Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.476$, $T_{max} = 0.539$
10 628 measured reflections
4186 independent reflections
3964 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 28.55°$ (97% complete to 26°)
$h = -17 \rightarrow 21$
$k = -14 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.043$
$S = 1.03$
4186 reflections
222 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0092 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.580 (6)

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

Zn(1)—N(11)	2.0363 (13)	Zn(1)—N(6)	2.0484 (13)
Zn(1)—N(1)	2.0429 (13)	Zn(1)—Cl(1)	2.2010 (4)
N(11)—Zn(1)—N(1)	104.76 (5)	N(11)—Zn(1)—Cl(1)	117.37 (4)
N(11)—Zn(1)—N(6)	104.45 (5)	N(1)—Zn(1)—Cl(1)	113.21 (4)
N(1)—Zn(1)—N(6)	102.41 (5)	N(6)—Zn(1)—Cl(1)	113.13 (4)

H atoms were added at calculated positions and refined using a riding model (including free rotation about C—C bonds for methyl groups). Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to $1.2U_{eq}$ (or $1.5U_{eq}$ for methyl H atoms) of the carrier atom.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXTL/PC*.

These studies were made possible by funding from the Monsanto Company whose support is greatly appreciated. EPSRC and Siemens plc generously supported the purchase of the SMART diffractometer. We wish to acknowledge the use of the EPSRC's Chemical Database Service at the Daresbury Laboratory, Cheshire, England (Fletcher *et al.*, 1996), for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1373). Services for accessing these data are described at the back of the journal.

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The Monomeric Form of a Cobalt(III) Complex of a Tetraaza Macrocyclic Ligand with a Dangling Carboxylate Arm

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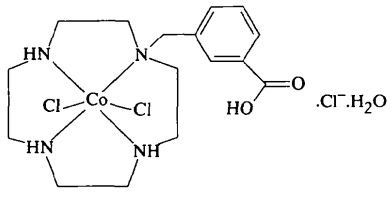
Abstract

The monomeric structure of *cis*-dichloro[3-(1,4,7,10-tetraazacyclododecan-1-yl)toluic acid-κ^4N]cobalt(III) chloride monohydrate, [$CoCl_2(C_{16}H_{26}N_4O_2)$]Cl.$H_2O$, has been determined. Previous work has only yielded crystals of the dinuclear complex or the monomeric complex in powdered form. Crystallization was effected from concentrated hydrochloric acid which contributed to the retention of the chlorides coordinated to the cobalt as well as providing the chloride counter-anion. Hydrogen bonding of the hydroxyl group of the carboxylic acid function to the chloride counter-anion played a significant role in the formation of crystals of this species.

Comment

Modelling of active sites of hydrolytic enzymes such as carboxypeptidase A has led to the design of the ligand 1,4,7,10-tetraazacyclododecane-*N*-*m*-toluic acid, L^{II}H. The first studies of its complexes (DelDonno *et al.*, 1990) yielded the dinuclear cobalt(III) complex. Its structure determination was useful in validating the design of the ligand which was intended to provide a specific chelation mode (*cis*-tetradentate) and to provide an additional nucleophilic function that would be unable to coordinate to the same metal ion. Later work (Zhang & Busch, 1993) led to the chloride of the monomeric complex, but only in powdered form.

The present single-crystal X-ray analysis establishes that the asymmetric unit of the title compound, (I), contains $[Co(L^{II}H)Cl_2]^+$ cations and free chloride anions, with one lattice water molecule. The structure of the cation is shown in Fig. 1.



(I)

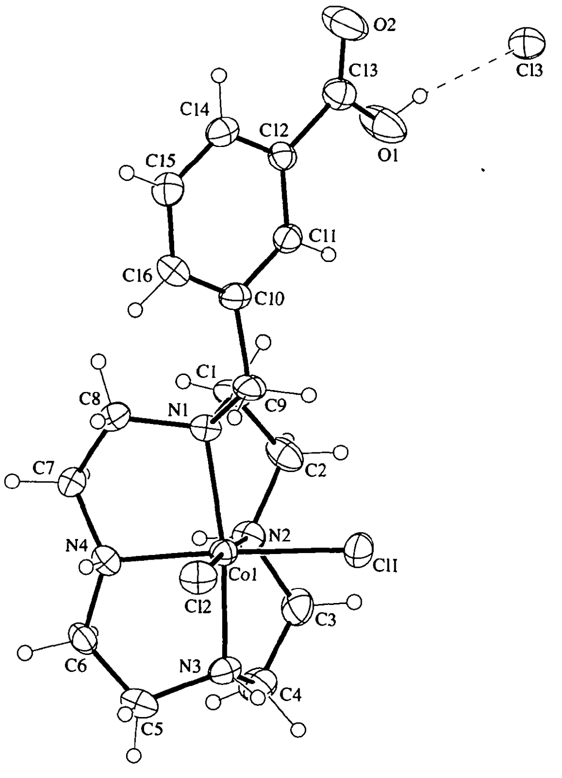


Fig. 1. View of the molecule showing the atomic numbering and the hydrogen-bonded free chloride ion. Displacement ellipsoids are drawn at the 50% probability level.

As previously observed (DelDonno *et al.*, 1990), the macrocycle is coordinated to the metal ion in a folded *cis* manner, with the Co^{3+} ion having a distorted octahedral geometry. Molecular distances are similar to those previously reported. The only well defined hydrogen bond is that between the hydroxyl group of the carboxylic acid function and the chloride counter-anion [O1···Cl3 3.00 (3) Å]. The solvent water molecule is weakly hydrogen bonded to Cl2 and Cl3 [3.43 (1) and 3.36 (1) Å, respectively]. The packing shows an edge-to-face π–π stacking interaction across a centre of inversion (symmetry code: $-x-1$, $1-y$, $-z$). The π–π distance is around 3.26 Å, with a ring-centre–ring-centre distance of 3.46 Å.

Experimental

The title complex was prepared according to the procedure of Zhang & Busch (1993). Small rectangular violet crystals of X-ray quality were obtained by dissolving pure $[Co(L^{II}H)Cl_2]Cl.H_2O$ in its powdered form in boiling concentrated hydrochloric acid and slowly cooling the solution.

Crystal data

$[CoCl_2(C_{16}H_{26}N_4O_2)]Cl.H_2O$
$M_r = 489.70$
Monoclinic
$P2_1/n$
$a = 7.3941\ (5)$ Å
$b = 10.532\ (1)$ Å
$c = 25.684\ (2)$ Å
$\beta = 90.585\ (5)°$
$V = 2000.09\ (5)$ Å^3
$Z = 4$
$D_x = 1.626$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4749 reflections
$\theta = 3$–$20°$
$\mu = 1.284$ mm^{-1}
$T = 180\ (2)$ K
Lath
0.40 × 0.20 × 0.08 mm
Purple

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.75$, $T_{max} = 0.96$
11 991 measured reflections
4685 independent reflections
3231 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 28.74°$ (97% complete to 26°)
$h = -9 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -32 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.100$
$S = 1.060$
4685 reflections
248 parameters
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 1.95P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

H atoms treated by a mixture of independent and constrained refinement
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Co1—N4	1.938 (3)	Co1—Cl1	2.2786 (10)
Co1—N2	1.941 (3)	Co1—Cl2	2.2826 (9)
Co1—N3	1.956 (3)	Cl3···O1	3.000 (3)
Co1—N1	2.054 (3)		
N4—Co1—N2	96.07 (12)	N3—Co1—Cl1	92.84 (9)
N4—Co1—N3	85.58 (11)	N1—Co1—Cl1	97.60 (8)
N2—Co1—N3	84.66 (11)	N4—Co1—Cl2	85.59 (8)
N4—Co1—N1	85.36 (11)	N2—Co1—Cl2	176.69 (9)
N2—Co1—N1	84.30 (11)	N3—Co1—Cl2	92.62 (8)
N3—Co1—N1	164.89 (11)	N1—Co1—Cl2	98.71 (8)
N4—Co1—Cl1	172.75 (8)	Cl1—Co1—Cl2	87.42 (4)
N2—Co1—Cl1	90.82 (9)		

The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures with different φ angles for the crystal; each 10 s exposure covered 0.3° in ω. The crystal-to-detector distance was 5.0 cm. Coverage of the unique set was over 97% complete to at least 26° in θ. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. The H atom attached to O1 was included and refined freely. Although the H atoms on the lattice water were visible on difference maps, they were not included. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

EPSRC and Siemens plc generously supported the purchase of the SMART diffractometer. The Warwick–Kansas collaboration has been supported by NATO.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1372). Services for accessing these data are described at the back of the journal.

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(1,3-Butadiynyl-C^1)(η^5-cyclopentadienyl)(triphenylphosphine-P)nickel(II)

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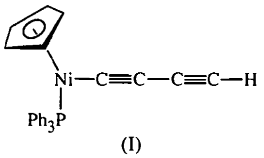
Abstract

The title compound, $[Ni(Cp)(PPh_3)(C{\equiv}C{-}C{\equiv}C{-}H)]$ or $[Ni(C_4H)(C_5H_5)(C_{18}H_{15}P)]$, has metal–ligand dimensions of Ni—P 2.1410 (4), Ni—C 1.8383 (15) Å and P—Ni—C 93.47 (5)°, and principal alkyne dimensions of C≡C 1.212 (2) and 1.187 (3) Å, and C≡C—C 177.94 (19) and 179.5 (2)°. Intra- and intermolecular C—H···C≡C interactions are present with the shortest C···C distance being 3.198 Å.

Comment

Transition metal σ-acetylide polymers have attracted much interest in recent years due to their potential applications in liquid-crystal technology and non-linear optics (Long, 1995). Attention has focused on the acetylide ligand π system (which can provide a pathway for electron-density delocalization between the metal centre and ligand) to determine the extent of mixing of the ligand- and metal-based orbitals, extensive delocalization being necessary for a large non-linear response in conducting materials (McGrady *et al.*, 1997; Whittall *et al.*, 1997). In contrast to monoacetylide derivatives, few diacetylide organometallic complexes have been structurally characterized to date (Sun *et al.*, 1992; Worth *et al.*, 1992). We report herein on the structure of the title compound, (I), which incorporates a σ-bonded 1,3-butadiynyl ligand.



(I)

Molecule (I) has a half-sandwich structure and contains the σ-bonded 1,3-butadiynyl ligand. A view of the molecule with our numbering scheme is given in Fig. 1 and selected dimensions are given in Table 1. The principal metal–ligand dimensions are Ni1—P1 2.1410 (4), Ni1—C1 1.8383 (15) Å and P1—Ni1—C1 93.47 (5)°.