

cations in series. The lack of interaction between chains is reflected in the poor quality of the crystals.

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Structure of Diaqua[1,6-bis(2-benzimidazolyl)-2,5-dithiahexane]nickel(II) Diperchlorate Monohydrate

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Abstract. $[\text{Ni}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)(\text{OH}_2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $M_r = 666.16$, monoclinic, $C2/c$, $a = 19.502$ (3), $b = 11.048$ (3), $c = 12.878$ (5) Å, $\beta = 109.96$ (3)°, $V = 2607.8$ Å³, $Z = 4$, $D_x = 1.697$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54184$ Å, $\mu = 50.4$ cm⁻¹, $F(000) = 1368$, $T = 293$ K. The final R value is 0.063 for 1763 observed [$I > 3\sigma(I)$] reflections. The Ni atom is octahedrally coordinated to the two pyridine N atoms of the benzimidazolyl groups, the two thioether S atoms and the two water O atoms. The anions, cations and hydrated water molecules are linked by a network of hydrogen bonds.

Experimental. A bluish green crystal of approximate dimensions 0.50 × 0.10 × 0.08 mm was mounted on a glass fibre. The observed systematic absences determined the space group to be Cc or $C2/c$, the latter being confirmed by the subsequent refinement. In the final full-matrix least-squares refinement all non-H atoms were assigned anisotropic thermal parameters; the H atoms were included in the structure-factor calculation with fixed isotropic tem-

perature factors ($B_{\text{iso}} = 4.0$ Å²). More details of the intensity data collection, structure solution and refinement are listed in Table 1. Final atomic coordinates are given in Table 2, distances and angles in Table 3.* Figs. 1 and 2 show the numbering scheme and a stereoview of the $[\text{Ni}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)(\text{OH}_2)_2]^{2+}$ cation, respectively.

Related literature. The structure determination is part of our studies of transition-metal complexes derived from open-chain tetradentate ligands containing NSSN donor atoms (Birker, Helder, Henkel, Krebs & Reedijk, 1982; Castiñeiras, Hiller, Strähle, Paredes & Sordo, 1985; Smits, Janssen, Beurskens, Van Rijn & Reedijk, 1987; Castiñeiras, Carballo,

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, further distances and angles, torsion angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52874 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Data-collection and structure-refinement parameters

Crystal shape	Parallelepiped
Diffractometer used	CAD-4, Enraf-Nonius
Method of intensity measurement	$\theta/2\theta$
No. and θ range (°) of reflections for lattice parameters	25, 19–34
Method used for absorption correction	DIFABS (Walker & Stuart, 1983)
Minimum absorption correction	0.8488
Maximum absorption correction	1.3803
Average absorption correction	0.9990
Maximum value of (sin θ/λ) in intensity measurement (Å ⁻¹)	0.5876
Range of h, k, l	0→22, 0→12, -15→15
Standard reflections	734, 820, 845, measured every 2 h, no intensity variation
Total No. of reflections measured and θ range (°)	2414, 65
No. of unique reflections and R_{int}	2258, 0.027
No. of observed reflections	1763
Criterion for observed reflections	$I > 3\sigma(I)$
Methods used to solve structure	Direct methods (Sheldrick, 1986)
Use of F or F^2 in LS refinement	F
Method of locating H atoms	ΔF map
Weighting scheme	$1/\sigma^2$
Parameters refined	174
Value of R	0.063
Value of wR	0.065
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.02
Max. height in final ΔF map	0.718 e Å ⁻³
Error in an observation of unit weight	3.269
Secondary-extinction coefficient	$1.6010(1) \times 10^{-6}$ (Zachariasen, 1963)
Source of atomic scattering factors	International Tables for X-ray Crystallography (1974)
Computer used	MicroVAX 3500
Programs used	VAXSDP, Version 3.0 (1986) (Frenz, 1978)

Table 2. Positional parameters and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses
$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Ni	0.000	0.3177 (1)	0.250	0.0396 (6)
S(1)	0.05058 (9)	0.4743 (2)	0.1640 (1)	0.0578 (8)
O(1)	0.0437 (2)	0.1817 (4)	0.1833 (3)	0.066 (2)
N(1)	0.0994 (2)	0.3364 (5)	0.3772 (4)	0.041 (2)
N(2)	0.2039 (3)	0.4310 (5)	0.4627 (4)	0.049 (3)
C(1)	0.1300 (3)	0.2895 (5)	0.4848 (5)	0.043 (3)
C(2)	0.1056 (3)	0.1972 (6)	0.5365 (5)	0.054 (3)
C(3)	0.1480 (4)	0.1711 (7)	0.6455 (5)	0.063 (4)
C(4)	0.2125 (4)	0.2329 (7)	0.6992 (5)	0.064 (4)
C(5)	0.2379 (3)	0.3232 (7)	0.6459 (5)	0.058 (3)
C(6)	0.1951 (3)	0.3497 (6)	0.5376 (5)	0.046 (3)
C(7)	0.1463 (3)	0.4186 (6)	0.3703 (5)	0.046 (3)
C(8)	0.1396 (3)	0.4875 (7)	0.2674 (6)	0.062 (4)
C(9)	0.0039 (4)	0.6036 (7)	0.1948 (7)	0.077 (5)
Perchlorate anion				
Cl	0.14059 (8)	0.1757 (2)	0.9877 (1)	0.0601 (9)
O(11)	0.4310 (3)	0.6444 (8)	0.5299 (6)	0.128 (5)
O(12)	0.3103 (4)	0.6131 (7)	0.4278 (6)	0.127 (6)
O(13)	0.1548 (5)	0.7047 (7)	0.505 (1)	0.204 (7)
O(14)	0.3470 (5)	0.640 (2)	0.5986 (6)	0.339 (4)
Solvent				
O(2)	0.500	0.5282 (7)	0.750	0.091 (3)

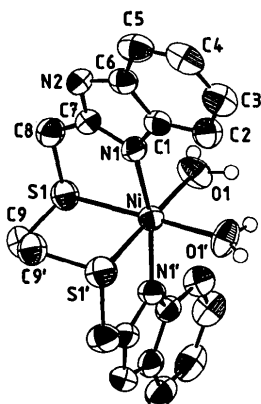
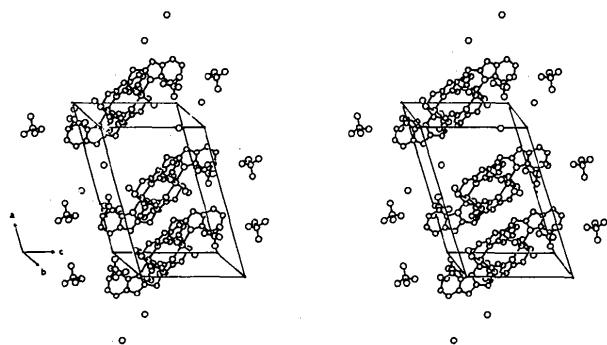
Fig. 1. Plot of the [Ni(C₁₈H₁₈N₄S₂)(OH₂)₂]²⁺ cation showing the numbering scheme.

Fig. 2. A stereoscopic view of part of the unit cell. For clarity the H atoms are omitted.

Table 3. Selected distances (Å) and angles (°) with e.s.d.'s in parentheses

Ni—S(1)	2.437 (2)	N(2)—C(7)	1.336 (6)
Ni—O(1)	2.054 (5)	C(1)—C(2)	1.39 (1)
Ni—N(1)	2.078 (4)	C(1)—C(6)	1.388 (8)
S(1)—C(8)	1.798 (6)	C(2)—C(3)	1.393 (8)
S(1)—C(9)	1.810 (8)	C(3)—C(4)	1.391 (9)
N(1)—C(1)	1.407 (7)	C(4)—C(5)	1.39 (1)
N(1)—C(7)	1.313 (8)	C(5)—C(6)	1.391 (8)
N(2)—C(6)	1.371 (9)	C(7)—C(8)	1.49 (1)
		C(9)—C(9')	1.49 (1)
Cl—O(11)	1.380 (6)	Cl—O(13)	1.352 (8)
Cl—O(12)	1.366 (7)	Cl—O(14)	1.28 (2)
O(11 ⁱⁱ)—H(11)	2.289 (8)	O(11 ⁱⁱ)—O(1)	2.980 (7)
O(2 ⁱⁱⁱ)—H(12)	1.739 (7)	O(2 ⁱⁱⁱ)—O(1)	2.710 (7)
O(11 ^{iv})—H(21)	2.168 (7)	O(11 ^{iv})—O(2)	2.982 (7)
O(12 ^{iv})—H(20)	2.074 (9)	O(12 ^{iv})—N(2)	3.036 (8)
S(1)—Ni—S(1')	89.55 (8)	N(1)—C(1)—C(6)	108.4 (5)
S(1)—Ni—O(1)	92.2 (1)	C(2)—C(1)—C(6)	121.5 (5)
S(1)—Ni—O(1')	177.7 (1)	C(1)—C(2)—C(3)	116.9 (6)
S(1)—Ni—N(1)	82.8 (1)	C(2)—C(3)—C(4)	121.6 (7)
S(1)—Ni—N(1')	89.2 (1)	C(3)—C(4)—C(5)	121.3 (6)
O(1)—Ni—O(1')	86.0 (2)	C(4)—C(5)—C(6)	116.9 (6)
O(1)—Ni—N(1)	89.6 (2)	N(2)—C(6)—C(1)	106.4 (5)
O(1)—Ni—N(1')	98.7 (2)	N(2)—C(6)—C(5)	131.9 (6)
N(1)—Ni—N(1')	168.6 (3)	C(1)—C(6)—C(5)	121.7 (6)
C(8)—S(1)—C(9)	101.9 (3)	N(1)—C(7)—N(2)	113.9 (5)
C(1)—N(1)—C(7)	104.5 (4)	N(1)—C(7)—C(8)	124.1 (5)
C(6)—N(2)—C(7)	107.0 (5)	N(2)—C(7)—C(8)	122.0 (6)
N(1)—C(1)—C(2)	130.1 (5)	S(1)—C(8)—C(7)	112.6 (5)
		S(1)—C(9)—C(9')	115.8 (5)
O(11)—Cl—O(12)	113.5 (6)	O(12)—Cl—O(13)	108.4 (5)
O(11)—Cl—O(13)	114.3 (6)	O(12)—Cl—O(14)	104.2 (8)
O(11)—Cl—O(14)	105.1 (6)	O(13)—Cl—O(14)	111 (2)
O(11 ⁱⁱ)—H(11)—O(1)	144.9 (3)	O(11 ^{iv})—H(21)—O(2)	171.6 (3)
O(2 ⁱⁱⁱ)—H(12)—O(1)	154.3 (2)	O(12 ^{iv})—H(20)—N(2)	154.5 (4)

Symmetry codes: (i) $-x, y, 0.5-z$; (ii) $x, y, z-1$; (iii) $0.5-x, 0.5-y, 1-z$; (iv) $0.5-x, 0.5+y, 1.5-z$.

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Structure of Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-(2,5,8,11,14-pentaoxapentadecane)barium(II)

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Abstract. $[\text{Ba}(\text{C}_5\text{HF}_6\text{O}_2)_2(\text{C}_{10}\text{H}_{22}\text{O}_5)]$, $M_r = 773.71$, triclinic, $P\bar{1}$, $a = 9.506(1)$, $b = 10.969(1)$, $c = 15.085(1)$ Å, $\alpha = 84.10(1)$, $\beta = 88.10(1)$, $\gamma = 65.31(1)^\circ$, $V = 1421.5(3)$ Å³, $Z = 2$, $D_x = 1.808$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 15.1$ cm⁻¹, $F(000) = 760$, $T = 100$ K, $R = 0.020$ for 6391 unique observed diffractometer data [$I \geq 2.5\sigma(I)$]. The barium cation is coordinated by all nine O atoms of the three ligands with Ba—O distances ranging from 2.683 to 2.893 Å. The 2,5,8,11,14-pentaoxapentadecane ligand is wrapped around the Ba in a plane. One hexafluoroacetylacetonate anion is found on top of this plane and one below. Both anions have the ZZ conformation. The absence of short intermolecular interactions explains why the compound sublimates easily.

Experimental. Data were collected at 100 K on an Enraf–Nonius CAD-4F diffractometer for a transparent, colorless crystal (0.6 × 0.5 × 0.5 mm), mounted on a glass fiber. The cell parameters were

calculated by least-squares from the SET4 setting angles of 25 reflections with $16 \leq \theta \leq 18^\circ$. 6755 reflections were scanned [$h - 12:12$, $k - 14:14$, $l - 19:0$; $\theta \leq 27.5^\circ$; $\omega/2\theta$ -scan mode; $\Delta\omega = (0.60 + 0.35 \tan\theta)^\circ$; Zr-filtered Mo $K\alpha$ radiation]. Three reference reflections (04 $\bar{2}$, 440, 30 $\bar{4}$) showed no decay during 64 h of X-ray exposure time. The data were corrected for Lp and for absorption [ABSORB (Spek, 1983), correction factors 1.75–2.15] resulting in the unique set of 6391 reflections [$I > 2.5\sigma(I)$] used in the structure determination. $\sigma^2(I) = \sigma_{cs}^2(I) + (pI)^2$ (McCandlish, Stout & Andrews, 1975) with $p = 0.015$. All non-H atoms were found by direct methods followed by peak optimization (SHELXS86; Sheldrick, 1986) in space group $P\bar{1}$. The correct space group, $P\bar{1}$, was inferred during refinement. The structure was refined on F by full-matrix least-squares procedures using anisotropic thermal parameters for all non-H atoms (SHELX76; Sheldrick, 1976). All H atoms were introduced at calculated positions (C—H = 0.98 Å) and refined in the riding mode on their carrier atoms with three isotropic thermal parameters. Convergence was

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