Hexaaquazinc(II) dipicrate trihydrate

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In the crystal structure of the title compound, $[Zn(H_2O)_6]$-$(C_6H_2N_3O_7)_2 \cdot 3H_2O$, the zinc cation complexes and picrate anions are stacked separately, extending along the b axis. No picrate species ligate to the metal cation. This lack of picrate coordination is atypical among metal picrate salts. We speculate that the size of the metal–aqua complex as related to the intermolecular distance of the picrate anions in the π stack can be a measure of the formation of such separated stacks in the crystal structures of divalent metal complexes with picrate anions. Picrate ions are linked to each other with short intermolecular $C \cdots C$ contacts of 3.223 (6) and 3.194 (6) Å in the stack.

Comment

The crystal structures of metal picrate salts that have been reported for main-group, transition, lanthanide and actinide metals are classified into two groups according to the coordination structure of the metal cation and the picrate anion (Harrowfield, 1996). Most of the salts belong to the first group, where the picrate anion can bind directly to the metal atom via a coordinate and/or ionic bonds. In the second group, the water molecules are coordinated instead of the picrate ions to form an aqua complex cation with the metal. These are rather exceptional, and so far only three examples have been reported, viz. hexaaquamagnesium dipicrate trihydrate (Harrowfield et al., 1995), tris(μ-hydroxo)hexaaquatriberyllium tris(picrate) hexahydrate (Cecconi et al., 1998) and hexaaquairon dipicrate dihydrate (Honda et al., 2003). The coordination mode may be determined according to the balance between the metal coordination and the stacking energy of the picrate anions (Harrowfield, 1996). Picrate anions tend to stack almost parallel to their molecular planes, regardless of whether the phenolate group is coordinated to the metal atom. The intermolecular interaction energy of the π stack is considered to be comparable to the difference between the coordination bond energies of the picrate anion and the aqua ligand to the metal cation. The second type of

structure will be formed when the π-stack energy exceeds the coordination bond energy of the picrate ion to the metal, which thus displaces water. The coordination is said to be controlled by the π-stack packing force. Thus, a further investigation of the crystal structures of metal picrates should contribute to the systematic understanding of the relationship between the structure formation and the intermolecular interactions. The crystal structure of a new 'no-picrate-coordination' complex, hexaaquazinc(II) dipicrate trihydrate, (I), is presented here and compared with those of other metal picrates.
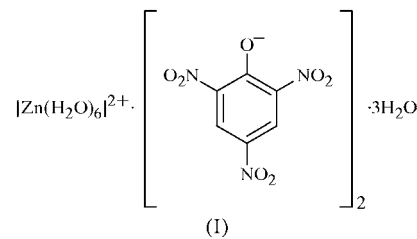

(I)

Fig. 1 shows the molecular structures of the hexaaquazinc cation and picrate anions, and selected bond lengths are summarized in Table 1. Six water molecules are coordinated to the central metal atom and no picrate species ligate to the metal atom. The crystal structure projected along the b axis is shown in Fig. 2. The unit cell contains four zinc cations and eight picrate anions. The cation complexes and picrate anions form separate stacks that extend along the b axis, and stacks consisting of the same species are aligned along the a axis. Picrate anions related through 2_1 screw symmetry stack in a head-to-tail manner, with the molecular planes almost parallel to the ac plane.

Similar packing motifs are observed in the Mg and Fe salts. In particular, the crystal structure of the Mg salt is similar to that of the present Zn salt. The monoclinic space group of $P2_1/c$ for the Mg salt is similar to that of $P2_1/n$ for the Zn salt, with a different direction of the glide symmetry. The unit-cell parameters [$a = 15.023$ (3) Å, $b = 6.718$ (4) Å, $c = 26.516$ (2) Å, $\beta = 109.55$ (1)° and $V = 2522$ Å^3] are similar to those of the Zn salt, with a reversed setting of a and c. The number of solvent water molecules in the unit cell (12) is also the same. The Fe salt crystallizes in a different space group (orthorhombic, $Pccn$) and the size of the unit cell is smaller [$a = 25.248$ (2) Å, $b = 7.1136$ (7) Å, $c = 13.1993$ (9) Å and $V = 2370.7$ (3) Å^3], partly because of the small number of solvent molecules in the unit cell (8). The average $M-O$ bond distance for the Zn complex is 2.09 (2) Å. This value is close to the distance of 2.06 (1) Å for the Mg complex and is slightly shorter than that for the Fe complex [2.12 (4) Å]. On the other hand, the Be salt adopts a structure that is different from that of the other three salts in the group; the metals form a trimeric cation, the picrate anions stack in a head-to-head and slipped parallel manner, and the cation and picrate stacks do not align with each other.

Fig. 3 illustrates the molecular stack of the picrate anions of the Zn salt when viewed from the c axis. The anions in the stack are linked to each other via short intermolecular contacts of 3.223 (6) and 3.194 (6) Å for $C3 \cdots C11^i$ and

C5···C9[ii], respectively [symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x, -y, -z + 1$]. Similar short C···C contacts in the stack are found in both the Mg (3.21 and 3.25 Å) and the Fe salts (3.06 and 3.08 Å). Successive anions of the stack are almost parallel to each other, with a dihedral angle between benzene planes of 6.5 (1)°. This value is close to the dihedral angle of 6.3° in the Mg salt. In the Fe salt, instead, the planes are not parallel to one another, subtending a much larger dihedral angle (24.7°). An intermolecular repulsion would be too large to keep the two planes parallel with very short contacts of ca 3.1 Å.

The π-stack contiguities of these salts are assumed to be similar when an 'average distance' between two benzene planes, which is estimated by calculating the average distance of the C atoms in one benzene ring from the least-squares plane formed by the C atoms in the other molecule, is used for comparison. The average distances for the Zn, Mg and Fe salts are 3.33 and 3.36, 3.35 and 3.36, and 3.45 and 3.50 Å, respectively. The benzene planes of the three independent picrate anions in the Be salt are almost parallel to each other, since the dihedral angles are all less than 2°, and the estimated average distances are 3.40, 3.46 and 3.51 Å. A high-level *ab initio* molecular orbital calculation has revealed that the optimal intermolecular distance for benzene molecules is 3.5 Å at a slipped-parallel orientation (Tsuzuki *et al.*, 2002). The average distances of the juxtaposed π-conjugated systems in the picrate stack seem to be slightly shorter than the most stable distance of benzene rings. An attractive electrostatic force due to a charge distribution introduced by the –NO$_2$ and –O$^-$ groups could contribute to the building up of the close π stacks.

The closest metal–metal distances between the aqua complexes in the Zn, Mg and Fe salts correspond to the *b*-axis lengths of their crystal lattices (6.69, 6.72 and 7.11 Å, respectively), that is, they are all approximately 7 Å and close to double the intermolecular spacings of the picrate anions in the π stacks. This ratio of the intermolecular spacings is consistent with the chemical stoichiometry ratio of the divalent metal cation to the monovalent picrate anion. We speculate that such intermolecular spacing of the aqua complex may be a measure of the formation of the crystal packing with separate stacks of aqua complexes and picrate anions in the divalent metal complex salts. For the Zn–, Mg– and Fe–aqua complexes, the intermolecular spacing is adequate to form the separate stack structure. On the other hand, when the intermolecular spacing is significantly larger than 7 Å because of the large size of the aqua complex, the segregated stack structure should become unstable and the picrate anion may develop a tendency to become coordinated to the metal by eliminating the aqua ligand.

In order to estimate the size of the aqua complex we assume that the average $M-O$ bond distance is the approximate size of the aqua-complex radius. The size of the complex is obtained by doubling the $M-O$ distance. This value does not take the H atoms of the aqua ligand into account but can be used to compare the size of other metal–aqua complexes by using the reported atomic coordinates, some of which do not contain accurate information on the positions of the H atoms. The sizes of the Zn–, Mg– and Fe–aqua complexes are thus estimated to be 4.17, 4.12 and 4.23 Å, respectively. They are all approximately 4 Å and adjacent complexes have an intermolecular separation of ca 3 Å. This separation is expected to be an optimal value for adjacent complexes to be energetically stable. Most of the metal cations in the picrate-coordinated group of divalent metal picrate salts that have been reported have a large ionic radius, and the minimum metal–O(ligand) distance is 2.46 Å for the Ca^{II} salts (Diakiw *et al.*, 1979). The size of the Ca–aqua complex would be approximately 5 Å, resulting in an intermolecular spacing of ca 8 Å, much larger than 7 Å. Although the $M-O$ distance is 2.11 Å in the trivalent cation Sc salt, some picrate anions are directly bound to the metal (Harrowfield *et al.*, 1994). The separate π-stack orientation would be unfavourable in terms of the electrostatic interaction energy between such a trivalent cation and the counter-anions. The cation charge can be considered as another factor for determining the picrate binding to the cation, as previously discussed (Harrowfield, 1996; Cecconi *et al.*, 1998).

Variable-temperature measurements from 300 down to 95 K were also conducted for the Zn salt and showed a linear
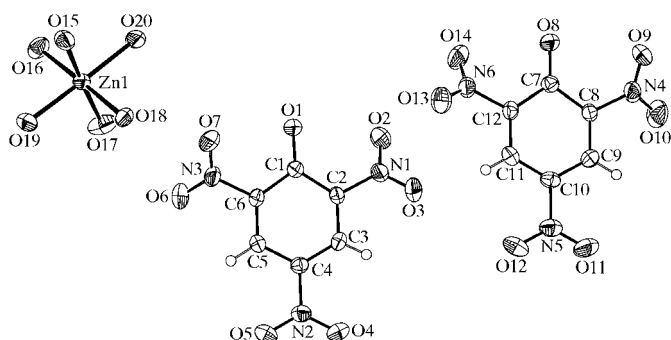

Figure 1
A displacement ellipsoid plot (50% probability level) of the title compound, showing the atomic labelling.
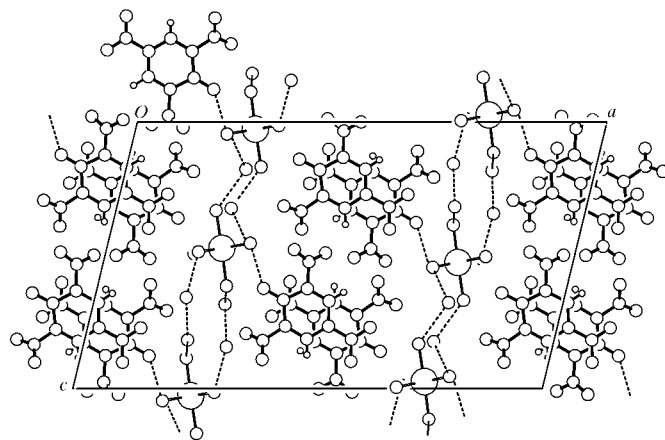

Figure 2
The crystal structure of the title compound, viewed from the *b* axis. Dashed lines depict intermolecular short contacts with O···O distances less than 2.8 Å, suggesting hydrogen-bond formation.

decrease of the lattice parameters. The thermal expansion coefficients for a, b, c, β and V were 1.32×10^{-5}, 9.90×10^{-5}, 2.53×10^{-5}, 6.57×10^{-6} and 1.34×10^{-4} K^{-1}, respectively. The value for V is close to the value of 1.30×10^{-4} K^{-1} for the Fe salt. Compared with the images observed at 300 K, the diffraction photographs at 95 K did not show any new appearances of diffraction spots or any diminution of existing spots. These results imply that the crystal is isomorphous between room temperature and 95 K. However, the diffraction spots disappeared and a powder diffraction pattern was observed at above 300 K. The d values of the diffraction lines were not consistent with the values that were estimated with the cell parameters of the single-crystal phase and indicated the occurrence of a phase transition.

Differential scanning calorimetry and thermal gravimetric analyses confirmed that the elimination of solvent water molecules begins at approximately this temperature (Matsukawa *et al.*, 2003). The high-temperature phase is stable below the phase-transition temperature under a dry environment on cooling but returns to the low-temperature phase rapidly on addition of water to the powder sample. The iron salts also exhibited a similar phase transition at *ca* 330 K, accompanied by the loss of two water solvent molecules from the unit cell. Note that the powder patterns of the non-water-solvated phases of the iron and zinc salts are almost identical to one another. The determination of the structure from the powder pattern of the high-temperature phase will be reported in the near future.
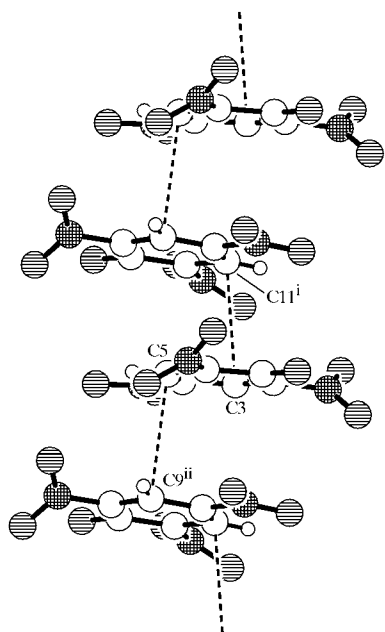

Figure 3
The molecular stack of picrate anions in the title compound, viewed from the c axis. Dashed lines indicate short intermolecular contacts with C···C distances less than 3.3 Å.

Experimental

The synthesis of the title compound was reported by Matsukawa *et al.* (2003). Single crystals were prepared by recrystallization from an aqueous solution.

Crystal data

[Zn(H2O)6](C6H2N3O7)2·3H2O	$V = 2509.5$ (3) Å^3
$M_r = 683.71$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 25.711$ (2) Å	$\mu = 1.10$ mm^{-1}
$b = 6.6934$ (4) Å	$T = 296$ K
$c = 15.007$ (1) Å	$0.64 \times 0.28 \times 0.16$ mm
$\beta = 103.656$ (6)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	5771 independent reflections
Absorption correction: ψ scan (North *et al.*, 1968)	3619 reflections with $F^2 > 2\sigma(F^2)$
$T_{min} = 0.732$, $T_{max} = 0.839$	$R_{int} = 0.015$
6370 measured reflections	3 standard reflections
	frequency: 60 min
	intensity decay: -5.2%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	380 parameters
$wR(F^2) = 0.134$	H-atom parameters not refined
$S = 1.31$	$\Delta\rho_{max} = 0.79$ e Å^{-3}
5771 reflections	$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—O15	2.065 (3)	Zn1—O18	2.087 (3)
Zn1—O16	2.078 (3)	Zn1—O19	2.112 (3)
Zn1—O17	2.071 (3)	Zn1—O20	2.101 (3)

The H atoms in the picrate anions were placed at calculated positions (C—H = 0.96 Å) and fixed during the final refinement, with U_{iso}(H) values of $1.5U_{eq}$ of the attached C atoms. Those in water molecules could not be reliably found in difference maps and were accordingly omitted from the model. However, short intermolecular contacts of O atoms between the water molecules and picrate anions suggest a complex hydrogen-bonding interaction between these entities.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *TEXSAN*.

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