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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.053

wR factor = 0.127

Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis[(4-nitrobenzyl)triphenylphosphinium] bis(maleonitriledithiolato)nickelate(II) dihydrate

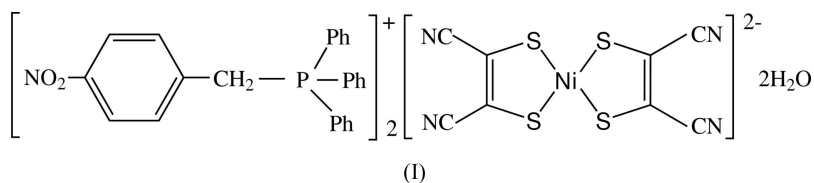
The title complex, $(\text{C}_{25}\text{H}_{21}\text{NO}_2\text{P})_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2] \cdot 2\text{H}_2\text{O}$ or $(\text{NO}_2\text{BzTPP})_2[\text{Ni}(\text{mnt})_2] \cdot 2\text{H}_2\text{O}$ [where NO_2BzTPP is (4-nitrobenzyl)triphenylphosphinium and mnt is maleonitriledithiolate], is reported. The Ni atom lies on a centre of symmetry. The square-planar Ni^{II} ion of the anion is coordinated by four S atoms of the two mnt^{2-} ligands. The benzene rings in the $[\text{NO}_2\text{BzTPP}]^+$ cation are twisted with respect to the plane of the P—C—C chain. Weak C—H...Ni interactions between the anion and cation and C—H... π , π — π and C—H...O interactions between cations are observed in the crystal structure.

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Comment

Since the ferromagnetic complex containing the $[\text{Ni}(\text{mnt})_2]^-$ anion (where mnt is maleonitriledithiolate), $[\text{NH}_4][\text{Ni}(\text{mnt})_2] \cdot \text{H}_2\text{O}$, was discovered in 1996 (Coomber *et al.*, 1996), related transition metal complexes have received attention in areas such as nonlinear optics and magnetic materials (Urichi *et al.*, 1998; Pullen *et al.*, 1998; Canadell, 1999; Robertson & Cronin, 2002; Nishijo *et al.*, 2003). A modular approach using organic cations has been employed to vary the stacking pattern of the $[\text{Ni}(\text{mnt})_2]^-$ anion, as small structural changes have been shown to result in significant changes in material properties (Robertson *et al.*, 1999; Nishijo *et al.*, 2000; Xie *et al.*, 2002; Ren *et al.*, 2002; Ni *et al.*, 2004). In order to study further the factors that determine the stacking pattern of $[\text{Ni}(\text{mnt})_2]^-$ complexes, we report here the structure of the new ion-pair title complex $[\text{NO}_2\text{BzTPP}]_2[\text{Ni}(\text{mnt})_2] \cdot 2\text{H}_2\text{O}$, (I).



The structure of (I) is shown in Fig. 1. The asymmetric unit consists of one cation, one-half of an anion with the Ni atom located on a crystallographic centre of symmetry, and one water molecule. In the $[\text{Ni}(\text{mnt})_2]^{2-}$ anion, the Ni^{II} ion is coordinated by four S atoms from two mnt ligands to give a square-planar coordination geometry. The bond lengths and bond angles are consistent with the corresponding values in $[\text{BrBzTPP}]_2[\text{Ni}(\text{mnt})_2] \cdot \text{H}_2\text{O}$ (Yang & Ni, 2006). The Ni—S bond lengths are slightly longer than in $[\text{BzTPP}][\text{Ni}(\text{mnt})_2]$ (Ni *et al.*, 2005). The CN groups of $[\text{Ni}(\text{mnt})_2]^{2-}$ are tipped slightly out of the NiS_4 plane with deviations of -0.045 (5) Å for N1 and 0.244 (5) Å for N2. In the $[\text{NO}_2\text{BzTPP}]^+$ cation, the deviations of the two O atoms from the C5—C10 benzene ring

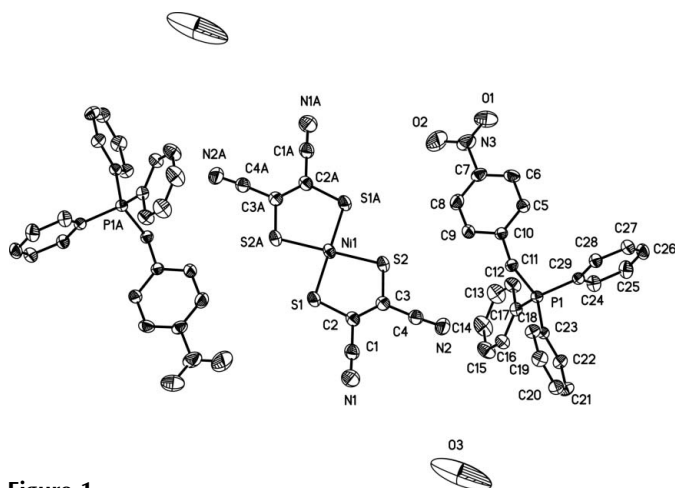


Figure 1
The structure of (I) showing 30% probability displacement ellipsoids with the atom-numbering scheme. All H atoms have been omitted for clarity. [Symmetry code: (A) $-x, 1 - y, 2 - z$.]

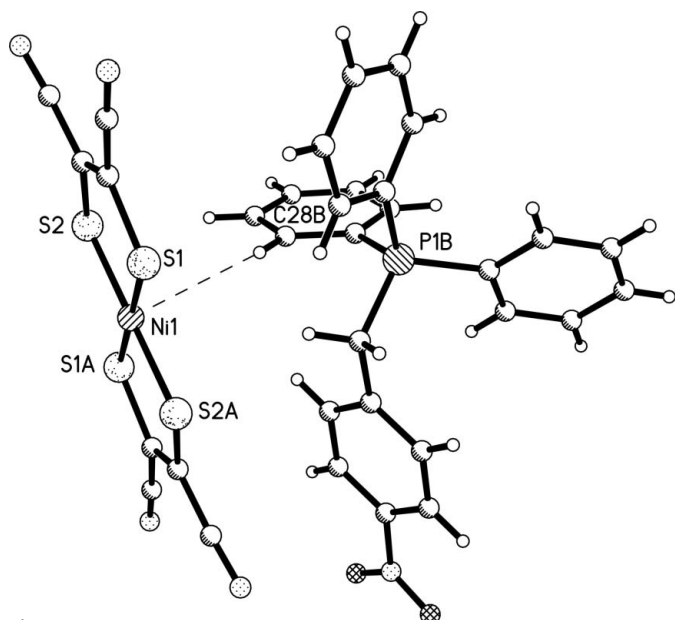


Figure 2
The C—H...Ni interaction (dashed line) between the cation and anion of (I) [Symmetry codes: (A) $-x, 1 - y, 2 - z$; (B) $-1 + x, y, z$.]

are 0.071 (6) and 0.187 (6) Å, respectively. The dihedral angles made by the four benzene rings with respect to the C10/C11/P1 reference plane are 98.6 (2)° for the C5—C10 ring, 61.4 (2)° for the C12—C17 ring, 4.5 (2)° for the C18—C23 ring and 93.3 (2)° for the C24—C29 ring.

An interesting structural feature of (I) is the presence of weak C—H...Ni hydrogen-bonding interactions between the anion and the cation (Fig. 2), with a C28...Ni1 distance of 3.760 (5) Å. Hydrogen-bonding interactions with Ni are rare (Yang & Ni, 2006), and are comparable with reported C—H...Cu interactions (Yang *et al.*, 2004; Braga *et al.*, 1997). Intermolecular cation–anion interactions are also observed (Fig. 3): C12ⁱ—H12ⁱ...O1 [symmetry code: (i) $1 - x, 2 - y, 2 - z$], with C12...O1 = 3.170 (6) Å; C20—H20... π , with a distance of 3.566 (6) Å between C20 and the centre of the

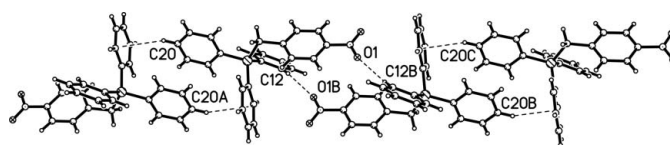


Figure 3
The weak intermolecular hydrogen bonds and π – π interactions (dashed lines) between the cations of (I). [Symmetry codes: (A) $2 - x, 1 - y, 1 - z$; (B) $1 - x, 2 - y, 2 - z$; (C) $1 - x, 2 - y, 2 - z$.]

C24—C29 ring; and a π – π interaction, with a distance of 3.513 (6) Å between neighbouring C18—C23 rings.

Experimental

1-(4-Nitrobenzyl)triphenylphosphonium bromide (NO₂BzTPPBr) was prepared by the literature method (Bulgarevich *et al.*, 1994). Disodium maleonitriledithiolate (Na₂mnt) was synthesized by a published procedure (Davison & Holm, 1967). The title compound was prepared by the direct reaction of 1:2:2 mol equivalents of NiCl₂·6H₂O (0.18 g, 0.75 mmol), Na₂mnt (0.28 g, 1.5 mmol) and (NO₂BzTPP)Br (0.72 g, 1.5 mmol) in methanol (40 ml). A red product was obtained and purified by recrystallization from a mixed solvent of methanol and water (2:1 v/v) (yield 92%). Analysis found: C 59.38, H 4.07, N 7.13%; calculated for C₅₈H₄₆N₆NiO₆P₂S₄: C 59.44, H 3.96, N 7.17%.

Crystal data

(C ₂₅ H ₂₁ NO ₂ P) ₂ [Ni(C ₄ N ₂ S ₂) ₂]·2H ₂ O	$V = 1415.7 (7) \text{ \AA}^3$
$M_r = 1171.90$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.375 \text{ Mg m}^{-3}$
$a = 10.931 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.962 (3) \text{ \AA}$	$\mu = 0.60 \text{ mm}^{-1}$
$c = 12.044 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\alpha = 82.94 (1)^\circ$	Block, red
$\beta = 82.70 (1)^\circ$	$0.45 \times 0.32 \times 0.18 \text{ mm}$
$\gamma = 84.42 (1)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	7009 measured reflections
φ and ω scans	4871 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	4220 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.801, T_{\max} = 0.897$	$R_{\text{int}} = 0.028$
	$\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 1.5P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.01$	$\Delta\rho_{\max} = 0.76 \text{ e \AA}^{-3}$
4871 reflections	$\Delta\rho_{\min} = -0.87 \text{ e \AA}^{-3}$
349 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ni1—S2	2.1580 (10)	S2—C3	1.739 (3)
Ni1—S1	2.1694 (10)	N1—C1	1.140 (5)
S1—C2	1.736 (4)	N2—C4	1.139 (5)
S2 ⁱ —Ni1—S1	88.13 (4)		

Symmetry code: (i) $-x, -y + 1, -z + 2$.

All H atoms were placed in geometrically calculated positions (C–H = 0.93–0.97 Å and O–H = 0.85 Å) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{O})$.

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

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