metal-organic compounds

Diaquabis(2,5-dihydroxybenzoato-κO)bis(1,10-phenanthroline-κ²N,N′)-strontium(II) bis(1,10-phenanthroline) tetrahydrate

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The title compound, $[Sr(C_7H_5O_4)_2(C_{12}H_8N_2)_2(H_2O)_2]\cdot 2C_{12}H_8N_2\cdot 4H_2O$, consists of an Sr^{II} complex, uncoordinated phenanthroline (phen) molecules and solvent water molecules. The Sr^{II} ion is located on a twofold axis and is coordinated by two phen ligands, two dihydroxybenzoate anions and two water molecules in a distorted tetragonal antiprismatic geometry. Partially overlapped arrangements exist between parallel coordinated and parallel uncoordinated phen rings; the face-to-face separations between the former (coordinated) and the latter (uncoordinated) rings are 3.436 (13) and 3.550 (14) Å, respectively. This difference suggests the effect of metal coordination on π–π stacking between phen rings.

Comment

As π–π stacking between aromatic rings plays an important role in electron-transfer processes in some biological systems (Deisenhofer & Michel, 1989), the nature of π–π stacking has attracted our attention in recent years. In a structure with typical π–π stacking, the face-to-face separation between parallel aromatic rings is much shorter than the van der Waals thickness of the aromatic ring. In order to understand the nature of π–π stacking, we have attempted to investigate the factors that prompt shorter separations of adjacent aromatic rings. A series of metal complexes incorporating aromatic ligands such as phenanthroline (Nie *et al.*, 2001), benzimidazole (Chen *et al.*, 2003), bipyridine (Xu *et al.*, 1996), diaminobithiazole (Luo *et al.*, 2004) and substituted benzoate (Cheng *et al.*, 2000) have been prepared in our laboratory, and their crystal structures have been determined. As part of our ongoing investigations into the nature of π–π stacking, the title compound, (I), including both coordinated and uncoordinated phenanthroline (phen), has been prepared. We present here its crystal structure in order to show the effect of metal coordination on π–π stacking between phen rings.

The crystal structure of (I) consists of an Sr^{II} complex, an uncoordinated phen molecule and solvent water molecules. The Sr^{II} ion is located on a crystallographic twofold axis. Two phen ligands chelate a single Sr^{II} ion, while two dihydroxybenzoate (dhba) anions and two water molecules complete the distorted SrN_4O_4 tetragonal antiprismatic coordination geometry (Fig. 1). The Sr—N and Sr—O bond distances (Table 1) are comparable to those found in related structures (Cambridge Structural Database, update of November 2006; Allen, 2002).

(I)
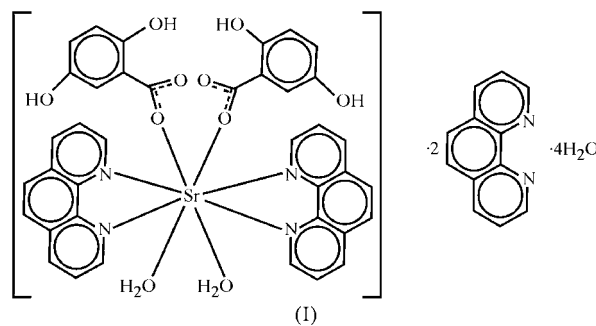
A partially overlapped arrangement of parallel phen rings is observed between coordinated and between uncoordinated phen rings (Fig. 2); this fact allowed us to study the effect of metal coordination on aromatic stacking. The face-to-face separation between parallel uncoordinated N3-phen and N3ii-phen rings is 3.550 (14) Å [symmetry code: (ii) $-x + \frac{3}{2}$, $-y + \frac{3}{2}$, $-z + 1$], which is close to the van der Waals thickness of an aromatic ring and reveals a rather weak π–π stacking, whereas the face-to-face separation between the parallel coordinated
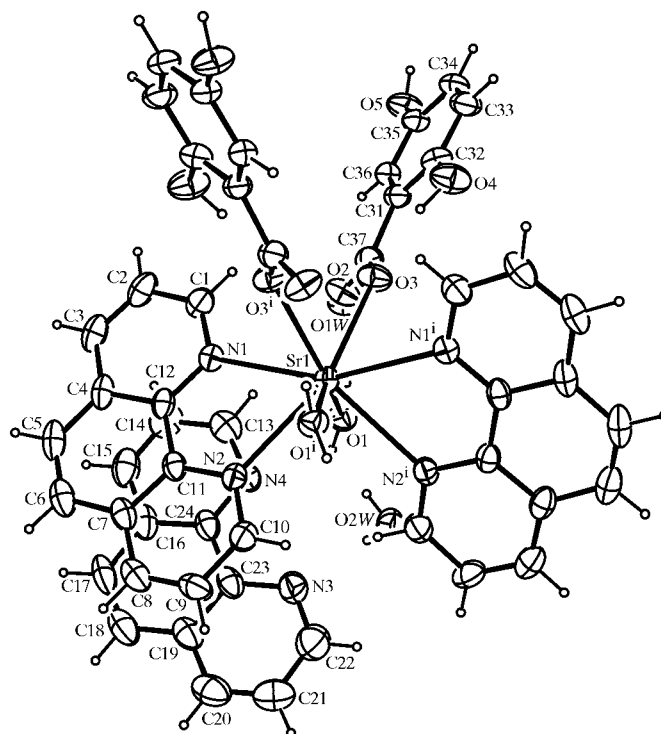

Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). [Symmetry code: (i) $-x + 1$, y, $-z + \frac{1}{2}$.]

N1-phen and N1^{iii}-phen rings [symmetry code: (iii) $-x + 1$, $-y + 1$, $-z + 1$] is 3.436 (13) Å, suggesting a stronger π–π stacking interaction.

Furthermore, the coordinated N1-phen ring is nearly parallel to the uncoordinated N3-phen ring, with a small dihedral angle of 7.03 (7)°. These two phen rings also partially overlap one another (Fig. 3). A *PLATON* calculation (Spek, 2003) shows the two different perpendicular distances from the centre-of-gravity of one benzene ring to the other benzene ring plane to be 3.519 and 3.489 Å. The mean value of 3.504 (15) Å is taken to represent the average face-to-face separation between nearly parallel uncoordinated and coordinated phen rings. It is perceivably shorter than the distance of 3.550 (14) Å between uncoordinated phen rings but longer than the distance of 3.436 (13) Å between coordinated phen rings.
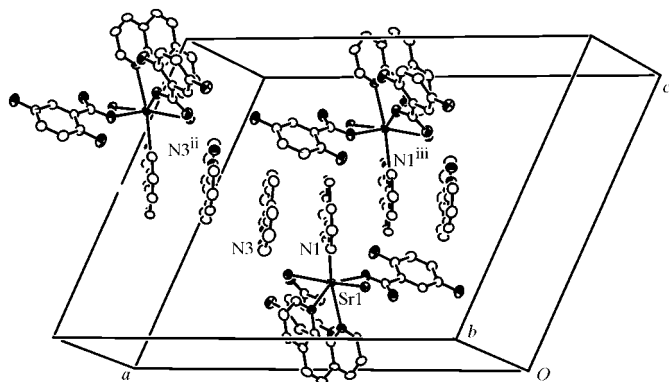

Figure 2
The packing of (I), showing the π–π stacking between phen rings. H atoms and solvent water molecules have been omitted for clarity. [Symmetry codes: (ii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$.]
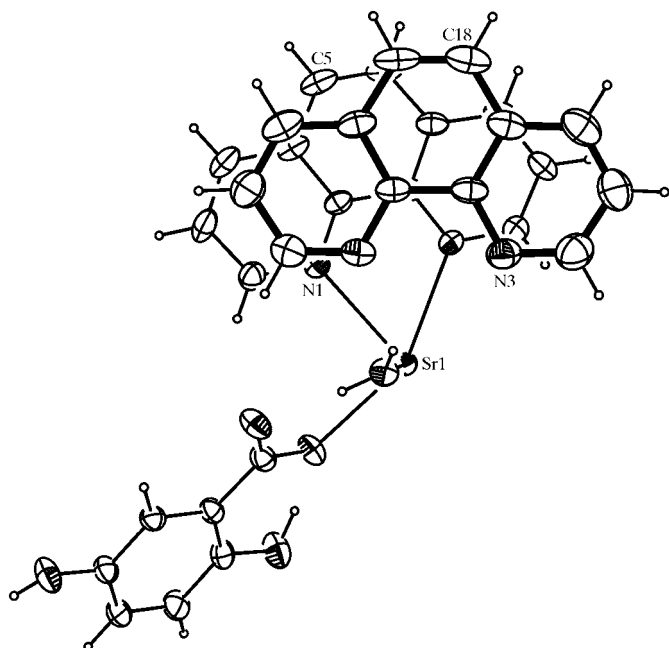

Figure 3
The partially overlapped arrangement between nearly parallel N1-phen and N3-phen rings.

A similar phenomenon was observed in the crystal structure of an Mn^{II} complex with the benzimidazole (bzim) ligand, which was determined by our group previously (Chen *et al.*, 2003). The face-to-face separation between parallel uncoordinated bzim rings is 3.60 (6) Å, but the separation between parallel coordinated bzim rings is 3.40 (4) Å.

These findings show the difference in face-to-face separations between coordinated aromatic rings and between uncoordinated aromatic rings, and suggest the effect of metal coordination on π–π stacking between aromatic rings, *i.e.* coordination to a metal cation may result in a shorter face-to-face separation and a stronger π–π stacking between aromatic rings.

Extensive hydrogen bonding occurs in the crystal structure of (I) (Table 2).

Experimental

Strontium nitrate (1 mmol), 2,5-dihydroxybenzoic acid (1 mmol), phen (1 mmol) and sodium carbonate (0.5 mmol) were dissolved in a water–ethanol mixture (15 ml, 2:1). The solution was refluxed for 2 h. After cooling to room temperature, the solution was filtered. Single crystals of (I) were obtained from the filtrate after 5 d.

Crystal data

[Sr(C7H5O4)2(C12H8N2)2(H2O)2]·· 2C12H8N2·4H2O	$\beta = 112.526$ (12)°
$M_r = 1222.75$	$V = 5771.5$ (8) Å^3
Monoclinic, $C2/c$	$Z = 4$
$a = 24.7846$ (16) Å	Mo $K\alpha$ radiation
$b = 13.2694$ (8) Å	$\mu = 1.01$ mm^{-1}
$c = 18.9986$ (13) Å	$T = 294$ (2) K
	$0.40 \times 0.24 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer	22817 measured reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	5189 independent reflections
	3468 reflections with $I > 2\sigma(I)$
$T_{min} = 0.645$, $T_{max} = 0.810$	$R_{int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	385 parameters
$wR(F^2) = 0.137$	H-atom parameters constrained
$S = 1.17$	$\Delta\rho_{max} = 0.92$ e Å^{-3}
5189 reflections	$\Delta\rho_{min} = -1.19$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Sr1—O1	2.582 (3)	Sr1—N1	2.731 (3)
Sr1—O3	2.563 (3)	Sr1—N2	2.710 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$N4	0.95	2.20	2.959 (5)	136
O1—H1$B\cdots$O2	0.91	1.94	2.759 (4)	150
O4—H4$A\cdots$O3	0.89	1.83	2.589 (4)	141
O5—H5$A\cdots$O1W^{iv}	0.82	1.79	2.589 (4)	163
O1W—H1$C\cdots$O2W^{iv}	0.91	1.87	2.729 (4)	155
O1W—H1$D\cdots$O2	0.89	1.94	2.699 (5)	143
O2W—H2$C\cdots$N3	0.90	2.09	2.950 (6)	160
O2W—H2$D\cdots$O5^{v}	0.88	2.31	2.961 (4)	131

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

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H atoms of hydroxy groups and water molecules were located in a difference Fourier map and refined as riding in their as-found relative positions $[U_{iso}(H) = 1.5U_{eq}(O)]$. Other H atoms were placed in calculated positions, with C—H distances of 0.93 Å, and refined in riding mode, with $U_{iso}(H)$ values of $1.2U_{eq}(C)$. The deepest hole is 0.001 Å from the Sr1 atom.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3052). Services for accessing these data are described at the back of the journal.

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