metal-organic papers

Bis(2,4,6-triamino-1,3,5-triazin-1-ium) bis(pyridine2,6-dicarboxylato)zincate(II) decahydrate

Zahra Aghajani,[a] Mahboubeh A. Sharif,[a] Hossein Aghabozorg[b]* and Azam Naderpour[a]

[a]Department of Chemistry, Islamic Azad University, Qom Branch, Qom, Iran, and [b]Department of Chemistry, Teacher Training University, PO Box 15614, Tehran, Iran

Correspondence e-mail:
aghabozorg@saba.tmu.ac.ir

The reaction of zinc(II) nitrate tetrahydrate with the proton-transfer compound LH_2 [LH_2 is (tataH)$_2$(pydc), where tata is 2,4,6-triamino-1,3,5-triazine (melamine) and pydcH$_2$ is pyridine-2,6-dicarboxylic acid] in aqueous solution leads to the formation of the title compound, (tataH)$_2$[Zn(pydc)$_2$].10H$_2$O or (C$_3$H$_7$N$_6$)$_2$[Zn(C$_7$H$_3$O$_4$)$_2$].10H$_2$O. The Zn^{II} atom has a distorted octahedral coordination environment. Extensive intermolecular N—H$\cdots$O and O—H$\cdots$O hydrogen bonding involving the tataH and pydc ligands and the water molecules forms an extended three-dimensional network.
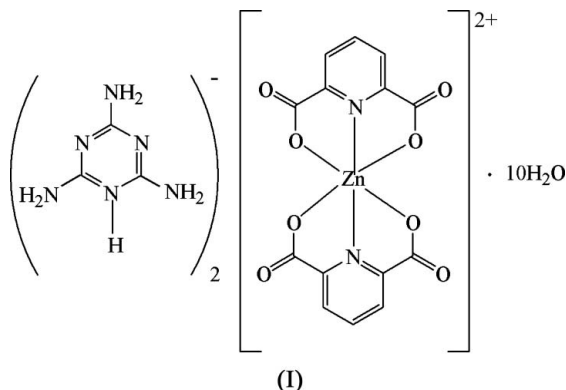
Comment

Hydrogen bonding plays a key role in chemical, catalytic and biochemical processes, as well as in supramolecular chemistry and crystal engineering (Epstein & Shubina, 2002). In order to study the hydrogen-bonding patterns in proton-transfer compounds, our research group has selected pyridine-2,6-dicarboxylic acid (pydcH$_2$) and 1,10-phenanthroline-2,9-dicarboxylic acid (phendcH$_2$) as proton donors, and 2,4,6-pyridinediamine (pyda), creatinine (creat), 1,10-phenanthroline (phen), N,N'-diethyl-2-amino-6-methyl-4-pyrimidinol (pyrim) and melamine (2,4,6-triamino-1,3,5-triazine, tata) as proton acceptors, resulting in the formation of new proton-transfer systems, such as (pydaH)(pydcH) (Aghabozorg, Akbari Saei & Ramezanipour, 2005), (creatH)(pydcH) (Moghimi *et al.*, 2004), (creatH)(phendcH) (Soleimannejad *et al.*, 2005), (pyrimH){H(Hpydc)$_2$} (Aghabozorg, Soleimannejad *et al.*, 2005), and (tataH$_2$)(pydc) and (tataH)$_2$(pydc) (Sharif *et al.*, 2006). The dicarboxylate fragments of the resulting proton-transfer compounds can function as suitable ligands in the synthesis of organo–metal complexes (Moghimi *et al.*, 2002*a,b*; Ranjbar *et al.*, 2003; Ranjbar, Aghabozorg & Moghimi, 2002; Ranjbar, Taghavipur *et al.*, 2002; Ranjbar *et al.*, 2001; Moghimi *et al.*, 2005). Here, we report the molecular structure of the title mononuclear complex, (tataH)$_2$-[Zn(pydc)$_2$].10H$_2$O, (I), in which the (pydc)$^{2-}$ ligands act as tridentate ligands through two O atoms and one N atom, and two 2,4,6-triamino-1,3,5-triazinium cations, (tataH)$^+$, act as counter-ions.

The structure of (I) is shown in Fig. 1 and geometric parameters are given in Table 1. The coordination geometry around the Zn^{II} atom is distorted octahedral. Atoms O1, O3, O5 and O8 form the equatorial plane with a small tetrahedral distortion (mean deviation 0.48 Å). The N atoms occupy the axial positions. The dihedral angle between the mean planes of the pyridine rings (A1 and A2, defined in Fig. 1) is 80.80 (9)°. The metal–ligand bond distances of (I) are consistent with those found in (pydaH)[Zn(pydc)(pydcH)]·3H$_2$O [Zn—N and Zn—O distances in the ranges 2.015 (2)–2.032 (2) and

2.0903 (19)–2.322 (2) Å, respectively; Ranjbar, Moghimi *et al.*, 2002 and (creatH)[Zn(pydc)(pydcH)]·4H$_2$O [Zn—N and Zn—O distances in the ranges 2.021 (3)–2.029 (3) and 2.114 (2)–2.141 (2) Å, respectively; Moghimi *et al.*, 2005]. In (tataH)$_2$[Zn(pydc)$_2$].10H$_2$O, (I), the Zn—N and Zn—O distances are in the ranges 2.032 (2)–2.036 (2) and 2.123 (2)–2.241 (2) Å, respectively. The dihedral angles between planes C1/A1, C2/A1, C1/C2, C1/A2 and C2/A2 are 3.8 (2), 1.95 (2), 4.9 (2), 78.9 (2) and 80.88 (9)°, respectively

(I)

.

In the crystal structure of (I), cations and anions are connected *via* hydrogen bonds and form a one-dimensional chain. In addition, the uncoordinated water molecules form a three-dimensional network through further hydrogen bonding (Fig. 2 and Table 2). It is interesting to note that the crystal packing (Fig. 2) is a layered structure. The space between the layers of [Zn(pydc)2]$^{2-}$ complex units is occupied by (tataH)$^+$ cations, which bridge the [Zn(pydc)2]$^{2-}$ units *via* hydrogen bonds. In addtion, each of the adjacent (pydc)$^{2-}$ planes of two

Figure 2
The crystal packing of (I). Hydrogen bonds are shown as dashed lines.

neighbouring [Zn(pydc)2]$^{2-}$ complex units is coplanar in such a way that sets of superimposed crosses are formed.

In conclusion, the intermolecular forces which exist between anions and cations in the title Zn^{II} complex consist of coulombic interactions as well as hydrogen bonding.

Experimental

The reaction of *L*H$_2$ (70 mg, 0.168 mmol) with Zn(NO$_3$)$_2$·4H$_2$O (22 mg, 0.084 mmol) in water (10 ml) gave colourless crystals of (tataH)$_2$[Zn(pydc)$_2$].10H$_2$O, (I). X-ray diffraction quality crystals were obtained by slow evaporation of the solvent at room temperature.

Crystal data

(C$_3$H$_7$N$_6$)$_2$[Zn(C$_7$H$_3$NO$_4$)$_2$]·10H$_2$O	$Z = 2$
$M_r = 830.03$	$D_x = 1.624$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.100$ (2) Å	Cell parameters from 1024
$b = 12.877$ (2) Å	reflections
$c = 13.209$ (2) Å	$\theta = 2.3–26.6°$
$\alpha = 87.739$ (4)°	$\mu = 0.82$ mm^{-1}
$\beta = 65.731$ (4)°	$T = 120$ (2) K
$\gamma = 80.709$ (3)°	Cube, colourless
$V = 1697.8$ (5) Å^3	$0.30 \times 0.30 \times 0.30$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	6529 independent reflections
φ and ω scans	5637 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)	$R_{int} = 0.017$
	$\theta_{max} = 26.0°$
$T_{min} = 0.791$, $T_{max} = 0.791$	$h = -13 \rightarrow 11$
10100 measured reflections	$k = -15 \rightarrow 15$
	$l = -13 \rightarrow 16$

Refinement

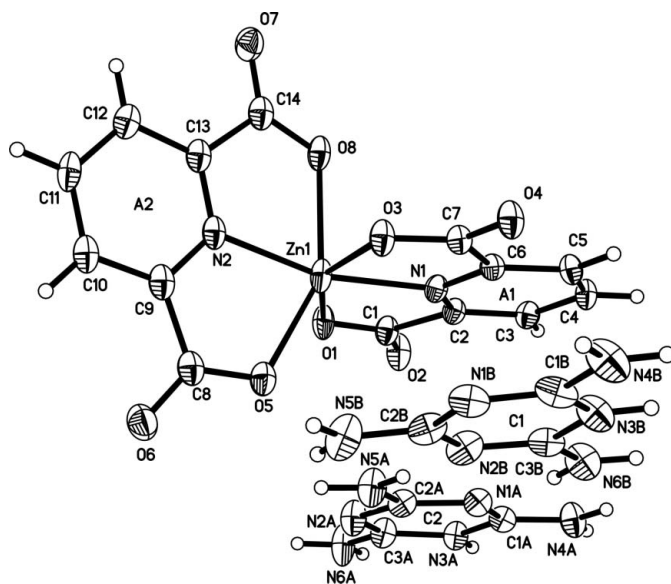|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 4.8947P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{max} < 0.001$
6529 reflections	$\Delta\rho_{max} = 1.22$ e Å^{-3}
507 parameters	$\Delta\rho_{min} = -0.76$ e Å^{-3}
H-atom parameters constrained	

Figure 1
The constituent ions of the title complex, with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres. The uncoordinated water molecules have been omitted for clarity. Rings A1, A2, C1 and C2 are discussed in the text.
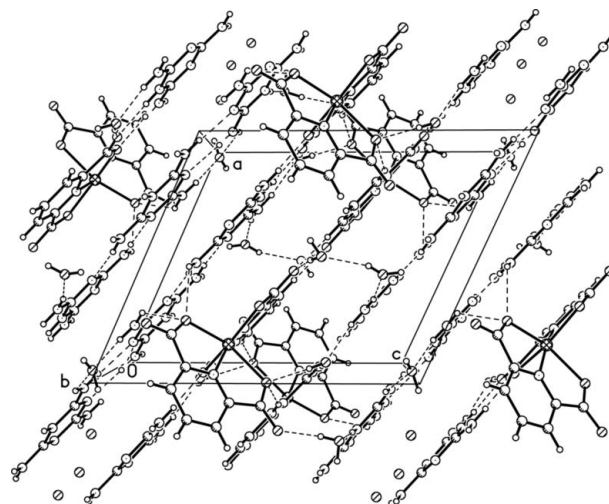
Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.032 (2)	Zn1—O5	2.153 (2)
Zn1—N2	2.036 (2)	Zn1—O3	2.2381 (19)
Zn1—O1	2.123 (2)	Zn1—O8	2.241 (2)
N1—Zn1—N2	163.14 (9)	O5—Zn1—O3	95.28 (8)
N1—Zn1—O1	77.47 (8)	N2—Zn1—O8	74.65 (9)
N2—Zn1—O5	76.83 (9)	O1—Zn1—O8	95.45 (8)
O1—Zn1—O5	92.87 (8)	O5—Zn1—O8	151.16 (7)
N1—Zn1—O3	74.84 (8)	O3—Zn1—O8	90.17 (8)
O1—Zn1—O3	152.04 (7)		
O8—Zn1—O1—C1	88.5 (2)	O1—Zn1—N2—C13	−97.3 (2)
O8—Zn1—O3—C7	−91.8 (2)	O3—Zn1—N2—C13	81.0 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3A—H3AA$\cdots$O4[i]	0.88	1.90	2.777 (3)	173
N4A—H4AA$\cdots$O7W[ii]	0.88	2.01	2.870 (4)	167
N4A—H4AB$\cdots$O1W[i]	0.88	2.00	2.866 (3)	170
N5A—H5AA$\cdots$N2B	0.88	2.08	2.950 (3)	172
N5A—H5AB$\cdots$O5	0.88	2.33	2.846 (3)	117
N6A—H6AB$\cdots$O3[i]	0.88	1.95	2.821 (3)	172
N3B—H3BA$\cdots$O4W	0.88	1.81	2.690 (3)	175
N4B—H4BA$\cdots$N1B[iii]	0.88	2.09	2.972 (3)	176
N4B—H4BB$\cdots$O6W[iii]	0.88	2.38	3.026 (4)	130
N5B—H5BA$\cdots$O6W	0.88	2.06	2.891 (4)	157
N5B—H5BB$\cdots$O5	0.88	2.35	2.991 (3)	130
N6B—H6BA$\cdots$N1A	0.88	2.30	3.179 (3)	173
N6B—H6BB$\cdots$O9W[iv]	0.88	2.40	3.148 (4)	143
N6B—H6BB$\cdots$O7W[ii]	0.88	2.54	3.078 (3)	120
O1W—H1WA$\cdots$O4	0.85	1.85	2.688 (3)	169
O1W—H1WB$\cdots$O8[v]	0.85	1.94	2.775 (3)	165
O2W—H2WA$\cdots$O7[i]	0.85	1.92	2.765 (3)	175
O2W—H2WB$\cdots$O1[vi]	0.85	2.00	2.846 (3)	175
O3W—H3WA$\cdots$O5W[i]	0.85	2.20	2.934 (3)	145
O3W—H3WB$\cdots$O2[i]	0.85	1.88	2.721 (3)	170
O4W—H4WB$\cdots$O7[v]	0.85	1.88	2.722 (3)	174
O4W—H4WA$\cdots$O9W[iv]	0.85	2.01	2.857 (4)	180
O4W—H4WA$\cdots$O1SB[vii]	0.85	2.20	2.764 (4)	124
O5W—H5WB$\cdots$O3W[viii]	0.85	2.05	2.878 (3)	165
O5W—H5WA$\cdots$O2W[vi]	0.85	1.87	2.716 (3)	172
O6W—H6WA$\cdots$O1SC[ix]	0.85	1.89	2.634 (5)	146
O6W—H6WA$\cdots$O8W[ix]	0.85	2.10	2.878 (4)	152
O6W—H6WB$\cdots$O8W′[x]	0.85	1.79	2.519 (4)	142
O6W—H6WB$\cdots$O8W[x]	0.85	2.12	2.947 (4)	165
O7W—H7WA$\cdots$O3W[x]	0.85	2.05	2.842 (3)	155
O7W—H7WB$\cdots$O9W[xi]	0.85	1.86	2.710 (4)	174
O9W—H9WA$\cdots$O6[xii]	0.85	1.84	2.682 (4)	168

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y + 1, -z$; (iii) $-x, -y + 1, -z$; (iv) $x - 1, y - 1, z$; (v) $-x, -y + 1, -z + 1$; (vi) $-x + 1, -y + 2, -z + 1$; (vii) $x, y - 1, z - 1$; (viii) $-x + 2, -y + 2, -z + 1$; (ix) $-x, -y + 2, -z + 1$; (x) $x, y, z - 1$; (xi) $-x + 3, -y + 2, -z$; (xii) $-x + 2, -y + 2, -z$.

All H atoms were placed in calculated positions, with N—H = 0.88–0.91 Å, O—H = 0.85 Å and C—H = 0.95 Å. They were included in a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(O). Two of the uncoordinated water molecules are disordered, one over two sites (O8W and O8W′) which were refined with fixed occupancies of 0.8 and 0.2, respectively, and one over three sites (O1SA, O1SB and O1SC), which were refined with fixed occupancies of 0.6, 0.2 and 0.2, respectively. H atoms were not included for the disordered O atoms, although they are included in the chemical formula. The largest residual electron-density peak is located 1.12 Å from atom O8.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Aghabozorg, H., Akbari Saei, A. & Ramezanipour, F. (2005). *Acta Cryst.* E**61**, o3242–o3244.
Aghabozorg, H., Soleimannejad, J., Sharif, M. A., Sheshmani, S. & Moghimi, A. (2005). *Anal. Sci.* **21**, x73–x74.
Bruker (1998). *SAINT-Plus* (Version 6.01) and *SMART* (Version 5.059). Bruker AXS Inc., Madison, Wisconsin, USA.
Epstein, L. M. & Shubina, E. S. (2002). *Coord. Chem. Rev.* **231**, 165–181.
Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M. & Chadha, R. K. (2002*a*). *Can. J. Chem.* **80**, 1687–1696.
Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M. & Chadha, R. K. (2002*b*). *J. Chem. Res. (S)*, pp. 477–479.
Moghimi, A., Sharif, M. A. & Aghabozorg, H. (2004). *Acta Cryst.* E**60**, o1790–o1792.
Moghimi, A., Sharif, M. A., Shokrollahi, A., Shamsipur, M. & Aghabozorg, H. (2005). *Z. Anorg. Allg. Chem.* **631**, 902–908.
Ranjbar, M., Aghabozorg, H. & Moghimi, A. (2002). *Acta Cryst.* E**58**, m304–306.
Ranjbar, M., Aghabozorg, H., Moghimi, A. & Yanovsky, A. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 626–628.
Ranjbar, M., Moghimi, A. & Aghabozorg, H. (2003). *Anal. Sci.* **19**, 803–804.
Ranjbar, M., Moghimi, A., Aghabozorg, H. & Yap, G. P. A. (2002). *Anal. Sci.* **18**, 219–220.
Ranjbar, M., Taghavipur, M., Aghabozorg, H., Moghimi, A., Jalali, F. & Shamsipur, M. (2002). *Polish J. Chem.* **76**, 785–794.
Sharif, M. A., Aghabozorg, H., Shokrollahi, A., Shamsipur, M., Moghimi, A. & Kickelbick, G. (2006). *Polish J. Chem.* Submitted.
Sheldrick, G. M. (1998). *SADABS* (Version 2.01) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Soleimannejad, J., Sharif, M. A., Sheshmani, S., Alizadeh, R., Moghimi, A. & Aghabozorg, H. (2005). *Anal. Sci.* **21**, x49–x50.