

## Two bicyclic dinuclear complexes generated from 3,3'-[1,3,4-thiadiazole-2,5-diyl-di(thiomethylene)]-dibenzoic acid (*L*) and dimethylformamide (DMF): [Cu(*L*)(DMF)]<sub>2</sub> and [Zn(*L*)(DMF)]<sub>2</sub>

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Received 11 December 2008

Accepted 22 December 2008

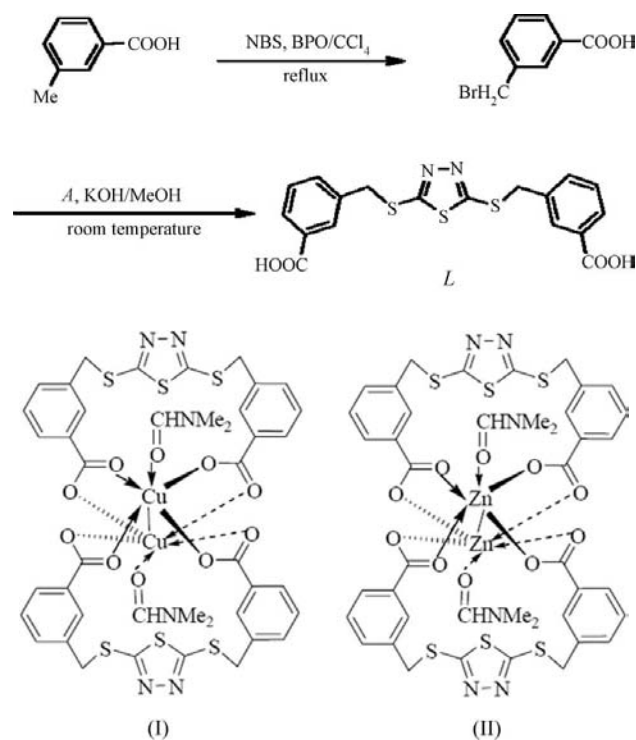
Online 14 January 2009

A new 1,3,4-thiadiazole bridging ligand, namely 3,3'-[1,3,4-thiadiazole-2,5-diyl-di(thiomethylene)]dibenzoic acid (*L*), has been used to create the novel isomorphous complexes bis{ $\mu$ -3,3'-[1,3,4-thiadiazole-2,5-diyl-di(thiomethylene)]dibenzoato}-bis[(*N,N*-dimethylformamide)copper(II)], [Cu<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>NO)<sub>2</sub>], (I), and bis{ $\mu$ -3,3'-[1,3,4-thiadiazole-2,5-diyl-di(thiomethylene)]dibenzoato}bis[(*N,N*-dimethylformamide)-zinc(II)], [Zn<sub>2</sub>(C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>NO)<sub>2</sub>], (II). Both exist as centrosymmetric bicyclic dimers constructed through the *syn-syn* bidentate bridging mode of the carboxylate groups. The two rings share a metal-metal bond and each of the metal atoms possesses a square-pyramidal geometry capped by the dimethylformamide molecule. The 1,3,4-thiadiazole rings play a critical role in the formation of a  $\pi$ - $\pi$  stacking system that expands the dimensionality of the structure from zero to one. The thermogravimetric analysis of (I) indicates decomposition of the coordinated ligands on heating. Compared with the fluorescence of *L* in the solid state, the fluorescence intensity of (II) is relatively enhanced with a slight redshift, while that of (I) is quenched.

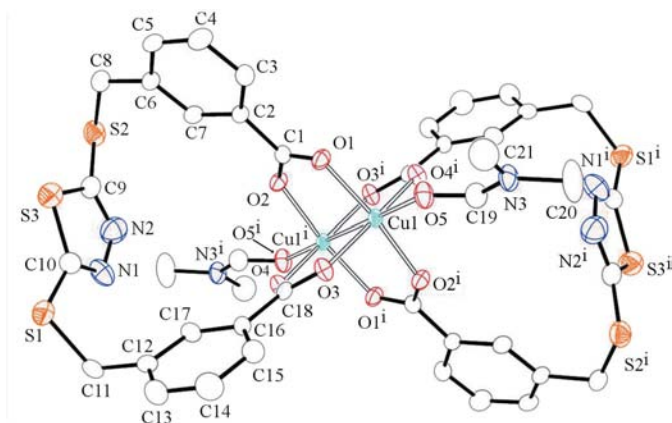
### Comment

Supramolecular chemistry has developed dramatically over recent decades. Numerous organometallic complexes have been designed for a number of potential applications, such as in synthetic chemistry (Sommerfeldt *et al.*, 2008), in gas storage (Rowell & Yaghi, 2005; Ma & Zhou, 2006), in selective absorption (Dong, Zhang *et al.*, 2007), as luminescence materials (Wang, Ma *et al.*, 2007; Huang *et al.*, 2007) and as magnetic materials (Halder *et al.*, 2002; Neville *et al.*, 2008). Although the principles for controlling the solid structures of

the target products still need to be classified and established, many rational synthetic strategies have been put forward (Dong, Jiang *et al.*, 2007; Zhang *et al.*, 2008). Among them, the selection of appropriate ligands as building blocks is undoubtedly a key point in manipulating the structures. 1,3,4-Thiadiazole derivatives are well known for their biological activities, such as anticancer (Chou *et al.*, 2003), antimicrobial (Mamolo *et al.*, 1996) and anti-inflammatory (Song *et al.*, 1999; Labanauskas *et al.*, 2001), yet very little has been reported on this system in supramolecular and materials chemistry (Tandon *et al.*, 1993, 1994; Huang, Du *et al.*, 2004; Huang, Song *et al.*, 2004). There are even fewer reports on ligands containing a carboxylic acid group and a 1,3,4-thiadiazole ring at the same time (Wang, Zhang *et al.*, 2007). Moreover, the 1,3,4-thiadiazole ring is itself a potentially versatile ligand, since the electron-rich and soft constituent S atom may significantly influence the properties of the ligand. With aromatic substituent groups, the ligand will show a strong tendency to completely or partly participate in intermolecular  $\pi$ - $\pi$  interactions, which may affect the packing arrangement of the crystal structures. We present here the synthesis of a new 1,3,4-thiadiazole-ring-bridged 3,3'-biphenylcarboxylate-type ligand (*L*) and two novel bicyclic dinuclear complexes, namely, [Cu(*L*)(DMF)]<sub>2</sub> (DMF is *N,N*-dimethylformamide), (I), and [Zn(*L*)(DMF)]<sub>2</sub>, (II). The X-ray crystal structures of (I) and (II) show that they are isomorphous. We have investigated the thermogravimetric behavior of (I), and the fluorescence properties of both complexes and ligand *L*.



Both complexes crystallize in the monoclinic space group *P*2<sub>1</sub>/*c* with a crystallographically imposed symmetry center. The large rings of the two *L* ligands give each molecule an overall 'figure-of-eight' shape. The zero-dimensional dinuclear



**Figure 1**

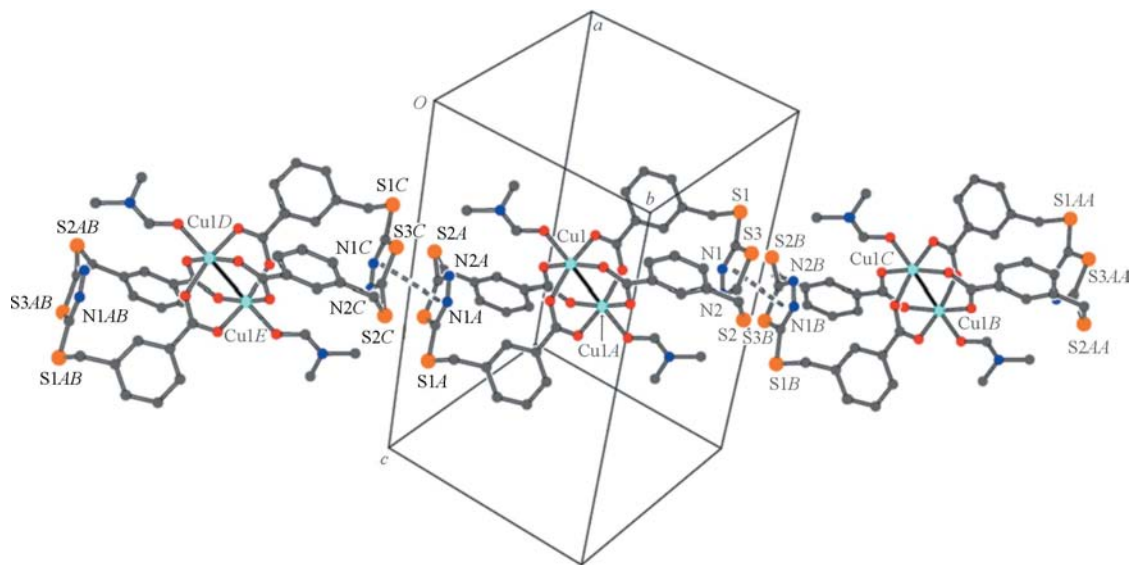
The molecular structure of (I) (displacement ellipsoids are shown at the 30% probability level), with H atoms omitted. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .]

structure is constructed through the *syn-syn* bidentate bridging mode of the carboxylate groups. In (I), ignoring the  $\text{Cu}\cdots\text{Cu}$  interaction, each  $\text{Cu}^{\text{II}}$  center lies in a  $\{\text{CuO}_5\}$  square-pyramidal coordination environment, with the apical position occupied by an O atom from a coordinated DMF molecule and the basal positions occupied by four carboxylate O atoms (Fig. 1). Two equivalent *L* ligands act as organic clips to bridge two  $\text{Cu}^{\text{II}}$  ions, thus forming a bicyclic dimer; the  $\text{Cu}-\text{O}$  distances range from 1.957 (4) to 1.967 (4) Å, and are consistent with the corresponding bond lengths in similarly five-coordinated  $\text{Cu}^{\text{II}}$  complexes (1.99 Å). The  $\text{Cu}-\text{O}$  (apical DMF) bond distance [2.134 (4) Å] is considerably longer, but slightly outside the 2.2–2.8 Å range for apical  $\text{Cu}-\text{O}$  bond distances. In contrast, while the  $\text{Zn}-\text{O}$  (carboxylate) distances in (II) range from 2.0269 (16) to 2.0440 (16) Å, the apical  $\text{Zn}-\text{O}$  (DMF) distance is significantly shorter at 1.9817 (15) Å. In (I), the  $\text{Cu}1\cdots\text{Cu}1(-x + 1, -y + 1, -z + 1)$  distance is 2.6344 (15) Å, which is less than the sum of the van

der Waals radii of two Cu atoms (2.8 Å; Song *et al.*, 2004) and thus implies a degree of metal–metal interaction. The  $\text{Cu}_2(\text{RCO}_2)_4$  core is, of course, equivalent to the well known classic dinuclear paddle-wheel structure of copper(II) carboxylates (Calvo *et al.*, 2008), in which the  $\text{Cu}\cdots\text{Cu}$  distance is 2.645 Å. The tetracarboxylate bridging framework can accommodate metal–metal separations of up to 3.452 Å (Zhou *et al.*, 2000). The  $\text{Zn}\cdots\text{Zn}$  separation of 2.9429 (5) Å for (II) is shorter than this maximum but much longer than the corresponding  $\text{Cu}\cdots\text{Cu}$  distance observed in (I).

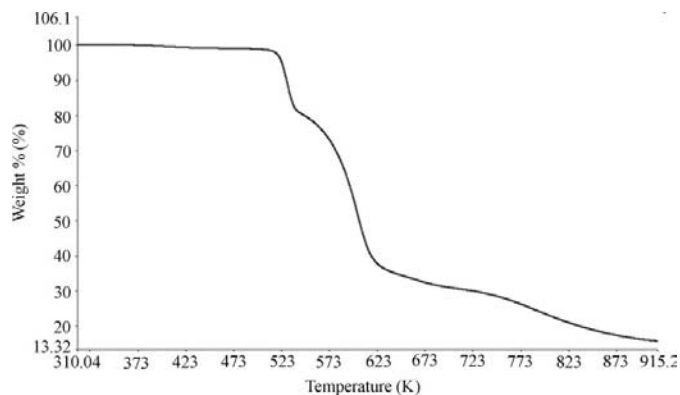
The ligand *L* is significantly twisted, as the two benzene rings on the same *L* ligand in (I) are rotated by 83.019 (3) and 80.281 (8)° with respect to the thiadiazole ring. There are intermolecular  $\pi-\pi$  interactions between the 1,3,4-thiadiazole rings, as shown in Fig. 2. The distance between the centroids of two neighboring thiadiazole rings is 3.563 (3) Å, and the two ring planes are absolutely parallel. Such interactions connect neighboring molecules into one-dimensional chains running along the crystallographic [110] direction. These one-dimensional chains then stack in a side-by-side fashion into sheets extending in the crystallographic (001) plane. The benzene rings in adjacent molecules are also parallel but are too far apart (*ca.* 4.45 Å) for normal  $\pi-\pi$  interactions. Thus, it is evident that the 1,3,4-thiadiazole rings play a critical role in the formation of the primary  $\pi-\pi$  interactions that propagate through the structure.

Both compounds are air stable and can retain their structural integrity at room temperature for a considerable length of time. However, the thermogravimetric plot of (I) (Fig. 3) shows a sharp mass loss of just under 20% from roughly 513–533 K, which is larger than the proportion of two DMF molecules (13.25%) but smaller than that of a ligand (37.97%), indicating that the coordinated ligands have decomposed on heating. In fact, a change of color from blue to yellow is also observed in the process of measuring the melting point of (I).

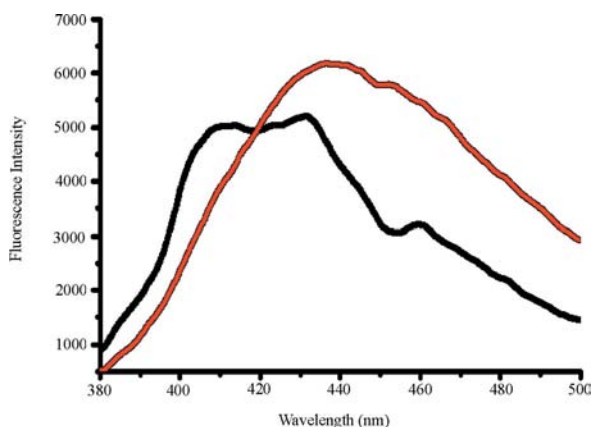


**Figure 2**

The crystal packing of (I), showing the  $\pi-\pi$  stacking interactions. H atoms have been omitted. Atoms labeled with the suffixes *A*, *B*, *C*, *AA* and *AB* are at the symmetry positions  $(-x + 1, -y + 1, -z + 1)$ ,  $(-x + 2, -y + 2, -z + 1)$ ,  $(x - 1, y - 1, z)$ ,  $(x + 1, y + 1, z)$  and  $(-x, -y, -z + 1)$ , respectively.



**Figure 3**  
Thermogravimetric analysis plot obtained by heating a powdered sample of (I) to 915 K under flowing nitrogen at 10 K min<sup>-1</sup>.



**Figure 4**  
Photoinduced emission spectra of *L* (black) and (II) (grey, or red in the electronic version of the paper) in the solid state.

Compound (I) consists of blue crystals insoluble in water and common organic solvents such as DMF, chloroform and methanol, while the colorless crystals of (II) can slightly dissolve in DMF. The luminescence properties of *L*, (I) and (II) were investigated in the solid state. *L* exhibits one emission maximum at 431 nm ( $\lambda_{\text{ex}} = 348$  nm; Fig. 4), while the fluorescence intensity of (II) is relatively enhanced with a slight redshift to 436 nm. By contrast, the fluorescence of (I) is quenched by Cu<sup>II</sup>, as commonly reported (Kessler, 1999).

This study demonstrates the utility of the 1,3,4-thiadiazole derivatives as organic ligands for constructing metal-organic complexes. We expect ligands of this type to be viable for the creation of more new complexes with interesting topologies and physical properties.

## Experimental

All the solvents and reagents were commercially available and were used as received. 2,5-Dimercapto-1,3,4-thiadiazole (*A*) (m.p. 441 K) was prepared according to the method described by Nie (2003). A carbon tetrachloride solution (20 ml) of 3-methylbenzoic acid (1.36 g, 10.0 mmol), 3-bromopyrrolidine-2,5-dione (NBS; 1.78 g, 10.0 mmol) and benzoyl peroxide (BPO; 0.020 g, 83.0 mmol) was boiled under reflux for 5 h. After cooling to room temperature, a pink precipitate

was obtained by filtration and subsequently washed with carbon tetrachloride and water. Recrystallization from methylene chloride provided a white solid, *viz.* 3-bromomethylbenzoic acid, in 92.3% yield.

A methanol solution (40 ml) of 3-bromomethylbenzoic acid (0.65 g, 3.0 mmol) was added dropwise to a methanol solution (30 ml) of *A* (0.20 g, 1.3 mmol) and potassium hydroxide (0.34 g, 6.0 mmol). The mixture was stirred at room temperature for 12 h. After removal of the solvent under vacuum, the residue was redissolved in water and filtered to give a clear solution. Acidification with 10% HCl aqueous solution followed by recrystallization from methanol provided the white precipitate *L* in 81.2% yield (m.p. 485–488 K). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.97 (*s*, 2H, COOH), 7.94–7.35 (*m*, 8H, *m*-C<sub>6</sub>H<sub>4</sub>), 4.51 (*s*, 4H, CH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu$  3455, 1689, 1638, 1455, 1398, 1311, 1291, 1239, 1205, 1040, 722.

A solution of Cu(OAc)<sub>2</sub> (2.0 mg, 0.010 mmol) in methanol (8 ml) was layered on to a solution of *L* (4.2 mg, 0.010 mmol) in DMF (8 ml). The solutions were left for about 3 d at room temperature and blue crystals of (I) were obtained (yield 83.3%, m.p. 525–527 K). IR (KBr, cm<sup>-1</sup>):  $\nu$  3443, 3064, 2927, 1656, 1622, 1578, 1441, 1397, 1114, 1039, 863, 801, 682, 669, 487.

A solution of Zn(OAc)<sub>2</sub> (2.2 mg, 0.010 mmol) in methanol (8 ml) was mixed with a solution of *L* (4.2 mg, 0.010 mmol) in DMF (8 ml). The solutions were left for about three weeks at room temperature and colorless crystals of (II) were obtained (yield 85.0%, m.p. 547–549 K). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.97 (*s*, 2H, COH), 7.94–7.34 (*m*, 16H, *m*-C<sub>6</sub>H<sub>4</sub>), 4.55 (*s*, 8H, CH<sub>2</sub>), 2.88 (*s*, 6H, CH<sub>3</sub>), 2.72 (*s*, 6H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu$  3432, 3068, 2934, 1630, 1580, 1498, 1440, 1403, 1372, 1217, 1078, 798, 700, 680, 665, 457.

## Compound (I)

### Crystal data

[Cu <sub>2</sub> (C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> S <sub>3</sub> ) <sub>2</sub> (C <sub>3</sub> H <sub>7</sub> NO) <sub>2</sub> ]	$V = 2279.5$ (14) Å <sup>3</sup>
$M_r = 1106.22$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.092$ (4) Å	$\mu = 1.27$ mm <sup>-1</sup>
$b = 11.165$ (4) Å	$T = 298$ (2) K
$c = 18.426$ (7) Å	$0.26 \times 0.09 \times 0.08$ mm
$\beta = 92.699$ (6)°	

### Data collection

Bruker SMART CCD area-detector diffractometer	11616 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4232 independent reflections
$T_{\text{min}} = 0.733$ , $T_{\text{max}} = 0.905$	2921 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.066$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.071$	300 parameters
$wR(F^2) = 0.186$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.77$ e Å <sup>-3</sup>
4232 reflections	$\Delta\rho_{\text{min}} = -0.65$ e Å <sup>-3</sup>

## Compound (II)

### Crystal data

[Zn <sub>2</sub> (C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> S <sub>3</sub> ) <sub>2</sub> (C <sub>3</sub> H <sub>7</sub> NO) <sub>2</sub> ]	$V = 2291.2$ (5) Å <sup>3</sup>
$M_r = 1109.88$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.0860$ (13) Å	$\mu = 1.39$ mm <sup>-1</sup>
$b = 11.2252$ (13) Å	$T = 173$ (2) K
$c = 18.440$ (2) Å	$0.49 \times 0.29 \times 0.15$ mm
$\beta = 93.169$ (2)°	

## Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.550$ ,  $T_{\max} = 0.819$

11782 measured reflections  
4246 independent reflections  
3873 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.084$   
 $S = 1.02$   
4246 reflections

300 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.33 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$

H atoms were placed in geometrically idealized positions and included as riding atoms [for (I): C–H = 0.97 (CH<sub>2</sub>), 0.93 (CH) and 0.96 Å (CH<sub>3</sub>); for (II): C–H = 0.99 (CH<sub>2</sub>), 0.95 (CH) and 0.98 Å (CH<sub>3</sub>); for both compounds,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  otherwise].

For both compounds, data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

We are grateful for financial support from the National Natural Science Foundation of China (grant Nos. 20871076 and 20671060), the National Basic Research Program of China (973 Program, grant No. 2007CB936000) and Shandong Natural Science Foundation (grant Nos. Z2004B01, J06D05 and 2006BS04040).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3180). Services for accessing these data are described at the back of the journal.

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