metal-organic papers

Bis[2-(benz(othia/oxa)zol-2-yl)phenolato-$\kappa^2 N,O$]-beryllium(II)

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In the crystal structure of the title compound, [Be(C$_{13}$H$_8$NO$_{1.265}$S$_{0.735}$)$_2$], the ring S atom in both benz(othia/oxa)zol-2-ylphenolate anions is disordered with respect to the O atom. The anions chelate to the Be atom in a tetragonal geometry; the neutral molecules are attracted to one another by intermolecular π–π stacking interactions, forming extended three-dimensional arrays.

Comment

Beryllium(II) complexes, being monomeric with tetrahedral geometries, have shown excellent electroluminescent properties (Li *et al.*, 2000; Hamada *et al.*, 1997). Some of them also have excellent electronic transfer properties (Hamada *et al.*, 1993). Beryllium(II) organometallic complexes have therefore been used both as emitters and as electron-transfer materials in organic diodes. For example, bis(10-hydroxybenzo[*h*]-quinolinato)beryllium performs better than Alq$_3$ (Hq = 8-hydroxyquinoline) when used as an electron-transfer material (Hamada *et al.*, 1993).
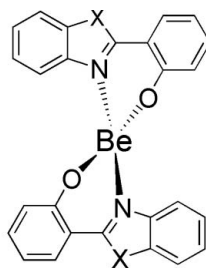
X = 0.265O + 0.735S

(I)

Beryllium(II) complexes with *N,O*-donor organic ligands, *viz.* 2-(2-hydroxyphenyl)benzoxazole and 2-(2-hydroxyphen-yl)benzothiazole, have been studied very recently in our group (Tong *et al.*, 2005). As expected, they have shown excellent photoluminescence, and are potential candidates for electroluminescent emitters. In order to relate their light-emitting nature and their molecular geometry, density functional theory (DFT) and time-dependent density functional theory (TDDFT) have been employed to calculate their geometrical and electronic structures. Their excellent light-emitting properties may be due in part to the planar configuration of deprotonated ligands upon ligation to Be^{II} ions. Moreover, such ligand planarity favors the formation of π–π stacking interactions, which, in turn, can help enhance their electron-transfer properties in organic diodes (Qiao *et al.*, 2004; Yu *et al.*, 2003; Sapochak *et al.*, 2002).
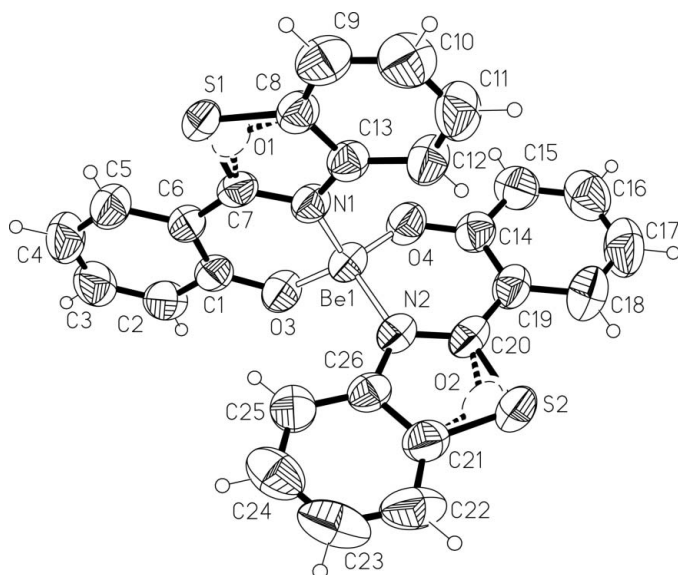
Figure 1
Molecular structure (*SHELXTL*; Sheldrick, 2000) of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. Minor-component O atoms are shown as broken ellipses.
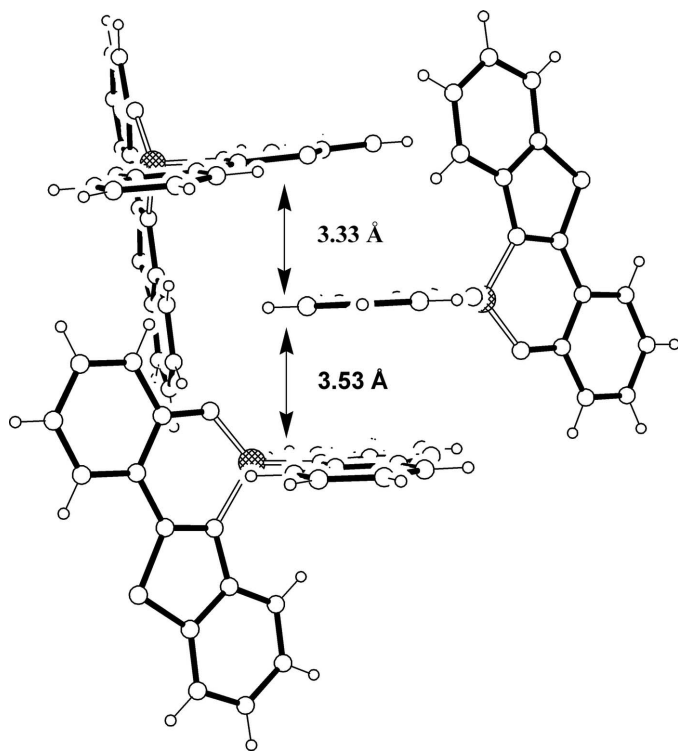

Figure 2
A perspective view of the intermolecular π–π stacking interactions.

In order to obtain other luminescent organic complex materials with different emitting wavelengths or improved light-emitting properties, we have synthesized mixed-ligand metal complexes with *N*,*O*-donor ligands; for example, the co-crystal mixed-ligand zinc(II) complex with 2-(2-hydroxy-phenyl)benzoxazole and 2-(2-hydroxyphenyl)benzothiazole
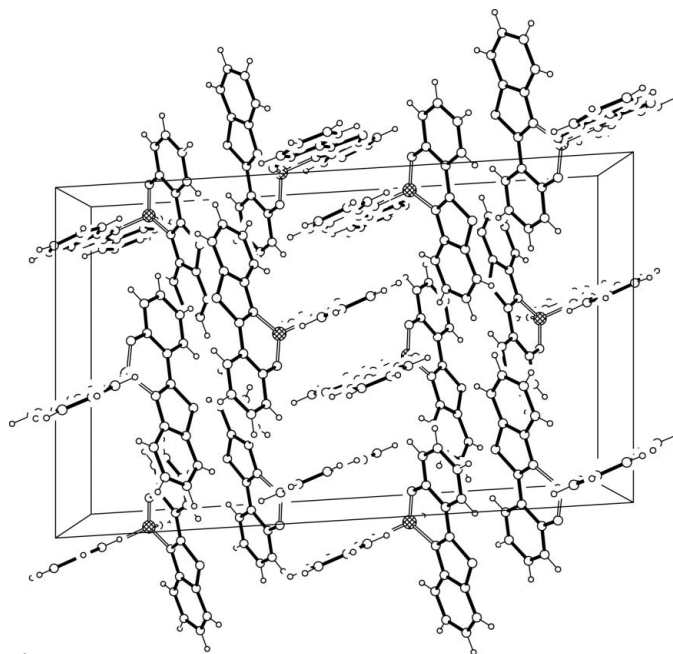

Figure 3
A perspective view of the crystal-stacking pattern along the crystallographic *b* axis.

has been reported (Tong *et al.*, 2004). It is also excellent with respect to photoluminescence. We report here another mixed-ligand complex of beryllium(II) with 2-(2-hydroxyphenyl)-benzoxazole and 2-(2-hydroxyphenyl)benzothiazole, the title compound, (I).

In the crystal structure of (I) (Fig. 1), two deprotonated ligands coordinate to the central Be^{II} ions, which is surrounded by an N_2O_2 environment. The S and O hetero-atoms in the ligand anion are statistically disordered. The refinement generates a formula of *ca* 0.735:0.265 ratio of S to O in each anion so that the compound can be regarded as a co-crystal, $[(C_{13}H_8NO_2)_2Be]_{0.265}[(C_{13}H_8NOS)_2Be]_{0.735}$, (I). The bond dimensions [1.744 (3)/1.748 (3) Å for Be—N and 1.564 (3)/1.573 (3) Å for Be—O] around the central Be^{II} atom are similar to those found in $[(C_{13}H_8NO_2)_2Be]$ and $[(C_{13}H_8NOS)_2Be]$ (Tong *et al.*, 2005). The dihedral angles between the phenolate and benz(othia/oxa)zole rings are *ca* 0.8 and 1.6°, indicating that they are essentially coplanar, as was found in $[(C_{13}H_8NO_2)_2Be]$ and $[(C_{13}H_8NOS)_2Be]$ (Tong *et al.*, 2005). There are strong intermolecular π–π stacking interactions in an antiparallel arrangement between adjacent molecules with interplanar distances of 3.53 and 3.33 Å (Fig. 2). Such interactions connect adjacent molecules, forming three-dimensional arrays (Fig. 3). Compound (I) exhibits excellent photoluminescence, which is probably due to the coplanarity of the phenolate and benz(othia/oxa)zole rings.

Experimental

The title compound, (I), was synthesized by a solvothermal method. A mixture of beryllium sulfate tetrahydrate (0.142 g, 0.8 mmol), 2-(2-hydroxyphenyl)benzoxazole (0.169 g, 0.8 mmol), 2-(2-hydroxyphenyl)benzothiazole (0.182 g, 0.8 mmol), potassium hydroxide (0.045 g,

0.8 mmol) and ethanol (13 ml) was stirred for 2 h at ambient temperature, and then transferred to a 23 ml Teflon-lined stainless steel container; the mixture was heated and reacted under autogenous pressure at 383 K for 7 d. After cooling to ambient temperature at a rate of 5 K h^{-1}, yellow crystals were obtained in a yield of *ca* 70%. Analysis found: C 68.65, H 3.57, N 6.25%; calculated for $C_{26}H_{16}BeN_2O_{2.53}S_{1.47}$: C 68.93, H 3.56, N 6.18%. Measurements performed on several specimens all gave the same structure, *i.e.* the co-crystal; neither bis[2-(benzoxazol-2-yl)phenolato]beryllium(II) nor bis[2-(benzthiazol-2-yl)phenolato]beryllium(II) could be found among the crystals.

Crystal data

$[Be(C_{13}H_8NO_{1.265}S_{0.735})_2]$
$M_r = 452.99$
Monoclinic, $C2/c$
$a = 24.3956 (16)$ Å
$b = 12.0400 (8)$ Å
$c = 14.7848 (10)$ Å
$\beta = 93.529 (1)°$
$V = 4334.4 (5)$ Å^3
$Z = 8$

$D_x = 1.388$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4822 reflections
$\theta = 2.4–26.8°$
$\mu = 0.22$ mm^{-1}
$T = 293 (2)$ K
Block, yellow
$0.34 \times 0.27 \times 0.13$ mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.928$, $T_{max} = 0.971$
12955 measured reflections

4712 independent reflections
3742 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.0°$
$h = -31 \rightarrow 23$
$k = -15 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.04$
4712 reflections
305 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 2.6031P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

In the ligand anions, the S heteroatom is disordered with respect to an O heteroatom, while the C atoms connected to them are not disordered. The S—C and corresponding O—C distances involving the disordered atoms were restrained to values of 1.74 and 1.38 Å, respectively, with corresponding deviations of 0.001 and 0.005 Å. These values are comparable to those found in bis[2-(benzthiazol-2-yl)phenolato]beryllium(II) (Tong *et al.*, 2005) and the parent 2-(2-hydroxyphenyl)benzothiazole (Aydin *et al.*, 1999; Stenson, 1970), and in, for example, 5-chloro-2-(4-*tert*-butylphenyl)benzoxazole (Mrozek *et al.*, 1999). The displacement parameters of the disordered atoms in each group were restrained to be equal to each other; additionally, the displacement parameters were restrained to be approximately isotropic. As the occupancy factor for both O atoms refined to 0.265, the occupancy factor for both S atoms were then assumed to be 0.735, *i.e.* $X = 0.265O + 0.735S$. The formula from the refinement is consistent with that from the elemental analysis.

The H atoms were placed at calculated positions and refined using a riding-model approximation (C—H = 0.93 Å for all aromatic ring H atoms), with their displacement parameters tied to those of the parent atoms; $U_{iso}(H) = 1.2U_{eq}(C)$ for all aromatic ring H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXL97*.

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