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Key indicators

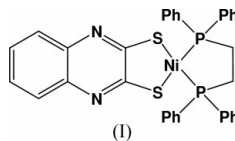
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.055
 wR factor = 0.156
Data-to-parameter ratio = 16.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**[1,2-Bis(diphenylphosphino)ethane]-
(2,3-quinoxalinedithiolato)nickel(II)**

A novel nickel(II) mixed-ligand complex, $[\text{Ni}(\text{C}_8\text{H}_4\text{N}_2\text{S}_2)(\text{C}_{26}\text{H}_{24}\text{P}_2)]$, containing a dithiolate and a phosphine derivative as ligands, was prepared from the reaction of $\text{Ni}(\text{dppe})\text{Cl}_2$ [dppe is 1,2-bis(diphenylphosphino)ethane] with H_2qdt (qdt is 2,3-quinoxalinedithiolate), using Et_3N as a base. The crystal structure of this compound shows a square-planar nickel environment. In the crystal structure, weak $\text{C}-\text{H}\cdots\text{S}$ interactions are the principal intermolecular forces, mediating the formation of ribbons along the b axis.

Received 30 January 2004
Accepted 15 March 2004
Online 20 March 2004

Comment

Diphosphine organodichalcogenide metal complexes have aroused a great deal of interest because of their possible use as catalysts (Thomas & Darkwa, 1998) and their relationship with anticancer activity (Jarrett & Sadier, 1991; Jarrett *et al.*, 1993). Some nickel complexes of this type are known to reversibly absorb sulfur dioxide (Darkwa, 1997). 2,3-Quinoxalinedithiol (H_2qdt) is a classical ligand and forms a series of complexes. These complexes are of interest because of their utilization as conductors (Simao *et al.*, 1999), ion-active substances of membrane electrodes (Inscore *et al.*, 2002) and models of molybdenum hydroxylase enzymes (Bode *et al.*, 1986). Recently, a homologous series of $(\text{dppe})M(\text{mnt})$ [dppe is 1,2-bis(diphenylphosphino)ethane and mnt is maleonitriledithiolate] and $(\text{PPh}_3)_2M(\text{mnt})$ complexes have been found to act as intermediates in the production of exohedrally substituted C_{60} complexes, and excellent model complexes for the spectroscopic and electrochemical behaviour of $\text{C}_{60}M(\text{mnt})$ complexes (Landis *et al.*, 1998). These complexes display some interesting chemistry. In the present paper, a structural study of $\text{Ni}(\text{dppe})(\text{qdt})$, (I), is presented.



The molecular structure of (I) is shown in Fig. 1. The Ni centre exists in a square-planar coordination geometry, composed of two P atoms from the dppe ligand and two S atoms from the qdt ligand. The five-membered ring, Ni1/P1/C33/C34/P2, is puckered, atoms C33 and C34 deviating from the Ni1/S1/S2/P1/P2 coordination plane by -0.332 (2) and 0.261 (2) \AA , respectively. The S1–Ni1–S2 and P1–Ni1–P2 bond angles in the five-membered ring are 91.96 (6) and 86.29 (6) $^\circ$, respectively. The average Ni–S bond distance is 2.166 (1) \AA , while the average Ni–P bond distance is 2.180 (1) \AA . These values are in agreement with those

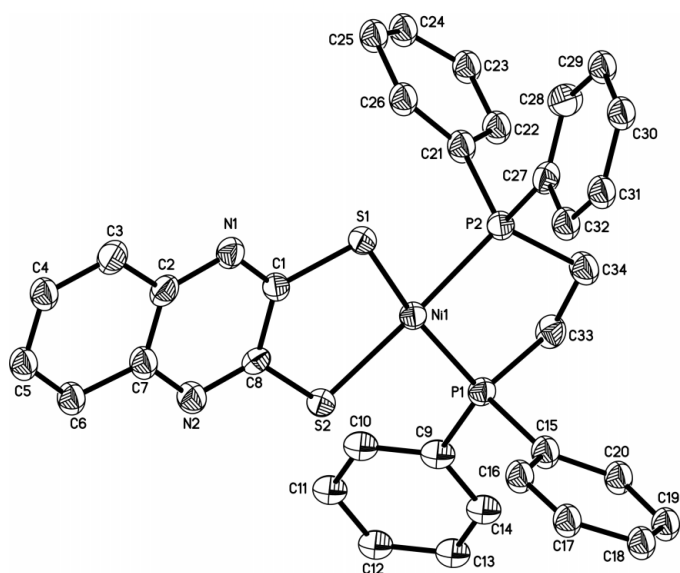


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. All H atoms have been omitted for clarity.

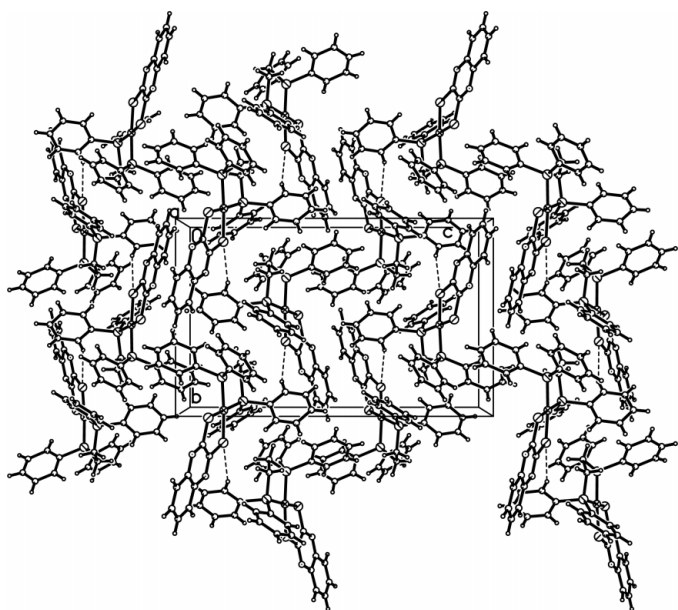


Figure 2
The crystal packing of the title complex, viewed down the *a* axis.

reported for similar complexes (Darkwa, 1997). The dihedral angle between the qdt plane and the Ni1/S2/P2 plane is $6.3(2)^\circ$. The neighbouring benzene planes make dihedral angles of $116.1(2)^\circ$ for the C9/C10/C11/C12/C13/C14 and C15/C16/C17/C18/C19/C20 planes, and $74.0(2)^\circ$ for the C21/C22/C23/C24/C25/C26 and C27/C28/C29/C30/C31/C32 planes.

The bond lengths and angles in (I) have unexceptional values (Table 1). The weak C—H...S interactions play an important role. There is a C20—H20...S2¹ [symmetry code: (i) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$] interaction, with a C20—S2¹ distance of $3.7479(3)$ Å and an H20...S2¹ distance of 2.89 Å. In the crystal structure, every molecule forms such contacts with two neighbours; atom H20 of the aromatic moiety acts as a donor, with atom S2 acting as a weak acceptor (see Fig. 2 and

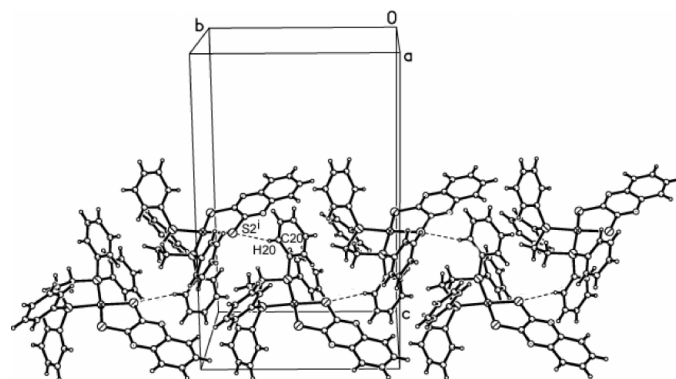


Figure 3
A view of the formation of ribbons along the *b* axis. [Symmetry code: (i) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

Table 2), so that ribbons are formed along the *b* axis. The complex is apolar.

Experimental

To a solution of Ni(dppe)Cl₂ (0.5 g, 0.945 mmol) and H₂qdt (0.184 g, 0.945 mmol) in dimethylformamide (60 ml) was added Et₃N (0.5 ml). The brown solution turned violet-red on addition of Et₃N and was stirred at room temperature for 2 h. After evaporating the solvent *in vacuo*, the red residue was recrystallized from CH₂Cl₂/hexane, yielding pure crystalline Ni(dppe)(qdt) (0.49 g, 80.3%). Red block-shaped single crystals of (I) suitable for X-ray structure determination were obtained by slow evaporation of the filtrate at room temperature over a period of several days. Analysis calculated for C₃₄H₂₈N₂NiP₂S₂: C 62.89, H 4.35, N 4.31%; found: C 62.59, H 4.46, N 4.50%. IR data (cm⁻¹): 3053 (w), 2974 (w), 2939 (w), 1552 (w), 1481 (s), 1434 (s), 1411 (m), 1364 (s), 1253 (s), 1177 (s), 1120 (s), 1101 (m), 878 (m), 818 (s), 761 (s), 747 (s), 691 (s), 665 (w), 598 (m), 525 (s), 482 (s), 441 (m), 423 (m).

Crystal data

[Ni(C₈H₄N₂S₂)(C₂₆H₂₄P₂)]
M_r = 649.35
 Orthorhombic, *P*2₁2₁2₁
a = 11.427 (1) Å
b = 12.947 (1) Å
c = 20.752 (2) Å
V = 3070.2 (5) Å³
Z = 4
D_x = 1.405 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 1624 reflections
 θ = 2.4–16.2°
 μ = 0.90 mm⁻¹
T = 293 (2) K
 Block, red
 0.32 × 0.25 × 0.16 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.76$, $T_{\max} = 0.86$
 16 591 measured reflections

5998 independent reflections
 5513 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -13 \rightarrow 14$
 $k = -15 \rightarrow 13$
 $l = -24 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.156$
 $S = 1.07$
 5998 reflections
 370 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 1.99P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------|-------------|------------|-------------|
| Ni1—S1 | 2.1656 (15) | P1—C33 | 1.822 (6) |
| Ni1—S2 | 2.1671 (14) | P2—C27 | 1.823 (6) |
| Ni1—P2 | 2.1791 (14) | P2—C34 | 1.827 (6) |
| Ni1—P1 | 2.1791 (15) | P2—C21 | 1.845 (5) |
| P1—C9 | 1.809 (6) | S1—C1 | 1.732 (5) |
| P1—C15 | 1.812 (5) | S2—C8 | 1.734 (5) |
| S1—Ni1—S2 | 91.96 (5) | C15—P1—Ni1 | 108.4 (2) |
| S1—Ni1—P2 | 89.41 (6) | C33—P1—Ni1 | 109.03 (19) |
| S2—Ni1—P2 | 175.21 (6) | C27—P2—C34 | 103.6 (3) |
| S1—Ni1—P1 | 170.01 (6) | C27—P2—C21 | 106.8 (3) |
| S2—Ni1—P1 | 93.06 (6) | C34—P2—C21 | 106.5 (3) |
| P2—Ni1—P1 | 86.29 (6) | C27—P2—Ni1 | 116.9 (2) |
| C9—P1—C15 | 107.9 (3) | C34—P2—Ni1 | 110.08 (19) |
| C9—P1—C33 | 103.4 (3) | C21—P2—Ni1 | 112.14 (18) |
| C15—P1—C33 | 103.6 (3) | | |

Table 2

Hydrogen-bonding geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------------|-------|--------------|--------------|----------------|
| C20—H20 \cdots S2 ⁱ | 0.93 | 2.89 | 3.748 (3) | 153 |

Symmetry code: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

All H atoms were positioned geometrically and refined as riding, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}$ of the parent atom ($C-H = 0.93-0.97$ Å). The Flack (1983) parameter was 0.04 (2).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (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*.

This work was funded by the National Natural Science Foundation of China, Jiangsu Science and Technology Department, and the Centre of Analysis and Determination of Nanjing University.

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