Monoclinic
$P2_1/n$
$a = 9.8504$ (7) Å
$b = 15.1177$ (10) Å
$c = 11.9574$ (8) Å
$\beta = 95.831$ (1)°
$V = 1771.4$ (2) Å^3
$Z = 4$
$D_x = 1.555$ Mg m^{-3}
D_m not measured

Cell parameters from 4254 reflections
$\theta = 5–25°$
$\mu = 1.709$ mm^{-1}
$T = 293$ (2) K
Pillar
0.30 × 0.29 × 0.20 mm
Colorless

Data collection

Siemens SMART CCD diffractometer
ω scan
Absorption correction: multi-scan based on 4062 symmetry-equivalent reflections (Sheldrick, 1990*b*)
$T_{\min} = 0.558$, $T_{\max} = 0.710$

10 962 measured reflections
4222 independent reflections
2648 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\max} = 28.82°$
$h = -12 \rightarrow 11$
$k = -19 \rightarrow 20$
$l = -6 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.131$
$S = 1.083$
4222 reflections
225 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 1.4143P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.024$
$\Delta\rho_{\max} = 0.535$ e Å^{-3}
$\Delta\rho_{\min} = -0.339$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn1—N3	2.115 (4)	Zn1—N4	2.197 (4)
Zn1—N1	2.149 (4)	Zn1—Cl1	2.284 (1)
Zn1—N2	2.174 (4)		
N3—Zn1—N1	132.3 (1)	N2—Zn1—N4	164.8 (2)
N3—Zn1—N2	89.6 (2)	N3—Zn1—Cl1	113.7 (1)
N1—Zn1—N2	86.4 (2)	N1—Zn1—Cl1	114.0 (1)
N3—Zn1—N4	94.0 (2)	N2—Zn1—Cl1	97.2 (1)
N1—Zn1—N4	80.2 (2)	N4—Zn1—Cl1	94.9 (1)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O3	0.91	2.32	3.218 (6)	170
N2—H1N2···O4	0.91	2.21	3.044 (6)	153
N4—H1N4···O1$^{\rm i}$	0.91	2.29	3.100 (6)	148

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Decay was monitored by repeating the initial frame at the end of data collection and analyzing the duplicate reflections; no decay was observed.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *SHELXL*93.

The authors thank the National Science Council for support under grants NSC86-2811-M007-0041, NSC87-2112-M007-009 and NSC87-2113-M007-041.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1404). Services for accessing these data are described at the back of the journal.

References

Alcock, N. W., Berry, A. & Moore, P. (1992). *Acta Cryst.* C**48**, 16–19.
Alcock, N. W., Herron, N. & Moore, P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1282–1288.
Fabbrizzi, L., Mealli, C. & Paoletti, P. (1979). *J. Chem. Res. (S)*, pp. 170–171.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Hay, R. W. & Tarafder, M. T. H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 823–827.
Ito, T., Kato, M. & Ito, H. (1984*a*). *Bull. Chem. Soc. Jpn*, **57**, 2634–2640.
Ito, T., Kato, M. & Ito, H. (1984*b*). *Bull. Chem. Soc. Jpn*, **57**, 2641–2649.
Kato, M. & Ito, T. (1985). *Inorg. Chem.* **24**, 509–514.
Melnik, M., Györyová, K., Skoršepa, J. & Holloway, C. E. (1995). *J. Coord. Chem.* **35**, 179–279.
Richman, J. E. & Atkins, T. J. (1974). *J. Am. Chem. Soc.* **96**, 2268–2270.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1995). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 714–716

trans-Dichloro[(1*RS*,4*RS*,5*SR*,7*RS*,8*SR*,11*SR*,12*RS*,14*SR*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N]cobalt(III) Perchlorate

Kaliyamoorthy Panneerselvam,[a] Tian-Huey Lu,[a] Shu-Fang Tung,[b] Guey-Sung Liu,[c] Ta-Yung Chi[c] and Chung-Sun Chung[c]

[a]*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300,* [b]*Southern Instrument Center, National Cheng Kung University, Tainan, Taiwan 701, and* [c]*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300. E-mail: thlu@phys.nthu.edu.tw*

(*Received 29 September 1997; accepted 17 December 1997*)

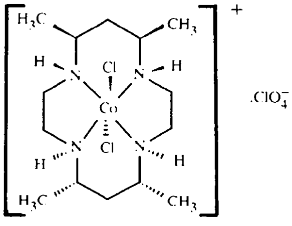
Abstract

The crystal and molecular structure of the title compound, [$CoCl_2(C_{14}H_{32}N_4)$]ClO_4, has been determined. The Co$^{\rm III}$ ion is six-coordinate with a distorted octahedral geometry consisting of the four N atoms of the

macrocyclic ligand in equatorial positions and the two Cl atoms in axial positions. The tetradentate macrocyclic ligand adopts its most stable configuration, with two six-membered rings in chair conformations and two five-membered rings in *gauche* forms.

Comment

Previous papers have dealt with copper(II) and nickel(II) complexes of the macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Hay *et al.*, 1982; Tahirov *et al.*, 1995; Wang *et al.*, 1996). In this study, we report the crystal structure of the cobalt(III) complex, (I), of this tetraaza macrocycle.



(I)

The cation of the title complex has an octahedral geometry around the metal center and has mirror as well as twofold symmetries. The asymmetric unit contains only one quarter of the formula unit. The $\mathrm{Co^{III}}$ ion is located at a center of symmetry, surrounded by four secondary N atoms of the macrocyclic ligand and two *trans*-disposed Cl atoms. All bond lengths and angles in the ligand moiety are normal. The macrocyclic ligand is the same as that obtained from the reduction of the $\mathrm{Ni^{II}}$ complex of *C-meso*-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene according to a previous report (Hay *et al.*, 1982) and the four chiral carbon centers are 5*SR*, 7*RS*, 12*RS* and 14*SR*. The tetradentate macrocyclic ligand adopts its most stable configuration, with two six-membered rings in chair conformations and two five-membered rings in *gauche* forms. The four methyl groups of the macrocyclic ligand are in equatorial positions. The four chiral nitrogen centers are 1*RS*, 4*RS*, 8*SR* and 11*SR*. The chiral H atoms have the *trans*-III type arrangement (Bosnich *et al.*, 1965). The central $\mathrm{Co^{III}}$ ion and four ligand N atoms are exactly coplanar. The Cl1—Co1—Cl1 and N1—Co1—N1 angles are exactly 180°, due to symmetry requirements. The Cl atom (Cl2) of the perchlorato group sits on the special position $0,0,\frac{1}{4}$. There is a hydrogen bond between an O atom of the perchlorato group and an amino group [$\mathrm{N1\cdots O1^{i}}$ 3.306 (5), $\mathrm{H1N1\cdots O1^{i}}$ 2.70 (5) Å and $\mathrm{N1—N1H1\cdots O1^{i}}$ 132 (4)°; symmetry code: (i) $1-x$, $-y$, z].

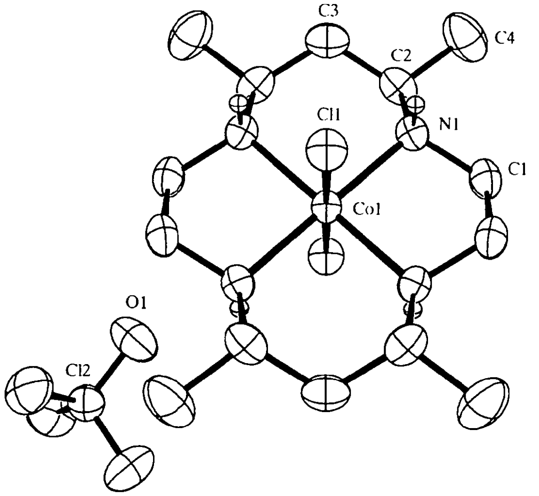


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been excluded, except for the H atoms of the amido groups, and all non-H atoms of one quarter of the formula unit are labeled.

Experimental

5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate was prepared according to the method of Kolinski & Korybut-Daszkiewicz (1975). To a suspension of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate (10 g) in methanol (200 ml) was added $\mathrm{NaBH_4}$ (5 g) in small portions at 273 K. Upon completion of the addition, the solution was refluxed for 2 h and cooled to room temperature. The white precipitate which formed was filtered and dissolved in sodium hydroxide solution (2 *M*). The aqueous solution was continuously extracted with chloroform. The chloroform solvent of the extract was removed on a rotary evaporator. The title complex was prepared according to the method of Hay *et al.* (1984). Cobalt(II) chloride hexahydrate (0.46 g) and (5*SR*,7*RS*,12*RS*,14*SR*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane (0.5 g) were dissolved in methanol (50 ml) to give a brown solution. The solution was aerated with a rapid stream of air for 2 h and then treated with concentrated HCl (37%, 3 ml). Aeration was continued until the solution volume was reduced to *ca* 35 ml. Water (25 ml) was then added followed by $\mathrm{HClO_4}$ (70–72%, 0.5 ml). A pale-green complex was obtained immediately and was filtered off, washed with ethanol, then diethyl ether and dried *in vacuo*. The green crystals were recrystallized from a mixture of HCl (0.1 *N*) and dimethyl sulfoxide.

Crystal data

$\mathrm{[CoCl_2(C_{14}H_{32}N_4)]ClO_4}$
$M_r = 485.72$
Tetragonal
$P4_2/m$
$a = 7.711\,(2)$ Å
$c = 17.076\,(2)$ Å
$V = 1015.2\,(4)$ Å^3
$Z = 2$
$D_x = 1.589$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.46$–$28.82°$
$\mu = 1.267$ mm^{-1}
$T = 293\,(2)$ K
Pillar
0.500 × 0.251 × 0.126 mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.637$, $T_{\max} = 0.852$
1376 measured reflections
1209 independent reflections
932 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 27.42°$
$h = -6 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections frequency: 60 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.133$
$S = 1.318$
1209 reflections
98 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 1.5088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.023$
$\Delta\rho_{\max} = 0.663$ e Å^{-3}
$\Delta\rho_{\min} = -0.644$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Co1	1/2	0	0	0.0275 (3)
Cl1	0.2851 (2)	0.1968 (2)	0	0.0389 (4)
N1	0.6270 (4)	0.1234 (4)	0.0856 (2)	0.0338 (7)
C1	0.5291 (6)	0.0927 (6)	0.1592 (2)	0.0421 (9)
C2	0.6709 (6)	0.3103 (5)	0.0743 (2)	0.0412 (10)
C3	0.7741 (9)	0.3335 (8)	0	0.0446 (14)
C4	0.7664 (11)	0.3865 (8)	0.1446 (4)	0.0693 (17)
Cl2	0	0	1/4	0.0433 (5)
O1	0.1143 (5)	0.0997 (5)	0.2026 (2)	0.0712 (11)

Table 2. *Selected geometric parameters (Å, °)*

Co1—N1	2.001 (3)	C1—C1^{i}	1.498 (9)
Co1—Cl1	2.2466 (14)	C2—C3	1.509 (6)
N1—C1	1.484 (5)	C2—C4	1.525 (7)
N1—C2	1.492 (5)	Cl2—O1	1.422 (3)
N1^{ii}—Co1—N1	180.0	C2—N1—Co1	118.4 (3)
N1—Co1—N1^{iii}	93.9 (2)	N1—C1—C1^{i}	107.7 (3)
N1—Co1—N1^{i}	86.1 (2)	N1—C2—C3	110.1 (4)
N1^{iii}—Co1—N1^{i}	180.0	N1—C2—C4	112.3 (4)
N1—Co1—Cl1^{ii}	87.72 (10)	C3—C2—C4	111.2 (5)
N1—Co1—Cl1	92.28 (10)	C2^{iii}—C3—C2	114.6 (5)
Cl1^{ii}—Co1—Cl1	180.0	O1^{iv}—Cl2—O1^{v}	108.9 (2)
C1—N1—C2	112.3 (3)	O1^{iv}—Cl2—O1	110.7 (4)
C1—N1—Co1	107.0 (2)	O1^{vi}—Cl2—O1	108.9 (2)

Symmetry codes: (i) $1 - x, -y, z$; (ii) $1 - x, -y, -z$; (iii) $x, y, -z$; (iv) $-x, -y, z$; (v) $-y, x, \frac{3}{2} - z$; (vi) $y, -x, \frac{3}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*93.

The authors thank the National Science Council for support under grants NSC87-2112-M007-009, NSC87-2811-M007-0048 and NSC87-2113-M007-041.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1261). Services for accessing these data are described at the back of the journal.

References

Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. 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.

Hay, R. W., Bembi, R. & House, D. A. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1921–1926.

Hay, R. W., Jeragh, B., Ferguson, G., Kaitner, B. & Ruhe, B. L. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1261–1266.

Kolinski, R. A. & Korybut-Daszkiewicz, B. (1975). *Inorg. Chim. Acta*, **14**, 237–245.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

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

Tahirov, T.-H., Lu, T.-H., Liu, G.-S., Chi, T.-Y. & Chung, C.-S. (1995). *Acta Cryst.* C**51**, 2018–2020.

Wang, A., Lee, T.-J., Chi, T.-Y., Liao, F.-L., Liu, G.-S. & Chung, C.-S. (1996). *Acta Cryst.* C**52**, 806–807.

Acta Cryst. (1998). C**54**, 716–719

R$_3$PAuCN Complexes: [{Ph$_2$(cyclohexyl)P}AuCN] and [{(*m*-Tolyl)$_3$P}AuCN]

A. R. AL-ARFAJ,[a] J. H. REIBENSPIES,[b] M. SAKHAWAT HUSSAIN[a]† AND A. A. ISAB[a]

[a]*Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia, and* [b]*Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA. E-mail: sakhawat@dpc.kfupm.edu.sa*

(*Received 22 September 1997; accepted 18 November 1997*)

Abstract

Linear complexes of cyanogold with cyclohexyldiphenylphosphine {cyano(cyclohexyldiphenylphosphine)gold(I), [Au(CN)(C$_{18}$H$_{21}$P)]} and tri(*m*-tolyl)phosphine {cyano[tri(*m*-tolyl)phosphine]gold(I), [Au(CN)(C$_{21}$H$_{21}$P)]} were synthesized and their crystal structures were compared with those of similar complexes. Irrespective of the differences in the anions (CN$^-$ *versus* Cl$^-$) or in the steric and electronic requirements of the various

---

† Work carried out during sabbatical leave at Texas A&M University, College Station, Texas, USA.