

## Hexakis(1*H*-imidazole- $\kappa N^3$ )nickel(II) bis[*O,O'*-diisopropyl dithiophosphate(1-)]

Qingli Hao,<sup>a</sup> Fangfang Jian,<sup>a</sup> Xujie Yang,<sup>a</sup> Xin Wang,<sup>a</sup> Ibrahim Abdul Razak,<sup>b</sup> S. Shanmuga Sundara Raj<sup>b</sup> and Hoong-Kun Fun<sup>b\*</sup>

<sup>a</sup>Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China, and <sup>b</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia  
Correspondence e-mail: hkfun@usm.my

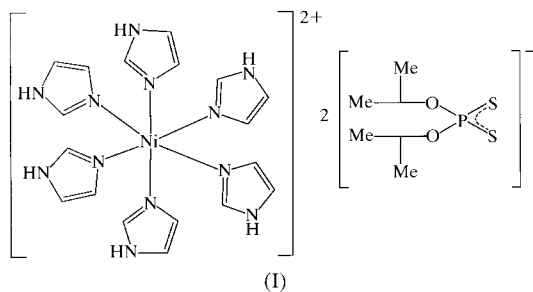
Received 15 August 2000

Accepted 19 September 2000

In the title complex, [Ni(Im)<sub>6</sub>](<sup>i</sup>Pr-dtp)<sub>2</sub> or [Ni(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>6</sub>](C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>, the coordination around the Ni atom, located on an inversion centre, is octahedral with all positions being occupied by tertiary N atoms of the imidazole moieties. Hydrogen bonds link the anions and cations into a two-dimensional network in the *bc* plane.

### Comment

Imidazole is of considerable interest as a ligand in that its presence in many biological systems (for example, in the histidyl residue of proteins) provides a potential binding site for metal ions. Imidazole itself is a monodentate ligand and forms complexes with metal ions through its tertiary N atom. Some complexes of imidazole and its derivatives with transition metal ions have been reported (Brooks & Davidson, 1960; Inoue *et al.*, 1966; Rao & Li, 1966; Eilbeck *et al.*, 1967; Davis & Smith, 1971). Complexes of copper(II) and cobalt(II) with carboxylate and imidazole ligands have been studied as models for metalloproteins since they both contain functionalities in the side chain (Sigel, 1980; Bernarducci *et al.*, 1983;



Abuhijleh & Woods, 1992). In addition, some of these copper(II) compounds were found to have a variety of pharmacological (Tamura *et al.*, 1987) and superoxide dismutase

activities (Bhirud & Srivastava, 1990). Some complexes of zinc(II) play an important role in biological organisms, especially in enzymatic reactions (Vallee & Wacker, 1970).

The asymmetric unit of the title complex, (I), is formed by one half of the hexakis(imidazole)nickel(II) molecule, with the Ni atom located at the center of symmetry, and one *O,O'*-diisopropyl dithiophosphate anion. The Ni1–N1, Ni1–N3 and Ni1–N5 bond distances agree with those of hexakis(imidazole)nickel(II) disalicylate [2.141 (1), 2.120 (1) and 2.124 (1) Å, respectively; Jian *et al.*, 1999] and hexakis(imidazole)nickel(II) bis(4-methoxybenzoate) [2.141 (2), 2.127 (2) and 2.140 (2) Å, respectively; Wang *et al.*, 2000]. The environment around the Ni atom is octahedral, with the N1, N1<sup>i</sup>, N3, N3<sup>i</sup>, N5 and N5<sup>i</sup> atoms occupying all the positions [symmetry code: (i)  $-x, -y, -z$ ]. The two P–S bond lengths of the anions are nearly the same. These bond lengths are different from those when the dialkyl dithiophosphate ligand is coordinated through its S atoms, *e.g.* 1.99 and 1.98 Å in [Ni{(EtO)<sub>2</sub>PS<sub>2</sub>}(py)<sub>2</sub>] (Ooi & Fernando, 1967), and 2.005 (6), 1.925 (6), 1.997 (8) and 1.926 (9) Å in [Zn{(i)PrO)<sub>2</sub>PS<sub>2</sub>}(bipy)] (Harrison *et al.*, 1986). The P–O and C–C bond lengths of the *O,O'*-diisopropyl dithiophosphate anions are comparable with reported values, while the O–C distances are shorter (Hoskins & Tiekink, 1985; Sanz-Aparicio *et al.*, 1986).

All the N–H atoms from the hexakis(imidazole)nickel(II) moiety form N–H...S intermolecular hydrogen bonds with the S atoms of the *O,O'*-diisopropyl dithiophosphate anions (Table 2). One of the S atoms also shows short S...S contacts [S2...S2( $-x, y, \frac{1}{2}-z$ ) 3.350 (2)°]. Hydrogen bonds link the anions and cations into a two-dimensional network parallel to the *bc* plane, with no interactions in the stacking (*i.e.* *a*) direction.

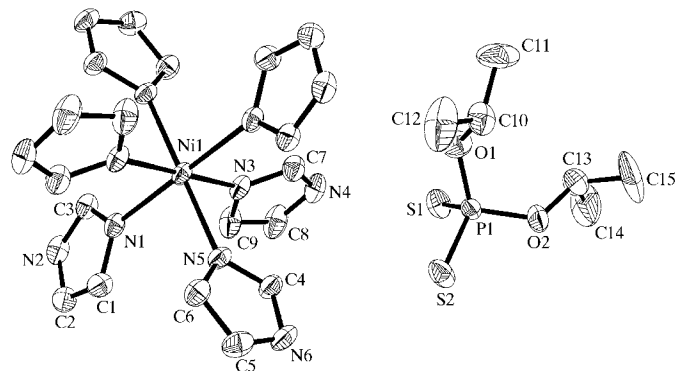


Figure 1

The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

### Experimental

The title compound was prepared by the addition of imidazole (0.06 mmol) to a solution of nickel(II) bis(*O,O'*-diisopropyl dithiophosphate) in EtOH (50 ml). The mixture was heated until dissolved, after which it was cooled and filtered. Light-blue single crystals suitable for X-ray analysis were obtained by recrystallization from anhydrous EtOH solution.

## Crystal data

[Ni(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>6</sub>](C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>  
*M<sub>r</sub>* = 893.73  
 Monoclinic, *C*2/*c*  
*a* = 24.7585 (4) Å  
*b* = 11.4460 (2) Å  
*c* = 16.5815 (1) Å  
 $\beta$  = 112.689 (1)°  
*V* = 4335.32 (11) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.369 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6747 reflections  
 $\theta$  = 1.78–28.38°  
 $\mu$  = 0.762 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Slab, light blue  
 0.40 × 0.34 × 0.12 mm

## Data collection

Siemens SMART CCD area-detector  
 $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.750, *T*<sub>max</sub> = 0.914  
 15 098 measured reflections  
 5353 independent reflections

3099 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.076  
 $\theta$ <sub>max</sub> = 28.45°  
*h* = -13 → 33  
*k* = -15 → 14  
*l* = -22 → 21  
 Intensity decay: negligible

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.072  
*wR* (*F*<sup>2</sup>) = 0.227  
*S* = 1.07  
 5353 reflections  
 241 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1162P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.32 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.65 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1–N3	2.108 (4)	P1–S2	1.9626 (18)
Ni1–N5	2.126 (3)	P1–S1	1.9690 (19)
Ni1–N1	2.140 (3)	O1–C10	1.407 (6)
P1–O2	1.568 (3)	O2–C13	1.441 (6)
P1–O1	1.603 (4)		
N3–Ni1–N5	88.45 (14)	N5–Ni1–N1	91.26 (13)
N3–Ni1–N1	89.03 (13)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N4–H4A···S1	0.86	2.49	3.288 (5)	155
N2–H2B···S2 <sup>i</sup>	0.86	2.59	3.442 (4)	173
N6–H6A···S2 <sup>ii</sup>	0.86	2.66	3.481 (4)	160

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

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms. The highest peak and deepest hole are located 0.94 and 0.78 Å, respectively, from the S1 atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 305/pfizik/610942. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1416). Services for accessing these data are described at the back of the journal.

## References

- Abuhijleh, A. L. & Woods, C. (1992). *Inorg. Chim. Acta*, **194**, 9–14.  
 Bernarducci, E. E., Bharadwaj, P. K., Lanancette, R. A., Jespersen, K. K., Potenza, J. A. & Schugar, M. J. (1983). *Inorg. Chem.* **22**, 3911–3920.  
 Bhirud, R. G. & Srivastava, T. S. (1990). *Inorg. Chim. Acta*, **173**, 121–125.  
 Brooks, P. & Davidson, N. (1960). *J. Am. Chem. Soc.* **82**, 2118–2123.  
 Davis, W. J. & Smith, J. (1971). *J. Chem. Soc. A*, pp. 317–324.  
 Eilbeck, W. J., Holmes, F. & Underhill, A. E. (1967). *J. Chem. Soc. A*, pp. 757–761.  
 Harrison, P. G., Begley, M. J., Kikabhai, T. & Killer, F. (1986). *J. Chem. Soc. Dalton Trans.* pp. 929–938.  
 Hoskins, B. F. & Tiekink, E. R. T. (1985). *Acta Cryst.* **C41**, 322–324.  
 Inoue, M., Kishita, M. & Kubo, M. (1966). *Bull. Chem. Soc. Jpn.* **39**, 1352.  
 Jian, F.-F., Wang, Z.-X., Bai, Z.-P., You, X.-Z., Fun, H.-K. & Chinnakali, K. (1999). *J. Chem. Crystallogr.* **29**, 359–363.  
 Ooi, S. & Fernando, Q. (1967). *Inorg. Chem.* **6**, 1558–1562.  
 Rao, G. N. & Li, N. C. (1966). *Can. J. Chem.* **44**, 1637–1642.  
 Sanz-Aparicio, J., Martinez-Carrera, S. & Garcia-Blanco, S. (1986). *Acta Cryst.* **C42**, 1121–1123.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sigel, H. (1980). *Inorg. Chem.* **19**, 1411–1413.  
 Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.  
 Tamura, H., Imai, H., Kuwahara, J. & Sugiura, Y. (1987). *J. Am. Chem. Soc.* **109**, 6870–6871.  
 Vallee, B. L. & Wacker, W. E. C. (1970). *The Proteins*, Vol. V, edited by H. Neurath, 2nd ed. New York: Academic Press.  
 Wang, Z., Zhang, Y., Razak, I. A., Shanmuga Sundara Raj, S., Fun, H.-K., Li, F. & Song, H. (2000). *Acta Cryst.* **C56**, 161–162.