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## Structure of Diaqua[1,6-bis(4-imidazolyl)-2,5-dithiahexane]nickel(II) Dinitrate

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**Abstract.** [Ni(C<sub>10</sub>H<sub>14</sub>N<sub>4</sub>S<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>,  $M_r = 473.12$ , triclinic,  $P\bar{1}$ ,  $a = 10.306$  (2),  $b = 10.483$  (2),  $c = 10.791$  (2) Å,  $\alpha = 62.46$  (1),  $\beta = 64.66$  (1),  $\gamma = 65.22$  (1)°,  $V = 897.9$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.750$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 13.6$  cm<sup>-1</sup>,  $F(000) = 448$ ,  $T = 293$  K, final  $R = 0.036$  for 2666 observed reflections. The Ni<sup>II</sup> ion is octahedrally coordinated by two imidazole N atoms and two thioether S atoms of the ligand 1,6-bis(4-imidazolyl)-2,5-dithiahexane, and two O atoms of coordinating water molecules. The Ni–N distances are 2.027 (3) and 2.050 (3) Å, the Ni–S distances 2.448 (1) and 2.453 (1) Å, and the Ni–O(aqua) distances 2.077 (2) and 2.084 (3) Å. The non-coordinating nitrate ions are hydrogen-bonded to the nitrogen H atoms of the imidazole groups of the ligand and to the water molecules, forming chains of cations in the structure.

**Introduction.** Coordination compounds with imidazole- and thioether-containing ligands are important as model systems for type I copper proteins. Recently a new method of synthesizing this kind of ligand has been developed (Bouwman & Driessen, 1988). One of the first ligands of this new series used in the preparation of coordination compounds is 1,6-bis(4-imidazolyl)-2,5-dithiahexane (bhdhx). The synthesis and characterization of several transition-metal compounds of bhdhx have been described recently (Bouwman, ten Hove, Driessen & Reedijk, 1988). The complexes with copper and nickel nitrates appeared to be X-ray isomorphous and the crystal structure of the copper compound [Cu(bhdhx)(NO<sub>3</sub>)<sub>2</sub>] has been determined (Bouwman, ten Hove, Driessen & Reedijk, 1988). A second modification of the nickel nitrate compound has been crystallized, and shows Weissenberg photographs different from those of the copper nitrate compound. The crystal structure of this compound, with stoichiom-

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) of the non-H atoms of  $[\text{Ni}(\text{bhdhx})(\text{H}_2\text{O})_2](\text{NO}_3)_2$

	$x$	$y$	$z$	$B_{\text{eq}}$
Ni	0.23199 (4)	0.22790 (4)	0.78998 (4)	2.21 (1)
S4	0.43673 (9)	0.01817 (9)	0.72690 (9)	2.85 (2)
S7	0.05431 (8)	0.11394 (8)	0.81390 (8)	2.63 (2)
O31	0.1201 (4)	0.8620 (3)	0.5479 (3)	5.7 (1)
O32	0.1139 (4)	0.6637 (3)	0.7344 (4)	6.6 (1)
O33	0.2941 (4)	0.6564 (4)	0.5422 (4)	6.6 (1)
O41	0.2481 (3)	0.6130 (3)	1.0462 (3)	4.71 (8)
O42	0.2747 (4)	0.4184 (3)	1.0094 (3)	4.95 (9)
O43	0.4219 (4)	0.5560 (5)	0.8615 (4)	7.7 (1)
O51	0.3652 (3)	0.3541 (2)	0.7519 (3)	3.21 (6)
O61	0.0530 (3)	0.3904 (3)	0.8646 (3)	3.79 (7)
N11	0.2164 (3)	-0.0067 (4)	1.2305 (3)	3.65 (8)
N13	0.2494 (3)	0.0963 (3)	0.9942 (3)	2.55 (7)
N21	0.3015 (4)	0.4039 (4)	0.3371 (3)	4.3 (1)
N23	0.2320 (3)	0.3261 (3)	0.5757 (3)	2.87 (7)
N30	0.1765 (4)	0.7286 (3)	0.6057 (3)	3.50 (8)
N40	0.3172 (3)	0.5285 (3)	0.9713 (3)	3.43 (8)
C5	0.3357 (4)	-0.0523 (4)	0.6818 (4)	3.51 (9)
C6	0.1801 (4)	-0.0581 (4)	0.7851 (4)	3.50 (9)
C10	0.4474 (4)	-0.1144 (4)	0.9082 (4)	3.17 (9)
C12	0.1749 (4)	0.1177 (4)	1.1212 (4)	3.16 (9)
C14	0.3425 (3)	-0.0493 (3)	1.0263 (3)	2.68 (8)
C15	0.3216 (4)	-0.1126 (4)	1.1730 (4)	3.6 (1)
C20	0.0177 (4)	0.2317 (5)	0.6404 (4)	3.9 (1)
C22	0.3294 (4)	0.3872 (4)	0.4556 (4)	3.6 (1)
C24	0.1407 (4)	0.3015 (4)	0.5305 (4)	3.15 (9)
C25	0.1847 (5)	0.3486 (5)	0.3822 (4)	4.4 (1)

Table 2. Geometry of  $[\text{Ni}(\text{bhdhx})(\text{H}_2\text{O})_2](\text{NO}_3)_2$

(a) Selected bond lengths ( $\text{\AA}$ ) involving non-H atoms

Ni S4	2.453 (1)	Ni O61	2.077 (2)
Ni S7	2.448 (1)	Ni N13	2.027 (3)
Ni O51	2.084 (3)	Ni N23	2.050 (3)

(b) Hydrogen-bond distances ( $\text{\AA}$ )

O51 O42	2.833 (5)	N21 O43 <sup>1</sup>	2.800 (5)
O51 O33	2.922 (4)	N11 O31 <sup>11</sup>	2.914 (4)
O61 O32	2.758 (5)		

(c) Selected bond angles ( $^\circ$ ) involving non-H atoms

S4 Ni S7	89.06 (4)	S7 Ni N23	83.2 (1)
S4 Ni O51	96.71 (6)	O51 Ni O61	85.8 (1)
S4 Ni O61	174.24 (7)	O51 Ni N13	94.1 (1)
S4 Ni N13	82.39 (7)	O51 Ni N23	90.9 (1)
S4 Ni N23	88.18 (8)	O61 Ni N13	92.3 (1)
S7 Ni O51	171.59 (6)	O61 Ni N23	97.0 (1)
S7 Ni O61	89.0 (1)	N13 Ni N23	169.8 (1)
S7 Ni N13	92.7 (1)		

Symmetry code: (i)  $1-x, 1-y, 1-z$ ; (ii)  $x, y-1, z+1$ .

etry  $[\text{Ni}(\text{bhdhx})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ , has been determined, and is reported here.

**Experimental.** Blue crystal grown from ethanol at room temperature with approximate dimensions  $0.10 \times 0.20 \times 0.50$  mm. Enraf-Nonius CAD-4 four-circle diffractometer, graphite-monochromatized  $\text{Mo K}\alpha$  radiation. Cell constants from setting angles of 25 reflections with  $11 \leq \theta \leq 14^\circ$ . Corrections for Lorentz and polarization effects. Absorption correction applied empirically, using  $\psi$  scans; transmission coefficients 0.93 to 1.00, normalized to unity.  $\theta_{\text{max}} = 25^\circ$ ,  $h$  0 to

12,  $k$  -12 to 12,  $l$  -12 to 12. Standard reflections 150, 005, 00 $\bar{5}$ , 0 $\bar{5}2$  and 610, intensity variation 1.8%. 3253 measured reflections, 3154 independent,  $R_{\text{int}} = 0.032$ , 488 reflections with  $I < 2\sigma(I)$  were classified as unobserved.

Patterson and Fourier methods.  $F$  used in LS refinement. The H atoms of the water molecules found in difference Fourier maps, all other H atoms placed at 0.98  $\text{\AA}$  from the parent atoms. Least-squares refinement of positional and non-H anisotropic thermal parameters; isotropic thermal factor of the H atoms refined.  $R = 0.036$ ,  $S = 1.71$ ,  $w = [2\text{Lp}F_o/\sigma(I)]^2$ ,  $wR = 0.058$ .  $\Delta_{\text{max}}/\sigma < 0.01$ . Max., min.  $\Delta\rho$  excursions in final difference synthesis 0.51, -0.30  $\text{e \AA}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous-dispersion corrections from Cromer & Liberman (1970). All calculations carried out using the Enraf-Nonius (1979) SDP system of programs on a Microvax II computer.

**Discussion.** Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.\* Selected bond distances, valence angles and hydrogen-bond contacts of the non-H atoms are given in Table 2. The asymmetric unit consists of one molecule of  $[\text{Ni}(\text{bhdhx})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ . An ORTEP projection (Johnson, 1965) of the asymmetric unit and the atomic labelling are given in Fig. 1.

The Ni<sup>II</sup> ion is octahedrally surrounded by two azole N atoms and two thioether S atoms of the ligand bhdhx,

\* Lists of H-atom coordinates, bond distances and angles, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44666 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

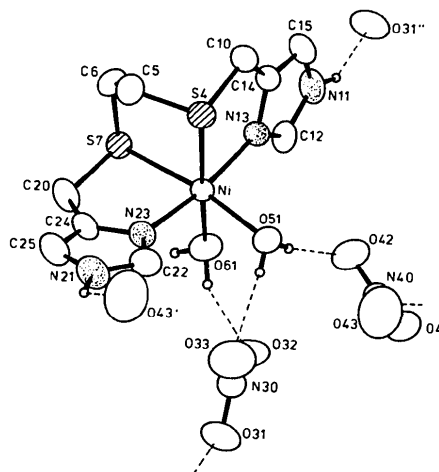


Fig. 1. ORTEP projection (Johnson, 1965) and atomic labelling of the molecular entity  $[\text{Ni}(\text{bhdhx})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ . For clarity the H atoms are omitted, except those which take part in hydrogen bonding.

and two O atoms of the water molecules. Distances from the central metal ion to the donor atoms lie in the broad range of 2.027 (3) to 2.453 (1) Å (see Table 2). The coordination geometry of Ni deviates from an ideal octahedron; the angles vary from 82.39 (7) for S4—Ni—N13 to 97.0 (1)° for O61—Ni—N23 (see Table 2).

The bhdhx molecule is not only coordinated to the Ni<sup>II</sup> ion but is also hydrogen-bonded, through the H atoms on the non-coordinating azole N atoms, to two of the O atoms of the nitrates, with N···O contacts of 2.800 (5) and 2.914 (4) Å. The presence of relatively strong hydrogen bridges was also inferred from the infrared spectrum of this compound, where strong bands in the 2500 to 3200 cm<sup>-1</sup> region occurred.

The precise coordination mode of the nitrates could not be inferred from the infrared spectrum as strong ligand bands occur in the same region as the nitrate absorptions (Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985).

Bond angles around the thioether S atoms are close to 100°, which indicates that one of the lone electron pairs on each of these S atoms is directed towards the Ni ion. The relatively long Ni—S contact of 2.45 Å suggests a weak bond, and is quite normal for Ni—S(thioether) distances (Setzer, Ogle, Wilson & Glass, 1983; Hill & Hope, 1974).

The imidazole rings are planar (distances to the least-squares planes not exceeding 0.008 Å). The

imidazole rings are not mutually coplanar; the dihedral angle is 87.7 (2)°. There is no intermolecular stacking of the aromatic rings. The packing of the molecules is due to normal van der Waals contacts and to the hydrogen bonds described above.

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## Structure of a Binuclear Copper(II) Complex: Tetrakis( $\mu$ -2-chloropropanoato)-bis(triphenylphosphine oxide)dicopper(II)

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**Abstract.** [Cu<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>ClO<sub>2</sub>)<sub>4</sub>{OP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}<sub>2</sub>],  $M_r = 1113.738$ , monoclinic,  $P2_1/n$ ,  $a = 11.191$  (8),  $b = 17.161$  (8),  $c = 13.102$  (4) Å,  $\beta = 91.69$  (3)°,  $V = 2515$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.47$ ,  $D_m = 1.45$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 12.1$  cm<sup>-1</sup>,  $F(000) = 1140$ ,

$T = 300$  K, final  $R = 0.061$  for 2698 observed reflections. The Cu<sup>II</sup> atoms are bridged by 2-chloropropanoate groups forming binuclear [Cu<sub>2</sub>(2-chloropropanoato)<sub>4</sub>(triphenylphosphine oxide)<sub>2</sub>] molecules. The Cu<sup>II</sup> atoms are coordinated by four O atoms from