

- Gil, E. R. de, de Burguera, M., Rivera, A. V. & Maxfield, P. (1977). *Acta Cryst.* **B33**, 578–579.
- Milbrath, D. S., Springer, J. P., Clardy, J. C. & Verkade, J. G. (1975). *Inorg. Chem.* **14**, 2665–2668.
- Patai, A. & Treinin, A. (1971). In *The Chemistry of the Azido Group*. London: Interscience.
- Rollin, Y., Troupel, M., Tuck, D. G. & Perichon, J. (1986). *J. Organomet. Chem.* **303**, 131–137.
- Rossi, A. & Hoffmann, R. (1975). *Inorg. Chem.* **14**, 365–374.
- Semmelhack, M. F., Helquist, P., Jones, L. D., Keller, L., Mendelson, L., Ryono, L. S., Smith, J. G. & Stauffer, R. D. (1981). *J. Am. Chem. Soc.* **103**, 6460–6471.
- Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Siemens (1993). *XSCANS*. Version 2.00a. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Zembayashi, M., Tamao, K., Yoshida, J.-I. & Kumada, M. (1977). *Tetrahedron Lett.* pp. 4089–4092.
- Zhou, Z.-H. & Yamamoto, T. (1991). *J. Organomet. Chem.* **414**, 119–127.

*Acta Cryst.* (1995). **C51**, 598–600

**trans-Bis(*O,O'*-diethyl dithiophosphato- $\kappa^2S, S'$ )bis(isoquinoline- $\kappa N$ )nickel(II)**

XIAO-YING HUANG

State Key Laboratory of Structural Chemistry,  
Fujian Institute of Research on the Structure of Matter,  
Academia Sinica, Fuzhou 350002, People's Republic  
of China

REN-GEN XIONG AND JUN-XIU DONG

Department of Chemistry and the State Key  
Laboratory of Structural Chemistry, Logistic  
Engineering College, Chongqing, 630042 Shicun,  
People's Republic of China

XIAO-ZENG YOU

Coordination Chemistry Institute and the State  
Key Laboratory of Structural Chemistry, Nanjing  
University, Nanjing, 210008 Jiangsu, People's Republic  
of China

(Received 13 April 1994; accepted 4 October 1994)

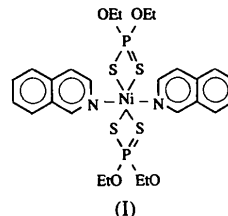
**Abstract**

In (*OC-6-12*)-bis(*O,O'*-diethyl dithiophosphato- $\kappa^2S, S'$ )-bis(isoquinoline- $\kappa N$ )nickel(II), [Ni(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>-(C<sub>9</sub>H<sub>7</sub>N)<sub>2</sub>], a distorted N<sub>2</sub>S<sub>4</sub> octahedron is formed around the central Ni atom. Two *O,O'*-diethyl dithiophosphate (dtp) ions act as bidentate ligands, each forming a four-membered chelate ring by coordination of its

two S atoms in the equatorial plane. Two axial isoquinoline ligands are coordinated to the metal atom through their N atoms. The Ni—S and Ni—N bond distances are 2.507 (2)–2.518 (1) Å and 2.118 (3) Å, respectively.

**Comment**

The structures of the triphenylphosphine and pyridine adducts of (diethyl dithiophosphato)nickel(II) have been reported (Liu, Lin, Yu, Zhu, Xu, Gou & You, 1991; Ooi & Fernando, 1967). In [Ni{(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>{P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}], the Ni atom displays square-pyramidal coordination (Liu *et al.*, 1991), whereas octahedral metal coordination was found in [Ni{(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] (Ooi & Fernando, 1967). Crystals of the title compound, (I), are composed of discrete molecules (Fig. 1) and each Ni atom lies on a crystallographic centre of symmetry. Two dtp ligands are bonded to nickel by their two S atoms, forming four-membered chelate rings in the equatorial plane; the octahedral coordination is completed by the N atoms of two isoquinoline ligands.



The Ni—S distances [2.507 (2) and 2.518 (1) Å] are slightly longer than those in [Ni{(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>{P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}] and [Ni(dtp)<sub>2</sub>] [2.43 (3) and 2.21 Å, re-

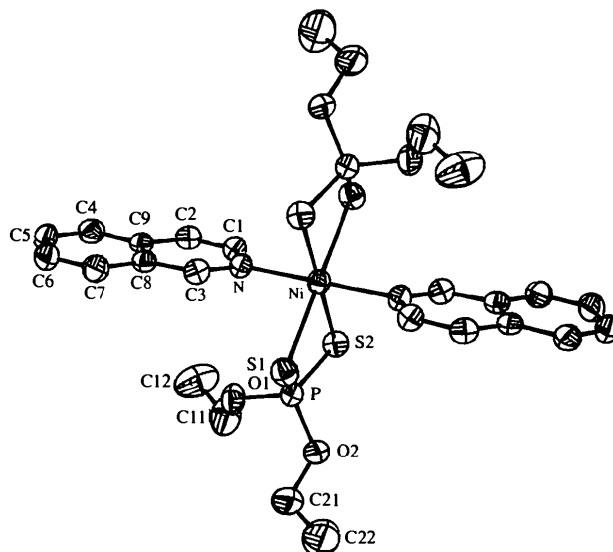


Fig. 1. Molecular structure (ORTEPII; Johnson, 1976) of the title complex showing 40% probability displacement ellipsoids. H atoms are omitted for clarity.

spectively] (Liu *et al.*, 1991; McConnell & Kastalsky, 1967). This probably reflects the change from octahedral coordination in the title compound to square pyramidal in the phosphine adduct and tetrahedral in [Ni(dtp)<sub>2</sub>]. The chelate angle S—Ni—S [81.39(5)°] agrees with values in [Ni{(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] (81.7°), [Ni{(C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] (81.51°) and [Ni{(C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>(C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>)<sub>2</sub>] (81.91°) (Ooi & Fernando, 1967; Liu, Lin, Xu, Yu & You, 1987; You, Xiong, Dong & Huang, 1994).

The C—C distances of 1.394(8) and 1.38(1) Å in the ethyl groups are significantly shorter than the typical C—C single-bond length (1.54 Å). This is probably a result of disorder, which is also apparent from the large displacement parameters of these atoms (see Table 1). The Ni—N distance of 2.118(3) Å is in fairly good agreement with similar distances in [Ni{(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] (2.11 Å) and [Ni{(C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] [2.116(4) Å].

**Experimental**

[Ni{(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub>}<sub>2</sub>] was dissolved in ethanol and excess isoquinoline was added until the colour of the solution changed from purple to green. Crystals of the title compound were obtained after the solution was left to evaporate at room temperature for two weeks.

*Crystal data*

[Ni(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>(C<sub>9</sub>H<sub>7</sub>N)<sub>2</sub>]  
*M<sub>r</sub>* = 687.45  
 Triclinic  
*P*1̄  
*a* = 7.997(4) Å  
*b* = 9.746(6) Å  
*c* = 10.979(2) Å  
 α = 78.87(3)°  
 β = 70.26(3)°  
 γ = 79.48(4)°  
*V* = 783.8(2) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 1.46 Mg m<sup>-3</sup>

*Data collection*

Enraf–Nonius CAD-4 diffractometer  
 ω-2θ scans  
 Absorption correction: refined from Δ*F* (DIFABS; Walker & Stuart, 1983)  
*T*<sub>min</sub> = 0.64, *T*<sub>max</sub> = 0.73  
 3668 measured reflections  
 3415 independent reflections

Mo *K*α radiation  
 λ = 0.71069 Å  
 Cell parameters from 25 reflections  
 θ = 13.97–14.93°  
 μ = 1.011 mm<sup>-1</sup>  
*T* = 296 K  
 Prisms  
 0.42 × 0.34 × 0.28 mm  
 Grey-green  
 2771 observed reflections [*I* > 3σ(*I*)]  
*R*<sub>int</sub> = 0.019  
 θ<sub>max</sub> = 27°  
*h* = 0 → 10  
*k* = -12 → 12  
*l* = -14 → 14  
 3 standard reflections frequency: 60 min intensity decay: 1.5%

*Refinement*

Refinement on *F*  
*R* = 0.049

*w* = 1/σ<sup>2</sup>(*F*)  
 (Δ/σ)<sub>max</sub> = 0.18

*wR* = 0.066  
*S* = 1.84  
 2771 reflections  
 178 parameters  
 H-atom parameters not refined; C—H = 0.95 Å

Δρ<sub>max</sub> = 0.44 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.62 e Å<sup>-3</sup>  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Ni	1	0	1	3.33(4)
S(1)	0.9410(1)	-0.0975(1)	0.8241(1)	4.44(7)
S(2)	1.2913(1)	0.0331(1)	0.8228(1)	4.20(6)
P	1.1573(1)	-0.0098(1)	0.7162(1)	3.94(6)
O(1)	1.0917(3)	0.1261(3)	0.6295(3)	5.2(2)
O(2)	1.2941(4)	-0.1028(3)	0.6126(3)	5.6(2)
N	0.8865(3)	0.2033(3)	0.9356(3)	3.6(2)
C(1)	0.9672(4)	0.3211(3)	0.9228(3)	3.7(2)
C(2)	0.8971(5)	0.4527(3)	0.8852(2)	3.8(2)
C(3)	0.7375(4)	0.2227(4)	0.9075(3)	3.9(2)
C(4)	0.6509(5)	0.6099(4)	0.8186(4)	4.5(3)
C(5)	0.4949(5)	0.6223(4)	0.7915(4)	4.9(3)
C(6)	0.4159(5)	0.5019(5)	0.7997(4)	5.1(3)
C(7)	0.4928(5)	0.3710(4)	0.8360(4)	4.6(3)
C(8)	0.6532(4)	0.3555(3)	0.8655(3)	3.5(2)
C(9)	0.7356(4)	0.4753(4)	0.8558(3)	3.5(2)
C(11)	1.2205(7)	0.2114(6)	0.5341(5)	7.6(4)
C(12)	1.180(4)	0.3529(7)	0.5518(6)	9.3(6)
C(21)	1.2406(9)	-0.1355(8)	0.5071(6)	9.6(6)
C(22)	1.279(1)	-0.2775(8)	0.4956(8)	10.7(8)

Table 2. Selected geometric parameters (Å, °)

Ni—N	2.118(3)	C(1)—C(2)	1.349(5)
Ni—S(2)	2.507(2)	C(2)—C(9)	1.406(5)
Ni—S(1)	2.518(1)	C(3)—C(8)	1.415(5)
S(1)—P	1.972(2)	C(4)—C(5)	1.357(5)
S(2)—P	1.973(1)	C(4)—C(9)	1.415(5)
P—O(1)	1.591(3)	C(5)—C(6)	1.405(6)
P—O(2)	1.584(3)	C(6)—C(7)	1.359(6)
O(1)—C(11)	1.448(5)	C(7)—C(8)	1.403(5)
O(2)—C(21)	1.467(6)	C(8)—C(9)	1.411(5)
N—C(3)	1.302(4)	C(11)—C(12)	1.394(8)
N—C(1)	1.380(4)	C(21)—C(22)	1.38(1)
N—Ni—S(2)	90.64(9)	C(1)—N—Ni	121.1(2)
N—Ni—S(1)	90.06(8)	C(2)—C(1)—N	123.0(3)
N—Ni—S(2')	89.4(1)	C(1)—C(2)—C(9)	120.4(3)
N—Ni—S(1')	89.94(8)	N—C(3)—C(8)	124.7(3)
S(2)—Ni—S(1)	81.39(5)	C(5)—C(4)—C(9)	120.1(4)
P—S(1)—Ni	81.26(5)	C(4)—C(5)—C(6)	120.5(3)
P—S(2)—Ni	81.53(5)	C(7)—C(6)—C(5)	120.9(3)
O(2)—P—O(1)	104.1(2)	C(6)—C(7)—C(8)	119.7(4)
O(2)—P—S(1)	113.9(1)	C(7)—C(8)—C(9)	120.0(3)
O(2)—P—S(2)	106.9(1)	C(7)—C(8)—C(3)	122.5(3)
O(1)—P—S(1)	106.3(1)	C(9)—C(8)—C(3)	117.5(3)
O(1)—P—S(2)	113.1(1)	C(2)—C(9)—C(8)	117.3(3)
S(1)—P—S(2)	112.29(7)	C(2)—C(9)—C(4)	123.9(3)
C(11)—O(1)—P	120.3(3)	C(8)—C(9)—C(4)	118.8(3)
C(21)—O(2)—P	119.8(3)	C(12)—C(11)—O(1)	111.8(5)
C(3)—N—C(1)	117.2(3)	C(22)—C(21)—O(2)	111.9(5)
C(3)—N—Ni	121.7(2)		

Symmetry code: (i) 2 - *x*, -*y*, 2 - *z*.

Data collection was performed using *CAD-4 Software* (Enraf–Nonius, 1989). The structure was solved by direct methods and difference Fourier syntheses, and refined by full-matrix least-squares methods with anisotropic displacement factors for all non-H atoms and isotropic displacement factors for H atoms. All calculations were performed on a MicroVAX 3100 computer with the *TEXSAN* crystallographic system (Molecular Structure Corporation, 1989).

This research is supported by a grant for a key research project from the State Science and Technology Commission, and the Tribology Laboratory of Tsinghu University.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances involving H atoms and torsion angles, have been deposited with the IUCr (Reference: MU1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Liu, S.-X., Lin, C.-C., Xu, Z., Yu, Y.-P. & You, X.-Z. (1987). *Chin. J. Org. Chem.* pp. 369–373.
- Liu, S.-X., Lin, C.-C., Yu, Y.-P., Zhu, D.-L., Xu, Z., Gou, S.-H. & You, X.-Z. (1991). *Acta Cryst.* **C47**, 43–45.
- McConnell, J. E. & Kastalsky, V. (1967). *Acta Cryst.* **22**, 853–859.
- Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Ooi, S. & Fernando, Q. (1967). *Inorg. Chem.* **6**, 1558–1562.
- Walker, N. & Stuart D. (1983). *Acta Cryst.* **A39**, 158–166.
- You, X.-Z., Xiong, R.-G., Dong, J.-X. & Huang, X.-Y. (1994). *Polyhedron*, **13**, 2763–2766.

*Acta Cryst.* (1995). **C51**, 600–602

## Bis(dicyanamide)bis(1,10-phenanthroline)-copper(II)

IVAN POTOČNÁK, MICHAL DUNAJ-JURČO, DUŠAN MIKLOŠ AND MÁRIA KABEŠOVÁ

Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia

LOTHAR JÄGER

Fachbereich Chemie, Martin-Luther-University, Halle-Wittenberg, 06120 Halle/Saale, Germany

(Received 1 July 1994; accepted 25 October 1994)

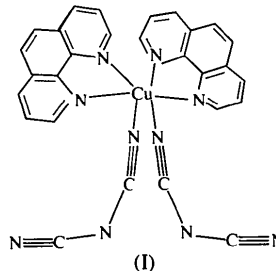
## Abstract

The title compound, [Cu(C<sub>2</sub>N<sub>3</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>], was prepared and its crystal structure was solved as a part of our study on synthesis, crystallochemistry and properties of copper compounds with pseudohalogenide anions. The structure, which is formed by discrete molecules, is presented. The dicyanamide and phen ligands are bonded to the Cu atom with elongated tetragonal bipyramidal

(4+2) coordination geometry, with the dicyanamide ligands in a *cis* arrangement.

## Comment

The crystal structure of the title compound, (I), is formed by discrete molecules held together by van der Waals forces. Fig. 1 shows a molecule of (I) with the atomic labelling scheme.



From a chemical point of view the structure studied is rather uncommon. Coordination polyhedra in copper compounds containing two phen (1,10-phenanthroline) molecules and two monoanions are mostly in the form of distorted trigonal bipyramids (or tetragonal pyramids) with an uncoordinated second monoanion. The Cu atom in (I) is coordinated by two phen molecules and by the dicyanamide anions in a *cis* arrangement, forming an elongated tetragonal bipyramid (4+2). One N atom (N1) of the dicyanamide anion occupies an axial position while the second (N10) is equatorial. The same coordination polyhedron was observed for [Cu(NCS)<sub>2</sub>(phen)<sub>2</sub>] and [Cu(NCSe)<sub>2</sub>(phen)<sub>2</sub>], but in these complexes the cyanate ligands (thio- or seleno-) occupy two equatorial positions (Kabešová & Kožíšková, 1992; Sedov, Kabešová, Dunaj-Jurčo, Gažo & Garaj, 1982). Cyano

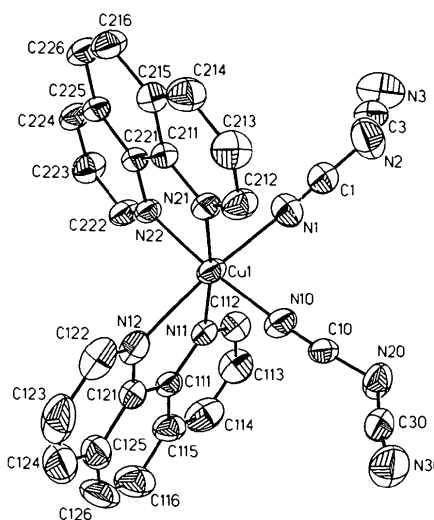


Fig. 1. ORTEP (Johnson, 1965) drawing of the formula unit and labelling of atoms. Displacement ellipsoids are drawn at the 40% probability level.