

Diaquabis[4-(4*H*-1,2,4-triazol-4-yl)-benzoato- κ^2O,O']cobalt(II), and the cadmium(II) and copper(II) analogues: new self-complementary hydrogen-bond donor/acceptor modules for designing hydrogen-bonded frameworks

Liliana V. Lukashuk,^a Andrey B. Lysenko,^a Eduard B. Rusanov,^b Alexander N. Chernega^b and Konstantin V. Domasevitch^{a*}

^aInorganic Chemistry Department, Kiev University, Volodimirskaya Str. 64, Kiev 01033, Ukraine, and ^bInstitute of Organic Chemistry, Murmanskaya Str. 5, Kiev 02094, Ukraine

Correspondence e-mail: dk@univ.kiev.ua

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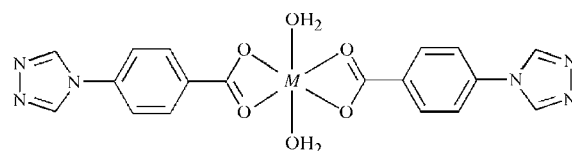
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In the isostructural title complexes, $[M(C_9H_6N_3O_2)_2(H_2O)_2]$ [$M = Co^{II}$, (I), Cd^{II} , (II), and Cu^{II} , (III); the metal centres reside on a twofold axis in the space group $C2/c$ for (I) and (II)], the metal centres are surrounded by four O atoms from two O,O' -bidentate carboxylate groups and by two *trans*-coordinated aqua ligands, forming a distorted octahedral environment. The molecules possess four hydrogen-bond donor (two aqua ligands) and four hydrogen-bond acceptor sites (two triazole groups), and aggregate by self-association, forming two-dimensional hydrogen-bonded frameworks [*via* $O-H\cdots N$ interactions; $O\cdots N = 2.749$ (3)– 2.872 (3) Å]. The layers are parallel and are tightly packed with short interlayer distances of 4.93, 4.95 and 5.01 Å for (I), (II) and (III), respectively.

Comment

The concept of hydrogen-bonded self-associated modules (Prins *et al.*, 2001) providing a multitude of interactions offers intriguing possibilities for structural design and development of novel materials, including nanotubes (Semetey *et al.*, 2002) and liquid crystals (Sautter *et al.*, 2001). An interesting perspective may be anticipated for molecular complexes containing a set of coordinated water molecules (donors of two hydrogen bonds) and heteroditopic bridging organic ligands (*e.g.* pyridinecarboxylates) which bear two different functional groups for anchoring the metal centre and for propagation of the secondary connections. The latter is feasible by simple interconnection of hydrogen-bond donor

and acceptor sites, which are offered by the tecton frames. Recently, 4-(1,2,4-triazol-4-yl)benzoic acid (HL) has been demonstrated to be an attractive candidate for this purpose (Zou *et al.*, 2005). Thus, the triazole functionality acts as a binding site towards the metal ion, while the carboxylate group supports hydrogen-bonding interactions, affording a three-dimensional hybrid hydrogen-bonded coordination polymer with fluorescence properties. Even more interesting is that the functionality of such a polydentate ligand allows a reverse situation for bis[4-(1,2,4-triazol-4-yl)benzoate]– $(H_2O)_2M^{II}$ complexes. In this case, the acid group can interact with the central atom, leaving the triazole termini non-coordinated and, therefore, capable of a hydrogen-bonding role. In these molecular modules, either of the coordinated aqua ligands can donate two hydrogen bonds, while the outer triazolyl groups supply four equal hydrogen-bond acceptor sites. The competition between the carboxylate and the triazole groups demonstrates the unique possibility for controlling and tuning the overall structure as well as functional properties through varying of the experimental conditions. We report here the crystal structures of new multiple hydrogen-bond donor/acceptor ‘self-complementary’ complexes $[ML_2(H_2O)_2]$ [$M = Co^{II}$, (I), Cd^{II} , (II), and Cu^{II} , (III)].



(I) $M = Co^{II}$, (II) $M = Cd^{II}$, (III) $M = Cu^{II}$

Compounds (I) and (II) are isomorphous, and their crystallographically unique parts comprise half-molecules with the metal atoms lying on a twofold axis (which is orthogonal to the direction defined by the two coordinated aqua ligands; Fig. 1). The Cu complex, (III), is not isostructural with (I) and (II), as the Jahn–Teller distortion within the coordination octahedron makes an impossible symmetry equivalence of *cis*-positioned bonds. Compound (III) crystallizes in the space group $P2_1/c$ and its asymmetric unit comprises one molecule of $[CuL_2(H_2O)_2]$ (Fig. 2). In all three cases, the molecular frames involve distorted octahedral MO_6 cores, which consist of two chelating carboxylate groups and two aqua molecules coordinated in the *trans* positions. It is important to note that such coordination behaviour and *trans* distribution of aryl-carboxylate ligands within the coordination sphere are rare for

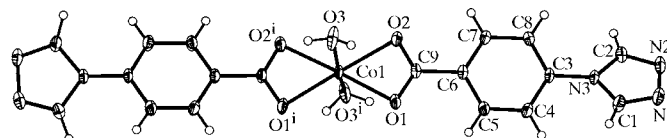


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.] The atom-labelling scheme and location of the asymmetric unit in the unit cell are identical for (II).

transition metal octahedral dications, although a similar configuration was observed for a $(\text{H}_2\text{O})_2\text{Cu}^{\text{II}}$ complex with two phthalate ligands (Goeta *et al.*, 1993).

For (I) and (II), the $M\text{—O}_{\text{CO}_2}$ bond lengths are similar, ranging from 2.1291 (12) to 2.1539 (11) Å and from 2.3008 (19) to 2.3275 (17) Å, respectively, and those for (II) are similar to those observed for the related *cis*- $(\text{C}_6\text{H}_5\text{CO}_2)_2\text{Cd}^{\text{II}}$ complexes [2.268–2.465 Å for $(\text{H}_2\text{O})_2(p\text{-ClC}_6\text{H}_5\text{CO}_2)_2\text{Cd}^{\text{II}}$, 2.258–2.509 Å for $(\text{H}_2\text{O})_2(p\text{-NO}_2\text{C}_6\text{H}_5\text{CO}_2)_2\text{Cd}^{\text{II}}$ (Rodesiler *et al.*, 1985) and 2.276–2.411 Å for $(\text{H}_2\text{O})_2\{\text{C}_6\text{H}_4(\text{COCH}_3)\text{CO}_2\}_2\text{Cd}^{\text{II}}$ (Viossat *et al.*, 2004)]. In (III), a more significant distortion from the regular octahedral geometry can be attributed to the Jahn–Teller effect, and it affords the elongation of the axial Cu–O carboxylate bonds [Cu1–O4 = 2.560 (2) Å and Cu1–O2 = 2.596 (2) Å]. Thus, the four equatorial positions are occupied by two carboxylate O atoms [Cu1–O1 = 1.9400 (15) Å and Cu1–O3 = 1.9377 (14) Å] and two water molecules [Cu1–O5 = 1.9806 (17) Å and Cu1–O6 = 1.9642 (18) Å], while for (I) and (II), the corresponding $M\text{—O}_{\text{aqua}}$ bonds are almost equal to the $M\text{—O}_{\text{CO}_2}$ bonds [Co1–O3 = 2.0552 (13) Å and Cd1–O3 = 2.280 (2) Å]. The *cis* angles in the coordination environment around the Cu centre range from 85.22 (7) to 126.85 (7)° [and are 55.99 (7) and 56.68 (7)° within the carboxylate chelate fragments], whereas the *trans* bond angles lie between 169.33 (8) and 177.14 (6)°. The distortion effect leads to anisobidentate coordination of the CO_2 fragments and it differentiates also the C–O bond lengths [O4–C18 =

1.237 (3) Å and O2–C9 = 1.240 (3) Å, and O1–C9 = 1.273 (3) Å and O3–C18 = 1.279 (3) Å]. The corresponding bond lengths in (I) and (II) are similar [O1–C9 and O2–C9 are in the range 1.255 (3)–1.269 (2) Å] and their values are normal for arylcarboxylates (*e.g.* 1.264–1.275 Å for the benzoic acid dimer; Bruno & Randaccio, 1980). The metallocycles actually lie in the same plane as the benzene rings of the ligand, but the triazole termini are rotated around the single C–N bond [the corresponding torsion angles C1–N3–C3–C4 and C2–N3–C3–C8 range from –24.6 (3) to –25.5 (4)° for (I) and (II), and are 28.3 (3) and 27.3 (3)° for (III)] and are characteristic for such a ligand system (Zou *et al.*, 2005).

The $[\text{ML}_2(\text{H}_2\text{O})_2]$ molecules can be considered as rectangular modules, in which the opposite triazole N atoms at the corners (acceptors of hydrogen bonds) are separated by a 20.5 Å spacer, while two aqua molecules (hydrogen-bond donors) around the metal centre are located at distances of *ca* 4.0 Å. Therefore, in the sense of the hydrogen-bond functionality, the molecules may be regarded as self-complementary (4+4) building blocks (Boldog *et al.*, 2003) and can generate complex framework structures by simple interconnection (O–H···N) of available hydrogen-bond donor and acceptor sites (Tables 1–3). The fixed orientation of the triazole and aqua complementary pair, and the direction of the H–O bond vectors from the aqua ligands, leads preferentially to a set of cyclic ten-membered hydrogen-bonded rings propagating parallel to the (001) direction (Fig. 3) and can be identified in the formalism of the graph-set analysis as $R_4^4(10)$ rings (Etter *et al.*, 1990). Obviously, the shape and conformation of the $[\text{ML}_2(\text{H}_2\text{O})_2]$ molecules are especially suitable for generation of two-dimensional hydrogen-bonded wave-like layers, which are situated parallel to each other, forming a tight packing motif with quite short interlayer separations of 4.93–5.01 Å. Additionally, the sheets are connected by a combination of weaker C–H···O hydrogen-bonding inter-

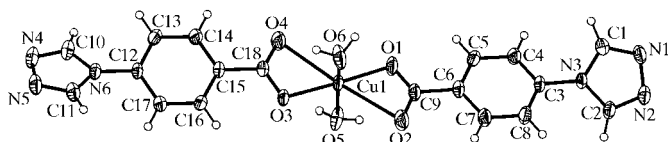


Figure 2

The molecular structure of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

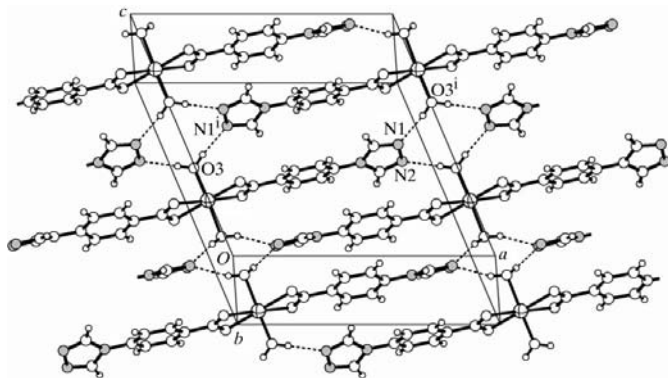


Figure 3

A projection of the structure of (I), showing the formation of an (001) layer with cyclic ten-membered hydrogen-bonded rings. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

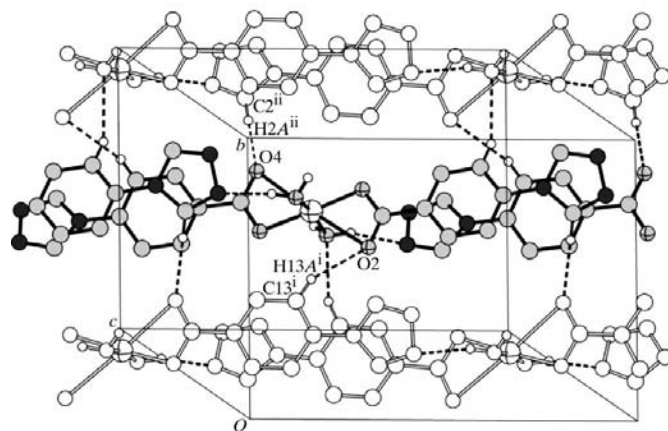


Figure 4

The packing of (III), showing the interlayer weak C–H···O hydrogen bonding involving phenylene and triazole groups; H atoms not involved in these interactions have been omitted. The hydrogen bonds are represented by dashed lines. [Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.]

actions (Fig. 4) (Desiraju & Steiner, 1999). In (I) and (II), atom O3 acts as a hydrogen-bond acceptor towards the C4—H4A($-\frac{1}{2} + x, \frac{1}{2} + y, z$) group of a molecule from a neighbouring layer. The packing pattern for (III) is similar. However, in this case, carbonyl atoms O2 and O4 (which occupy very distal axial positions within the coordination octahedron and are sterically available for the additional interactions) also manifest hydrogen-bond acceptor properties towards the phenylene C13—H13A($-x, y - \frac{1}{2}, -z + \frac{1}{2}$) and triazole C2—H2A($-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$) groups, respectively (Table 3). Such a non-equivalent environment precludes an evident inversion symmetry of the molecule. This weaker C—H...O hydrogen bonding generates an even more complicated three-dimensional structure by interconnection of the O—H...N hydrogen-bonded layers.

The tectons represent a rare type of a self-complementary (four donor/acceptor) building block that may find further application in the design of the solid-state architecture.

Experimental

All materials were of reagent grade and were used as received. The organic ligand HL was prepared according to a typical procedure (Bartlett & Humphrey, 1967). Complexes (I)–(III) were prepared in a similar fashion using a hydrothermal technique. In a typical synthesis, Co(CH₃COO)₂·4H₂O (0.0249 g, 0.1 mmol), HL (0.0189 g, 0.1 mmol) and water (5 ml) in a Teflon vessel were placed in a steel bomb and heated to 413 K for 24 h. The mixture was cooled slowly to room temperature over a period of 72 h, which afforded well shaped pink crystals of (I) (yield 0.0141 g, 60%).

Compound (I)

Crystal data

[Co(C₉H₆N₃O₂)₂(H₂O)₂]
M_r = 471.30
 Monoclinic, *C*2/*c*
a = 13.5266 (9) Å
b = 9.8617 (7) Å
c = 14.4429 (9) Å
 β = 112.083 (3)°
V = 1785.3 (2) Å³
Z = 4
 Mo *K*α radiation
 μ = 1.02 mm⁻¹
T = 213 (2) K
 0.18 × 0.16 × 0.16 mm

Data collection

Siemens SMART CCD diffractometer
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.838, *T_{max}* = 0.854
 7599 measured reflections
 2057 independent reflections
 1607 reflections with *I* > 2σ(*I*)
R_{int} = 0.030

Refinement

R[*F*² > 2σ(*F*²)] = 0.028
wR(*F*²) = 0.068
S = 0.94
 2057 reflections
 141 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.38 e Å⁻³
 $\Delta\rho_{\min}$ = -0.31 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H1...N1 ⁱ	0.85	1.97	2.780 (2)	159
O3—H2...N2 ⁱⁱ	0.85	2.05	2.843 (2)	154
C4—H4A...O3 ⁱⁱⁱ	0.94	2.63	3.428 (2)	143

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x - 1, y, z$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$.

Compound (II)

Crystal data

[Cd(C₉H₆N₃O₂)₂(H₂O)₂]
M_r = 524.77
 Monoclinic, *C*2/*c*
a = 13.7301 (6) Å
b = 9.8915 (5) Å
c = 14.8111 (10) Å
 β = 112.063 (3)°
V = 1864.21 (18) Å³
Z = 4
 Mo *K*α radiation
 μ = 1.23 mm⁻¹
T = 296 (2) K
 0.18 × 0.16 × 0.16 mm

Data collection

Siemens SMART CCD diffractometer
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.810, *T_{max}* = 0.828
 6196 measured reflections
 2213 independent reflections
 1941 reflections with *I* > 2σ(*I*)
R_{int} = 0.021

Refinement

R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.086
S = 1.06
 2213 reflections
 141 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.67 e Å⁻³
 $\Delta\rho_{\min}$ = -0.33 e Å⁻³

Table 2

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H1...N1 ⁱ	0.86	1.94	2.788 (2)	166
O3—H2...N2 ⁱⁱ	0.86	2.01	2.836 (2)	159
C4—H4A...O3 ⁱⁱⁱ	0.93	2.56	3.331 (2)	141

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x - 1, y, z$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$.

Compound (III)

Crystal data

[Cu(C₉H₆N₃O₂)₂(H₂O)₂]
M_r = 475.91
 Monoclinic, *P*2₁/*c*
a = 13.4483 (4) Å
b = 10.0101 (3) Å
c = 14.4749 (5) Å
 β = 111.674 (2)°
V = 1810.83 (10) Å³
Z = 4
 Mo *K*α radiation
 μ = 1.26 mm⁻¹
T = 296 (2) K
 0.50 × 0.20 × 0.20 mm

Data collection

Siemens SMART CCD diffractometer
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.571, *T_{max}* = 0.787
 13821 measured reflections
 4301 independent reflections
 3232 reflections with *I* > 2σ(*I*)
R_{int} = 0.036

Table 3

Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H1...N5 ⁱ	0.85	2.05	2.872 (3)	163
O5—H2...N1 ⁱⁱ	0.85	1.99	2.790 (3)	157
O6—H3...N2 ⁱⁱⁱ	0.85	1.98	2.799 (3)	162
O6—H4...N4 ^{iv}	0.85	1.98	2.749 (3)	149
C2—H2A...O4 ^v	0.93	2.23	3.158 (3)	175
C4—H4A...O5 ^{vi}	0.93	2.52	3.368 (3)	152
C13—H13A...O2 ^{vii}	0.93	2.54	3.371 (3)	150

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $x - 1, y, z$; (iv) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	280 parameters
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
4301 reflections	$\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

All H atoms were located in difference maps and then treated as riding atoms using default C—H and O—H bond lengths, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$.

For all compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.700.00; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3077). Services for accessing these data are described at the back of the journal.

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