

Table 3. Deviations (Å) of atoms from the least-squares plane defined by Pt, S(1), S(2), Cl(1) and Cl(2) for five related complexes

Complexes: (a) *cis*-[PtCl₂(*rac-cis*-PrSOCH₂CH₂SOPr)] (this work), (b) *cis*-[PtCl₂(*rac-cis*-PhSOCH=CHSOPh)] (Filgueiras, Holland, Johnson & Raithby, 1982), (c) *cis*-[PtCl₂(*rac*-PhSOCH₂CH₂SOPh)] (Cattalini, Michelin, Marangoni & Pelizzi, 1979), (d) *cis*-[PtCl₂(*meso*-PhSOCH₂CH₂SOPh)] (Cattalini, Michelin, Marangoni & Pelizzi, 1979) and (e) [PtCl₂(C₄H₈OS)₂] (Melanson, de la Chevrotière & Rochon, 1985).

	(a)	(b)	(c)	(d)	(e)
Pt	0.012 (1)	0.012	0.011	0.000	0.001
S(1)	-0.097 (4)	-0.008	-0.005	0.130	0.022
S(2)	0.094 (4)	0.002	-0.001	-0.130	0.001
Cl(1)	-0.094 (5)	-0.008	-0.001	-0.121	0.001
Cl(2)	0.085 (5)	0.002	-0.005	0.121	0.030

The structure was solved by the Patterson method and successive Fourier electron density difference maps, and refined by full-matrix least-squares procedures with anisotropic temperature factors for all non-H atoms. The positions of all H atoms were generated geometrically in the final stages of refinement. Anomalous-dispersion corrections were taken from Cromer & Liberman (1970) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms. Programs used were *SDP* (Enraf–Nonius, 1985), *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

This work has received partial support from CNPq, FAPESP and FINEP, which are hereby gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Cattalini, L., Michelin, G., Marangoni, G. & Pelizzi, G. (1979). *J. Chem. Soc. Dalton Trans.* pp. 96–101.
- Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
- Filgueiras, C. A. L., Holland, P. R., Johnson, B. F. G. & Raithby, P. R. (1982). *Acta Cryst.* **B38**, 954–956.
- Johnson, R. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Melanson, R., de la Chevrotière, C. & Rochon, F. D. (1985). *Acta Cryst.* **C41**, 1428–1431.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S38.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1995). **C51**, 621–623

An Aminobenzylidioxocyclam Nickel(II) Complex

JUSTIN K. MORAN, MARILYN M. OLMSTEAD AND
CLAUDE F. MEARES

Department of Chemistry, University of California,
Davis, California 95616-0935, USA

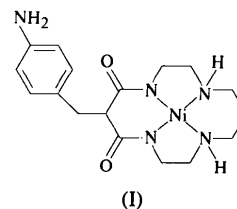
(Received 16 June 1994; accepted 17 October 1994)

Abstract

The title compound, [6-(4-aminobenzyl)-1,11-diaza-4,8-diazanidacyclotetradecane-5,7-dione(2-)- $\kappa^4 N^{1,4,8,11}$]-nickel(II), [Ni(C₁₇H₂₅N₅O₂)], has mirror symmetry with Ni—N(amide) and Ni—N(amine) bond distances of 1.862 (5) and 1.925 (5) Å, respectively. The aromatic ring of the side chain is tipped 21.3 (3)° towards the plane containing the Ni and four N atoms. The distance from the Ni atom to the center of the aromatic ring is 3.551 (5) Å.

Comment

Polyazamacrocyclic ligands have many applications in chemistry, biology and medicine. We have been examining the use of carbon-substituted polyazamacrocycles as bifunctional chelating agents (BCAs) (Moi, Meares, McCall, Cole & DeNardo, 1985). We report here the X-ray crystal structure of an aminobenzylidioxocyclam nickel complex, (I).



The most striking feature of the aminobenzylidioxocyclam nickel structure is that the aromatic ring of the side chain sits 3.551 (5) Å above the Ni atom, with N(amide)—Ni—*Ctr* (where *Ctr* is the center of the aromatic ring) and N(amine)—Ni—*Ctr* angles of 86.3 (1) and 96.3 (1)°, respectively. The aromatic ring is nearly parallel to the plane containing the four N atoms, making a dihedral angle of 21.3 (3)° with it. This is quite different from the structure observed in the previously reported phenyldioxocyclam nickel complex, where the phenyl ring is perpendicular to the plane of the four N atoms with an H atom directed towards the Ni atom (Chinn, Busch & Alcock, 1993).

The structure displays the expected square-planar geometry about the nickel(II) atom coordinated by

the two deprotonated amide N atoms and the two amine N atoms of the macrocyclic ring. The Ni—N(amide) and Ni—N(amine) distances are 1.862 (5) and 1.925 (5) Å, respectively. These bond distances are similar to the values reported for the phenyldioxocyclam nickel structure. The six-membered ring incorporating the two amine N atoms has a chair conformation, while the six-membered dioxo ring adopts a partial-boat conformation. The C—C bond in each the two five-membered rings is in a *gauche* configuration. The two aliphatic amine H atoms are directed towards the same side of the coordination plane, *i.e.* away from the aromatic ring.

In the unit cell, the discrete molecules are linked by hydrogen bonding between the H atoms of the aminobenzyl N atom and the carbonyl O atoms of two other dioxocyclam moieties. The O1...N3($x - \frac{1}{2}, 2 - y, z + \frac{1}{2}$) distance is 2.863 (5) Å. If the H atoms are allowed to refine, the aminobenzyl N atom is slightly pyramidalized with a C11...N3—H3A angle of 117 (1)°; this amounts to a displacement of the H atoms in the direction of the hydrogen bond. An examination of the phenyl ring

geometry shows that the phenyl H atoms remain in the plane of the ring if the constraints of the riding model are removed. Since a few of the macrocyclic C—H distances refined to unreasonably short values in this model, the results are reported for the riding model.

The structures of two other metal-dioxocyclam complexes have been reported, one of a Pt^{II}-methyl-dioxocyclam (Kimura, Korenari, Shionoya & Shino, 1988) and the other of a Tc^V-dioxocyclam (Marchi, Rossi, Magon, Duatti, Casellato, Graziani, Vidal & Riche, 1990). With the exception of the side chain, both of these complexes have structures similar to that reported here.

Experimental

To a solution of 6-aminobenzyl-dioxocyclam (0.45 g, 1.4 mmol) in 16 ml of dimethyl sulfoxide was added nickel(II) perchlorate hexahydrate (1.48 g, 5.6 mmol) and diisopropylethylamine (1.5 ml, 8.7 mmol). After stirring at room temperature for 3 h, a precipitate formed. The solid was filtered and washed with fresh dimethyl sulfoxide. The yellow solid [yield 0.41 g (75%)] was recrystallized from hot dimethyl sulfoxide.

Crystal data

[Ni(C₁₇H₂₅N₅O₂)]

$M_r = 390.13$

Orthorhombic

$Pmn2_1$

$a = 9.415 (3) \text{ \AA}$

$b = 8.103 (2) \text{ \AA}$

$c = 11.957 (3) \text{ \AA}$

$V = 912.2 (4) \text{ \AA}^3$

$Z = 2$

$D_x = 1.420 \text{ Mg m}^{-3}$

Mo K α radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 24 reflections

$\theta = 5.2\text{--}18.5^\circ$

$\mu = 1.084 \text{ mm}^{-1}$

$T = 130 (2) \text{ K}$

Prism

$0.22 \times 0.20 \times 0.16 \text{ mm}$

Yellow

Data collection

Siemens R3m/V diffractometer

ω scans

Absorption correction:

refined from ΔF (XABS; Hope & Moezzi, undated)

$T_{\min} = 0.79$, $T_{\max} = 0.86$

1796 measured reflections

1272 independent reflections

1134 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0128$

$\theta_{\max} = 27.50^\circ$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 10$

$l = -15 \rightarrow 1$

2 standard reflections

monitored every 198 reflections

intensity decay: none

Refinement

Refinement on F^2

$R(F) = 0.0291$

$wR(F^2) = 0.0709$

$S = 1.022$

1272 reflections

124 parameters

H atoms riding with C—H =

0.96 and N—H = 0.94 Å

$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.017$

$\Delta\rho_{\max} = 0.262 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.245 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

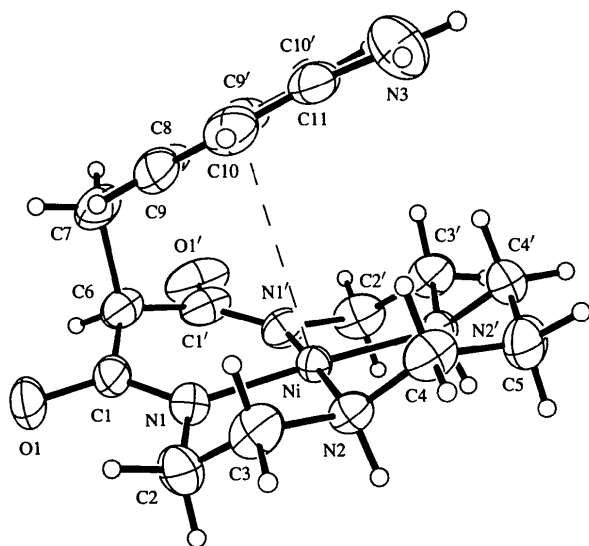


Fig. 1. Molecular structure of the title compound showing 50% probability displacement ellipsoids.

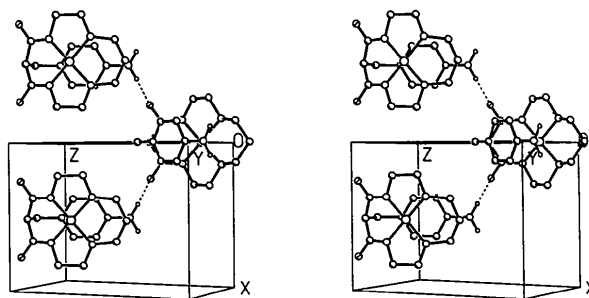


Fig. 2. Packing diagram showing the hydrogen bonding between molecules.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	U_{eq}
Ni	0	0.63340 (6)	0.02252 (6)	0.02670 (14)
O1	0.2444 (4)	0.6394 (3)	0.3011 (3)	0.0662 (10)
N1	0.1442 (6)	0.6147 (4)	0.1284 (4)	0.0386 (11)
N2	0.1493 (5)	0.6418 (4)	-0.0873 (3)	0.0318 (10)
N3	0	1.2000 (6)	-0.1284 (5)	0.067 (2)
C1	0.1378 (5)	0.6460 (5)	0.2371 (3)	0.0456 (10)
C2	0.2816 (4)	0.5796 (5)	0.0782 (4)	0.0492 (11)
C3	0.2856 (4)	0.6737 (5)	-0.0299 (4)	0.0472 (11)
C4	0.1339 (4)	0.7518 (5)	-0.1857 (3)	0.0432 (9)
C5	0	0.7172 (9)	-0.2505 (6)	0.051 (2)
C6	0	0.7012 (7)	0.2877 (5)	0.045 (2)
C7	0	0.8929 (6)	0.3001 (5)	0.053 (2)
C8	0	0.9841 (6)	0.1907 (4)	0.0448 (13)
C9	0.1252 (4)	1.0244 (4)	0.1380 (3)	0.0449 (9)
C10	0.1266 (4)	1.0999 (4)	0.0327 (5)	0.0495 (10)
C11	0	1.1372 (6)	-0.0198 (5)	0.0470 (13)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Ni—N1 ⁱ	1.862 (5)	C2—C3	1.501 (5)
Ni—N2 ⁱ	1.925 (5)	C6—C7	1.561 (7)
O1—C1	1.263 (5)	C7—C8	1.502 (7)
N1—C1	1.325 (6)	C8—C9	1.375 (5)
N1—C2	1.454 (7)	C9—C10	1.401 (7)
N2—C3	1.479 (6)	C10—C11	1.381 (5)
N3—C11	1.394 (7)		
N1 ⁱ —Ni—N1	93.6 (3)	N1—C1—C6	119.5 (5)
N1 ⁱ —Ni—N2 ⁱ	86.24 (10)	N1—C2—C3	106.2 (4)
C1—N1—Ni	128.2 (4)	N2—C4—C5	112.2 (4)
C2—N1—Ni	112.6 (4)	C1 ⁱ —C6—C7	109.6 (3)
C4—N2—Ni	119.4 (3)	C8—C7—C6	114.1 (4)
O1—C1—N1	123.4 (5)	C9—C8—C7	121.0 (2)
O1—C1—C6	117.1 (4)	C10—C11—N3	120.2 (3)

Symmetry code: (i) $-x, y, z$.

Data collection: Siemens P3 software. Cell refinement: Siemens P3 software. Data reduction: XDISK (Siemens, 1991). Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1990). Software used to prepare material for publication: SHELXL93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Chinn, P., Busch, D. H. & Alcock, N. W. (1993). *Acta Cryst.* **C49**, 1284–1286.
- Hope, H. & Moezzi, B. (undated). *XABS. Program to Provide an Empirical Absorption Correction Based on F_o and F_c Differences*. Univ. of California, Davis, USA.
- Kimura, E., Korenari, S., Shionoya, M. & Shino, M. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1166–1168.
- Marchi, A., Rossi, R., Magon, L., Duatti, A., Casellato, A., Graziani, R., Vidal, M. & Riche, F. J. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1935–1940.
- Moi, M. K., Meares, C. F., McCall, M. J., Cole, W. C. & DeNardo, S. J. (1985). *Anal. Biochem.* **148**, 249–253.
- Sheldrick, G. M. (1990). *SHELXTL-Plus. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XDISK. Data Reduction Program*. Version 3.11. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1995). **C51**, 623–625

Tetrakis(acetonitrile-*N*)copper(I) Hexafluorophosphate(V) Acetonitrile Solvate

JANE R. BLACK, WILLIAM LEVASON AND
MICHAEL WEBSTER

*Department of Chemistry, University of Southampton,
Southampton SO17 1BJ, England*

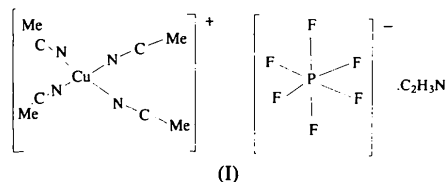
(Received 28 June 1994; accepted 2 November 1994)

Abstract

The chemical species in the asymmetric unit of the title complex, $[\text{Cu}(\text{C}_2\text{H}_3\text{N})_4]\text{PF}_6 \cdot \text{C}_2\text{H}_3\text{N}$, consist of tetrahedral $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ cations [Cu—N 1.968 (6)–2.030 (6) $\text{\AA}$], $[\text{PF}_6]^-$ anions and acetonitrile solvate molecules.

Comment

As part of a study of Cu^{I} complexes with Group 15 and Group 16 donors, we have been studying $[\text{Cu}\{\text{PhSe}(\text{CH}_2)_n\text{SePh}\}_2]^+$ cations. Multinuclear NMR studies show that these exist in solution in acetonitrile as the Se-bonded complexes, with no evidence for substitution by the solvent. Colourless crystals, grown from the mixture by vapour diffusion of diethyl ether, formed over several days but turned white after a few seconds exposure to air. The crystals have been subjected to X-ray examination and shown to be those of the acetonitrile adduct $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6 \cdot \text{MeCN}$, (I).



The cations almost have the expected tetrahedral geometry with N—Cu—N angles in the range 102.7 (3)–114.0 (3) $^\circ$ (see Table 2), and with nearly linear Cu—N—C [168.0 (6)–177.4 (6) $^\circ$] and N—C—C [176.5 (8)–