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## Key indicators

Single-crystal X-ray study

$T = 293$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å

Disorder in solvent or counterion

$R$  factor = 0.052

$wR$  factor = 0.149

Data-to-parameter ratio = 14.4

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

Bis[(4-bromobenzyl)triphenylphosphonium] bis(1,2-dicyanoethane-1,2-dithiolato- $\kappa^2S,S'$ )-nickel(II) monohydrate

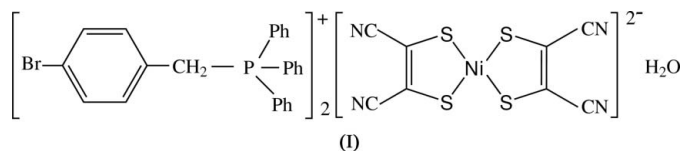
The synthesis and crystal structure of the title complex,  $(\text{C}_{25}\text{H}_{21}\text{BrP})_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2] \cdot \text{H}_2\text{O}$  or  $[\text{BrBzTPP}]_2[\text{Ni}(\text{mnt})_2] \cdot \text{H}_2\text{O}$  [where BrBzTPP is (4-bromobenzyl)triphenylphosphonium and mnt is 1,2-dicyanoethane-1,2-dithiolate or maleonitriledithiolate], is reported. The  $\text{Ni}^{\text{II}}$  ion of the  $[\text{Ni}(\text{mnt})_2]^{2-}$  anion is coordinated by four S atoms of two mnt ligands and exhibits the expected square-planar coordination geometry. The  $[\text{BrBzTPP}]^+$  cation adopts a conformation where the four benzene rings are twisted with respect to the plane of the P—C—C chain which links them. The Ni atom lies on a centre of symmetry. Weak C—H...Ni and C—H...S interactions between the anions and cations may play a role in the packing and stabilization of the crystal structure.

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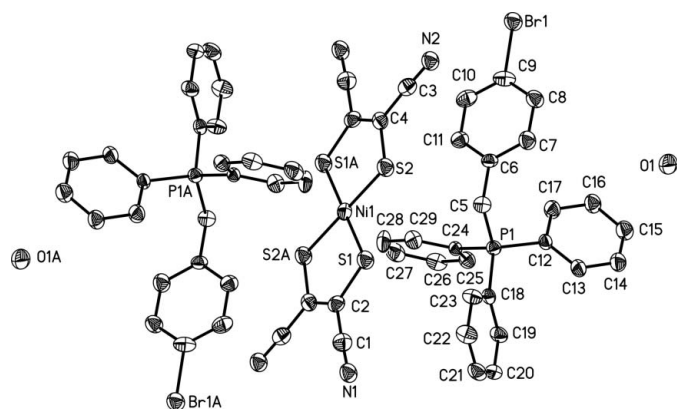
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## Comment

Recently, maleonitriledithiolate transition metal complexes have received attention in many areas, such as magnetic materials, non-linear optics and conduction (Robertson & Cronin, 2002; Urichi *et al.*, 1998; Pullen *et al.*, 1998; Nishijo *et al.*, 2003; Canadell, 1999). The discovery in 1996 of the ferromagnetic complex containing the  $[\text{Ni}(\text{mnt})_2]^{2-}$  anion,  $\text{NH}_4\text{Ni}(\text{mnt})_2 \cdot \text{H}_2\text{O}$ , strongly stimulated interest in these complexes (Coomber *et al.*, 1996). The introduction of organic cations was recognized as a powerful strategy to tune the stacking pattern of the anion in order to obtain molecular materials with unusual magnetic properties. Magnetic coupling between  $[\text{Ni}(\text{mnt})_2]^{2-}$  anions is very sensitive, both to the overlap of neighbouring  $[\text{Ni}(\text{mnt})_2]^{2-}$  anions and to intermolecular contacts. Small structural changes can result in large changes in the materials properties of these complexes, due to the subtle interplay between ferromagnetic and anti-ferromagnetic components of intermolecular interactions (Xie *et al.*, 2002; Ren *et al.*, 2002; Ni *et al.*, 2004; Nishijo *et al.*, 2000; Robertson *et al.*, 1999). With a view to examining the effects of some larger organic cations on the stacking pattern of  $[\text{Ni}(\text{mnt})_2]$  complexes, we report here the synthesis and crystal structure of the title ion-pair complex,  $[\text{BrBzTPP}]_2[\text{Ni}(\text{mnt})_2]$ , (I).



The structure of (I), with the labelling of the non-H atoms, is shown in Fig. 1. The  $\text{Ni}^{\text{II}}$  atom, lying on a centre of symmetry, exhibits the expected square-planar coordination


**Figure 1**

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

geometry. The CN groups of the  $[\text{Ni}(\text{mnt})_2]^{2-}$  anion are tipped slightly out of the plane; the deviations from the plane are  $-0.049$  (6) Å for atom N1,  $-0.168$  (6) Å for N2,  $0.047$  (6) Å for N1<sup>i</sup> and  $0.166$  (6) Å for N2<sup>i</sup> [symmetry code: (i)  $1 - x, 2 - y, 1 - z$ ]. The Ni–S bond distances are 2.167 (1) and 2.155 (1) Å, and the S–Ni–S bond angles within the five-membered rings are 91.93 (5) and 88.07 (5)°. For comparison, in the structure of  $[\text{BzTPP}][\text{Ni}(\text{mnt})_2]$  (BzTPP is benzyltriphenylphosphonium; Ni *et al.*, 2005), the Ni–S bond distances are slightly longer. The  $[\text{BrBzTPP}]^+$  cation of (I) adopts a conformation whereby the four benzene rings are twisted with respect to the C6/C5/P1 reference plane. The dihedral angles made by the four benzene rings with the C6/C5/P1 reference plane are 96.4 (2)° for the C6–C11 ring, 63.0 (2)° for the C12–C17 ring, 6.1 (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 a weak  $\text{C}29^{\text{i}} \cdots \text{H}19^{\text{i}} \cdots \text{Ni}1$  intermolecular interaction [symmetry code: (i)  $1 - x, 2 - y, 1 - z$ ], with a  $\text{C}29^{\text{i}} \cdots \text{Ni}1$  distance of 3.767 (5) Å (Fig. 2). Similar C–H  $\cdots$  M interactions have been reported in the literature for other metal complexes (Yang *et al.*, 2004; Braga *et al.*, 1997). Intermolecular C–H  $\cdots$  S interactions are also observed in the crystal structure:  $\text{C}5 \cdots \text{H}5\text{A} \cdots \text{S}2$ , with a  $\text{C}5 \cdots \text{S}2$  distance of 3.710 (5) Å, and  $\text{C}7^{\text{ii}} \cdots \text{H}7^{\text{ii}} \cdots \text{S}2$  [symmetry code: (ii)  $1 - x, 1 - y, 1 - z$ ], with a  $\text{C}5 \cdots \text{S}2$  distance of 3.710 (5) Å (Fig. 2).

## Experimental

The title compound was prepared by the direct reaction of 1:2:2 mole equivalents of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{mnt}$  and 1-(4-bromobenzyl)triphenylphosphonium bromide ( $[\text{BrBzTPP}]\text{Br}$ ) in methanol (30 ml). A red product was formed and this was purified by recrystallization from a solution in a mixture (2:1) of methanol and water (yield 86%). Block single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a methanol solution at room temperature after about two weeks. Analysis, found: C 56.89, H 3.75, N 4.38%; calculated for  $\text{C}_{58}\text{H}_{44}\text{Br}_2\text{N}_4\text{NiO}_2\text{P}_2\text{S}_4$ : C 57.02, H 3.63, N 4.59%. IR data (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3450 (s), 3059 (w), 2935 (w), 2889 (w), 2193 (s), 1637 (s), 1629 (s), 1588 (m), 1560 (m), 1523 (s), 1486 (s), 1439 (s), 1401 (m), 1340 (s),

1319 (s), 1148 (s), 1111 (s), 1073 (m), 1012 (m), 997 (m), 860 (m), 832 (m), 738 (m), 723 (m), 708 (m), 690 (m), 627 (m), 527 (s), 506 (s), 477 (m), 450 (m).

## Crystal data

$(\text{C}_{25}\text{H}_{21}\text{BrP})_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2] \cdot \text{H}_2\text{O}$   
 $M_r = 1221.68$   
 Triclinic,  $P\bar{1}$   
 $a = 10.896$  (2) Å  
 $b = 11.047$  (2) Å  
 $c = 11.753$  (2) Å  
 $\alpha = 82.25$  (1)°  
 $\beta = 84.30$  (1)°  
 $\gamma = 84.00$  (1)°  
 $V = 1388.9$  (4) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.461$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1337 reflections  
 $\theta = 2.5$ – $21.8$ °  
 $\mu = 2.04$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, red  
 $0.4 \times 0.3 \times 0.2$  mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\text{min}} = 0.49$ ,  $T_{\text{max}} = 0.66$   
 6889 measured reflections

4782 independent reflections  
 4049 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$   
 $\theta_{\text{max}} = 25.0$ °  
 $h = -12 \rightarrow 12$   
 $k = -13 \rightarrow 11$   
 $l = -13 \rightarrow 13$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.149$   
 $S = 1.02$   
 4782 reflections  
 332 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 1.95P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.51$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.39$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ni1–S2	2.1552 (12)	P1–C12	1.783 (4)
Ni1–S1	2.1672 (13)	P1–C18	1.789 (4)
N1–C1	1.131 (6)	P1–C24	1.799 (4)
N2–C3	1.140 (6)	P1–C5	1.803 (4)
S1–C2	1.720 (5)	Br1–C9	1.890 (4)
S2–C4	1.740 (5)		
S2 <sup>i</sup> –Ni1–S1	91.93 (5)	C12–P1–C24	108.30 (18)
S2–Ni1–S1	88.07 (5)	C18–P1–C24	108.17 (17)
C2–S1–Ni1	103.35 (16)	C12–P1–C5	110.8 (2)
C4–S2–Ni1	103.52 (15)	C18–P1–C5	107.89 (18)
C12–P1–C18	111.88 (18)	C24–P1–C5	109.77 (19)

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

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

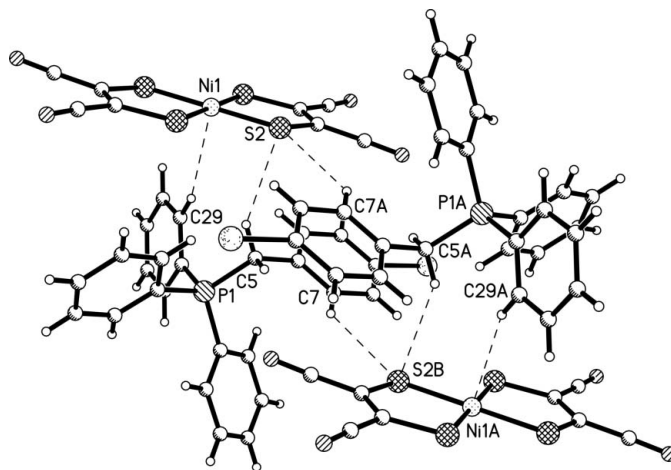
Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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**Figure 2**

The intermolecular interactions (dashed lines) between the cation and anion of (I). [Symmetry codes: (A)  $1 - x, 1 - y, 1 - z$ ; (B)  $1 - x, 2 - y, 1 - z$ .]