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Butyltriphenylphosphonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III)

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In the title complex, $(C_{22}H_{24}P)[Ni(C_3S_5)_2]$ or $(BuPh_3P)$-$[Ni(dmit)_2]$ (where $BuPh_3P$ is the butyltriphenylphosphonium cation and dmit is the 2-thioxo-1,3-dithiole-4,5-dithiolate anion), each Ni atom is tetracoordinated by four dmit S atoms, forming a nearly square-planar arrangement. The average Ni—S bond length is 2.16Å, much smaller than 2.21Å for the Ni^{2+} ion in $[Ni(dmit)_2]^{2-}$. The other bond distances are also shorter, close to the corresponding double-bond value. The $[Ni(dmit)_2]^-$ anions and butyltriphenylphosphonium counter-cations form a layered arrangement in the crystal structure.

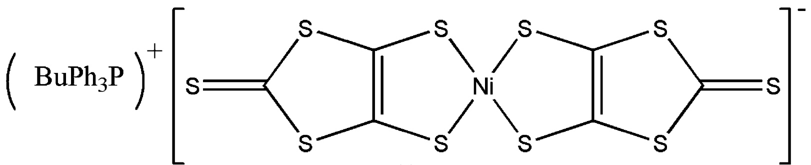
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.042
wR factor = 0.103
Data-to-parameter ratio = 20.7

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

Comment

As conjugated charge-transfer complexes, $Q[M(dmit)_2]$ complexes (M is a transition metal and Q is the counter-cation) have been used as electrical conductors and superconductors (Svenstrup & Becher, 1995; Cassoux, 1999; Pullen & Olk, 1999; Robertson & Cronin, 2002). Recently, many of these dmit complexes have been reported as possessing good second-order (Fang *et al.*, 1994; Zhai *et al.*, 1999) and third-order non-linear optical (NLO) properties (Winter *et al.*, 1992; Zuo *et al.*, 1996; Wang *et al.*, 1999; Bai *et al.*, 1999; Dai *et al.*, 2000; Liu *et al.*, 2002). This is because the highly conjugated structure and charge-transfer between the metal and the dmit ligand result in large NLO effects and fast responses (McDonagh *et al.*, 1999). The title complex, (I), a new salt of the general form $Q[M(dmit)_2]$, is also a new NLO material.



(I)

In the asymmetric unit of (I) (Fig. 1), there is one $[Ni(dmit)_2]^-$ anion and one $BuPh_3P^+$ cation. The Ni^{3+} ion is coordinated by four S atoms from two dmit molecules. The S—Ni—S bond angles for the vicinal S atoms are in the range 86.86 (3)–93.05 (3)°, with an average value of 90.01°. The other two S—Ni—S angles of 177.79 (4) and 178.83 (4)° are close to 180°. Together, these data indicate that the NiS_4 core adopts a nearly square-planar configuration.

The Ni—S bond lengths (Table 1) range from 2.1543 (8) to 2.1634 (9) Å, with an average of 2.16 Å, much smaller than 2.21Å for the Ni^{2+} ion in $Q_2[Ni(dmit)_2]$ (Lindqvist *et al.*, 1979). This indicates that oxidation has taken place at the central Ni atom, which is in accordance with those observed elsewhere

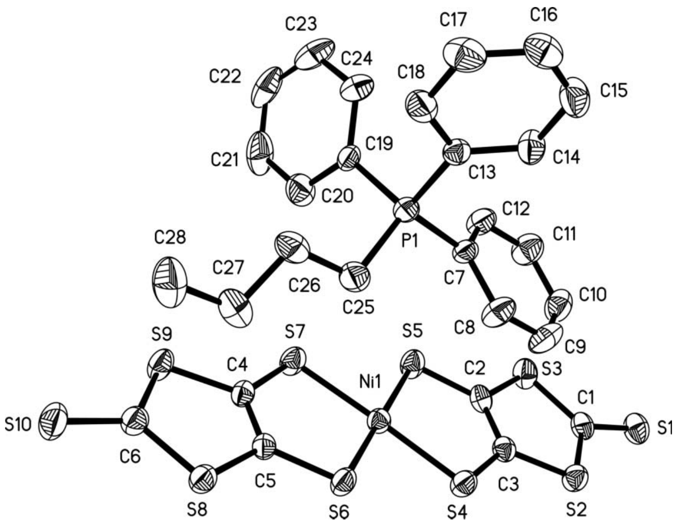


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

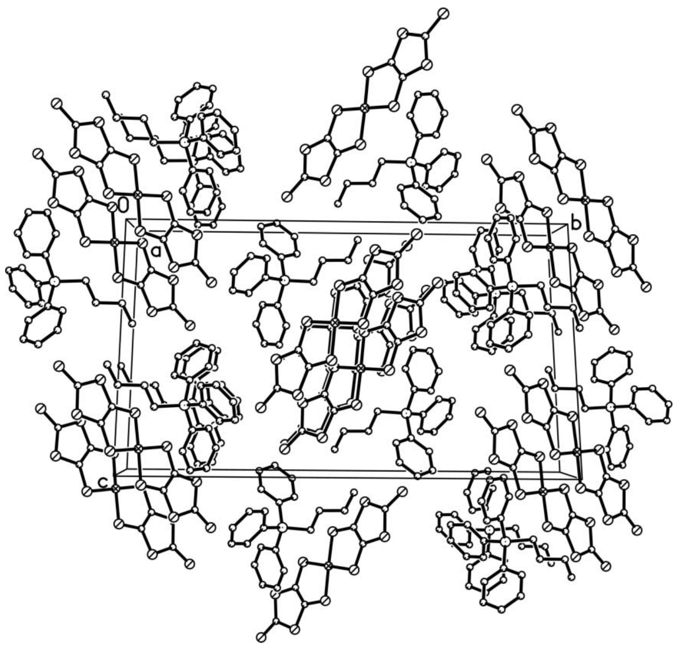


Figure 2
The packing of (I), viewed along the *a* axis. H atoms have been omitted.

for Ni (Lindqvist *et al.*, 1982; Diemen *et al.*, 1988). The C6—S10 and C1—S1 distances are 1.632 (3) and 1.642 (3) Å, respectively. The remaining C—S bonds vary from 1.704 (3) to 1.749 (3) Å and are close to the value 1.71 Å reported for a C═S double bond (Lindqvist *et al.*, 1979). The C—C bond lengths of the ion are 1.345 (3) and 1.362 (4) Å, close to the corresponding double-bond value 1.34 Å.

All the data show that the $[Ni(dmit)_2]^-$ ring system has a high degree of electron delocalization. In addition, the introduction of Ni^{3+} allows the possibility of low-energy charge transfer due to an unfilled *d* electron shell of Ni^{3+}. These will greatly enhance the NLO properties of the materials.

Experimental

The synthesis of (I) involved a modification of literature methods (Steimeck & Kirmse, 1979; Wang *et al.*, 1998). To degassed dimethylformamide (DMF, 40 ml), CS_2 (20 ml) was added and the mixture was cooled to 273 K. Sodium (1.21 g) was added to the solution and the mixture was vigorously stirred with cooling until the reaction was complete. MeOH (several ml) was slowly added. To this solution, separate solutions of $NiCl_2\cdot 6H_2O$ (3.71 g) dissolved in 25–28% aqueous ammonia (40 ml), and then $BuPh_3PBr$ (10.45 g) in water (30 ml), were added consecutively with stirring at room temperature. The mixture was stirred overnight, and the product was isolated by filtration and washed with water and MeOH, affording black crystals of (I). The high optical-quality single crystals used for the X-ray structure analysis were obtained by slow evaporation of an acetone solution.

Crystal data

$(C_{22}H_{24}P)[Ni(C_3S_5)_2]$
$M_r = 770.75$
Monoclinic, $P2_1/c$
$a = 8.373$ (1) Å
$b = 26.177$ (4) Å
$c = 16.005$ (2) Å
$\beta = 111.678$ (2)°
$V = 3259.9$ (8) Å^3
$Z = 4$
$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.31$ mm^{-1}
$T = 298$ (2) K
Prism, black
0.31 × 0.21 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998) $T_{min} = 0.688$, $T_{max} = 0.838$
19383 measured reflections
7491 independent reflections
4815 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.103$
$S = 0.92$
7491 reflections
362 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S6	2.1543 (8)	C3—S4	1.704 (3)
Ni1—S7	2.1580 (8)	C3—S2	1.740 (3)
Ni1—S4	2.1618 (8)	C4—C5	1.345 (3)
Ni1—S5	2.1634 (9)	C4—S7	1.716 (3)
C1—S1	1.642 (3)	C4—S9	1.737 (3)
C1—S2	1.723 (3)	C5—S6	1.714 (3)
C1—S3	1.724 (3)	C5—S8	1.749 (3)
C2—C3	1.362 (4)	C6—S10	1.632 (3)
C2—S5	1.705 (3)	C6—S9	1.723 (3)
C2—S3	1.738 (3)	C6—S8	1.732 (3)
S6—Ni1—S7	92.97 (3)	S4—Ni1—S5	93.05 (3)
S6—Ni1—S4	86.86 (3)	C3—S4—Ni1	102.10 (10)
S7—Ni1—S4	177.79 (4)	C2—S5—Ni1	102.01 (10)
S6—Ni1—S5	178.83 (4)	C5—S6—Ni1	102.16 (10)
S7—Ni1—S5	87.17 (3)	C4—S7—Ni1	102.27 (9)

All H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.96 (for CH_2 groups), 0.97 (for CH_3 groups) or 0.93Å (for C_6H_5 groups); their isotropic dis-

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placement parameters were set at 1.2 (1.5 for CH_3 groups) times U_{eq} of their parent atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Bai, J. F., Zuo, J. L., Tan, W. L., Ji, W., Shen, Z., Fun, H. K., Chinnakali, K., Razak, I. A., You, X. Z. & Che, C. M. (1999). *J. Mater. Chem.* **9**, 2419–2423.

Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1998). *SMART* (Version 5.054), *SADABS* (Version 2.0) and *SAINT* (Version 6.36a). Bruker AXS Inc., Madison, Wisconsin, USA.

Cassoux, P. (1999). *Coord. Chem. Rev.* **185–186**, 213–232.

Dai, J., Bian, G. Q., Wang, X., Xu, Q. F., Zhou, M. Y., Munakata, M., Maekawa, M., Tong, M. H., Sun, Z. R. & Zeng, H. P. (2000). *J. Am. Chem. Soc.* **122**, 11007–11008.

Diemen, J. H. van, Groeneveld, L. R., Lind, A., de Graaff, R. A. G., Haasnoot, J. G. & Reedijk, J. (1988). *Acta Cryst.* C**44**, 1898–1902.

Fang, Q., Jiang, M. H., Qu, Z., Cai, J. H., Lei, H., Yu, W. T. & Zhuo, Z. (1994). *J. Mater. Chem.* **4**, 1041–1045.

Lindqvist, O., Andersen, L., Sieler, J., Steimecke, G. & Hoyer, E. (1982). *Acta Chem. Scand. Ser. A*, **36**, 855–856.

Lindqvist, O., Sjolin, L., Sieler, J., Steimecke, G. & Hoyer, E. (1979). *Acta Chem. Scand. Ser. A*, **33**, 445–448.

Liu, C. M., Zhang, D. Q., Song, Y. L., Zhang, C. L., Li, Y. L. & Zhu, D. B. (2002). *Eur. J. Inorg. Chem.* **7**, 1591–1594.

McDonagh, A. M., Humphrey, M. G., Samoc, M. & Luther-Davies, B. (1999). *Organometallics*, **18**, 5195–5199.

Pullen, A. E. & Olk, R. M. (1999). *Coord. Chem. Rev.* **188**, 211–262.

Robertson, N. & Cronin, L. (2002). *Coord. Chem. Rev.* **227**, 93–127.

Steimeck, G. & Kirmse, R. (1979). *Phosphorus Sulfur*, **7**, 49–55.

Svenstrup, N. & Becher, J. (1995). *Synthesis*, pp. 215–235.

Wang, C. S., Batsanov, A. S., Bryce, M. R. & Howard, J. A. K. (1998). *Synthesis*, pp. 1615–1618.

Wang, S. F., Huang, W. T., Zhang, T. Q., Yang, H., Gong, Q. H., Okuma, Y., Horikiri, M. & Miura, Y. F. (1999). *Appl. Phys. Lett.* **75**, 1845–1847.

Winter, C. S., Oliver, S. N., Manning, R. J., Rush, J. D., Hill, C. A. S. & Underhill, A. E. (1992). *J. Mater. Chem.* **2**, 443–447.

Zhai, J., Huang, C. H., Wei, T. X., Gan, L. B. & Cao, H. (1999). *Polyhedron*, **18**, 1513–1518.

Zuo, J. L., Yao, T. M., You, F., You, X. Z., Fun, H.-K. & Yip, B. C. (1996). *J. Mater. Chem.* **6**, 1633–1637.

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