metal-organic compounds

Bis(μ-2-{5-[(pyridin-4-ylmethyl)sulfanyl]-1,3,4-oxadiazol-2-yl}phenolato)bis[(acetylacetonato)copper(II)]: a novel binuclear metallocycle

Jing Xiao, Jian-Ping Ma, Ru-Qi Huang and Yu-Bin Dong*

College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, People's Republic of China
Correspondence e-mail: yubindong@sdnu.edu.cn

The new asymmetric ligand 2-{5-[(pyridin-4-ylmethyl)sulfanyl]-1,3,4-oxadiazol-3-yl}phenol (HL) has been used to synthesize the novel discrete title binuclear metallocycle, [Cu$_2$-(C$_{14}$H$_{10}$N$_3$O$_2$S)$_2$(C$_5$H$_7$O$_2$)$_2$] or Cu$_2$$L$$_2$(acac)$_2$ (acac is acetylacetonate). Each Cu^{II} centre is five-coordinate and adopts a square-pyramidal geometry. Two ligands are connected by two Cu^{II} cations to form the dinuclear metallocycle, which lies across a crystallographic inversion centre. Discrete molecules are linked into a two-dimensional structure through weak Cu···S, C—H···π and π–π interactions.

Comment

Increasing effort is currently being devoted to research into supramolecular compounds, which have been widely used in molecular absorption and separation (Rowsell & Yaghi, 2005; Noro *et al.*, 2010), heterogeneous catalysis (Dang *et al.*, 2010), magnetism (Maspoch *et al.*, 2004) and luminescent materials (Ono *et al.*, 2009). Many high-dimensional supramolecular networks, extended from low-dimensional molecules, have been successfully constructed through various intermolecular interactions. These interactions are fundamental for the tuning and prediction of crystal structures (Goswami *et al.*, 2007). Over recent decades, weak Cu···S (Breneman & Parker, 1993), C—H···π (Munshi *et al.*, 2004) and π–π (Khavasi & Fard, 2010) interactions have attracted much attention as they all have a dramatic effect on molecular packing features.

In order to investigate these three weak intermolecular interactions further, we have prepared a new asymmetric ligand, *viz.* 2-{5-[(pyridin-4-ylmethyl)sulfanyl]-1,3,4-oxadiazol-3-yl}phenol (HL), and used it to synthesize the title complex, Cu$_2$$L$$_2$(acac)$_2$ (acac is acetylacetonate), (I). Complex (I) is a discrete binuclear metallocycle. It is soluble in common

organic solvents such as chloroform, acetone and *N,N*-dimethylformamide.

(I)
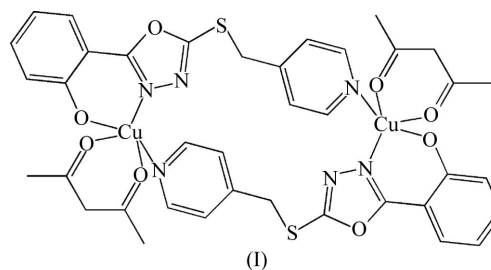
Complex (I) crystallizes in the triclinic space group $P\bar{1}$ with one five-coordinate Cu^{II} centre in the asymmetric unit. The dinuclear metallocycle therefore lies across a crystallographic inversion centre. Each Cu^{II} centre adopts a [4+1] square-pyramidal coordination geometry (Fig. 1): two O atoms from the acetylacetonate anion, one oxadiazole N atom and one hydroxy O atom are located in the equatorial plane, with Cu1—O1 = 1.929 (3) Å, Cu1—O2 = 1.939 (3) Å, Cu1—N1 = 1.978 (3) Å and Cu1—O3 = 1.939 (2) Å, and one pyridine N atom occupies the axial position, with Cu1—N3^i = 2.354 (3) Å [symmetry code: (i) −x + 1, −y + 2, −z + 2], which is elongated due to Jahn–Teller distortion.

The benzene ring and the central oxadiazole ring of each ligand are almost coplanar; the dihedral angle is 5.5 (2)°. However, the pyridine ring is nearly perpendicular to the oxadiazole ring; the dihedral angle between them is 81.3 (1)°. The Cu^{II}···Cu^{II} distance is 8.763 (1) Å. The two pyridine rings are exactly parallel by symmetry and the corresponding centroid–centroid distance is 5.934 (1) Å.

In the solid state, complex (I) assembles into a two-dimensional supramolecular network through weak Cu···S,
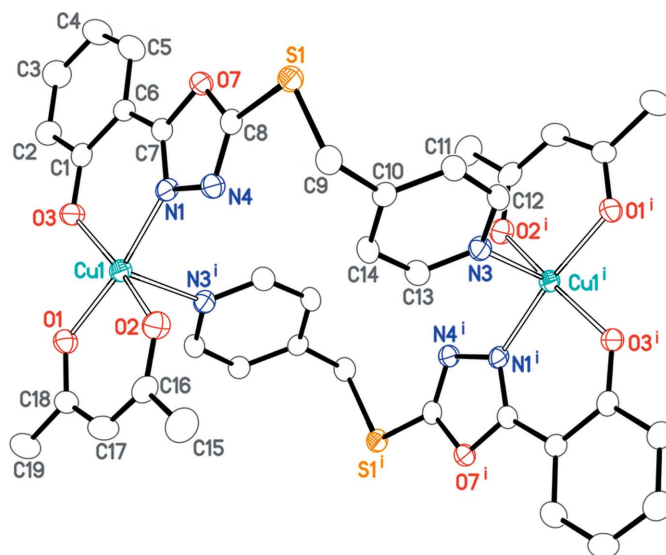
Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) −x + 1, −y + 2, −z + 2.]
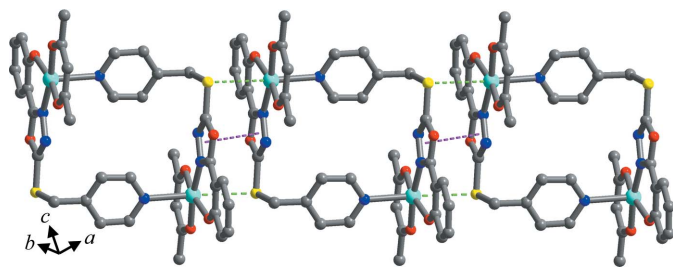
Figure 2

The one-dimensional chain of (I), constructed by weak Cu···S interactions (green dashed lines in the electronic version of the paper) and π–π interactions (purple dashed lines). H atoms have been omitted for clarity.
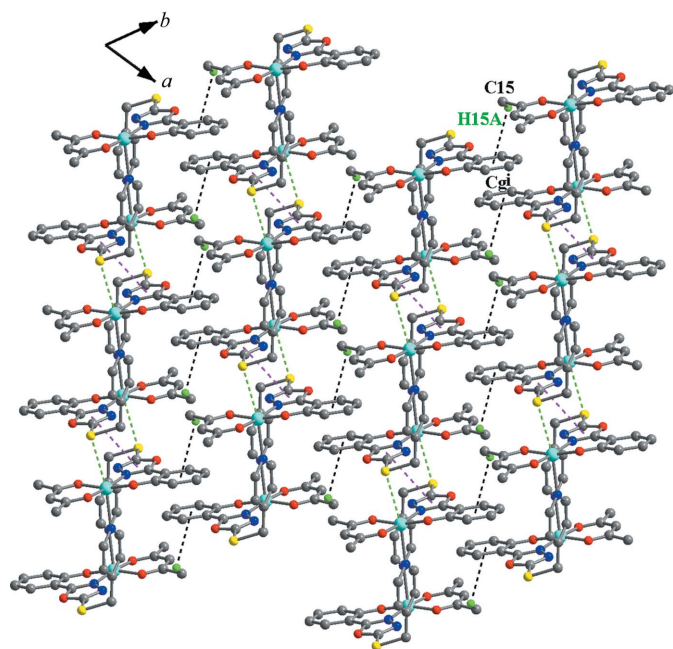
Figure 3

A view along the crystallographic c axis of the two-dimensional sheet of (I), constructed by weak Cu···S (green dashed lines in the electronic version of the paper), π–π (purple dashed lines) and C—H···π interactions (C15—H15A···Cg^i; black dashed lines between the chains). H atoms not involved in C—H···π interactions have been omitted for clarity. [Symmetry code: (i) x, $y + 1$, z.]

C—H···π and π–π interactions. Discrete molecules are linked into one-dimensional chains along the crystallographic [1$\overline{1}$0] direction through weak Cu···S and π–π interactions (Fig. 2). The Cu···S distance is 3.235 (1) Å, comparable with the value of 3.220 (1) Å for (2,2′-bipyridine)bis(thiocyanato-κN)-copper(II) reported by Parker *et al.* (1994). The π–π interactions occur between pairs of centrosymmetrically related parallel oxadiazole rings and the centroid–centroid distance is 3.798 (8) Å. Further, the parallel one-dimensional chains extend to form a two-dimensional sheet in the ab plane through the C—H···π interaction C15—H15A···Cg^i, where Cg^i denotes the centroid of the C1–C6 ring at the symmetry-related position (x, $y + 1$, z) (Fig. 3). The H···π distance is 3.234 (5) Å and the C—H···π angle is 110.2 (2)°, which are

close to the values reported for 3-(2,4-dimethylphenyloxy-methyl)-3,4-dihydroisocoumarin (Goswami *et al.*, 2007) of 3.11 Å and 157 (2)°, respectively.

In summary, a discrete binuclear metallocycle has been successfully synthesized. Weak Cu···S, C—H···π and π–π interactions link the discrete molecules into a two-dimensional structure. This study demonstrates that weak intermolecular interactions play a crucial role in constructing high-dimensional supramolecular networks. Meanwhile, the metallocycle can also be used as a secondary building block because the five-coordinate Cu^{II} atoms have free coordination positions, and studies employing this property are underway.

Experimental

For the preparation of HL, KOH (1.52 g, 27.1 mmol) was added with stirring to a solution of 5-(2-hydroxyphenyl)-1,3,4-oxadiazole-2-thiol (1.81 g, 9.3 mmol) and 4-(chloromethyl)pyridine hydrochloride (2.28 g, 13.8 mmol) in methanol (50 ml) at ambient temperature. The mixture was stirred for 24 h at ambient temperature and the reaction monitored by thin-layer chromatography. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using ethyl acetate as eluent to afford HL as a white solid (yield 1.08 g, 42%; m.p. 387–389 K). IR (KBr pellet, ν, cm^{-1}): 3443 (s), 2360 (w), 1625 (s), 1597 (s), 1415 (m), 1254 (m), 1186 (m), 1060 (w), 983 (m), 907 (m), 764 (w), 701 (m), 671 (w); ^{1}H NMR (300 MHz, CDCl$_3$, 298 K, TMS): δ 9.76 (s, 1H, –OH), 8.63 (d, 2H, –C$_5$H$_4$N), 7.67–7.64 (d, 1H, –C$_6$H$_4$–), 7.51–7.50 (d, 2H, –C$_5$H$_4$N), 7.46–7.41 (q, 1H, –C$_6$H$_4$–), 7.27–7.21 (d, 1H, –C$_6$H$_4$–), 7.12–7.09 (d, 1H, –C$_6$H$_4$–), 7.01–6.96 (q, 1H, –C$_6$H$_4$–), 4.50 (s, 2H, –CH$_2$–). Elemental analysis calculated for C$_{14}$H$_{11}$N$_3$O$_2$S: C 58.93, H 3.89, N 14.73%; found: C 58.82, H 3.98, N 14.67%.

For the preparation of (I), a solution of Cu(acac)$_2$ (5.57 mg, 0.028 mmol) in methanol (5 ml) was layered onto a solution of HL (8.01 mg, 0.028 mmol) in CH$_2$Cl$_2$ (5 ml). The solutions were left for about two weeks at room temperature and blue crystals of (I) were obtained (yield 10.12 mg, 75%). IR (KBr pellet, ν, cm^{-1}): 3443 (m), 2360 (w), 1610 (s), 1586 (s), 1443 (m), 1264 (s), 1152 (m), 1089 (w), 1007 (m), 977 (m), 927 (m), 768 (m), 704 (m), 669 (w).

Crystal data

[Cu$_2$(C$_{14}$H$_{10}$N$_3$O$_2$S)$_2$(C$_5$H$_7$O$_2$)$_2$]	$\gamma = 62.741$ (3)°
$M_r = 893.91$	$V = 943.9$ (3) Å^3
Triclinic, $P\overline{1}$	$Z = 1$
$a = 9.934$ (2) Å	Mo $K\alpha$ radiation
$b = 10.069$ (2) Å	$\mu = 1.30$ mm^{-1}
$c = 11.627$ (2) Å	$T = 298$ K
$\alpha = 68.146$ (3)°	$0.35 \times 0.18 \times 0.06$ mm
$\beta = 88.758$ (3)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4983 measured reflections
	3455 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	2864 reflections with $I > 2\sigma(I)$
$T_{min} = 0.659$, $T_{max} = 0.926$	$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	255 parameters
$wR(F^2) = 0.124$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 1.03$ e Å^{-3}
3455 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}

metal-organic compounds

H atoms were placed in idealized positions and treated as riding, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aryl H atoms and H17, C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene H atoms, and C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *SMART* (Bruker, 2003); cell refinement and data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics and software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

References

Breneman, G. L. & Parker, O. J. (1993). *Polyhedron*, **12**, 891–895.
Bruker (2003). *SADABS, SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dang, D.-B., Wu, P.-Y., He, C., Xie, Z. & Duan, C.-Y. (2010). *J. Am. Chem. Soc.* **132**, 14321–14323.
Goswami, S., Gupta, V. K., Brahmbhatt, D. I. & Pandya, U. R. (2007). *J. Chem. Crystallogr.* **37**, 213–217.
Khavasi, H. R. & Fard, M. A. (2010). *Cryst. Growth Des.* **10**, 1892–1896.
Maspoch, D., Ruiz-Molina, D. & Veciana, J. (2004). *J. Mater. Chem.* **14**, 2713–2723.
Munshi, P., Venugopala, K. N., Jayashree, B. S. & Row, T. N. G. (2004). *Cryst. Growth Des.* **4**, 1105–1107.
Noro, S. I., Akutagawa, T. & Nakamura, T. (2010). *Chem. Commun.* pp. 3134–3136.
Ono, K., Klosterman, J. K., Yoshizawa, M., Sekiguchi, K., Tahara, T. & Fujita, M. (2009). *J. Am. Chem. Soc.* **131**, 12526–12527.
Parker, O. J., Wilson, B. L. & Breneman, G. L. (1994). *Acta Cryst.* C**50**, 1681–1683.
Rowsell, J. L. C. & Yaghi, O. M. (2005). *Angew. Chem. Int. Ed.* **44**, 4670–4679.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.