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Bis(benzyltriphenylphosphonium) bis(1,2-dicyanoethene-1,2-dithiolato)nickel(II)

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Key indicators

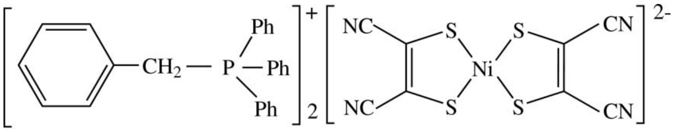
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
R factor = 0.038
wR factor = 0.107
Data-to-parameter ratio = 14.4

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

The asymmetric unit of the title compound, $(C_{25}H_{22}P)_2[Ni(C_4N_2S_2)_2]$ or $(BzTPP)_2[Ni(mnt)_2]$ (where BzTPP is 1-benzyltriphenylphosphonium and mnt is maleonitriledithiolate), consists of one $(BzTPP)^+$ cation and one-half of a centrosymmetric $[Ni(mnt)_2]^{2-}$ anion. The Ni^{II} atom of the anion is coordinated by four S atoms from two mnt^{2-} ligands and exhibits the expected square-planar coordination geometry. The $(BzTPP)^+$ cation adopts a conformation where the four phenyl rings are twisted with respect to the plane of the P—C—C chain that links them. Weak C—H···N and C—H···π interactions are present in the crystal structure.

Comment

A major reason for the interest in maleonitriledithiolate (mnt^{2-}) transition metal complexes is their potential application as magnetic materials, in non-linear optics and as conducting materials (Urichi *et al.*, 1998; Pullen *et al.*, 1998; Canadell, 1999; Robertson & Cronin, 2002; Nishijo *et al.*, 2003). Introduction of organic cations is a powerful strategy to tune the stacking pattern of the $[Ni(mnt)_2]^{2-}$ anion and thereby obtain molecular materials with unusual physical properties, because small structural changes can result in large changes in the material properties of the $[Ni(mnt)_2]^{2-}$ complexes (Robertson *et al.*, 1999; Nishijo *et al.*, 2000; Ni *et al.*, 2004). To examine the effects of larger organic cations on the stacking pattern of $[Ni(mnt)_2]^{2-}$ complexes, we prepared the title complex $(BzTPP)_2[Ni(mnt)_2]$, (I), where BzTPP is 1-benzyltriphenylphosphonium.



(I)

The asymmetric unit of (I) comprises one $(BzTPP)^+$ cation and half of a centrosymmetric $[Ni(mnt)_2]^{2-}$ anion (Fig. 1). For the $(BzTPP)^+$cation, the four phenyl rings are twisted with respect to the C10/C11/P1 reference plane, with dihedral angles of 85.5 (2)° for the C5–C10 ring, 85.3 (2)° for the C12–C17 ring, 16.9 (2)° for the C18–C23 ring and 79.6 (2)° for the C24–C29 ring. The NiS_4 core of the $[Ni(mnt)_2]^{2-}$ anion exists in a slightly distorted square-planar geometry in which Ni^{II} is coordinated by four S atoms from two mnt ligands. The Ni—S bond distances are slightly longer than those found in $(BzTPP)[Ni(mnt)_2]$ (Ni *et al.*, 2005).

The geometries of the anion and the cation of (I) are essentially identical to those of the Ni^{III} complex,

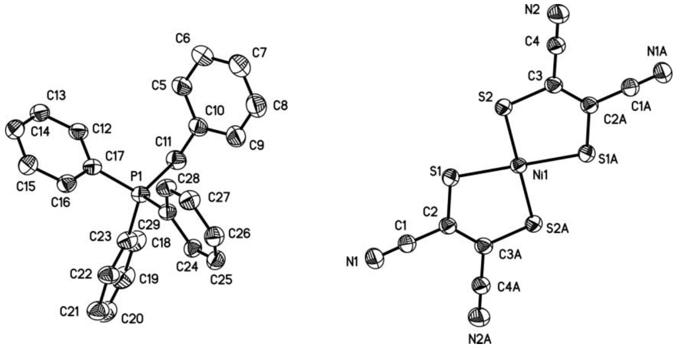


Figure 1
The structure of the ions of (I) showing 30% probability displacement ellipsoids with the numbering scheme. H atoms have been omitted. [Symmetry code: (A) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$]

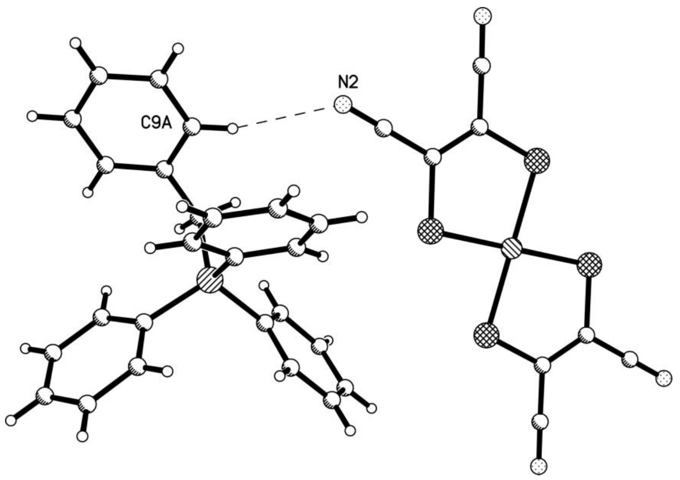


Figure 2
The weak hydrogen bond (dashed line) between the cation and the anion. [Symmetry code: (A) $x, 1 + y, z$].

(BzTPP)[Ni(mnt)$_2$] (Ni *et al.*, 2005). However, the stacking pattern of the title complex is significantly different from that of (BzTPP)[Ni(mnt)$_2$], in which the anions form segregated columns that are not present in (I). A weak hydrogen bond is observed between atom C9 of the anion and N2 of the cation (Table 2, Fig. 2). There are also two weak C—H$\cdots\pi$ hydrogen bonds between neighboring cations (Table 2), which result in the formation of ribbons of cations (Fig. 3). These anion–cation and cation–cation contacts may play an important role in the stabilization of the crystal structure of (I).

Experimental

Benzyltriphenylphosphonium bromide (BzTPPBr) was prepared by the literature method (Bulgarevich *et al.*, 1994). Disodium maleonitriledithiolate (Na$_2$mnt) was synthesized by a published procedure (Davison & Holm, 1967). The title compound was prepared by the direct reaction of 1:2:2 molar equivalents of NiCl$_2$·6H$_2$O (0.24 g, 1.0 mmol), Na$_2$mnt (0.28 g, 1.5 mmol) and (BzTPP)Br(0.57 g,1.6 mmol) in methanol (40 ml). The red product was purified by recrystallization from a 2:1 mixture of CH$_3$CN and iso-PrOH (yield 79%). Red block-shaped single crystals suitable for X-ray analysis were obtained after two weeks by slow evaporation of a CH$_3$CN solution at room temperature. Analysis found: C 66.53, H 4.33, N 5.18%; calculated for $C_{58}H_{44}N_4NiP_2S_4$: C 66.61, H 4.24, N 5.36%.

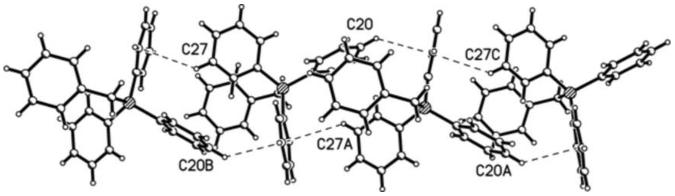


Figure 3
The weak hydrogen bonds between cations (dashed lines) and the formation of the ribbons. [Symmetry codes: (A) $1 - x, -y, -z$; (B) $1 - x, -1 - y, -z$; (C) $1 - x, -y, -z$.]

Crystal data

$(C_{25}H_{22}P)_2[Ni(C_4N_2S_2)_2]$
$M_r = 1045.86$
Monoclinic, $P2_1/n$
$a = 9.3845$ (5) Å
$b = 14.6825$ (9) Å
$c = 18.8748$ (11) Å
$\beta = 99.443$ (1)°
$V = 2565.5$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.65$ mm^{-1}
$T = 291$ (2) K
0.41 × 0.34 × 0.15 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.766$, $T_{\max} = 0.901$
13425 measured reflections
4508 independent reflections
3985 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.107$
$S = 1.03$
4508 reflections
313 parameters
175 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—S1	2.1684 (8)	S1—C2	1.727 (3)
Ni1—S2	2.1743 (7)	S2—C3	1.737 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9—H9$\cdots$N2$^{\rm i}$	0.93	2.57	3.478 (5)	165
C20—H20$\cdots Cg1^{\rm ii}$	0.93	3.15	3.852 (5)	133
C27—H27$\cdots Cg1^{\rm iii}$	0.93	3.17	3.727 (3)	120

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$. $Cg1$ is the centroid of atoms C12–C17.

All H atoms were placed in geometrically calculated positions (C—H = 0.93–0.97 Å) with $U_{\rm iso} = 1.2U_{\rm eq}$(parent atom).

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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