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Bis[1-(3-cyanobenzyl)triphenylphosphonium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickelate(II)

Chun-lin Ni,* Jia-rong Zhou and Yong Hou

Department of Applied Chemistry, College of Science, South China Agricultural University, Guangzhou, 510642, People's Republic of China
Correspondence e-mail: ctgunicl@163.com

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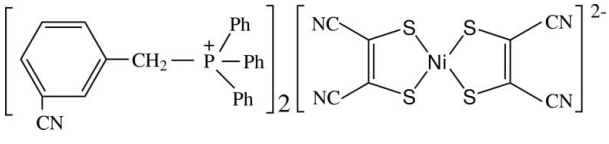
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.061; wR factor = 0.139; data-to-parameter ratio = 14.2.

The title complex, $(C_{26}H_{21}NP)_2[Ni(C_4N_2S_2)_2]$, is a salt of the mCNBzTPP$^+$cation and the $[Ni(mnt)_2]^{2-}$ anion [mCNBzTPP$^+$ is the 1-(3-cyanobenzyltriphenylphosphonium) cation and mnt^{2-} is the maleonitriledithiolate anion] and was prepared by the direct reaction of $NiCl_2$, Na_2mnt and $(mCNBzTPP)^+\cdot Br^-$ in ethanol. The asymmetric unit consists of two unique mCNBzTPP$^+$cations and half each of two $[Ni(mnt)_2]^{2-}$ anions with each Ni atom lying on an inversion centre. The Ni^{II} ions adopt a square-planar coordination geometry, binding to the S atoms of two mnt^{2-} ligands. Both $[mCNBzTPP]^+$ cations adopt conformations in which their four aromatic rings are twisted with respect to the planes that include the P atoms and the two C atoms linking them to the 3-cyanobenzyl rings. Three weak C—H···N hydrogen bonds play an important role in stabilizing the crystal structure.

Related literature

For details of other square-planar M(dithiolene)$_2$ complexes, see: Robertson & Cronin (2002); Ni *et al.* (2004); Nishijo *et al.* (2003); Canadell (1999). For the structures of related $Ni(mnt)_2^{2-}$ complexes with square-planar geometry and a substituted triphenylphosphonium counter-ion, see: Ni *et al.* (2005); Yang & Ni (2006); Liu & Ni, 2006; Zhou *et al.* (2007).



Experimental

Crystal data

$(C_{26}H_{21}NP)_2[Ni(C_4N_2S_2)_2]$
M_r = 1095.89
Monoclinic, $P2_1/n$
a = 19.158 (4) Å
b = 14.956 (3) Å
c = 19.598 (4) Å
β = 108.785 (4)°
V = 5316.3 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.63 mm^{-1}
T = 298 (2) K
0.34 × 0.22 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.834, T_{max} = 0.912
25624 measured reflections
9356 independent reflections
6235 reflections with $I > 2\sigma(I)$
R_{int} = 0.076

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.139
S = 1.09
9356 reflections
661 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10···N4^{i}	0.93	2.57	3.479 (7)	165
C33—H33···N2^{ii}	0.93	2.62	3.452 (6)	149
C36—H36···N2^{i}	0.93	2.47	3.250 (6)	141

Symmetry codes: (i) $x, y, z-1$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); 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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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2398).

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supplementary materials

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Bis[1-(3-cyanobenzyl)triphenylphosphonium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickelate(II)

C. Ni, J. Zhou and Y. Hou

Comment

Much effort has been devoted to the study of square planar *M*(dithiolene)$_2$ complexes (Robertson & Cronin, 2002; Ni *et al.*, 2004; Nishijo *et al.*, 2003; Canadell, 1999). Recently, we have carried out a systematic investigation on the coordination chemistry of salts containing Ni(mnt)$_2$ anion and substituted benzyltriphenylphosphonium cations and obtained some Ni(mnt)$_2^{2-}$-based molecular solids (Ni *et al.*, 2005; Yang & Ni, 2006; Liu & Ni, 2006; Zhou *et al.*, 2007). In this paper, we report the structure of the title compound, Fig. 1. There are two halves of non-equivalent Ni(mnt)$_2^{2-}$ anions and two (mCNBzTPP)$^+$ cations in the asymmetric unit. For the two Ni(mnt)$_2^{2-}$ anions. The Ni1 and Ni2 atoms are each coordinated to four sulfur atoms and exhibit square planar coordination geometry with the Ni atoms lying on inversion centres. The N atoms of the four unique CN groups deviate from the C1/C2/Ni1/S1/S2 or C5/C6/Ni2/S3/S4 planes by 0.029 (3) Å for N1, −0.077 (3) Å for N2, −0.216 (2) Å for N3 and −0.242 (2) Å for N4 respectively.

The two (mCNBzTPP)$^+$ cations adopt a conformation where four phenyl rings are twisted with respect to the plane including the P atom and the two C atoms linking it to the 3-cyanobenzyl ring. For the cation containing P1, the dihedral angles are 88.7 (3) for the C9/C10/C11/C12/C13/C14 ring, 84.0 (2) ° for the C17/C18/C19/C20/C21/C22 ring, 24.4 (2) ° for the C23/C24/C25/C26/C27/C28 ring, and 87.7 (2) ° for the C29/C30/C31/C32/C33/C34 ring. For the cation containing P2, the dihedral angles are 90.6 (3) for the C35/C36/C37/C38/C39/C40 ring, 93.2 (2) ° for the C43/C44/C45/C46/C47/C48 ring, 23.0 (2) ° for the C49/C50/C51/C52/C53/C54 ring, and 82.1 (2) ° for the C55/C56/C57/C58/C59/C60 ring. The deviations of the N5 and N6 atoms from the C9/C10/C11/C12/C13/C14 and C35/C36/C37/C38/C39/C40 phenyl ring planes are −0.052 (2)Å and 0.130 (2) Å respectively.

The crystal structure is stabilized by C10—H10···N4, C33—H33···N2 and C36—H36···N hydrogen bonds, Fig 2, Table 1.

Experimental

The title compound was prepared by the direct reaction of $NiCl_2{\cdot}6H_2O$, Na_2mnt and (mCNBzTPP)$^+$Br$^-$ in methanol. Red block-shaped single crystals were obtained by slow evaporation of a CH_3CN solution at room temperature over two weeks.

Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq} (C) for aromatic and 0.97 Å, U_{iso} = 1.2U_{eq} (C) for CH_2 atoms.

Figures

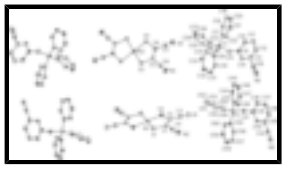

Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms. Labelled atoms are related to unlabelled atoms by the symmetry operations $-x+1, -y, -z+2$ and $-x+2, -y, -z+2$.

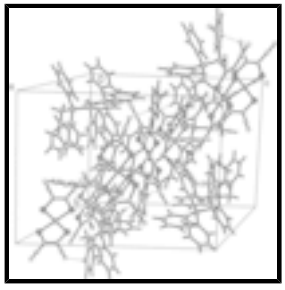

Fig. 2. Crystal packing of (I) showing the C—H···N hydrogen bonds between the anions and cations drawn as dashed lines.

Bis[1-(3-cyanobenzyl)triphenylphosphonium] bis(1,2-dicyanoethene-1,2- dithiolato-κ^2S,S')nickelate(II)

Crystal data

$(C_{26}H_{21}NP)_2[Ni(C_4N_2S_2)_2]$	$F_{000} = 2264$
$M_r = 1095.89$	$D_x = 1.369$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 957 reflections
$a = 19.158$ (4) Å	$\theta = 2.6$–22.9º
$b = 14.956$ (3) Å	$\mu = 0.63$ mm^{-1}
$c = 19.598$ (4) Å	$T = 298$ (2) K
$\beta = 108.785$ (4)º	Block, red
$V = 5316.3$ (19) Å^3	0.34 × 0.22 × 0.15 mm
$Z = 4$	

Data collection

Bruker Smart Apex CCD diffractometer	9356 independent reflections
Radiation source: fine-focus sealed tube	6235 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.076$
$T = 298$(2) K	$\theta_{max} = 25.0$º
φ and ω scans	$\theta_{min} = 2.2$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -22 \rightarrow 22$
$T_{min} = 0.834$, $T_{max} = 0.912$	$k = -17 \rightarrow 8$
25624 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.061$	H-atom parameters constrained
$wR(F^2) = 0.139$	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.015$
9356 reflections	$\Delta\rho_{max} = 0.83$ e Å^{-3}
661 parameters	$\Delta\rho_{min} = -0.73$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.0000	1.0000	0.05280 (19)
Ni2	1.0000	0.0000	1.0000	0.05428 (19)
C1	0.42984 (18)	0.1858 (2)	0.98368 (18)	0.0558 (9)
C2	0.45351 (18)	0.1800 (2)	0.92638 (19)	0.0589 (9)
C3	0.4419 (2)	0.2543 (3)	0.8777 (2)	0.0668 (10)
C4	0.3917 (2)	0.2625 (3)	0.9953 (2)	0.0682 (11)
C5	0.9070 (2)	0.1704 (2)	0.97231 (18)	0.0587 (9)
C6	0.96210 (19)	0.1926 (2)	0.94730 (18)	0.0568 (9)
C7	0.9619 (2)	0.2757 (3)	0.9121 (2)	0.0655 (10)
C8	0.8462 (2)	0.2295 (3)	0.9644 (2)	0.0664 (10)
C9	0.6312 (2)	0.2789 (3)	0.07367 (19)	0.0657 (10)
C10	0.6713 (3)	0.3359 (4)	0.0437 (2)	0.0982 (16)
H10	0.7084	0.3127	0.0279	0.118*
C11	0.6563 (3)	0.4260 (4)	0.0376 (3)	0.122 (2)
H11	0.6835	0.4630	0.0174	0.146*
C12	0.6027 (3)	0.4618 (3)	0.0604 (3)	0.1008 (16)
H12	0.5934	0.5229	0.0566	0.121*
C13	0.5623 (3)	0.4066 (3)	0.0892 (2)	0.0733 (11)
C14	0.5765 (2)	0.3156 (3)	0.09584 (18)	0.0617 (10)
H14	0.5486	0.2790	0.1155	0.074*
C15	0.6486 (2)	0.1806 (3)	0.08122 (17)	0.0658 (10)
H15A	0.6652	0.1617	0.0416	0.079*
H15B	0.6040	0.1477	0.0778	0.079*
C16	0.5037 (3)	0.4444 (3)	0.1115 (2)	0.0886 (14)
C17	0.78815 (18)	0.2373 (2)	0.18514 (17)	0.0524 (9)
C18	0.8438 (2)	0.2316 (3)	0.1540 (2)	0.0670 (10)
H18	0.8475	0.1814	0.1274	0.080*
C19	0.8927 (2)	0.2998 (3)	0.1626 (2)	0.0858 (13)
H19	0.9298	0.2958	0.1417	0.103*
C20	0.8882 (3)	0.3739 (3)	0.2014 (3)	0.0920 (14)

H20	0.9223	0.4199	0.2070	0.110*
C21	0.8336 (3)	0.3806 (3)	0.2323 (2)	0.0834 (13)
H21	0.8307	0.4311	0.2590	0.100*
C22	0.7827 (2)	0.3126 (3)	0.22363 (19)	0.0653 (10)
H22	0.7450	0.3176	0.2437	0.078*
C23	0.76030 (19)	0.0478 (2)	0.15672 (18)	0.0527 (9)
C24	0.7239 (2)	−0.0135 (3)	0.1050 (2)	0.0703 (11)
H24	0.6769	−0.0011	0.0738	0.084*
C25	0.7578 (3)	−0.0931 (3)	0.1001 (2)	0.0819 (13)
H25	0.7337	−0.1341	0.0647	0.098*
C26	0.8260 (3)	−0.1129 (3)	0.1461 (3)	0.0789 (12)
H26	0.8481	−0.1672	0.1422	0.095*
C27	0.8621 (2)	−0.0529 (3)	0.1983 (2)	0.0777 (12)
H27	0.9088	−0.0663	0.2298	0.093*
C28	0.8297 (2)	0.0267 (3)	0.2043 (2)	0.0661 (10)
H28	0.8540	0.0670	0.2403	0.079*
C29	0.68050 (19)	0.1447 (2)	0.23794 (18)	0.0498 (8)
C30	0.60572 (19)	0.1288 (2)	0.2250 (2)	0.0593 (9)
H30	0.5734	0.1263	0.1781	0.071*
C31	0.5804 (2)	0.1170 (3)	0.2823 (2)	0.0721 (11)
H31	0.5302	0.1083	0.2736	0.087*
C32	0.6266 (3)	0.1177 (3)	0.3513 (2)	0.0750 (12)
H32	0.6084	0.1089	0.3894	0.090*
C33	0.7008 (2)	0.1317 (3)	0.3643 (2)	0.0729 (11)
H33	0.7330	0.1313	0.4114	0.088*
C34	0.7278 (2)	0.1462 (2)	0.30799 (19)	0.0638 (10)
H34	0.7778	0.1570	0.3172	0.077*
C35	0.1902 (2)	0.3078 (3)	0.07543 (17)	0.0595 (9)
C36	0.2387 (2)	0.3790 (3)	0.0796 (2)	0.0723 (11)
H36	0.2871	0.3675	0.0818	0.087*
C37	0.2153 (3)	0.4658 (3)	0.0803 (2)	0.0841 (13)
H37	0.2482	0.5123	0.0829	0.101*
C38	0.1447 (3)	0.4850 (3)	0.0772 (2)	0.0800 (13)
H38	0.1294	0.5439	0.0779	0.096*
C39	0.0969 (2)	0.4154 (3)	0.0731 (2)	0.0683 (11)
C40	0.1188 (2)	0.3278 (3)	0.07163 (17)	0.0623 (10)
H40	0.0851	0.2818	0.0680	0.075*
C41	0.2163 (2)	0.2123 (2)	0.07693 (17)	0.0617 (10)
H41A	0.2541	0.2090	0.0539	0.074*
H41B	0.1754	0.1749	0.0498	0.074*
C42	0.0227 (3)	0.4321 (3)	0.0721 (2)	0.0849 (13)
C43	0.32015 (19)	0.2503 (2)	0.21637 (18)	0.0550 (9)
C44	0.3895 (2)	0.2469 (3)	0.20863 (19)	0.0642 (10)
H44	0.4022	0.1993	0.1845	0.077*
C45	0.4392 (2)	0.3137 (3)	0.2365 (2)	0.0781 (12)
H45	0.4858	0.3114	0.2315	0.094*
C46	0.4205 (3)	0.3839 (3)	0.2717 (2)	0.0821 (13)
H46	0.4545	0.4291	0.2905	0.099*
C47	0.3521 (3)	0.3884 (3)	0.2798 (2)	0.0799 (12)

H47	0.3399	0.4361	0.3042	0.096*
C48	0.3014 (2)	0.3214 (3)	0.25145 (19)	0.0669 (10)
H48	0.2546	0.3244	0.2561	0.080*
C49	0.2971 (2)	0.0648 (2)	0.1677 (2)	0.0581 (9)
C50	0.2752 (2)	0.0107 (3)	0.1084 (2)	0.0779 (12)
H50	0.2386	0.0297	0.0669	0.094*
C51	0.3071 (3)	−0.0713 (3)	0.1102 (3)	0.0985 (16)
H51	0.2919	−0.1078	0.0697	0.118*
C52	0.3601 (3)	−0.1002 (3)	0.1694 (4)	0.0963 (16)
H52	0.3815	−0.1561	0.1697	0.116*
C53	0.3825 (3)	−0.0470 (3)	0.2295 (3)	0.0910 (14)
H53	0.4193	−0.0667	0.2705	0.109*
C54	0.3509 (2)	0.0355 (3)	0.2293 (2)	0.0768 (11)
H54	0.3656	0.0713	0.2702	0.092*
C55	0.18144 (19)	0.1573 (2)	0.20786 (18)	0.0534 (9)
C56	0.1109 (2)	0.1369 (2)	0.1647 (2)	0.0597 (9)
H56	0.1003	0.1313	0.1151	0.072*
C57	0.0561 (2)	0.1250 (3)	0.1953 (2)	0.0723 (11)
H57	0.0084	0.1118	0.1662	0.087*
C58	0.0715 (3)	0.1324 (3)	0.2675 (3)	0.0786 (12)
H58	0.0338	0.1257	0.2875	0.094*
C59	0.1418 (3)	0.1498 (3)	0.3114 (2)	0.0778 (12)
H59	0.1521	0.1529	0.3611	0.093*
C60	0.1974 (2)	0.1626 (2)	0.2818 (2)	0.0658 (10)
H60	0.2451	0.1747	0.3113	0.079*
N1	0.4317 (2)	0.3151 (3)	0.84045 (19)	0.0875 (11)
N2	0.3606 (2)	0.3238 (3)	1.0040 (2)	0.1000 (13)
N3	0.9608 (2)	0.3414 (2)	0.8829 (2)	0.0867 (11)
N4	0.7969 (2)	0.2761 (3)	0.9571 (2)	0.0936 (12)
N5	0.4584 (3)	0.4751 (3)	0.1290 (3)	0.1336 (19)
N6	−0.0351 (2)	0.4436 (3)	0.0736 (2)	0.1084 (14)
P1	0.71916 (5)	0.15259 (6)	0.16601 (5)	0.0517 (2)
P2	0.25325 (5)	0.17021 (6)	0.16846 (5)	0.0535 (3)
S1	0.44310 (5)	0.09780 (7)	1.04475 (5)	0.0612 (3)
S2	0.49732 (6)	0.08587 (7)	0.91018 (5)	0.0721 (3)
S3	0.90439 (5)	0.06748 (7)	1.01219 (6)	0.0694 (3)
S4	1.03274 (5)	0.11747 (7)	0.95286 (5)	0.0627 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0455 (4)	0.0584 (4)	0.0527 (4)	0.0018 (3)	0.0133 (3)	0.0064 (3)
Ni2	0.0468 (4)	0.0560 (4)	0.0551 (4)	0.0025 (3)	0.0096 (3)	0.0013 (3)
C1	0.0410 (19)	0.061 (2)	0.063 (2)	0.0029 (18)	0.0134 (17)	0.0062 (19)
C2	0.051 (2)	0.062 (2)	0.063 (2)	0.0034 (19)	0.0166 (18)	0.009 (2)
C3	0.063 (3)	0.069 (3)	0.073 (3)	0.007 (2)	0.028 (2)	0.007 (2)
C4	0.066 (3)	0.069 (3)	0.073 (3)	0.004 (2)	0.027 (2)	0.003 (2)
C5	0.055 (2)	0.057 (2)	0.056 (2)	0.012 (2)	0.0077 (18)	0.0009 (18)

C6	0.054 (2)	0.058 (2)	0.056 (2)	0.0011 (19)	0.0143 (18)	0.0000 (19)
C7	0.070 (3)	0.065 (3)	0.063 (2)	0.006 (2)	0.025 (2)	0.001 (2)
C8	0.070 (3)	0.066 (3)	0.061 (2)	0.004 (2)	0.018 (2)	0.002 (2)
C9	0.059 (2)	0.078 (3)	0.054 (2)	0.012 (2)	0.0104 (19)	0.010 (2)
C10	0.085 (3)	0.122 (5)	0.097 (3)	0.024 (3)	0.043 (3)	0.045 (3)
C11	0.123 (5)	0.116 (5)	0.142 (5)	0.015 (4)	0.064 (4)	0.070 (4)
C12	0.127 (5)	0.075 (3)	0.102 (4)	0.008 (3)	0.039 (3)	0.035 (3)
C13	0.096 (3)	0.061 (3)	0.058 (2)	0.007 (3)	0.019 (2)	0.012 (2)
C14	0.069 (3)	0.058 (3)	0.057 (2)	0.001 (2)	0.0195 (19)	0.0055 (19)
C15	0.058 (2)	0.080 (3)	0.058 (2)	0.005 (2)	0.0168 (19)	−0.009 (2)
C16	0.134 (5)	0.057 (3)	0.080 (3)	0.015 (3)	0.042 (3)	0.007 (2)
C17	0.050 (2)	0.053 (2)	0.055 (2)	0.0036 (17)	0.0169 (17)	0.0043 (18)
C18	0.079 (3)	0.056 (2)	0.076 (3)	−0.004 (2)	0.039 (2)	0.000 (2)
C19	0.092 (3)	0.068 (3)	0.121 (4)	−0.011 (3)	0.066 (3)	−0.001 (3)
C20	0.097 (4)	0.062 (3)	0.131 (4)	−0.026 (3)	0.056 (3)	−0.008 (3)
C21	0.102 (4)	0.048 (3)	0.108 (3)	−0.011 (3)	0.046 (3)	−0.016 (2)
C22	0.072 (3)	0.057 (2)	0.074 (2)	0.005 (2)	0.035 (2)	−0.004 (2)
C23	0.054 (2)	0.046 (2)	0.059 (2)	−0.0021 (18)	0.0206 (19)	−0.0077 (18)
C24	0.058 (2)	0.072 (3)	0.080 (3)	−0.002 (2)	0.021 (2)	−0.024 (2)
C25	0.087 (3)	0.068 (3)	0.099 (3)	−0.012 (3)	0.042 (3)	−0.031 (3)
C26	0.089 (3)	0.049 (3)	0.118 (4)	0.006 (2)	0.059 (3)	−0.006 (3)
C27	0.072 (3)	0.059 (3)	0.100 (3)	0.016 (2)	0.025 (2)	−0.003 (2)
C28	0.066 (3)	0.055 (2)	0.073 (2)	0.000 (2)	0.015 (2)	−0.008 (2)
C29	0.051 (2)	0.040 (2)	0.060 (2)	0.0013 (16)	0.0196 (18)	−0.0042 (17)
C30	0.047 (2)	0.056 (2)	0.071 (2)	0.0061 (18)	0.0144 (19)	0.0035 (19)
C31	0.058 (2)	0.065 (3)	0.106 (3)	0.006 (2)	0.043 (3)	0.011 (3)
C32	0.086 (3)	0.071 (3)	0.085 (3)	−0.001 (2)	0.051 (3)	0.003 (2)
C33	0.076 (3)	0.075 (3)	0.068 (2)	−0.002 (2)	0.024 (2)	−0.002 (2)
C34	0.060 (2)	0.069 (3)	0.064 (2)	−0.006 (2)	0.024 (2)	−0.005 (2)
C35	0.064 (2)	0.065 (3)	0.050 (2)	0.003 (2)	0.0187 (18)	0.0066 (19)
C36	0.070 (3)	0.078 (3)	0.081 (3)	−0.004 (2)	0.040 (2)	0.006 (2)
C37	0.099 (4)	0.065 (3)	0.098 (3)	−0.012 (3)	0.046 (3)	0.010 (3)
C38	0.093 (3)	0.061 (3)	0.098 (3)	0.006 (3)	0.048 (3)	0.019 (2)
C39	0.075 (3)	0.063 (3)	0.075 (3)	0.012 (2)	0.034 (2)	0.015 (2)
C40	0.059 (2)	0.067 (3)	0.060 (2)	−0.004 (2)	0.0176 (19)	0.007 (2)
C41	0.056 (2)	0.072 (3)	0.058 (2)	−0.001 (2)	0.0185 (18)	−0.0052 (19)
C42	0.095 (4)	0.068 (3)	0.101 (3)	0.019 (3)	0.045 (3)	0.031 (2)
C43	0.055 (2)	0.051 (2)	0.056 (2)	−0.0016 (18)	0.0136 (18)	−0.0009 (18)
C44	0.062 (2)	0.056 (2)	0.077 (3)	−0.005 (2)	0.026 (2)	−0.001 (2)
C45	0.065 (3)	0.064 (3)	0.106 (3)	−0.013 (2)	0.028 (2)	0.002 (3)
C46	0.083 (3)	0.063 (3)	0.090 (3)	−0.022 (3)	0.013 (3)	0.005 (2)
C47	0.108 (4)	0.052 (3)	0.075 (3)	−0.005 (3)	0.021 (3)	−0.009 (2)
C48	0.077 (3)	0.056 (2)	0.070 (2)	0.001 (2)	0.027 (2)	−0.007 (2)
C49	0.057 (2)	0.049 (2)	0.073 (2)	−0.0080 (19)	0.029 (2)	−0.010 (2)
C50	0.076 (3)	0.070 (3)	0.091 (3)	−0.002 (2)	0.031 (2)	−0.025 (2)
C51	0.112 (4)	0.070 (3)	0.132 (5)	−0.007 (3)	0.067 (4)	−0.032 (3)
C52	0.112 (4)	0.050 (3)	0.159 (5)	0.006 (3)	0.088 (4)	−0.001 (3)
C53	0.085 (3)	0.068 (3)	0.125 (4)	0.017 (3)	0.040 (3)	0.012 (3)
C54	0.083 (3)	0.059 (3)	0.089 (3)	0.006 (2)	0.028 (3)	−0.003 (2)

C55	0.053 (2)	0.047 (2)	0.061 (2)	0.0034 (18)	0.0197 (19)	−0.0019 (18)
C56	0.061 (2)	0.052 (2)	0.065 (2)	0.0040 (19)	0.017 (2)	0.0067 (19)
C57	0.062 (3)	0.065 (3)	0.093 (3)	0.002 (2)	0.031 (2)	0.010 (2)
C58	0.078 (3)	0.059 (3)	0.118 (4)	0.006 (2)	0.060 (3)	0.012 (3)
C59	0.104 (4)	0.069 (3)	0.075 (3)	0.006 (3)	0.050 (3)	0.004 (2)
C60	0.074 (3)	0.060 (3)	0.065 (2)	0.000 (2)	0.024 (2)	−0.001 (2)
N1	0.095 (3)	0.079 (3)	0.090 (3)	0.008 (2)	0.032 (2)	0.023 (2)
N2	0.107 (3)	0.089 (3)	0.117 (3)	0.029 (3)	0.056 (3)	0.002 (2)
N3	0.104 (3)	0.066 (2)	0.099 (3)	0.012 (2)	0.045 (2)	0.013 (2)
N4	0.082 (3)	0.097 (3)	0.102 (3)	0.032 (2)	0.031 (2)	0.006 (2)
N5	0.211 (6)	0.083 (3)	0.142 (4)	0.051 (3)	0.106 (4)	0.015 (3)
N6	0.104 (3)	0.093 (3)	0.147 (4)	0.027 (3)	0.068 (3)	0.046 (3)
P1	0.0482 (5)	0.0511 (6)	0.0556 (5)	0.0023 (4)	0.0166 (4)	−0.0061 (5)
P2	0.0509 (6)	0.0529 (6)	0.0574 (5)	−0.0007 (5)	0.0182 (4)	−0.0080 (5)
S1	0.0583 (6)	0.0668 (6)	0.0607 (6)	0.0045 (5)	0.0221 (5)	0.0076 (5)
S2	0.0835 (7)	0.0727 (7)	0.0708 (6)	0.0205 (6)	0.0397 (6)	0.0171 (5)
S3	0.0596 (6)	0.0699 (7)	0.0816 (7)	0.0097 (5)	0.0268 (5)	0.0137 (6)
S4	0.0561 (6)	0.0621 (6)	0.0705 (6)	0.0069 (5)	0.0215 (5)	0.0061 (5)

Geometric parameters (Å, °)

Ni1—S2^{i}	2.1661 (10)	C29—C30	1.392 (4)
Ni1—S2	2.1661 (10)	C29—P1	1.795 (3)
Ni1—S1	2.1709 (10)	C30—C31	1.370 (5)
Ni1—S1^{i}	2.1709 (10)	C30—H30	0.9300
Ni2—S4^{ii}	2.1695 (10)	C31—C32	1.357 (5)
Ni2—S4	2.1695 (10)	C31—H31	0.9300
Ni2—S3	2.1709 (10)	C32—C33	1.377 (5)
Ni2—S3^{ii}	2.1709 (10)	C32—H32	0.9300
C1—C2	1.342 (4)	C33—C34	1.378 (5)
C1—C4	1.416 (5)	C33—H33	0.9300
C1—S1	1.742 (4)	C34—H34	0.9300
C2—C3	1.434 (5)	C35—C40	1.379 (5)
C2—S2	1.720 (4)	C35—C36	1.398 (5)
C3—N1	1.143 (5)	C35—C41	1.510 (5)
C4—N2	1.137 (5)	C36—C37	1.375 (5)
C5—C6	1.341 (5)	C36—H36	0.9300
C5—C8	1.430 (5)	C37—C38	1.365 (6)
C5—S3	1.735 (4)	C37—H37	0.9300
C6—C7	1.421 (5)	C38—C39	1.371 (5)
C6—S4	1.735 (4)	C38—H38	0.9300
C7—N3	1.135 (4)	C39—C40	1.379 (5)
C8—N4	1.145 (5)	C39—C42	1.437 (6)
C9—C14	1.372 (5)	C40—H40	0.9300
C9—C10	1.397 (6)	C41—P2	1.816 (3)
C9—C15	1.505 (5)	C41—H41A	0.9700
C10—C11	1.375 (7)	C41—H41B	0.9700
C10—H10	0.9300	C42—N6	1.130 (5)

C11—C12	1.357 (7)	C43—C48	1.376 (5)
C11—H11	0.9300	C43—C44	1.386 (5)
C12—C13	1.370 (6)	C43—P2	1.784 (4)
C12—H12	0.9300	C44—C45	1.367 (5)
C13—C14	1.387 (5)	C44—H44	0.9300
C13—C16	1.445 (6)	C45—C46	1.365 (5)
C14—H14	0.9300	C45—H45	0.9300
C15—P1	1.821 (3)	C46—C47	1.371 (6)
C15—H15A	0.9700	C46—H46	0.9300
C15—H15B	0.9700	C47—C48	1.381 (5)
C16—N5	1.128 (6)	C47—H47	0.9300
C17—C22	1.378 (5)	C48—H48	0.9300
C17—C18	1.392 (5)	C49—C50	1.366 (5)
C17—P1	1.781 (3)	C49—C54	1.383 (5)
C18—C19	1.357 (5)	C49—P2	1.788 (4)
C18—H18	0.9300	C50—C51	1.367 (6)
C19—C20	1.363 (6)	C50—H50	0.9300
C19—H19	0.9300	C51—C52	1.344 (7)
C20—C21	1.371 (5)	C51—H51	0.9300
C20—H20	0.9300	C52—C53	1.370 (6)
C21—C22	1.381 (5)	C52—H52	0.9300
C21—H21	0.9300	C53—C54	1.374 (6)
C22—H22	0.9300	C53—H53	0.9300
C23—C24	1.377 (5)	C54—H54	0.9300
C23—C28	1.392 (5)	C55—C60	1.383 (5)
C23—P1	1.790 (3)	C55—C56	1.378 (5)
C24—C25	1.375 (5)	C55—P2	1.792 (3)
C24—H24	0.9300	C56—C57	1.377 (5)
C25—C26	1.361 (6)	C56—H56	0.9300
C25—H25	0.9300	C57—C58	1.355 (5)
C26—C27	1.370 (6)	C57—H57	0.9300
C26—H26	0.9300	C58—C59	1.369 (6)
C27—C28	1.365 (5)	C58—H58	0.9300
C27—H27	0.9300	C59—C60	1.381 (5)
C28—H28	0.9300	C59—H59	0.9300
C29—C34	1.380 (4)	C60—H60	0.9300
$S2^{i}$—Ni1—S2	180.0	C32—C33—C34	120.4 (4)
$S2^{i}$—Ni1—S1	87.41 (4)	C32—C33—H33	119.8
S2—Ni1—S1	92.59 (4)	C34—C33—H33	119.8
$S2^{i}$—Ni1—$S1^{i}$	92.59 (4)	C29—C34—C33	119.9 (4)
S2—Ni1—$S1^{i}$	87.41 (4)	C29—C34—H34	120.1
S1—Ni1—$S1^{i}$	180.000 (1)	C33—C34—H34	120.1
$S4^{ii}$—Ni2—S4	180.0	C40—C35—C36	117.9 (4)
$S4^{ii}$—Ni2—S3	87.69 (4)	C40—C35—C41	121.5 (4)
S4—Ni2—S3	92.31 (4)	C36—C35—C41	120.6 (4)
$S4^{ii}$—Ni2—$S3^{ii}$	92.31 (4)	C37—C36—C35	120.4 (4)
S4—Ni2—$S3^{ii}$	87.69 (4)	C37—C36—H36	119.8

S3—Ni2—S3^{ii}	180.00 (5)	C35—C36—H36	119.8
C2—C1—C4	121.2 (3)	C38—C37—C36	121.4 (4)
C2—C1—S1	120.8 (3)	C38—C37—H37	119.3
C4—C1—S1	118.0 (3)	C36—C37—H37	119.3
C1—C2—C3	118.9 (3)	C37—C38—C39	118.4 (4)
C1—C2—S2	121.6 (3)	C37—C38—H38	120.8
C3—C2—S2	119.4 (3)	C39—C38—H38	120.8
N1—C3—C2	177.7 (4)	C40—C39—C38	121.4 (4)
N2—C4—C1	179.4 (5)	C40—C39—C42	118.1 (4)
C6—C5—C8	121.1 (3)	C38—C39—C42	120.5 (4)
C6—C5—S3	121.6 (3)	C39—C40—C35	120.5 (4)
C8—C5—S3	117.2 (3)	C39—C40—H40	119.7
C5—C6—C7	120.9 (3)	C35—C40—H40	119.7
C5—C6—S4	120.4 (3)	C35—C41—P2	111.6 (2)
C7—C6—S4	118.5 (3)	C35—C41—H41A	109.3
N3—C7—C6	178.7 (5)	P2—C41—H41A	109.3
N4—C8—C5	179.0 (5)	C35—C41—H41B	109.3
C14—C9—C10	118.0 (4)	P2—C41—H41B	109.3
C14—C9—C15	121.8 (4)	H41A—C41—H41B	108.0
C10—C9—C15	120.2 (4)	N6—C42—C39	177.6 (5)
C11—C10—C9	120.5 (5)	C48—C43—C44	119.8 (3)
C11—C10—H10	119.7	C48—C43—P2	121.5 (3)
C9—C10—H10	119.7	C44—C43—P2	118.0 (3)
C12—C11—C10	121.1 (5)	C45—C44—C43	119.9 (4)
C12—C11—H11	119.5	C45—C44—H44	120.1
C10—C11—H11	119.5	C43—C44—H44	120.0
C11—C12—C13	119.1 (5)	C44—C45—C46	120.1 (4)
C11—C12—H12	120.5	C44—C45—H45	120.0
C13—C12—H12	120.5	C46—C45—H45	120.0
C14—C13—C12	120.7 (4)	C47—C46—C45	120.8 (4)
C14—C13—C16	120.2 (4)	C47—C46—H46	119.6
C12—C13—C16	119.0 (4)	C45—C46—H46	119.6
C9—C14—C13	120.6 (4)	C46—C47—C48	119.5 (4)
C9—C14—H14	119.7	C46—C47—H47	120.2
C13—C14—H14	119.7	C48—C47—H47	120.2
C9—C15—P1	113.0 (2)	C43—C48—C47	119.9 (4)
C9—C15—H15A	109.0	C43—C48—H48	120.1
P1—C15—H15A	109.0	C47—C48—H48	120.1
C9—C15—H15B	109.0	C50—C49—C54	119.6 (4)
P1—C15—H15B	109.0	C50—C49—P2	120.9 (3)
H15A—C15—H15B	107.8	C54—C49—P2	119.5 (3)
N5—C16—C13	179.0 (6)	C51—C50—C49	119.8 (5)
C22—C17—C18	119.6 (3)	C51—C50—H50	120.1
C22—C17—P1	121.0 (3)	C49—C50—H50	120.1
C18—C17—P1	119.1 (3)	C52—C51—C50	121.2 (5)
C19—C18—C17	119.7 (4)	C52—C51—H51	119.4
C19—C18—H18	120.1	C50—C51—H51	119.4
C17—C18—H18	120.1	C51—C52—C53	119.7 (5)
C18—C19—C20	121.0 (4)	C51—C52—H52	120.1

C18—C19—H19	119.5	C53—C52—H52	120.1
C20—C19—H19	119.5	C54—C53—C52	120.2 (5)
C19—C20—C21	120.0 (4)	C54—C53—H53	119.9
C19—C20—H20	120.0	C52—C53—H53	119.9
C21—C20—H20	120.0	C53—C54—C49	119.4 (4)
C20—C21—C22	120.1 (4)	C53—C54—H54	120.3
C20—C21—H21	120.0	C49—C54—H54	120.3
C22—C21—H21	120.0	C60—C55—C56	119.8 (3)
C17—C22—C21	119.6 (4)	C60—C55—P2	120.3 (3)
C17—C22—H22	120.2	C56—C55—P2	119.8 (3)
C21—C22—H22	120.2	C55—C56—C57	119.7 (4)
C24—C23—C28	119.4 (3)	C55—C56—H56	120.2
C24—C23—P1	121.5 (3)	C57—C56—H56	120.2
C28—C23—P1	119.1 (3)	C58—C57—C56	120.3 (4)
C25—C24—C23	119.3 (4)	C58—C57—H57	119.8
C25—C24—H24	120.3	C56—C57—H57	119.8
C23—C24—H24	120.3	C57—C58—C59	120.7 (4)
C26—C25—C24	121.1 (4)	C57—C58—H58	119.7
C26—C25—H25	119.4	C59—C58—H58	119.7
C24—C25—H25	119.4	C58—C59—C60	119.9 (4)
C25—C26—C27	119.9 (4)	C58—C59—H59	120.1
C25—C26—H26	120.1	C60—C59—H59	120.1
C27—C26—H26	120.1	C55—C60—C59	119.5 (4)
C28—C27—C26	120.1 (4)	C55—C60—H60	120.2
C28—C27—H27	119.9	C59—C60—H60	120.2
C26—C27—H27	119.9	C17—P1—C23	108.84 (16)
C27—C28—C23	120.1 (4)	C17—P1—C29	110.34 (16)
C27—C28—H28	119.9	C23—P1—C29	109.18 (15)
C23—C28—H28	119.9	C17—P1—C15	108.13 (17)
C34—C29—C30	119.4 (3)	C23—P1—C15	109.27 (16)
C34—C29—P1	118.4 (3)	C29—P1—C15	111.05 (17)
C30—C29—P1	121.9 (3)	C43—P2—C49	109.69 (17)
C31—C30—C29	119.2 (3)	C43—P2—C55	111.52 (17)
C31—C30—H30	120.4	C49—P2—C55	109.65 (16)
C29—C30—H30	120.4	C43—P2—C41	105.81 (17)
C32—C31—C30	121.7 (4)	C49—P2—C41	109.37 (17)
C32—C31—H31	119.2	C55—P2—C41	110.73 (16)
C30—C31—H31	119.2	C1—S1—Ni1	102.29 (13)
C31—C32—C33	119.3 (4)	C2—S2—Ni1	102.74 (12)
C31—C32—H32	120.3	C5—S3—Ni2	102.43 (13)
C33—C32—H32	120.3	C6—S4—Ni2	102.97 (13)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) −*x*+2, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···N4^{iii}	0.93	2.57	3.479 (7)	165
C33—H33···N2^{iv}	0.93	2.62	3.452 (6)	149

C36—H36···N2^{iii}	0.93	2.47	3.250 (6)	141

Symmetry codes: (iii) *x*, *y*, *z*−1; (iv) *x*+1/2, −*y*+1/2, *z*−1/2.

Fig. 1

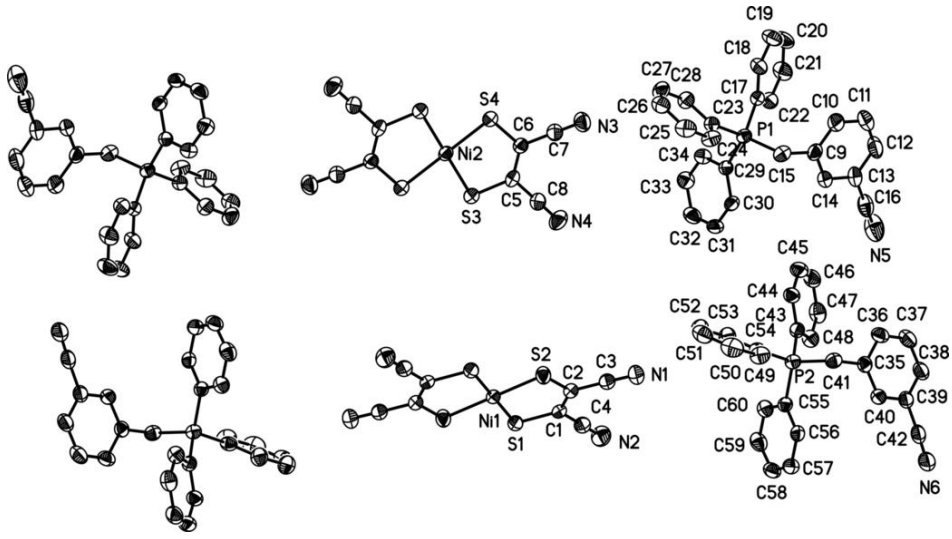

Fig. 2