

A novel 18-membered metallocycle in {2,5-bis[3-(1*H*-1,3-imidazol-1-ylmethyl)phenyl]-1,3,4-oxadiazole}-dichloridocobalt(II)

Yan Wu, Gui-Ge Hou, Jian-Ping Ma and Yu-Bin Dong*

College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, People's Republic of China
Correspondence e-mail: yubindong@sdu.edu.cn

Received 25 March 2010

Accepted 6 May 2010

Online 13 May 2010

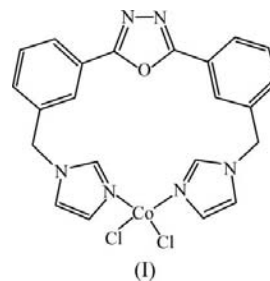
The title molecular complex, $[\text{CoCl}_2(\text{C}_{22}\text{H}_{18}\text{N}_6\text{O})]$, features a novel 18-membered Co-containing metallocycle. The Co^{II} atom lies in a fairly regular tetrahedral geometry defined by two imidazole N-atom donors from one 2,5-bis[3-(1*H*-1,3-imidazol-1-ylmethyl)phenyl]-1,3,4-oxadiazole (*L*) ligand and two chloride anions. The coordinating orientation of the *L* ligand plays an important role in constructing the metallocycle complex. The complexes form a three-dimensional supramolecular assembly *via* nonclassical C—H...Cl and C—H...N hydrogen bonds and π — π interactions.

Comment

Supramolecular compounds are currently an active field of chemistry due to their novel structural topologies, their potential application in gas storage (Yaghi *et al.*, 2003; Rowsell & Yaghi, 2005), and their magnetic (Zhao *et al.*, 2003; Wang *et al.*, 2006; Neville *et al.*, 2008), catalytic (Wu & Lin, 2007) and optical properties (Wang *et al.*, 2007; Huang *et al.*, 2007). Recently, many high-dimensional supramolecular networks, extended from low-dimensional metal-containing molecules through hydrogen bonds, have been achieved by carefully selecting as building blocks organic ligands containing appropriate functional groups (Yaghi *et al.*, 1998; Cho *et al.*, 2006; Ma & Lin, 2008; Cheng *et al.*, 2001; Choi *et al.*, 1999; Choi & Suh, 1999). However, other supramolecular interactions, such as π — π stacking and nonclassical hydrogen bonds, have been somewhat less well documented. Recently, Nichol & Clegg (2006) reported a series of structures of organic complexes formed by weak intermolecular interactions (C—H...*X* hydrogen bonding and π — π stacking) between acids and bases when classical hydrogen bonding is not possible.

In metal–organic frameworks, the geometry of the organic ligands is one of the most important factors in determining the structure of the framework. Recently, our group reported a study of the M^{II} ($M = \text{Cu}, \text{Cd}, \text{Mn}$ and Co) coordination

chemistry of 2,5-bis[3-(1*H*-1,2,4-triazol-1-ylmethyl)phenyl]-1,3,4-oxadiazole (*L2*; Zhao *et al.*, 2009). In that study, the divergent arrangement of *L2* favours the formation of discrete bird-like spiro-metallocyclic complexes. In order to investigate further how the coordinating orientations of related organic ligands affect the structures of supramolecular complexes, we synthesized the ligand 2,5-bis[3-(1*H*-1,3-imidazol-1-ylmethyl)phenyl]-1,3,4-oxadiazole (*L*) and its complex $[\text{CoCl}_2\text{L}_2]$, (I), the structure of which we report here.



Compound (I) crystallizes in the triclinic crystal system (space group $P\bar{1}$) with two CoCl_2L molecules per unit cell and one in the asymmetric unit ($Z = 2$). The Co^{II} atom is coordinated by two imidazole N-atom donors from one chelating *L* ligand and two chloride anions in a tetrahedral geometry (Fig. 1 and Table 1). The two benzene rings and the central oxadiazole ring of *L* are almost coplanar, and the planes of the two terminal triazole rings are nearly perpendicular to that of the Ph-Ox-Ph unit (Ph is a benzene ring and Ox is the 1,3,4-oxadiazole ring), with dihedral angles of 90.0 (2) and 80.6 (2)°. The two flexible imidazolymethylene arms of each *L* ligand are bent markedly inwards and converge at the Co^{II} centre to form a metallocycle consisting of 18 atoms. The distances across the ring are $\text{Co1}\cdots\text{O1} = 6.287$ (4) Å and $\text{C19}\cdots\text{C4} = 8.239$ (7) Å. The coordination behaviour of the imidazole

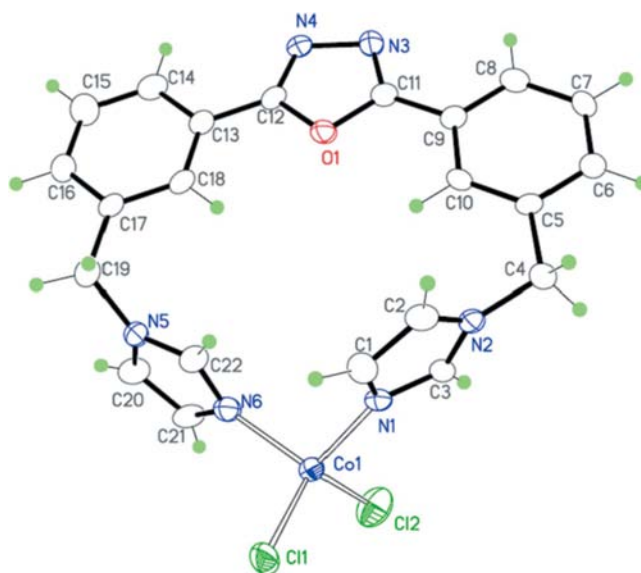
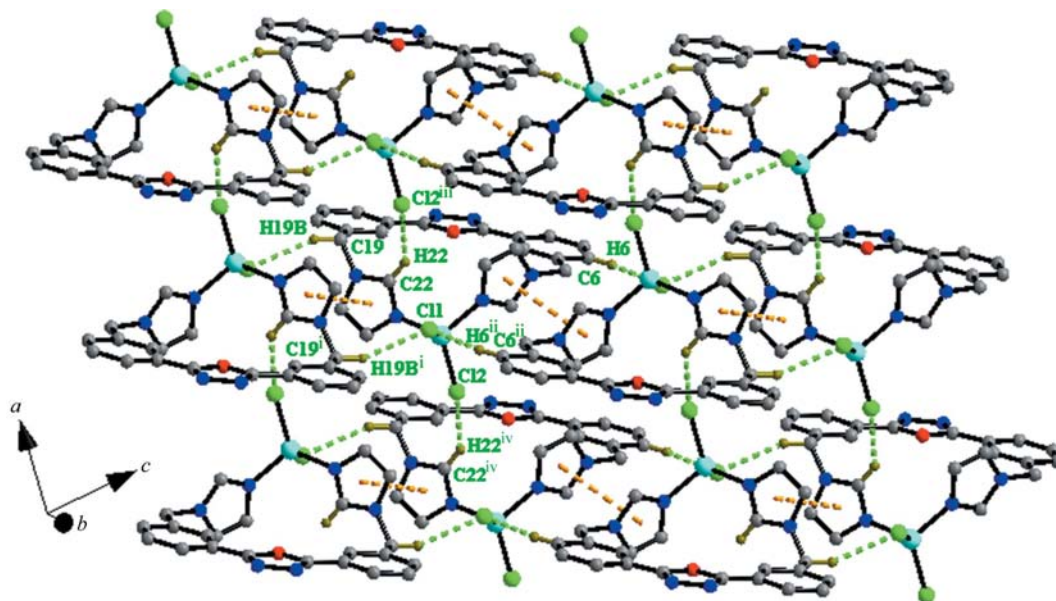


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.


Figure 2

The two-dimensional sheet of (I) constructed by C–H···Cl hydrogen bonds (green dashed lines in the electronic version of the paper) and π – π stacking interactions (orange dashed lines). Some H atoms have been omitted. [Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $-x, -y + 2, -z + 1$; (iii) $x + 1, y, z$; (iv) $x - 1, y, z$.]

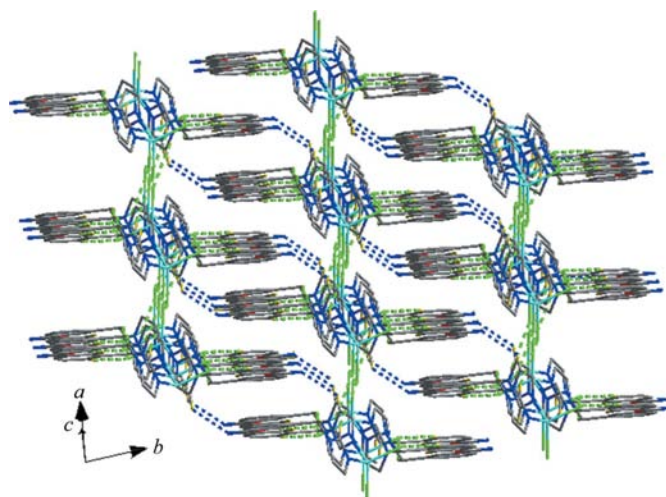
ligand *L* is similar to that of the related triazole ligand *L2* (Zhao *et al.*, 2009), which is also coordinated to a single metal centre to form a large ring with corresponding dimensions of $ca\ 6.6 \times 8.3\ \text{\AA}$, respectively. Therefore, the minor change in the central five-membered ring results in very little change in the coordinating orientation of the ligands; both are ideally oriented to form large metalocycles.

Complex (I) assembles into a three-dimensional supramolecular network through nonclassical C–H···Cl and C–H···N hydrogen bonds and π – π interactions. Two hydrogen bonds, *viz.* C19–H19B···Cl1ⁱ and C6–H6···Cl1ⁱⁱ [symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $-x, -y + 2, -z + 1$], link the discrete molecules into one-dimensional chains along the crystallographic *c* axis (Fig. 2). These parallel chains extend into a two-dimensional sheet in the *ac* plane *via* the C22–H22···Cl2ⁱⁱⁱ hydrogen bond [symmetry code: (iii) $x + 1, y, z$]. Thallapally & Nangia (2001) defined a C–H···Cl contact as short, medium or long using the criteria $H\cdots Cl < 2.6\ \text{\AA}$, $H\cdots Cl = 2.6\text{--}3.0\ \text{\AA}$ and $H\cdots Cl > 3.0\ \text{\AA}$, respectively. The H···Cl distances in (I) (Table 2) belong to the intermediate class of contact. The packing within the layers is also reinforced by π – π interactions between pairs of centrosymmetrically related parallel imidazole rings, with centroid–centroid distances of 3.837 (3) and 3.666 (3) \AA for pairs of rings involving atoms N1/N2/C1–C3 and atoms N5/N6/C20–C22, respectively.

The two-dimensional sheets are connected to each other along the *b* axis *via* C–H···N hydrogen bonds (Fig. 3). The C–H···N contacts and C–H···N angles (Table 2) are within typically observed ranges (Alshahateet *et al.*, 2004). The Ph–Ox–Ph ring systems protrude from either side of the layers and interleave in a parallel fashion, with centroid–centroid contacts of 3.738 (3) and 3.802 (3) \AA for interactions between

one benzene (atoms C5–C10) and one Ox (atoms O1/N3/N4/C11/C12) ring and between the two different benzene rings, respectively.

In summary, a three-dimensional supramolecular compound driven by C–H···Cl and C–H···N hydrogen bonds has been successfully synthesized from an 18-membered Co-containing metalocyclic complex. This study demonstrates that nonclassical hydrogen bonds play an important role in constructing high-dimensional supramolecular compounds, which may provide a new method for constructing novel functional materials.


Figure 3

The C–H···N hydrogen bonds (blue dashed lines in the electronic version of the paper) and π – π interactions (orange dashed lines) crosslinking the two-dimensional sheets of (I) into the extended three-dimensional supramolecular structure.

Experimental

KOH (2.80 g, 50 mmol) was added with stirring to a solution of bis(3-bromomethylphenyl)oxadiazole (2.04 g, 5 mmol) and imidazole (0.69 g, 10 mmol) in tetrahydrofuran (THF; 50 ml) at ambient temperature. The mixture was stirred for 12 h at ambient temperature (monitored by thin-layer chromatography). After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using THF as eluent to afford *L* as a yellow solid (yield 0.87 g, 2.27 mmol, 45%). IR (KBr pellet, ν , cm^{-1}): 3405 (*m*), 1546 (*s*), 1504 (*w*), 1445 (*m*), 1283 (*m*), 1231 (*s*), 1188 (*m*), 1107 (*m*), 1074 (*s*), 983 (*w*), 907 (*m*), 818 (*m*), 721 (*vs*), 661 (*m*), 627 (*m*), 428 (*w*); ^1H NMR (300 MHz, CDCl_3 , TMS): δ 8.11–8.08 (*d*, 2H, *m*- C_6H_4), 8.03 (*s*, 2H, *m*- C_6H_4), 7.79 (*s*, 2H, $-\text{C}_3\text{H}_3\text{N}_2$), 7.57–7.52 (*t*, 2H, *m*- C_6H_4), 7.35–7.33 (*d*, 2H, *m*- C_6H_4), 7.15 (*s*, 2H, $-\text{C}_3\text{H}_3\text{N}_2$), 6.97 (*s*, 2H, $-\text{C}_3\text{H}_3\text{N}_2$), 5.26 (*s*, 4H, $-\text{CH}_2-$); elemental analysis calculated for $\text{C}_{22}\text{H}_{18}\text{N}_6\text{O}$: C 69.11, H 4.71, N 21.99%; found: C 69.20, H 4.77, N 22.01%.

A solution of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (5.47 mg, 0.023 mmol) in CH_3OH (5 ml) was layered on to a solution of *L* (8.3 mg, 0.022 mmol) in CH_2Cl_2 (8 ml). The system was left for about two weeks at room temperature and blue crystals of (*I*) were obtained (yield 8.33 mg, 74%). IR (KBr pellet, ν , cm^{-1}): 3109 (*m*), 1548 (*m*), 1522 (*m*), 1490 (*w*), 1429 (*vs*), 1327 (*m*), 1097 (*w*), 1069 (*s*), 952 (*w*), 803 (*w*), 763 (*m*), 723 (*vs*), 684 (*w*), 658 (*m*), 631 (*w*).

Crystal data

$[\text{CoCl}_2(\text{C}_{22}\text{H}_{18}\text{N}_6\text{O})]$	$\gamma = 87.592$ (7°)
$M_r = 512.25$	$V = 1115.9$ (9) \AA^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.313$ (3) \AA	Mo $K\alpha$ radiation
$b = 11.056$ (5) \AA	$\mu = 1.04$ mm^{-1}
$c = 14.572$ (7) \AA	$T = 173$ K
$\alpha = 74.376$ (6) $^\circ$	$0.45 \times 0.15 \times 0.05$ mm
$\beta = 79.570$ (7) $^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	5791 measured reflections
Absorption correction: multi-scan SADABS (Bruker, 2003)	4068 independent reflections
$T_{\min} = 0.653$, $T_{\max} = 0.950$	2984 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$	289 parameters
$wR(F^2) = 0.146$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.78$ e \AA^{-3}
4068 reflections	$\Delta\rho_{\text{min}} = -0.54$ e \AA^{-3}

H atoms were placed in idealized positions and treated as riding, with C–H = 0.95 (CH) or 0.99 \AA (CH_2) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2003); cell refinement: SMART; 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: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

The authors are grateful for financial support from the National Natural Science Foundation of China (grant Nos.

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cl1–Co1	2.2370 (16)	Co1–N1	2.018 (4)
Cl2–Co1	2.2447 (19)	Co1–N6	2.018 (4)
N1–Co1–N6	106.49 (15)	Cl1–Co1–Cl2	117.60 (6)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C2–H2 \cdots N4 ⁱ	0.95	2.48	3.198 (6)	133
C22–H22 \cdots Cl2 ⁱⁱ	0.95	2.78	3.529 (5)	136
C6–H6 \cdots Cl1 ⁱⁱⁱ	0.95	2.75	3.629 (5)	155
C19–H19B \cdots Cl1 ^{iv}	0.99	2.68	3.557 (5)	148

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $-x, -y+2, -z+1$; (iv) $-x+1, -y+2, -z$.

20871076 and 20671060), the Shangdong Natural Science Foundation (grant No. JQ200803), and the PhD Programmes Foundation of the Ministry of Education of China (grant No. 200804450001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3243). Services for accessing these data are described at the back of the journal.

References

- Alshahateet, S. F., Bishop, R., Craig, D. C. & Scudder, M. L. (2004). *Cryst. Growth Des.* **4**, 837–844.
- Bruker (2003). *SADABS, SAINT and SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheng, D. P., Khan, M. A. & Houser, R. P. (2001). *Inorg. Chem.* **40**, 6858–6859.
- Cho, S. H., Ma, B. Q., Nguyen, S. T., Hupp, J. T. & Albrecht-Schmitt, T. E. (2006). *Chem. Commun.* pp. 2563–2565.
- Choi, H. J., Lee, T. S. & Suh, M. P. (1999). *Angew. Chem. Int. Ed.* **38**, 1405–1408.
- Choi, H. J. & Suh, M. P. (1999). *Inorg. Chem.* **38**, 6309–6312.
- Huang, Y.-L., Huang, M.-Y., Chan, T.-H., Chang, B. C. & Lii, K. L. (2007). *Chem. Mater.* **19**, 3232–3237.
- Ma, L. & Lin, W.-B. (2008). *J. Am. Chem. Soc.* **130**, 13834–13835.
- Neville, S. M., Halder, G. J., Chapman, K. W., Duriska, M. B., Southon, P. D., Cashion, J. D., Letard, J. F., Moubaraki, B., Murray, K. S. & Kepert, C. J. (2008). *J. Am. Chem. Soc.* **130**, 2869–2876.
- Nichol, G. S. & Clegg, W. (2006). *Cryst. Growth. Des.* **6**, 451–460.
- Rowell, J. L. C. & Yaghi, O. M. (2005). *Angew. Chem.* **117**, 4748–4758.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Thallapally, P. K. & Nangia, A. (2001). *CrystEngComm*, **3**, 114–119.
- Wang, Y.-T., Tang, G.-M., Liu, Z.-M. & Yi, X.-H. (2007). *Cryst. Growth Des.* **7**, 2272–2275.
- Wang, X.-Y., Wang, L., Wang, Z.-M. & Gao, S. (2006). *J. Am. Chem. Soc.* **128**, 674–675.
- Wu, C.-D. & Lin, W.-B. (2007). *Angew. Chem. Int. Ed.* **46**, 1075–1078.
- Yaghi, O. M., Li, H. L., Davis, C., Richardson, D. T. & Groy, L. (1998). *Acc. Chem. Res.* **31**, 474–484.
- Yaghi, O. M., O'Keefe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. & Kim, J. (2003). *Nature (London)*, **423**, 705–714.
- Zhao, B., Cheng, P., Dai, Y., Cheng, C., Liao, D.-Z., Yan, S.-P., Jiang, Z.-H. & Wang, G.-L. (2003). *Angew. Chem. Int. Ed.* **42**, 934–936.
- Zhao, X.-X., Ma, J.-P., Shen, D.-Z., Huang, R.-Q. & Dong, Y.-B. (2009). *CrystEngComm*, **7**, 1–11.