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Mendeleev Commun., 2010, **20**, 109–110
Mendeleev Communications

Synthesis and crystal structure of two new dinuclear oxalato-bridged copper(II) complexes containing bis(2-pyridyl)amine as a ligand

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DOI: 10.1016/j.mencom.2010.03.015

Two new dinuclear oxalate-bridged copper(II) complexes $[Cu_2(dpyam)_2(\mu\text{-}C_2O_4)(DMF)_2](I)_{1.6}(NO_3)_{0.4}$ and $[Cu_2(dpyam)_2(\mu\text{-}C_2O_4)(DMF)_2](ClO_4)_2$ (dpyam = di-2-pyridylamine) were prepared directly from their components by the molar ratio method and their crystal structures were determined by X-ray crystallography.

Over the last two decades increasing interest has been devoted to study of exchange interactions between metal ions through extended bridging groups in dinuclear and polynuclear metal complexes.[1] Dinuclear copper(II) complexes with the oxalate dianion acting as a bis-didentate bridging ligand are suitable model compounds for magneto-structural correlations.[2–14] General trends of magnetic behaviours of these compounds are well established, the oxalate bridge being very efficient in transmission of the antiferromagnetic interactions between the two copper(II) atoms.[4] The crystal structures, spectroscopic properties and magneto-structural correlation of the most relevant complexes were described previously.[5] The exchange interaction between copper ions *via* the oxalate bridge is strongly dependent on the geometry around the copper ions, which is sensitive to the nature of counterions, solvent molecules and terminal ligands. In order to extend the investigation by modifying to other counterions and solvents, this paper reports the synthesis and the results of the structure determination of dinuclear oxalate-bridged copper(II) complexes, $[Cu_2(dpyam)_2(\mu\text{-}C_2O_4)(DMF)_2](I)_{1.6}(NO_3)_{0.4}$ **1** and $[Cu_2(dpyam)_2(\mu\text{-}C_2O_4)(DMF)_2](ClO_4)_2$ **2**.†

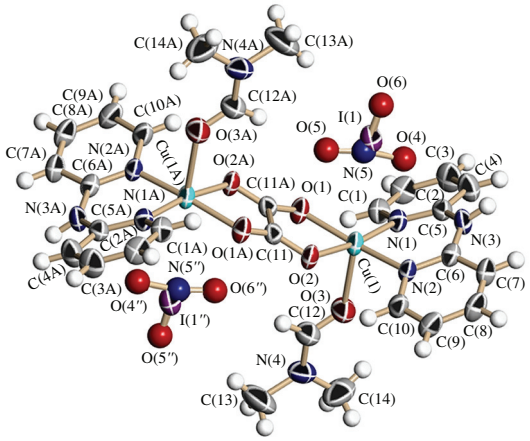

Figure 1 Plot of the structure of $[Cu_2(dpyam)_2(\mu\text{-}C_2O_4)(DMF)_2](I)_{1.6}(NO_3)_{0.4}$ **1**. Atoms with an 'A' are generated by a mirror plane. Selected bond lengths (Å): Cu(1)–N(1) 1.970(3), Cu(1)–N(2) 1.987(3), Cu(1)–O(1) 2.021(2), Cu(1)–O(2) 1.992(2), Cu(1)–O(3) 2.270(3), Cu(1)–O(4) 2.990(1), Cu(1)–O(5) 3.298(1), Cu(1)–I(1) 3.415(1), Cu(1)–Cu(1A) 5.219(1); selected bond angles (°): N(1)–Cu(1)–N(2) 91.35(1), N(1)–Cu(1)–O(2) 171.66(1), N(2)–Cu(1)–O(2) 92.09(1), N(1)–Cu(1)–O(1) 92.95(1), N(2)–Cu(1)–O(1) 171.67(1), O(2)–Cu(1)–O(1) 82.74(9), N(1)–Cu(1)–O(3) 90.29(1), N(2)–Cu(1)–O(3) 92.85(1), O(2)–Cu(1)–O(3) 97.12(1), O(1)–Cu(1)–O(3) 94.26(1).

The structure of **1** consists of the centrosymmetric dinuclear cation $[Cu_2(dpyam)_2(\mu\text{-}C_2O_4)(DMF)_2]^{2+}$ and non-coordinating I^- and NO_3^- anions in site occupancies of 0.8 and 0.2, respectively (Figure 1).‡ Each Cu^{II} centre is pentacoordinated to two nitrogen atoms of a dpyam ligand and two oxygen atoms of the oxalate bridge [Cu–N/O distances vary from 1.970(3) to 2.021(2) Å] in the basal plane, with the axial site occupied by an oxygen atom of DMF [*d*(Cu–O) 2.270(3) Å] giving approximately CuN_2O_2O' chromophore. The Cu···I (3.415 Å) and Cu···ONO_2 (2.990 Å) distances are quite long, which have been considered as a very weak interaction.[15] Several parameters are used to define the coordination environment around the pentacoordinated metal center, and one of the most commonly used parameters is the factor τ ($\tau = 0$ for an ideal square pyramid, and $\tau = 1$ for an ideal trigonal bipyramid), the value of which is zero, suggesting an almost ideal square pyramidal geometry of Cu^{II}. The four basal atoms are not coplanar, showing a slight tetrahedral distortion with a dihedral angle of 9.8(1)° formed

† *Synthesis of* **1**: a hot DMF solution (10 ml) of dpyam (0.17 g, 1.0 mmol) was added to a hot aqueous solution (10 ml) of $Cu(NO_3)_2{\cdot}3H_2O$ (0.24 g, 1.0 mmol). The mixture was heated at 80 °C with continuous stirring for 10 min; then, an aqueous solution (10 ml) of $H_2C_2O_4$ (0.06 g, 0.5 mmol) and an aqueous solution (10 ml) of KI (0.16 g, 1.0 mmol) were slowly added subsequently. After standing at room temperature for a few weeks, green crystals of complex **1** were obtained. Yield, ~55%. FTIR (KBr pellets, ν/cm^{-1}): 1660 (s), 1365 (w), 1341 (m), 845 (m). Electronic spectrum (solid-state) shows a broad band at 14610 cm^{-1} with a lower energy shoulder at 10520 cm^{-1} assigned to the d_{xy}, d_{yz}, $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions. Found (%): C, 36.05; H, 3.49; N, 12.76. Calc. for $C_{28}H_{32}N_{8.4}Cu_2O_{7.2}I_{1.6}$ (%): C, 36.10; H, 3.46; N, 12.63.

Synthesis of **2**: a hot solution of dpyam (0.17 g, 1.0 mmol) in DMF (10 ml) was added to a hot aqueous solution (10 ml) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.37 g, 1.0 mmol), then $H_2C_2O_4$ (0.03 g, 0.25 mmol) in water (10 ml) was added. The mixture was heated at 80 °C with continuous stirring for 10 min. The resulting green solution was allowed to evaporate at room temperature. After a few weeks, green crystals of complex **2** were obtained, which were filtered off and dried in air. Yield, ~70%. FTIR (KBr pellets, ν/cm^{-1}): 1668 (s), 1341 (m), 1120 (s), 1116 (s), 1100 (s), 1069 (s), 845 (m). Electronic spectrum (solid-state) shows a broad band at 14910 cm^{-1} with a lower energy shoulder at 10525 cm^{-1} assigned to the d_{xy}, d_{yz}, $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions. Found (%): C, 37.35; H, 3.63; N, 12.48. Calc. for $C_{28}H_{32}N_8Cu_2O_{14}Cl_2$ (%): C, 37.26; H, 3.57; N, 12.41.

between the CuN_2 and CuO_2 planes. The copper atoms are slightly (by 0.004 Å) displaced from the basal planes toward the apical positions and are slightly linked through a bis-didentate oxalate molecule with a Cu···Cu separation of 5.219(1) Å; the dihedral angle formed between the basal plane and the oxalate plane of 16.4(1)° agrees with the planar central Cu–ox–Cu core.[7] The non-coordinated iodide and nitrate anions occur in the same positions in the lattice structure, which have 80 and 20% occupancies for I^- and NO_3^-, respectively. The weak hydrogen bonding occurs between the amine N atom and the I^- (N···I distances 3.656 Å) and the N_{amine} and $O_{nitrate}$ (N···O distances 2.974 Å) of neighbouring units.

The structure of complex **2** (Figure 2)‡ is isotypic only in terms of Cu^{II} based complex with **1**. The geometry around the copper atom can be considered as an almost square pyramidal environment ($\tau = 0$). The corresponding Cu–O and Cu–N distances in the basal plane are in the range from 1.972(2) to 2.011(2) Å, while the axial $Cu–O_{DMF}$ bond distance [2.204(2) Å] is significantly longer than those in the basal plane. The four donor atoms on the equatorial plane are not perfectly planar, showing a small tetrahedral distortion, with a dihedral angle of 15.5(1)° formed between the CuO_2 and CuN_2 planes. Both copper atoms are linked through an oxalate bridge, with a Cu···Cu distance of 5.221(6) Å and the dihedral angle formed between the basal plane and the oxalate plane is 17.4(1)°. The copper atom is lifted 0.008 Å out of that plane toward the apical position. The perchlorate anion is close to the coordination sphere of Cu(1) but the quite long $Cu···OClO_3$ distance of 3.041 Å seems to indicate a very weak interaction. The hydrogen bonding occurs between the amine N atom and an O atom of neighbouring perchlorate with a N···O contact of 2.998(1) Å.

‡ *Crystallographic data for* **1**: at 273(2) K crystals of $C_{28}H_{32}N_{8.4}Cu_2O_{7.2}I_{1.6}$ are triclinic, space group $P\bar{1}$, $a = 8.4614(4)$, $b = 8.9112(4)$ and $c = 12.3824(6)$ Å, $\alpha = 71.913(1)°$, $\beta = 76.329(1)°$, $\gamma = 80.225(1)°$, $V = 857.68(7)$ Å^3, $Z = 1$, $M = 973.50$, $d_{calc} = 1.889$ g cm^{-3}, μ(MoKα) = 3.095 cm^{-1}, $F(000) = 476$.

Crystallographic data for **2**: at 293(2) K crystals of $C_{28}H_{32}N_8Cu_2O_{14}Cl_2$ are triclinic, space group $P\bar{1}$, $a = 8.4780(5)$, $b = 9.1158(6)$ and $c = 12.7487(8)$ Å, $\alpha = 70.055(10)°$, $\beta = 74.391(10)°$, $\gamma = 77.445(1)°$, $V = 883.39(10)$ Å^3, $Z = 1$, $M = 902.60$, $d_{calc} = 1.679$ g cm^{-3}, μ(MoKα) = 1.434 cm^{-1}, $F(000) = 460$.

Intensities of 4658 and 10621 reflections for **1** and **2**, respectively, were collected at 273 K for **1** and at 293 K for **2**, on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinements were performed using the program SAINT [Siemens. SAINT, Version 4]. An empirical absorption correction with the SADABS program[16] was applied, which resulted in transmission coefficients ranging from 0.527 to 1.000 for complex **1** and from 0.776 to 1.000 for complex **2**.

The structures were solved by direct methods and refined by a full matrix least-squares method on F^2_{obs} with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package. For **1** and **2**, respectively, the refinement converged to $wR_2 = 0.0878$ and 0.0976, GOF = 1.037 and 1.041 for all independent reflections [$R_1 = 0.0340$ and 0.0480 was calculated against F for 3083 and 4245 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXS-97 and SHELXL-97. For complex **1**, the I^- anion has an occupancy factor of 0.80. Simultaneously, there is a nitrogen atom from NO_3^- ion practically coincident with the I^- with an occupancy factor of 0.20. Introducing the fractional NO_3^- ion into the model caused the R value to drop from 0.062 to 0.034. All hydrogen atoms in **2** were located in a difference Fourier map and refined isotropically, while all hydrogen atoms in **1** were fixed and allowed to ride on attached atoms. The ClO_4^- anion in **2** is disordered, with two conformers having occupancy factors of 0.5.

CCDC 689326 and 689327 contain 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.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

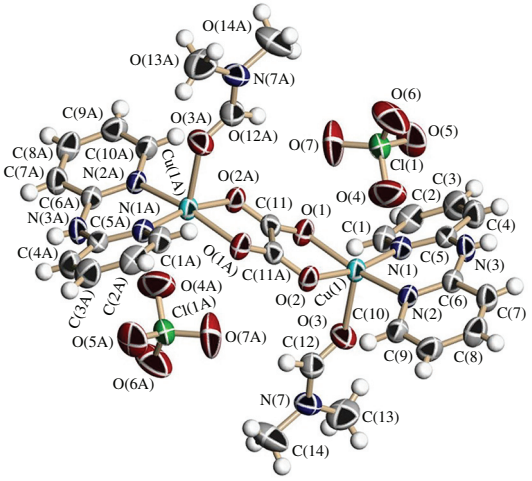

Figure 2 Plot of the structure of $[Cu_2(dpyam)_2(\mu\text{-}C_2O_4)(DMF)_2](ClO_4)_2$ **2**. Atoms with an 'A' are generated by a mirror plane. Selected bond lengths (Å): Cu(1)–N(1) 1.972(2), Cu(1)–N(2) 1.983(2), Cu(1)–O(1) 2.011(1), Cu(1)–O(2) 1.994(2), Cu(1)–O(3) 2.204(2), Cu(1)–O(4) 3.041(1), Cu(1)–Cu(1A) 5.221(6); selected bond angles (°): N(1)–Cu(1)–N(2) 91.22(9), N(1)–Cu(1)–O(2) 168.16(9), O(2)–Cu(1)–O(1) 82.76(8), N(1)–Cu(1)–O(3) 91.76(9), N(2)–Cu(1)–O(2) 92.59(9), N(2)–Cu(1)–O(3) 94.56(9), N(1)–Cu(1)–O(1) 91.25(9), O(2)–Cu(1)–O(3) 99.10(9), N(2)–Cu(1)–O(1) 167.84(9), O(1)–Cu(1)–O(3), 97.26(9).

This study was supported by the Thailand Research Fund, Khon Kean University, the Center of Excellence for Innovation in Chemistry (PERCH-CIC) and Commission on Higher Education, Ministry of Education.

References

1 (*a*) R. D. Willet, D. Gatteschi and O. Kahn, *Magneto-Stuctural Correlations in Exchange Coupled Systems, Nato ASI Series C*, D. Reidel, Dordrecht, The Netherlands, 1985, p. 140; (*b*) O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993.
2 Z. Smékal, J. Kameníček, P. Klasová, G. Wrzeszcz, Z. Šindelář, P. Kopel and Z. Zák, *Polyhedron*, 2002, **21**, 1203.
3 L. Zhang, W.-M. Bu, S.-P. Yan, Z.-H. Jiang, D.-Z. Liao and G.-L. Wang, *Polyhedron*, 2000, **19**, 1105.
4 (*a*) M. Julve, M. Verdaguer, O. Kahn, A. Gleizes and M. Philoche-Levisalles, *Inorg. Chem*., 1983, **22**, 368; (*b*) M. Julve, M. Verdaguer, M. Philoche-Levisalles and O. Kahn, *Inorg. Chem*., 1984, **23**, 3808.
5 (*a*) S. Youngme and P. Gunnasoot, *Transition Met. Chem*., 2004, **29**, 840; (*b*) S. Youngme, A. Cheansirisomboon, C. Danvirutai, N. Chaichit, C. Pakawatchai, G. A. van Albada and J. Reedijk, *Inorg. Chem. Commun*., 2006, **9**, 973.
6 R. Vicente, A. Escuer, J. Ferretjans, H. Stoeckli-Evans, X. Solans and M. Font-Bardía, *J. Chem. Soc., Dalton Trans.*, 1997, 167.
7 O. Castillo, A. L. Iñaki Muga, J. M. Gutiérrez-Zorrilla, J. Sertucha, P. Vitoria and P. Román, *Polyhedron*, 1999, **18**, 1235.
8 B. J. Hathaway, *Struct. Bonding (Berlin)*, 1984, **57**, 55.
9 S. C. Manna, J. Ribas, E. Zangrando and N. R. Chaudhuri, *Inorg. Chim. Acta*, 2007, **360**, 2589.
10 Z. Smékal, J. Kameníček, P. Klasová, G. Wrzeszcz, Z. Sindelár, P. Kopel and Z. Zak, *Polyhedron*, 2002, **21**, 1203.
11 J. L. Shaw, G. T. Yee, G. Wang, D. E. Benson, C. Gokdemir and C. J. Ziegler, *Inorg. Chem*., 2005, **44**, 5060.
12 M. Du, Y.-M. Guo and X.-H. Bu, *Inorg. Chim. Acta*, 2002, **335**, 136.
13 B. Bag, N. Mondal, S. Mitra, V. Gramlich, J. Ribas and M. S. E. Fallah, *Polyhedron*, 2001, **20**, 2113.
14 R. Lescouëzeca, G. Marinescu and J. Vaissermann, *Inorg. Chim. Acta*, 2003, **350**, 131.
15 S. A. Moggach, K. W. Galloway, A. R. Lennir, P. Parois, N. Rowantree, E. K. Brechin, J. E. Warren, M. Murrie and S. Parsons, *CrystEngComm*, 2009, **11**, 2601.
16 G. M. Sheldrick, *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany.

Received: 30th June 2009; Com. 09/3358