

A host-guest complex of diaquabis-[1-hydroxy-2(1*H*)-pyridinethionato-*O,S*]magnesium(II) and 2,2'-dithio-bis(pyridine *N*-oxide)

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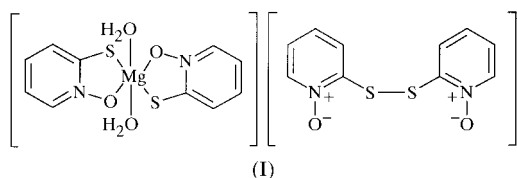
Received 12 August 1999

Accepted 22 October 1999

The title compound, $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2] \cdot \text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S}_2$, is a two-component host-guest material. The 2,2'-dithiobis(pyridine *N*-oxide) molecule has crystallographic twofold symmetry. The metal complex lies on an inversion centre and associates *via* C—H...S interactions into chains which thread the 2,2'-dithiobis(pyridine *N*-oxide) lattice in perpendicular directions. Hydrogen bonds exist between the water molecules of the diaquamagnesium units and the N—O groups of the host lattice.

Comment

1-Hydroxypyridine-2(1*H*)-thione, pyriothione, has been widely studied as a result of its fungicidal properties (Albert *et al.*, 1956; Chandler & Segel, 1978; Bond & Jones, 1999). Pyriothione is readily oxidized to the disulfide, *i.e.* 2,2'-dithiobis(pyridine *N*-oxide) (DTPO), which also displays fungicidal activity (Paulus, 1993). The crystal structure of DTPO consists of a three-dimensional C—H...O-bonded lattice composed of two interpenetrated homochiral networks (Bodige *et al.*, 1997). The DTPO lattice has been shown to be suitable for guest inclusion by the formation of the host-guest complexes $[\text{TCNB}][\text{DTPO}]_2(\text{H}_2\text{O})_4$ and $[\text{PMDA}][\text{DTPO}]_2$, where TCNB and PMDA represent 1,2,4,5-tetracyanobenzene and pyromellitic dianhydride, respectively (Bodige *et al.*, 1997). The title compound, $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2] \cdot \text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S}_2$, (I), is a host-guest material in which a diaquamagnesium complex of pyriothione is incorporated into a DTPO lattice.

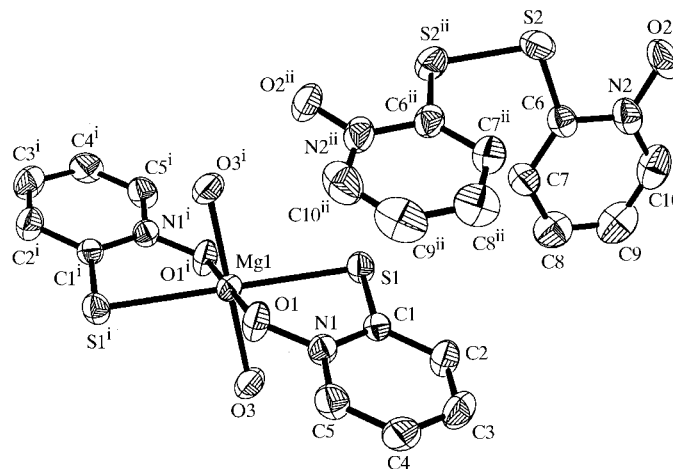


The Mg atom of the $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2]$ unit occupies a centre of symmetry and adopts distorted octahedral coordination

via two bidentate pyriothione ligands and two water molecules (Fig. 1). The pyriothione ligands are tilted with respect to the equatorial plane defined by O1, S1, O1ⁱ and S1ⁱ [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$], forming an angle of 27.5 (1)°. The DTPO molecule is chiral as a result of the fixed C6—S2—S2ⁱⁱ—C6ⁱⁱ torsion angle [symmetry code: (ii) $-x, y, \frac{1}{2} - z$]; both enantiomers are present in the crystal. The magnitude of this torsion angle, 80.3 (1)°, is considerably less than the value of 90.2 (2)° observed in DTPO itself, showing the DTPO lattice to be distorted significantly on incorporation of the $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2]$ guest.

The $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2]$ units in (I) are linked *via* C—H...S interactions [C4...S1ⁱⁱⁱ 3.565 (2) Å and C4—H4...S1ⁱⁱⁱ 147.6°; symmetry code: (iii) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$] into chains running parallel to [110] and $[\bar{1}10]$. The C—H...O network observed in DTPO is disrupted by guest insertion and the dominant interactions in (I) are hydrogen bonds between the water molecules of the diaquamagnesium units and the N—O groups of the DTPO lattice [H100...O2^{iv} 1.91 (2) Å and O3—H100...O2^{iv} 174 (2)°; H101...O2^v 2.02 (2) Å and O3—H101...O2^v 160 (2)°; symmetry codes: (iv) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (v) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$] (Fig. 2).

The structure of (I) may be related to that of $[\text{PMDA}][\text{DTPO}]_2$ in which PMDA molecules associate *via* C—H...O interactions to yield chains similar to the $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2]_n$ chains in (I). These thread the DTPO lattice in one direction giving rise to a solid-state polypseudorotaxane structure. The planar nature of the PMDA chains allows for face-to-face aromatic interactions between the PMDA molecules and the DTPO lattice. In (I), however, the diaquamagnesium unit introduces water molecules above and below the plane of the $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2]_n$ chains, facilitating additional hydrogen-bond interactions with the DTPO lattice and giving rise to the new three-dimensional architecture.


Figure 1

The molecular units in (I) showing displacement ellipsoids at 50% probability [symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (ii) $-x, y, \frac{1}{2} - z$]. H atoms have been omitted.

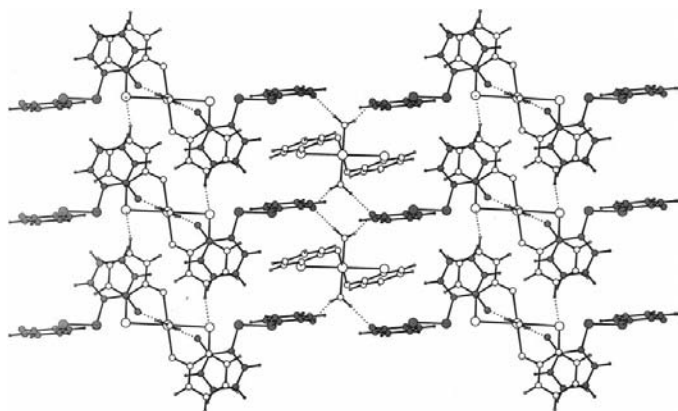


Figure 2

View of (I) parallel to [110] with the DTPO lattice shaded grey. $[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2]_n$ chains run vertically and normal to the plane of the page. $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{S}$ interactions are indicated by dotted lines.

Experimental

$\text{C}_5\text{H}_5\text{NOS}$ and $\text{Mg}(\text{OAc})_2$ were dissolved in an $\text{EtOH}/\text{H}_2\text{O}$ mixture with stirring. The solvent was removed by evaporation and the resulting powder was recrystallized from EtOH to yield single crystals of (I).

Crystal data

$[\text{Mg}(\text{C}_5\text{H}_4\text{NOS})_2(\text{H}_2\text{O})_2]_n$
 $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S}_2$
 $M_r = 564.95$
 Monoclinic, $C2/c$
 $a = 8.101(2) \text{ \AA}$
 $b = 13.564(3) \text{ \AA}$
 $c = 21.573(4) \text{ \AA}$
 $\beta = 91.13(3)^\circ$
 $V = 2370.1(8) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.583 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.5\text{--}15.0^\circ$
 $\mu = 0.474 \text{ mm}^{-1}$
 $T = 296(2) \text{ K}$
 Block, colourless
 $0.6 \times 0.3 \times 0.3 \text{ mm}$

Data collection

Rigaku AFC-7R four-circle diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.840$, $T_{\max} = 0.867$
 2910 measured reflections
 2721 independent reflections
 2179 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 17$
 $l = -28 \rightarrow 28$
 3 standard reflections every 200 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.096$
 $S = 1.016$
 2721 reflections
 166 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 1.5439P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.017$$

$$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$$

The water H atoms, H100 and H101, were located in a difference Fourier map and refined with a fixed isotropic displacement parameter of 0.05 \AA^2 and a restrained O—H distance of $0.82(2) \text{ \AA}$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1998); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994) and *CAMERON* (Pearce *et al.*, 1993); software used to prepare material for publication: *SHELXL97*.

The authors thank the EPSRC and Avecia (formerly Zeneca Specialties) for funding and Dr Neil Feeder for assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1120). Services for accessing these data are described at the back of the journal.

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