. Solomon, U.M. Sundaram, T.E. Machonkin, Chem. Rev. 96 (1996) 2563.
- [10] D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268.
- [11] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M. da Silva, A.J.L. Pombeiro, Angew. Chem., Int. Ed. 44 (2005) 4345.
- [12] A.M. Kirillov, Y.Y. Karabach, M. Haukka, Inorg. Chem. 47 (2008) 162.
- [13] K.S. Murray, Adv. Inorg. Chem. 43 (1995) 261.
- [14] R.E.P. Winpenny, Adv. Inorg. Chem. 52 (2001) 1.
- [15] C. Janiak, Dalton Trans. (2003) 2781.
- [16] S. Kitagawa, R. Kitaura, S.-i. Noro, Angew. Chem., Int. Ed. 43 (2004) 2334.
- [17] R.L. Carlin, Magnetochemistry, Springer-Verlag, Berlin, Heidelberg, 1986.
- [18] L.-M. Zheng, S. Gao, P. Yin, X.-Q. Xin, Inorg. Chem. 43 (2004) 2151.
- [19] T.D. Harris, M.V. Bennett, J. Am. Chem. Soc. 132 (2010) 3980.
- [20] J.-R. Li, Q. Yu, Y. Tao, X.-H. Bu, J. Ribas, S.R. Batten, Chem. Commun. (2007) 2290.
- [21] M. Yuan, F. Zhao, W. Zhang, Z.-M. Wang, S. Gao, Inorg. Chem. 46 (2007) 11235.
- [22] A. Rodríguez-Diéguez, M.A. Palacios, A. Sironi, E. Colacio, Dalton Trans. (2008) 2887.
- [23] V.L. Pecoraro (Ed.), Manganese Redox Enzymes, VCH, New York, 1992, p. 1228.
- [24] K. Wieghardt, Angew. Chem. Int., Ed. Engl. 28 (1989) 1153.
- [25] E. Coronado, Magnetic Molecular Materials, in: D. Gattes-chi, O. Khan, J.E. Miller, F. Palacio (Eds.), Nato ASI Series, vol. E198, Kluwer Academic Publisher, Dordrecht, 1991, pp. 267–279.
- [26] M. Sarkar, R. Clérac, C. Mathoniére, N.G.R. Hearns, V. Bertolasi, D. Ray, Inorg. Chem. 49 (2010) 6575.
- [27] E. Colacio, J.M. Dominguez-Vera, R. Kivekäs, J.M. Moreno, A. Romerosa, J. Ruiz, Inorg. Chim. Acta 212 (1993) 115.
- [28] Z.N. Chen, S.X. Liu, J. Qiu, Z.M. Wang, J.L. Huang, W.X. Tang, J. Chem. Soc., Dalton Trans. (1994) 2989.
- [29] CSD Search, Supporting Information.
- [30] C.-S. Liu, J.-J. Wang, Inorg. Chem. 46 (2007) 6299.
- [31] Y. Sevryugina, D.D. Vaughn, M.A. Petrukhina, Inorg. Chim. Acta 360 (2007) 3103.
- [32] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Germany, 1997.
- [33] ABSPACK, version 1, Oxford Diffraction, Abingdon, 2005.
- [34] P. Talukder, S. Sen, S. Mitra, L. Dahlenberg, C. Desplanches, J.-P. Sutter, Eur. J. Inorg. Chem. (2006) 329.
- [35] C. Biswas, M.G.B. Drew, S. Asthana, C. Desplanches, A. Ghosh, J. Mol. Struct. 965 (2010) 39.
- [36] N. Mondal, M.K. Saha, B. Bag, S. Mitra, G. Rosair, M.S.E. Fallah, Polyhedron 20 (2001) 579.
- [37] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
- [38] J.C.A. Boyens, J. Cryst. Mol. Struct. 8 (1978) 317.
- [39] K. Nakamoto, Infrared Spectra of Inorganic Compounds, Wiley, New York, 1970.
- [40] S. Chattopadhyay, M.S. Ray, M.G.B. Drew, A. Figuerola, C. Diaz, A. Ghosh, Polyhedron 25 (2006) 2241.
- [41] S. Biswas, A. Ghosh, Polyhedron 39 (2012) 31.
- [42] M.S. Ray, R. Bhattacharya, S. Chaudhuri, L. Right, G. Boceli, G. Mukhopadhyay, A. Ghosh, Polyhedron 22 (2003) 617.
- [43] D. Maity, S. Chattopadhyay, A. Ghosh, M.G.B. Drew, G. Mukhopadhyay, Polyhedron 28 (2009) 812.