

References

- Faridoon, Ni Dhubbghaill, O., Spalding, T. R., Ferguson, G., Kaitner, B., Fontaine, X. L. R., Kennedy J. D. & Reed, D. (1988). *J. Chem. Soc. Dalton Trans.* pp. 2739–2745.
- Ferguson, G., Coughlan, S., Spalding, T. R., Fontaine, X. L. R., Kennedy J. D. & Stibr, B. (1990). *Acta Cryst.* **C46**, 1402–1405.
- Frenz, B. A. (1983). *Enraf-Nonius Structure Determination Package; SDP User's Guide*. Version of 6 January 1983. Enraf-Nonius, Delft, The Netherlands.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Mingos, D. M. P., Forsyth, M. I. & Welch, A. J. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1363–1374.
- Spek, A. L. (1991). *PLATON-91*. Univ. of Utrecht, Holland.
- Spek, A. L. (1992). *PLUTON-92*. Univ. of Utrecht, Holland.

Acta Cryst. (1993). **C49**, 961–963

Structure of (1,4,7,10,13-Pentaazacyclopentadecane- $N^1, N^4, N^7, N^{10}, N^{13}$)(perchlorato- O)nickel(II) Perchlorate

TIAN-HUEY LU

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300

WEI-JEN LAN AND CHUNG-SUN CHUNG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

(Received 23 June 1992; accepted 26 October 1992)

Abstract

The structure consists of Ni^{II} with distorted octahedral N_5O coordination. The five $Ni-N$ distances span a very narrow range: 2.051 (7)–2.083 (8) Å. All five five-membered chelate rings are in stable *gauche* form; the chelate angles $N-Ni-N$ of these rings are in the range 82.6 (4)–84.7 (4)°. This structure is expected to be the most stable isomer of $[Ni(C_{10}H_{25}N_5)(ClO_4)]^+$. Four hydrogen bonds between amine groups and perchlorate ions help stabilize the crystal structure.

Comment

There is a great deal of interest in the crystal structures of the complexes of transition metals coordinated with macrocyclic ligands. The macrocyclic ligands form much more stable complexes with 3d transition metals than complexes formed with the corresponding open-chain ligands (Cabbiness & Margerum, 1969). A large volume of work has been

published on tetraaza macrocyclic ligands and their complexes, but little information is available on the pentaaza macrocyclic systems. In order to expand the knowledge in the field of coordination chemistry of pentaaza macrocyclic complexes, we have investigated the X-ray crystal structure of the title compound.

1,4,7,10,13-Pentaazacyclopentadecane was prepared by a published procedure (Bencini, Fabbrizzi & Poggi, 1981). The title complex was obtained by mixing the ligand with a hot equimolar aqueous solution of $Ni(ClO_4)_2 \cdot 6H_2O$. After refluxing for 2 h, the blue-violet crystals were obtained by slow evaporation of the solution. These crystals were recrystallized twice from methanol.

The structure consists of discrete $[Ni([15]aneN_5)(ClO_4)]^+$ cations. Five N atoms from the macrocyclic ligand and one O atom from the perchlorate ion constitute the distorted octahedral coordination polyhedron of the Ni atom. N(1), N(2), N(4) and N(5) of the macrocyclic ligand form a plane; the displacements of the atoms from this plane are shown in Fig. 1. The macrocyclic pentaamine is in a folded structure; the N(3) atom is *cis* to the other N atoms. An O atom of a perchlorate ion is *trans* to N(3); the other perchlorate ion is located far from the bonding range and has a disordered structure. The five $Ni-N$ distances span a very narrow range [2.051 (7)–2.083 (8) Å] and are slightly shorter than the average $Ni-N$ distance for six-coordinate Ni^{II} tetraamine complexes (Lu, Chung & Ashida, 1991). The five-membered chelate rings, except the one that contains disordered C(1) and C(2) atoms, are in stable *gauche* form; the chelate angles $N-Ni-N$ of these rings are in the range 82.6 (4)–84.7 (4)°. This

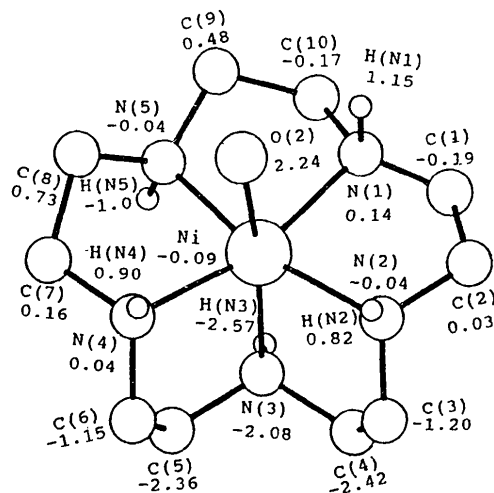


Fig. 1. A perspective view of the molecule excluding two perchlorate ions and the H atoms attached to the C atoms. The atom-numbering scheme is shown as well as the displacements of the atoms from the best plane formed by the atoms N(1), N(2), N(4) and N(5).

structure is expected to be the most stable isomer of $[\text{Ni}(\text{I}5)\text{aneN}_3](\text{ClO}_4)^+$. The dihedral angles between the planes $\text{N}(2)\text{NiN}(3)$ and $\text{N}(1)\text{NiN}(4)$, $\text{N}(2)\text{NiN}(3)$ and $\text{N}(1)\text{NiN}(2)$, as well as $\text{N}(3)\text{NiN}(4)$ and $\text{N}(4)\text{NiN}(5)$ are $108.5(5)$, $107.7(7)$ and $78.1(4)^\circ$, respectively. Four hydrogen bonds between amine H atoms and perchlorate O atoms help stabilize the crystal structure: $\text{N}(1)\text{—H}(\text{N}1)\cdots\text{O}(2)$, $\text{N}(2)\text{—H}(\text{N}2)\cdots\text{O}(2)$, $\text{N}(2)\text{—H}(\text{N}2)\cdots\text{O}(8)$ and $\text{N}(4)\text{—H}(\text{N}4)\cdots\text{O}(2)$ with $\text{N}\cdots\text{O}$ bond lengths of 3.12 (2), 3.09 (1), 3.12 (1) and 2.87 (1) Å, and with $\text{N—H}\cdots\text{O}$ bond angles of $112.7(6)$, $101.5(5)$, $139.5(6)$ and $101.4(5)^\circ$, respectively.

Experimental

Crystal data

$[\text{Ni}(\text{ClO}_4)(\text{C}_{10}\text{H}_{25}\text{N}_5)](\text{ClO}_4)$

$M_r = 472.95$

Monoclinic

$P2_1/n$

$a = 9.822(5) \text{ \AA}$

$b = 13.676(7) \text{ \AA}$

$c = 13.998(4) \text{ \AA}$

$\beta = 96.86(3)^\circ$

$V = 1866.8(14) \text{ \AA}^3$

$Z = 4$

Data collection

Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

empirical, based on Ψ scan (North, Phillips & Mathews, 1968)

$T_{\min} = 0.73573$, $T_{\max} = 0.7395$

6552 measured reflections

3281 independent reflections

Refinement

Refinement on F

Final $R = 0.066$

$wR = 0.074$

$S = 2.03$

2534 reflections

265 parameters

Only H-atom U 's refined

$w = 1.0$

$(\Delta/\sigma)_{\max} = 0.421$

$D_x = 1.683 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.7093 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 9.5\text{--}14.0^\circ$

$\mu = 1.39 \text{ mm}^{-1}$

$T = 298(3) \text{ K}$

Rectangular pillar

$0.53 \times 0.38 \times 0.34 \text{ mm}$

Blue-violet

2534 observed reflections

$[I \geq 2.5(I)]$

$R_{\text{int}} = 0.05$

$\theta_{\max} = 25.0^\circ$

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 16$

$l = -16 \rightarrow 16$

3 standard reflections

frequency: 60 min

intensity variation: $\pm 2.0\%$

$\Delta\rho_{\max} = 0.83(6) \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.72(6) \text{ e \AA}^{-3}$

Extinction coefficient:

$0.53(4)$ (length in mm)

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

O(4)	0.3081 (8)	0.1939 (6)	0.4317 (5)	7.8 (4)
O(1)	0.2231 (10)	0.3380 (7)	0.3709 (8)	10.6 (6)
O(2)	0.2816 (7)	0.2197 (6)	0.2655 (4)	6.2 (3)
O(3)	0.4552 (8)	0.2994 (8)	0.3621 (6)	9.1 (5)
O(5)	0.6997 (8)	0.0518 (7)	0.3565 (5)	8.2 (4)
O(6)*	0.7833 (11)	0.0300 (8)	0.2128 (9)	8.8 (6)
O(6D)*	0.721 (7)	0.076 (5)	0.168 (5)	9.2 (18)
O(7)	0.5499 (8)	0.0462 (7)	0.2151 (6)	9.7 (5)
O(8)	0.7025 (12)	0.1802 (7)	0.2493 (8)	11.3 (6)
N(1)	0.2346 (12)	0.4032 (8)	0.1334 (13)	12.4 (10)
N(2)	0.4783 (8)	0.3069 (8)	0.1313 (6)	6.7 (5)
N(3)	0.3189 (7)	0.2551 (7)	-0.0376 (5)	5.6 (4)
N(4)	0.2709 (11)	0.1076 (6)	0.0913 (7)	7.1 (5)
N(5)	0.0664 (7)	0.2486 (7)	0.0839 (5)	5.6 (4)
C(1)	0.3433 (22)	0.4583 (10)	0.1270 (18)	11.8 (12)
C(2)	0.4786 (18)	0.4129 (13)	0.1502 (12)	10.4 (9)
C(3)	0.5519 (11)	0.2811 (15)	0.0516 (8)	9.8 (11)
C(4)	0.4595 (11)	0.2982 (14)	-0.0432 (8)	9.0 (9)
C(5)	0.3056 (15)	0.1536 (11)	-0.0721 (8)	8.7 (7)
C(6)	0.3408 (19)	0.0809 (10)	0.0090 (9)	10.4 (9)
C(7)	0.1240 (19)	0.0780 (10)	0.0816 (11)	9.8 (9)
C(8)	0.0339 (14)	0.1545 (13)	0.1245 (10)	9.0 (8)
C(9)	0.0138 (11)	0.3352 (13)	0.1281 (9)	8.5 (8)
C(10)	0.0934 (17)	0.4222 (11)	0.1001 (10)	8.7 (8)

*Occupancy: O(6) 0.85; O(6D) 0.15.

Table 2. Selected bond lengths (Å) and angles (°)

Ni—O(2)	2.344 (6)	N(1)—C(1)	1.316 (23)
Ni—N(1)	2.063 (10)	N(1)—C(10)	1.434 (19)
Ni—N(2)	2.082 (8)	N(2)—C(2)	1.477 (21)
Ni—N(3)	2.051 (8)	N(2)—C(3)	1.442 (17)
Ni—N(4)	2.083 (8)	N(3)—C(4)	1.512 (15)
Ni—N(5)	2.051 (7)	N(3)—C(5)	1.471 (17)
Cl(1)—O(4)	1.418 (8)	N(4)—C(6)	1.456 (18)
Cl(1)—O(1)	1.419 (9)	N(4)—C(7)	1.489 (20)
Cl(1)—O(2)	1.430 (6)	N(5)—C(8)	1.456 (17)
Cl(1)—O(3)	1.419 (7)	N(5)—C(9)	1.458 (17)
Cl(2)—O(5)	1.394 (8)	C(1)—C(2)	1.46 (3)
Cl(2)—O(6)	1.421 (10)	C(3)—C(4)	1.535 (16)
Cl(2)—O(6D)	1.38 (7)	C(5)—C(6)	1.516 (19)
Cl(2)—O(7)	1.418 (8)	C(7)—C(8)	1.54 (3)
Cl(2)—O(8)	1.437 (9)	C(9)—C(10)	1.50 (3)
O(2)—Ni—N(1)	90.4 (7)	N(1)—C(1)—C(2)	117.6 (13)
O(2)—Ni—N(2)	88.4 (3)	N(2)—C(2)—C(1)	113.5 (10)
O(2)—Ni—N(3)	160.2 (3)	N(2)—C(3)—C(4)	109.4 (10)
O(2)—Ni—N(4)	80.7 (3)	N(3)—C(4)—C(3)	110.2 (9)
O(2)—Ni—N(5)	90.6 (3)	N(3)—C(5)—C(6)	111.8 (8)
N(1)—Ni—N(2)	82.6 (4)	N(4)—C(6)—C(5)	109.9 (9)
N(1)—Ni—N(3)	106.7 (7)	N(4)—C(7)—C(8)	112.1 (9)
N(1)—Ni—N(4)	164.3 (6)	N(5)—C(8)—C(7)	106.6 (10)
N(1)—Ni—N(5)	82.8 (4)	N(3)—C(4)—H(7)	109.9 (12)
N(2)—Ni—N(3)	84.1 (3)	Ni—O(2)—Cl(1)	139.3 (4)
N(2)—Ni—N(4)	109.9 (4)	Ni—N(1)—C(1)	110.8 (10)
N(2)—Ni—N(5)	165.3 (4)	Ni—N(1)—C(10)	108.5 (9)
N(3)—Ni—N(4)	84.7 (4)	Ni—N(2)—C(2)	108.7 (8)
N(3)—Ni—N(5)	101.3 (3)	Ni—N(2)—C(3)	109.1 (7)
N(4)—Ni—N(5)	84.4 (4)	Ni—N(3)—C(4)	109.3 (6)
O(4)—Cl(1)—O(1)	106.1 (6)	Ni—N(3)—C(5)	108.6 (7)
O(4)—Cl(1)—O(2)	110.3 (5)	Ni—N(4)—C(6)	107.3 (8)
O(4)—Cl(1)—O(3)	110.8 (5)	Ni—N(4)—C(7)	107.0 (8)
O(1)—Cl(1)—O(2)	108.2 (5)	Ni—N(5)—C(8)	106.2 (7)
O(1)—Cl(1)—O(3)	112.3 (6)	Ni—N(5)—C(9)	106.9 (7)
O(2)—Cl(1)—O(3)	108.9 (5)	C(1)—N(1)—C(10)	130.3 (16)
O(5)—Cl(2)—O(6)	108.3 (6)	C(2)—N(2)—C(3)	113.0 (12)
O(5)—Cl(2)—O(7)	111.3 (5)	C(4)—N(3)—C(5)	113.5 (10)
O(5)—Cl(2)—O(8)	109.6 (6)	C(6)—N(4)—C(7)	113.9 (11)
O(6)—Cl(2)—O(7)	108.7 (6)	C(8)—N(5)—C(9)	116.4 (11)
O(6)—Cl(2)—O(8)	106.0 (7)	N(1)—C(10)—C(9)	106.9 (11)
O(7)—Cl(2)—O(8)	112.9 (6)	N(5)—C(9)—C(10)	108.2 (10)

The structure was solved by the Patterson function. Refinement was by full-matrix least squares using anisotropic temperature factors. The H atoms were found by theoretical calculations using isotropic temperature factors. Calculations were performed using *NRCVAX* (Gabe, Le Page, White & Lee, 1987). The high

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

B_{eq} is the mean of the principal axes of the thermal ellipsoid.				
	x	y	z	B_{eq}
Ni	0.27621 (10)	0.25947 (7)	0.10217 (7)	3.46 (4)
Cl(1)	0.31919 (22)	0.26321 (20)	0.35774 (14)	5.02 (10)
Cl(2)	0.6803 (3)	0.07706 (17)	0.25933 (17)	5.10 (10)

value of the R factor seems to arise from the easily disordered perchlorate group, although two sets of independent data were taken and averaged.

The authors thank the National Science Council, Taiwan, for support under grants NSC82-0208-M007-32 and NSC82-0208-M007-119. They are also indebted to Ms Shu-Fang Tung for collection of the X-ray diffraction data.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55785 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1020]

References

- Bencini, A., Fabbrizzi, L. & Poggi, A. (1981). *Inorg. Chem.* **20**, 2544–2549.
 Cabbiness, D. K. & Margerum, D. W. (1969). *J. Am. Chem. Soc.* **91**, 6540–6541.
 Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* **A43**, C-294.
 Lu, T.-H., Chung, C.-S. & Ashida, T. (1991). *J. Chin. Chem. Soc.* **38**, 147–153.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Acta Cryst. (1993). **C49**, 963–965

Structures of $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ and $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$

Y. GAO, J. GUERY AND C. JACOBONI

Laboratoire des Fluorures - URA 449, Faculté des Sciences, Université du Maine, 72017 Le Mans CEDEX, France

(Received 11 May 1992; accepted 25 November 1992)

Abstract

μ -Difluoro-bis[bis(dimethyl sulfoxide)trifluorozirconium], $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$, crystallizes in a monoclinic space group; the structure is built up from isolated $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ bipolyhedra formed by edge sharing of $[\text{ZrF}_5(\text{dmsO})_2]$ pentagonal bipyramids. Diaqua(dimethyl sulfoxide)tetrafluorozirconium dihydrate, $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, crystallizes as a triclinic structure composed of isolated $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]$ pentagonal bipyramids with two non-coordinated H_2O molecules; the F—H and O—H hydrogen-bonding scheme has been determined.

Comment

The structure of tetrafluoro bis(dimethyl sulfoxide) zirconium (I) is built up from isolated $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ bipolyhedra formed by F1—F1 edge-sharing of $[\text{ZrF}_5(\text{dmsO})_2]$ pentagonal bipyramids; the two molecules of dmsO are in the *trans* configuration (Fig. 1). The structure of diaqua tetrafluoro dimethyl sulfoxide zirconium dihydrate (II) is composed of isolated $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]$ pentagonal bipyramids and two non-coordinated water molecules (Fig. 2); the three-dimensional network is ensured by hydrogen bonding as shown in Fig. 3. The distances of possible hydrogen bonds are F1—H51 2.01(3), F2—H22 1.91(3), F3—H32 1.80(3), F4—H42 1.98(4), O4—H21 1.94(4), O4—H52 1.96(3) and O5—H31 1.80(4) Å.

The S—O distances [1.537(3) and 1.541(3) Å for (I), 1.539(1) Å for (II)] are longer than the value of 1.471 Å found for the free dmsO molecule (Viswamitra & Kannan,

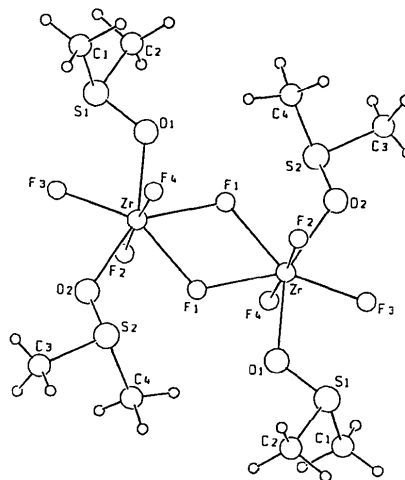


Fig. 1. View of $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ showing atomic labelling scheme.

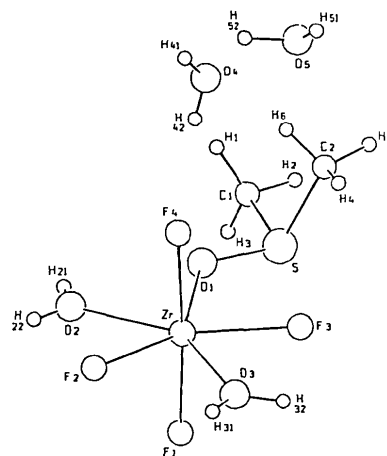


Fig. 2. View of $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ showing atomic labelling scheme.