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Intramolecular π–π stacking in diaquabis(2-hydroxybenzoato-κO)bis(1,10-phenanthroline-κ²N,N′)strontium(II)

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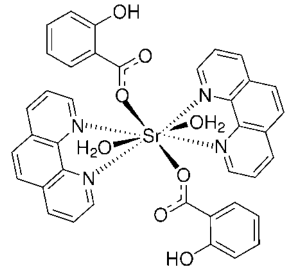
In the title compound, $[Sr(C_7H_5O_3)_2(C_{12}H_8N_2)_2(H_2O)_2]$, the Sr^{II} ion is located on a twofold rotation axis and assumes a distorted square-antiprism SrN_4O_4 coordination geometry, formed by two phenanthroline (phen) ligands, two 2-hydroxybenzoate anions and two water molecules. Within the mononuclear complex molecule, intramolecular *π–π* stacking is observed between nearly parallel coordinated phen ligands, while normal intermolecular *π–π* stacking occurs between parallel phen ligands of adjacent complex molecules. Classic O—H⋯O and weak C—H⋯O hydrogen bonding helps to stabilize the crystal structure.

Comment

As *π–π* stacking between aromatic rings plays an important role in electron-transfer processes in some biological systems (Deisenhofer & Michel, 1989), it has attracted our attention in recent years. Because *π–π* stacking is usually observed between adjacent molecules, it is considered as a type of intermolecular interaction. In order to understand the nature of *π–π* stacking, a series of metal complexes incorporating aromatic ligands such as phenanthroline (phen) (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) has been prepared and their crystal structures determined in our laboratory. As part of our ongoing investigation into the nature of *π–π* stacking, the title Sr^{II} complex, (I), has recently been prepared and its X-ray crystal structure, which shows unusual intramolecular *π–π* stacking, is presented here.

The molecular structure of (I) is shown in Fig. 1. The Sr^{II} ion is located on a twofold rotation axis and coordinated by two phen ligands, two 2-hydroxybenzoate anions and two water molecules in a distorted square-antiprism coordination geometry. Coordinated bond distances and angles are listed in Table 1. In order to compare the coordination geometry, a search of the Cambridge Structure Database (Version 5.28, updated in November 2006; Allen, 2002) was performed. Table 2 summarizes the Sr—N bond distances in (I) and the maximum and minimum Sr—N bond distances in the Sr^{II} complexes with a phen ligand reported previously. The atomic deviations of the Sr^{II} ion from the chelating phen ligands are also listed in Table 2 in order to compare coplanarities. These values show that in all these Sr^{II} complexes the Sr^{II} ion is nearly coplanar with the phen mean plane. In (I), however, the Sr^{II} ion deviates from the phen mean planes by 1.374 (3) Å, the chelating phen ligand tilting with respect to the Sr1/N1/N2 plane by a larger dihedral angle of 33.49 (7)°. This clearly indicates the poor overlap between the atomic orbitals of the Sr^{II} ion and phen N atoms in the structure. However, the average Sr—N bond of 2.795 (3) Å is similar to the values found in related Sr^{II} complexes (Table 2). These facts suggest a more electrostatic nature of the Sr—N bonds in (I).



(I)

The two phen ligands, which are related by the twofold rotation axis, are nearly parallel to each other, the dihedral angle being 10.47 (2)°. The partially overlapped arrangement

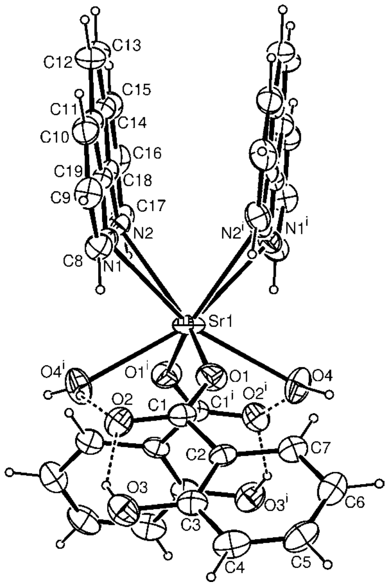


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. One disordered water H atom has been omitted for clarity and the remaining H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.]

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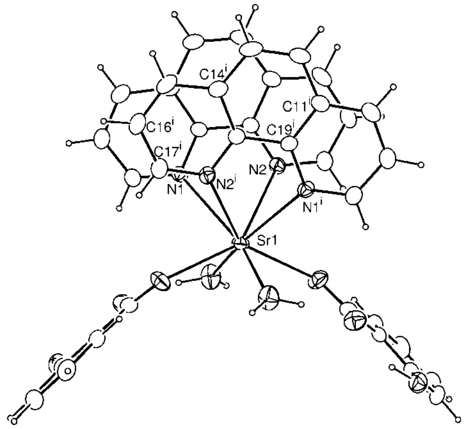

Figure 2
A diagram showing the intramolecular π–π stacking in (I) between N1-phen and N1^{i}-phen. [Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.]

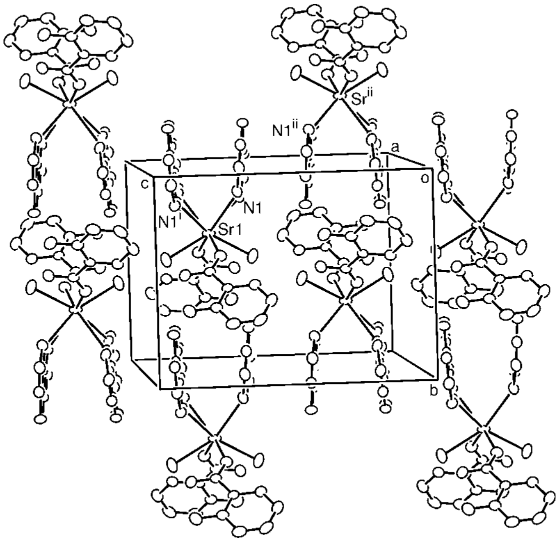

Figure 3
A unit-cell packing diagram for (I), showing both intra- and intermolecular π–π stacking. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $1 - x, -y, 1 - z$.]

between these two nearly parallel phen ligands is shown in Fig. 2. Atoms C11^{i}, C14^{i}, C16^{i}, C17^{i} and C19^{i} of the N1^{i}-containing phen ligand [symmetry code: (i) $1 - x, y, \frac{3}{2} - z$] are displaced from the N1-phen mean plane by 3.470 (4), 3.537 (4), 3.413 (5), 3.139 (5) and 3.250 (4) Å, respectively, with an average value of 3.362 (5) Å, appreciably shorter than the van der Waals thickness of an aromatic ring (3.70 Å; Cotton & Wilkinson, 1972). A *PLATON* calculation (Spek, 2003) shows a short $Cg\cdots Cg$ separation of 3.511 (2) Å between the two phen ligands, involving the N1-pyridine and the C12^{i}-benzene rings. These facts suggest the existence of intramolecular π–π stacking between the coordinated phen ligands within the mononuclear complex. As expected, intermolecular π–π stacking is also observed between parallel phen ligands of adjacent molecules of the complex (Fig. 3). The face-to-face separation between parallel N1-phen and N1^{ii}-phen is 3.422 (8) Å [symmetry code: (ii) $1 - x, -y, 1 - z$].

This structure determination reveals that π–π stacking interactions can be not only intermolecular but also intramolecular in nature, somehow correlating to their hydrogen-bonding counterparts. Classic O—H$\cdots$O and weak C—H$\cdots$O hydrogen bonds also occur in the crystal structure of (I) (Table 3). Intramolecular O—H$\cdots$O hydrogen bonds form internal loops (Fig. 1). Intermolecular O—H$\cdots$O and weak C—H$\cdots$O hydrogen bonding, in turn, helps to stabilize the crystal structure.

Experimental

A water–ethanol solution (20 ml, 1:1 *v*/*v*) containing $SrCO_3$ (0.15 g, 1 mmol), 2-hydroxybenzoic acid (0.27 g, 2 mmol) and Na_2CO_3 (0.05 g, 0.5 mmol) was refluxed for 0.5 h. Phen (0.20 g, 1 mmol) was added to the solution and the mixture was refluxed for a further 4 h. After cooling to room temperature, the solution was filtered and the filtrate was kept at room temperature. Single crystals of (I) were obtained from the filtrate after 3 d.

Crystal data

$[Sr(C_7H_5O_3)_2(C_{12}H_8N_2)_2(H_2O)_2]$
$M_r = 758.28$
Orthorhombic, *Pbcn*
$a = 23.411$ (4) Å
$b = 10.409$ (2) Å
$c = 13.722$ (3) Å
$V = 3343.8$ (11) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.67$ mm^{-1}
$T = 295$ (3) K
0.35 × 0.29 × 0.27 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.548$, $T_{max} = 0.640$
25451 measured reflections
3111 independent reflections
2383 reflections with $I > 2\sigma(I)$
$R_{int} = 0.083$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.113$
$S = 1.18$
3111 reflections
231 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Water and hydroxy H atoms were located in a difference Fourier map and were refined as riding in their as-found relative positions, with $U_{iso}(H) = 1.5U_{eq}(O)$. Water atom H4*B* is disordered over two sites (H4*B*1 and H4*B*2) and their occupancies were set at 0.5. Aromatic H atoms were placed in calculated positions, with C—H = 0.93 Å, and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$.

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 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 1
Selected bond lengths (Å).

Sr1—O1	2.505 (3)	Sr1—N1	2.872 (3)
Sr1—O4	2.618 (3)	Sr1—N2	2.718 (3)

Table 2
Comparison of the Sr—N bond distances (Å) and the atomic deviation(s) (Å) of Sr1 from the phen plane(s) in (I) and in analogous complexes.

Complex	$Sr—N_{min}$	$Sr—N_{max}$	$Sr—phen_{min}$	$Sr—phen_{max}$
(I)	2.718 (3)	2.872 (3)	1.374 (3)	
(II)	2.775	2.808	0.062	
(III)	2.766 (7)	2.772 (6)	0.003	
(IV)	2.709 (14)	2.825 (17)	0.442 (3)	0.519 (3)
(V)	2.573 (3)	2.810 (4)	0.111 (1)	0.456 (1)
(VI)	2.680 (9)	2.847 (9)	0.184 (1)	0.244 (1)
(VII)	2.613 (3)	2.714 (3)	0.007 (1)	0.396 (1)
(VIII)	2.710 (3)	2.731 (3)	0.224 (1)	

Notes: (II) tetraaquabis(1,10-phenanthroline)strontium(II) diperchlorate bis(1,10-phenanthroline) (no s.u. values are available; Smith *et al.*, 1977); (III) tetraaquabis(1,10-phenanthroline)strontium(II) diiodide bis(1,10-phenanthroline) (Kepert *et al.*, 1996); (IV) bis(dipivaloylmethanato)bis(1,10-phenanthrolinato)strontium(II) (Soboleva *et al.*, 1995); (V) *catena*-poly[[hexakis[(μ_2-cyano)aqua(1,10-phenanthroline)]diiron(III)-tristrontium(II)] 1,10-phenanthroline solvate hydrate] (Datta *et al.*, 2003); (VI) *catena*-poly[bis(μ_2-cyano)bis(dimethylformamide)tricyanonitrosylbis(1,10-phenanthroline)-iron(II)strontium(II)] (RoyChowdhury *et al.*, 2004); (VII) bis(μ_2-cyano)triaquatetracyano(nitrato-*O*,*O*′)tetrakis(1,10-phenanthroline)iron(III)distrontium(II) hydrate (Datta *et al.*, 2002); (VIII) diaquabis(2,5-dihydroxybenzoato)bis(1,10-phenanthroline)-strontium(II) bis(1,10-phenanthroline) tetrahydrate (Xu *et al.*, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3058). Services for accessing these data are described at the back of the journal.

Table 3
Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O3—H3$\cdots$O2	0.97	1.63	2.492 (4)	145
O4—H4*A*$\cdots$O2^{i}	0.92	1.85	2.715 (4)	157
O4—H4*B*1$\cdots$O4^{ii}	0.81	2.10	2.853 (4)	156
C9—H9$\cdots$O3^{iii}	0.93	2.52	3.368 (5)	152
C10—H10$\cdots$O3^{iv}	0.93	2.55	3.389 (5)	150

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

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