

C(5), O(1), O(2), O(3) lie in a plane. The C(5)—O(1) [1.329 (4) Å] and C(5)—O(2) [1.311 (4) Å] bonds are longer than C(5)—O(3) [1.238 (4) Å], which has some double-bond character. However, the carbonate chelation is symmetrical, in contrast to the results previously reported for this structure. The carbonate plane makes an angle of 4.9 (1)° with the plane formed by Co(1), O(1), O(2).

Both ethylenediamine molecules show a similar disposition of their chelate rings (λ conformation in the λ enantiomer), with torsion angles N(1)—C(1)—C(2)—N(2) and N(3)—C(3)—C(4)—N(4) of 53.2 (5) and 51.1 (5)°, respectively, very close to the value of 51.6° found in the (+)-[Co(en)₂Cl₂]Cl·H₂O complex (Matsumoto, Ooi & Kuroya, 1970). In addition, this complex shows the same configuration about the central atom as that in λ $\delta\delta(+)$ -[Co^{III}(en)₂Cl₂]Cl while the other enantiomer is Δ $\delta\delta$. Hydrogen bonding includes the chloride ion and the O(1) and O(3) atoms of the carbonate ligand, which are hydrogen bonded to the H atoms of the amine. Symmetry operations and geometrical data for this network are collected in Table 2.

References

- BEURSKENS, G., NOORDIK, J. H. & BEURSKENS, P. T. (1980). *Cryst. Struct. Commun.* **9**, 23–28.
 GARCÍA-GRÁNDA, S., CALVO-PÉREZ, V. & GÓMEZ-BELTRÁN, F. (1992). *Acta Cryst.* Submitted.
 GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.
 HEALY, P. C., KENNARD, C. H. L., SMITH, G. & WHITE, A. H. (1981). *Cryst. Struct. Commun.* **10**, 883–889.
 KIRIYAMA, K. & IGAKI, M. (1988). *Bull. Chem. Soc. Jpn*, **61**, 2817–2823.
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
 MATSUMOTO, K., OOI, S. & KUROYA, H. (1970). *Bull. Chem. Soc. Jpn*, **43**, 3801–3804.
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
 NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
 NORTH, A. C. T., PHILIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1993). **C49**, 324–326

Structure of Diaqua[1,8-bis(2-pyridyl)-3,6-dithiaoctane-*N,N',S,S'*]nickel(II) Diperchlorate at 243 K

BY ELENA BERMEJO, ALFONSO CASTIÑEIRAS* AND RICARDO DOMINGUEZ

Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain

AND JOACHIM STRÄHLE AND WOLFGANG HILLER†

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany

(Received 16 March 1992; accepted 18 June 1992)

Abstract. [Ni(C₁₆H₂₀N₂S₂)(H₂O)₂](ClO₄)₂. *M_r* = 598.12, monoclinic, *P*2₁/*n*, *a* = 11.639 (1), *b* = 13.216 (1), *c* = 15.698 (2) Å, β = 107.48 (1)°, *V* = 2303.2 Å³, *Z* = 4, *D_x* = 1.725 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.70930 Å, μ = 13.072 cm⁻¹, *F*(000) = 1232, *T* = 243 K, final *R* = 0.040 for 3444 observed [*I* > 3 σ (*I*)] reflections. The Ni atom is octahedrally coordinated to the two pyridine N atoms in a *trans* arrangement [Ni—N = 2.104 (2) and 2.106 (2) Å], the two thio-

ether S atoms with a *cis* geometry [Ni—S = 2.4073 (8) and 2.4038 (8) Å] and the two water O atoms [Ni—O = 2.130 (2) and 2.105 (2) Å]. The packing in the crystal results in hydrogen-bond interactions between the water molecules and the perchlorate anions.

Experimental. The title compound was synthesized by reaction of Ni(ClO₄)₂·6H₂O with 1,8-bis(2-pyridyl)-3,6-dithiaoctane (bpdto) in ethyl alcohol. Recrystallization from ethyl alcohol and slow evaporation of the solvent afforded prismatic bluish green single crystals. A specimen (0.15 × 0.25 ×

* Author to whom correspondence should be addressed.

† Permanent address: Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-8046 Garching, Germany.

Table 1. *Data-collection and structure-refinement parameters*

Crystal shape	Prismatic
Diffractometer	Enraf-Nonius CAD-4
Method of intensity measurement	$\omega/2\theta$
No. and θ range ($^\circ$) of reflections for lattice parameters	25, 9–13
Method used for absorption correction	DIFABS11 (Walker & Stuart, 1983)
Minimum absorption correction	0.856
Maximum absorption correction	1.103
Average absorption correction	0.992
Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurement (\AA^{-1})	0.638
Range of h, k, l	0→14, 0→16, -20→20
Standard reflections	04 $\bar{8}$, 42 $\bar{7}$, 22 $\bar{8}$ measured every 1 h, no intensity variation
Total No. of reflections measured and θ range ($^\circ$)	5470, 3–27 (167 unobserved reflections, 233 systematic absences included)
No. of unique reflections, R_{int}	4864, 0.021
No. of observed reflections	3444
Criterion for observed reflections	$I > 3\sigma(I)$
Method used to solve structure	Direct methods (Sheldrick, 1986)
Method of locating H atoms	From ΔF synthesis
Weighting scheme	$1/\sigma^2(F)$
No. of parameters refined	370
R	0.040
wR	0.042
Maximum Δ/σ	0.01
Maximum height in final ΔF map ($e \text{\AA}^{-3}$)	0.763
E.s.d. in an observation of unit weight	1.925
Secondary-extinction coefficient	$5.97(1) \times 10^{-8}$ (Zachariasen, 1963)
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.2A)
Computer used	MicroVAX 3500
Programs used	SDP-VAX, version 3.0 (1986) (Frenz, 1978)

0.20 mm) was mounted on a glass fibre. The structure was solved using direct methods which revealed the positions of all non-H atoms. In the final full-matrix least-squares refinement on F all non-H atoms were assigned anisotropic temperature parameters, and the H-atom positions were refined with B_{iso} fixed at 4.0\AA^2 . More details of the intensity data collection, structure solution and refinement are listed in Table 1. Final positional parameters are given in Table 2, and bond lengths and bond angles in Table 3.* The atomic labelling scheme and molecular structure are shown in Fig. 1, and a stereoview of the unit cell is presented in Fig. 2 (SCHAKAL; Keller, 1988).

Related literature. Crystal structures of related compounds have been reported: 1,8-bis(2-pyridyl)-3,6-dithiaoctane (bpdto) (Castiñeiras, Paredes &

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances, bond angles, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55504 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England. [CIF reference: SH1005]

Table 2. *Positional and equivalent isotropic thermal parameters (\AA^2)*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.				
	x	y	z	U_{eq}
Ni	0.97018 (4)	-0.01087 (4)	0.24140 (3)	0.0188 (2)
Ligand				
S(1)	1.18215 (9)	-0.03997 (8)	0.26749 (7)	0.0263 (4)
S(2)	1.01205 (9)	0.08313 (8)	0.61469 (9)	0.0239 (4)
N(1)	0.9996 (3)	0.1308 (3)	0.3053 (2)	0.024 (1)
N(2)	0.9526 (3)	-0.1513 (3)	0.1752 (2)	0.022 (2)
C(1)	0.9193 (4)	0.1583 (3)	0.3472 (3)	0.024 (2)
C(2)	0.9237 (4)	0.2493 (4)	0.3908 (3)	0.032 (2)
C(3)	1.0159 (5)	0.3156 (4)	0.3930 (3)	0.037 (2)
C(4)	1.0990 (4)	0.2877 (4)	0.3511 (3)	0.037 (2)
C(5)	1.0903 (4)	0.1960 (3)	0.3078 (3)	0.027 (2)
C(6)	1.1830 (4)	0.1683 (3)	0.2620 (3)	0.033 (2)
C(7)	1.2616 (4)	0.0780 (4)	0.3043 (3)	0.033 (2)
C(8)	1.2171 (4)	-0.1132 (4)	0.3695 (3)	0.035 (2)
C(9)	1.1500 (4)	-0.0810 (4)	0.4327 (3)	0.033 (2)
C(10)	0.9545 (4)	-0.2175 (3)	0.3691 (3)	0.030 (2)
C(11)	0.8629 (4)	-0.2391 (3)	0.2784 (3)	0.028 (2)
C(12)	0.9132 (4)	-0.2387 (3)	0.2006 (3)	0.023 (2)
C(13)	0.9186 (4)	-0.3283 (3)	0.1565 (3)	0.030 (2)
C(14)	0.9643 (4)	-0.3300 (4)	0.0848 (3)	0.032 (2)
C(15)	1.0055 (4)	-0.2407 (4)	0.0592 (3)	0.032 (2)
C(16)	0.9979 (4)	-0.1538 (3)	0.1058 (3)	0.027 (2)
Water				
O(1)	0.7797 (2)	0.0041 (2)	0.2088 (2)	0.027 (1)
O(2)	0.9417 (3)	0.0708 (2)	0.1217 (2)	0.028 (1)
Anions				
Cl(1)	0.3738 (1)	0.12819 (9)	0.61252 (7)	0.0394 (5)
O(11)	0.3657 (5)	0.2283 (3)	0.6339 (3)	0.101 (3)
O(12)	0.3229 (4)	0.0664 (3)	0.6654 (3)	0.092 (2)
O(13)	0.4944 (5)	0.1071 (6)	0.6272 (5)	0.179 (5)
O(14)	0.3181 (7)	0.1111 (6)	0.5263 (3)	0.194 (5)
Cl(2)	0.70311 (9)	-0.06421 (8)	-0.04713 (7)	0.0290 (5)
O(21)	1.3088 (3)	0.5060 (3)	0.4549 (2)	0.050 (2)
O(22)	1.1606 (3)	0.5300 (3)	0.5250 (2)	0.051 (2)
O(23)	1.1121 (3)	0.5495 (3)	0.3702 (2)	0.048 (2)
O(24)	1.2336 (3)	0.6685 (3)	0.4662 (3)	0.050 (2)

Table 3. *Selected distances (\AA) and angles ($^\circ$)*

Ni—S(1)	2.407 (1)	Ni—S(2)	2.404 (1)
Ni—O(1)	2.129 (2)	Ni—O(2)	2.105 (3)
Ni—N(1)	2.103 (4)	Ni—N(2)	2.107 (4)
Ligand			
S(1)—C(7)	1.816 (5)	C(15)—C(16)	1.379 (7)
S(1)—C(8)	1.810 (5)	N(2)—C(16)	1.346 (6)
S(2)—C(9)	1.808 (4)	C(1)—C(2)	1.377 (7)
S(2)—C(10)	1.819 (4)	C(2)—C(3)	1.178 (8)
N(1)—C(1)	1.344 (6)	C(3)—C(4)	1.373 (8)
N(1)—C(5)	1.354 (6)	C(4)—C(5)	1.378 (7)
N(2)—C(12)	1.347 (6)	C(5)—C(6)	1.510 (7)
C(12)—C(13)	1.383 (6)	C(6)—C(7)	1.529 (6)
C(13)—C(14)	1.382 (7)	C(8)—C(9)	1.497 (8)
C(14)—C(15)	1.378 (8)	C(10)—C(11)	1.528 (6)
		C(11)—C(12)	1.505 (7)
Anions			
Cl(1)—O(11)	1.375 (4)	Cl(2)—O(21)	1.443 (4)
Cl(1)—O(12)	1.415 (5)	Cl(2)—O(22)	1.438 (4)
Cl(1)—O(13)	1.381 (6)	Cl(2)—O(23)	1.421 (3)
Cl(1)—O(14)	1.333 (5)	Cl(2)—O(24)	1.423 (4)
Hydrogen bonds			
H(11)—O(1)	0.88 (7)	H(21)—O(2)	0.73 (6)
H(11)—O(12)	1.92 (6)	H(21)—O(21)	2.07 (6)
H(12)—O(1)	0.78 (6)	H(22)—O(2)	0.84 (7)
H(12)—O(22)	2.07 (5)	H(22)—O(11'')	2.00 (6)
O(1)—O(12)	2.760 (4)	O(2)—O(11'')	2.823 (4)
O(1)—O(22)	2.836 (3)	O(2)—O(21)	2.800 (4)
S(1)—Ni—S(2)	88.98 (3)	S(1)—Ni—O(1)	174.56 (7)
S(1)—Ni—O(2)	96.45 (7)	S(1)—Ni—N(1)	92.82 (8)
S(1)—Ni—N(2)	83.45 (7)	S(1)—Ni—O(1)	93.01 (7)

Table 3 (cont.)

S(2)—Ni—O(2)	171.38 (7)	S(2)—Ni—N(1)	87.11 (8)
S(2)—Ni—N(2)	94.69 (7)	O(1)—Ni—O(2)	82.2 (1)
O(1)—Ni—N(1)	92.34 (9)	O(1)—Ni—N(2)	91.33 (9)
O(2)—Ni—N(1)	85.9 (1)	O(2)—Ni—N(2)	92.61 (9)
N(1)—Ni—N(2)	175.8 (1)		

Ligand

S(1)—C(7)—C(6)	110.5 (2)	N(1)—C(5)—C(4)	121.0 (4)
S(1)—C(8)—C(9)	114.3 (3)	N(1)—C(5)—C(6)	119.7 (3)
S(2)—C(9)—C(8)	114.2 (2)	C(4)—C(5)—C(6)	119.4 (3)
S(2)—C(10)—C(11)	111.9 (2)	C(5)—C(6)—C(7)	113.8 (3)
C(7)—S(1)—C(8)	102.7 (2)	C(10)—C(11)—C(12)	115.1 (3)
C(9)—S(2)—C(10)	103.0 (2)	N(2)—C(12)—C(11)	119.5 (3)
C(1)—N(1)—C(5)	117.7 (3)	N(2)—C(12)—C(13)	121.0 (3)
C(12)—N(2)—C(16)	118.0 (3)	C(11)—C(12)—C(13)	119.5 (3)
N(1)—C(1)—C(2)	123.4 (4)	C(12)—C(13)—C(14)	120.6 (3)
C(1)—C(2)—C(3)	118.7 (3)	C(13)—C(14)—C(15)	118.5 (3)
C(2)—C(3)—C(4)	118.2 (3)	C(14)—C(15)—C(16)	118.4 (3)
C(3)—C(4)—C(5)	120.9 (3)	N(2)—C(16)—C(15)	123.6 (3)

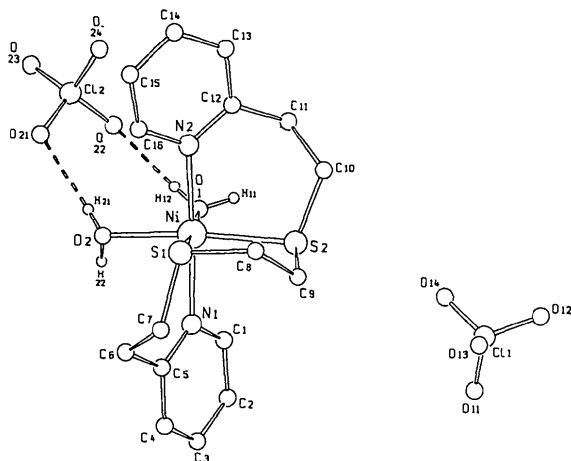
Anions

O(11)—Cl(1)—O(12)	109.9 (3)	O(21)—Cl(2)—O(22)	108.0 (2)
O(11)—Cl(1)—O(13)	107.1 (3)	O(21)—Cl(2)—O(23)	110.2 (2)
O(11)—Cl(1)—O(14)	111.3 (4)	O(21)—Cl(2)—O(24)	109.9 (2)
O(12)—Cl(1)—O(13)	111.7 (3)	O(22)—Cl(2)—O(23)	109.7 (2)
O(12)—Cl(1)—O(14)	109.7 (3)	O(22)—Cl(2)—O(24)	108.6 (2)
O(13)—Cl(1)—O(14)	107.1 (4)	O(23)—Cl(2)—O(24)	110.5 (2)

Hydrogen bonds

O(1)—H(11)—O(12) ^a	163 (5)	O(2)—H(21)—O(21)	172 (6)
O(1)—H(12)—O(22)	169 (5)	O(2)—H(22)—O(11 ^b)	162 (5)

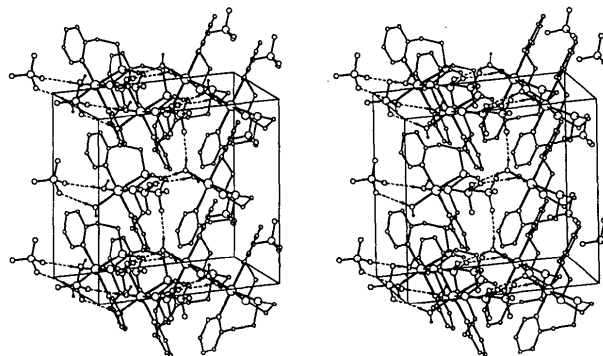
Symmetry code: (i) $1 - x, -y, 1 - z$; (ii) $0.5 + x, 0.5 - y, z - 0.5$.

Fig. 1. Molecular structure of [Ni(C₁₆H₂₀N₂S₂)(H₂O)₂](ClO₄)₂.

Hiller, 1984); (bpdto)copper(I) hexafluorophosphate and perchlorato(bpdto)copper(II) perchlorate (Brubaker, Brown, Yoo, Kinsey, Kutchan & Motte, 1979); diaqua(bpdto)cobalt(II) diperchlorate (Castiñeiras, Hiller, Strähle, Paredes & Sordo, 1985); tricarbonyl(bpdto)molybdenum (Fischer, 1987);

tetraiodo(bpdto)dimercury(II) (Castiñeiras, Díaz, Florencio, García-Blanco & Martínez-Carrera, 1988a); tetrabromo(bpdto)dimercury(II) (Castiñeiras, Díaz, Florencio, García-Blanco & Martínez-Carrera, 1988b).

This work was supported by a grant from Dirección General de Investigación Científica y Técnica (Spain) (PS88-0051).

Fig. 2. Stereoview of the unit cell. *c* is vertical, *a* is horizontal and *b* is in the plane of the paper.

References

- BRUBAKER, G. R., BROWN, J. N., YOO, M. K., KINSEY, R. A., KUTCHAN, T. M. & MOTTE, E. A. (1979). *Inorg. Chem.* **18**, 299–302.
- CASTIÑEIRAS, A., DÍAZ, G., FLORENCIO, F., GARCÍA-BLANCO, S. & MARTÍNEZ-CARRERA, S. (1988a). *J. Crystallogr. Spectrosc. Res.* **18**, 395–401.
- CASTIÑEIRAS, A., DÍAZ, G., FLORENCIO, F., GARCÍA-BLANCO, S. & MARTÍNEZ-CARRERA, S. (1988b). *Z. Anorg. Allg. Chem.* **567**, 101–110.
- CASTIÑEIRAS, A., HILLER, W., STRÄHLE, J., PAREDES, M. V. & SORDO, J. (1985). *Acta Cryst.* **C41**, 41–43.
- CASTIÑEIRAS, A., PAREDES, M. V. & HILLER, W. (1984). *Acta Cryst.* **C40**, 2078–2079.
- FISCHER, B. (1987). Master's thesis. Univ. of Tübingen, Germany.
- FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP - A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTROF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.
- KELLER, E. (1988). *SCHAKAL*. Program for plotting molecular and crystal structures. Univ. of Freiburg, Germany.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.