ω scans
Absorption correction:
  empirical *via* ψ scans
  (North *et al.*, 1968)
  $T_{\min} = 0.463$, $T_{\max} = 0.520$
7090 measured reflections
6024 independent reflections

$R_{\rm int} = 0.081$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 11$
$k = -1 \rightarrow 27$
$l = -1 \rightarrow 18$
3 standard reflections
  frequency: 60 min
  intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.100$
$S = 1.015$
5938 reflections
339 parameters
H-atom parameters
  constrained

$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.014$
$\Delta\rho_{\max} = 0.811$ e Å^{-3}
$\Delta\rho_{\min} = -0.744$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

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

Pt—C1	2.106 (10)	P1—N1	1.632 (9)
Pt—P2	2.213 (3)	P1—C6	1.827 (10)
Pt—P1	2.289 (3)	P2—N3	1.648 (9)
Pt—Cl1	2.391 (3)	P2—N2	1.667 (9)
Cl2—P1	2.088 (4)	P2—C7	1.840 (10)
C1—Pt—P2	95.2 (3)	N1—P1—Pt	118.6 (4)
C1—Pt—P1	178.6 (3)	C6—P1—Pt	108.1 (3)
P2—Pt—P1	85.39 (11)	Cl2—P1—Pt	113.7 (2)
C1—Pt—Cl1	87.7 (3)	N3—P2—N2	102.4 (5)
P2—Pt—Cl1	170.37 (11)	N3—P2—C7	109.8 (5)
P1—Pt—Cl1	91.51 (11)	N2—P2—C7	102.9 (5)
N1—P1—C6	105.5 (5)	N3—P2—Pt	116.2 (3)
N1—P1—Cl2	107.2 (3)	N2—P2—Pt	122.4 (4)
C6—P1—Cl2	102.2 (4)	C7—P2—Pt	102.1 (4)

All non-H atoms were located by direct methods and subsequent alternate cycles of difference Fourier synthesis and full-matrix least-squares refinement. The resulting structural model was refined to convergence with allowance for anisotropic thermal motion of the non-H atoms. H atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to 1.3 times the $U_{\rm eq}$ of their carrier atoms. According to some of the U^{ij} values of the tertiary butyl C atoms, rotational disorder about the C1—C2 bond was suggested for this substituent, but was not accounted for during refinement. The highest peaks in the final difference map were located less than 1.0 Å from the Pt atom.

Data collection: *CAD*-4-*PC* (Enraf-Nonius, 1995). Cell refinement: *CAD*-4-*PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1171). Services for accessing these data are described at the back of the journal.

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A monohelical cobalt(II) complex of a quinquepyridine ligand

YOU-JUN FU,[a] ZHANG-SHOU GAO,[a] HAO YANG,[b] WENNING DAI,[b] DEFEN WANG,[b] HONGWEN HU,[b] WENXIA TANG,[b] ZEYING ZHANG[c] AND THOMAS C. W. MAK[c]

[a]*State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China,* [b]*State Key Laboratory of Coordination Chemistry, Chemistry Department, Nanjing University, Nanjing 210093, People's Republic of China, and* [c]*Chemistry Department, Chinese University of Hong Kong, Shatin, New Territories, Hong Kong. E-mail: zsgao@hosts.icm.sdu.edu.cn*

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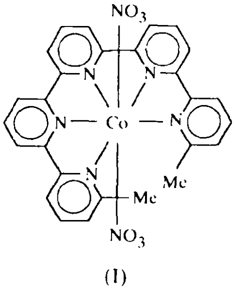
Abstract

The monohelical mononuclear title complex, (6,6''''-dimethyl-2,2':6',2'':6'',2''':6''',2''''-quinquepyridine-κ^5N)-bis(nitrato)cobalt(II), $[\mathrm{Co(NO_3)_2(C_{27}H_{21}N_5)}]$, was obtained by the reaction of the quinquepyridine ligand (dmqpy) with hydrated cobalt nitrate, $\mathrm{Co(NO_3)_2(H_2O)_4}$. In the complex, the coordination geometry of the $\mathrm{Co^{II}}$ atom is a distorted pentagonal bipyramid, with the dmqpy ligand twisted about the equatorial plane and the two $\mathrm{NO_3^-}$ ions occupying the apical positions.

Comment

Oligopyridines have aroused much interest, due to their ability to form helical complexes with the first row transition metals (Constable, 1992). 2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine (qpy) is a typical ligand that can form both homo- and hetero-dinuclear double helicates (Barley & Constable, 1988; Constable & Walker, 1992). We have previously found that dmqpy forms double helical complexes with silver(I) (Fu *et al.*, 1996), while unsubstituted qpy produces only a mononuclear near-planar pentacoordinated complex under the same conditions (Constable *et al.*, 1988). We now report that 6,6⁗-dimethyl-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (dmqpy) forms only a monohelical complex with cobalt(II) nitrate, in which the NO_3^- ions occupy apical positions.

Both enantiomers of the monohelicate $[Co(dmqpy)(NO_3)_2]$, (I), are present in the centrosymmetric crystal structure. The helical configuration of the ligand is achieved by a series of twists about the C—C bonds between adjacent pyridine rings, to avoid the significant steric effect that would be arise if the terminal methyl groups were in a completely coplanar conformation. The dihedral angles are 9.4 (3) and 15.1 (4)° for rings 1 and 2, and 2 and 3, respectively (using the N atom numbers). Cobalt(II) is heptacoordinate, with a distorted pentagonal bipyramidal geometry; the dmqpy molecule twists about the equatorial plane and the apical positions are occupied by two monodentate NO_3^- anions (Fig. 1).



(I)

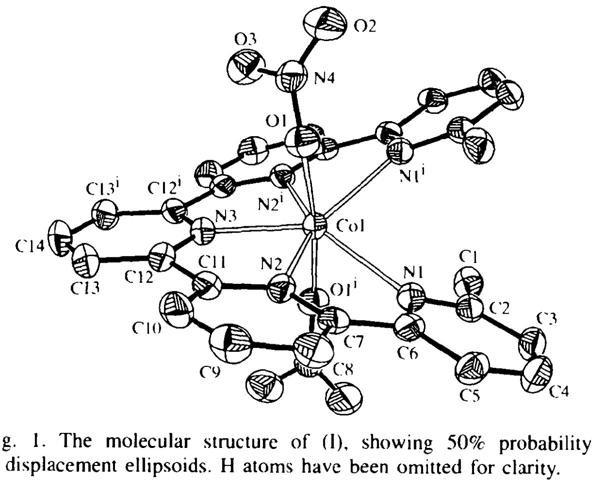


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title complex was prepared by refluxing a suspension of dmqpy (0.072 mmol, 30 mg) in methanol containing $Co(NO_3)_2(H_2O)_4$ (0.074 mmol, 20 mg) for about 2 h. After filtration, suitable crystals were obtained by slow vapour diffusion of diethyl ether. Satisfactory chemical analyses were obtained.

Crystal data

$[Co(NO_3)_2(C_{27}H_{21}N_5)]$
$M_r = 598.4$
Monoclinic
$C2/c$
$a = 17.380 (3)$ Å
$b = 11.600 (2)$ Å
$c = 13.418 (3)$ Å
$\beta = 110.92 (3)°$
$V = 2527 (1)$ Å^3
$Z = 4$
$D_x = 1.573$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–15°$
$\mu = 0.739$ mm^{-1}
$T = 292 (2)$ K
Needle
0.60 × 0.20 × 0.05 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (Kopfmann & Huber, 1968)
$T_{\min} = 0.841$, $T_{\max} = 0.964$
2997 measured reflections
2904 independent reflections

2995 reflections with $|F_o| \geq 4\sigma(|F_o|)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 25.5°$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.054$
$wR = 0.061$
$S = 1.25$
2904 reflections
188 parameters
H atoms riding, $U_{\rm iso}$ fixed
$w = 1/[\sigma^2(|F_o|) + 0.0004|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.059$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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	0.23100 (1)	1/4	0.0364 (3)
N1	0.4065 (2)	0.3804 (3)	0.1782 (3)	0.041 (1)
N2	0.4156 (2)	0.1769 (3)	0.0991 (3)	0.040 (1)
N3	1/2	0.0461 (4)	1/4	0.043 (1)
C1	0.4347 (3)	0.4906 (4)	0.3438 (4)	0.058 (2)
C2	0.3952 (3)	0.4784 (4)	0.2255 (4)	0.047 (2)

C3	0.3461 (3)	0.5683 (4)	0.1661 (5)	0.058 (2)
C4	0.3078 (3)	0.5561 (4)	0.0582 (5)	0.064 (2)
C5	0.3153 (3)	0.4540 (4)	0.0099 (7)	0.051 (2)
C6	0.3650 (3)	0.3680 (4)	0.0723 (3)	0.041 (2)
C7	0.3722 (3)	0.2544 (4)	0.0269 (3)	0.040 (2)
C8	0.3357 (3)	0.2248 (5)	−0.0813 (4)	0.052 (2)
C9	0.3440 (3)	0.1147 (5)	−0.1117 (4)	0.061 (2)
C10	0.3853 (3)	0.0338 (4)	−0.0364 (4)	0.057 (2)
C11	0.4190 (3)	0.0672 (4)	0.0684 (4)	0.044 (2)
C12	0.4616 (3)	−0.0108 (4)	0.1591 (4)	0.046 (2)
C13	0.4610 (3)	−0.1304 (4)	0.1560 (5)	0.063 (2)
C14	1/2	−0.1893 (6)	1/4	0.076 (4)
N4	0.6548 (3)	0.2077 (4)	0.1865 (3)	0.052 (2)
O1	0.5772 (2)	0.2202 (3)	0.1460 (3)	0.053 (1)
O2	0.6996 (3)	0.2646 (4)	0.1542 (4)	0.091 (2)
O3	0.6839 (2)	0.1334 (3)	0.2573 (3)	0.069 (2)

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

Co1—N1	2.336 (3)	Co1—N3	2.144 (5)
Co1—N2	2.127 (3)	Co1—O1	2.259 (4)
N1—Co1—N2	71.6 (1)	N1—Co1—N1^{i}	84.2 (2)
N1—Co1—N3	137.9 (1)	N2—Co1—N1^{i}	138.9 (1)
N2—Co1—N3	72.8 (1)	O1—Co1—N1^{i}	79.4 (1)
N1—Co1—O1	105.4 (1)	N4—Co1—N2^{i}	145.7 (2)
N2—Co1—O1	75.9 (1)	O1—Co1—N2^{i}	102.2 (1)
N3—Co1—O1	86.8 (1)	O1—Co1—O1^{i}	173.7 (2)

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

Although voids of about 1350 Å were identified by *PLATON* (Spek, 1998), no significant residual electron density was found.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1249). Services for accessing these data are described at the back of the journal.

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Trimethylphosphonium trichlorogermanate(II)

Gabriele Kociok-Köhn, Johannes G. Winter and Alexander C. Filippou*

Institut für Anorganische und Allgemeine Chemie der Humboldt Universität zu Berlin, Hessische Straße 1-2, 10115 Berlin, Germany. E-mail: filippou@chemie.hu-berlin.de

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Abstract

The title compound, [HPMe$_3$][GeCl$_3$], features pseudo-tetrahedral [HP(CH$_3$)$_3$]$^+$ and trigonal-pyramidal GeCl$_3^-$ units that form a strongly distorted perovskite structure. The Ge^{II} centre shows a distorted octahedral environment with three short Ge—Cl bonds [average Ge—Cl = 2.3071 (9) Å] and three much longer interionic Ge· · ·Cl distances [average Ge· · ·Cl = 4.1372 (12) Å].

Comment

[HPMe$_3$][GeCl$_3$], (1), was originally obtained as a by-product in the course of the attempted crystallization of GeCl$_2$(PMe$_3$), (2). Compound (2) was prepared from GeCl$_2$(1,4-dioxane) and P(CH$_3$)$_3$ in benzene and investigated as an intermediate in the reaction of Cp*M*(CO)$_3$GeCl$_2$H (Cp = C$_5$H$_5$; *M* = Mo, W) with P(CH$_3$)$_3$ to give *trans*-Cp*M*(CO)$_2$[P(CH$_3$)$_3$]GeCl$_2$H (Filippou *et al.*, 1997). Compound (1) was then selectively obtained as a yellow solid from (2) and HCl, and was fully characterized. Compound (1), with its nearly cubic lattice constants, crystallizes in a strongly distorted perovskite structure similar to the low-temperature modification of [N(CH$_3$)$_4$][GeCl$_3$], (3) (Depmeier *et al.*, 1980). The Ge^{II} centre has a distorted octahedral environment with three short Ge—Cl bonds [average Ge—Cl = 2.3071 (9) Å] and three much longer Ge· · ·Cl contacts [average Ge· · ·Cl = 4.1372 (12) Å]. The tendency of Ge^{II} to form trigonal-pyramidal GeCl$_3^-$ units is thus clear. The non-bonded Ge· · ·Cl distances are similar to those in (3) [4.069 (8), 4.122 (8) and 4.322 (4) Å]. However, in (1), the presence of a cation with different substituents leads to a distortion, as is reflected in the different non-bonded Ge· · ·Cl distances; two of these are slightly shorter and one is slightly longer than in (3) (Table 2). Fig. 1 shows compound (1) as the distorted perovskite structure type. Another orthorhombic example of this structure type is given by the powder structure of [HN(CH$_3$)$_3$][GeCl$_3$] (Möller & Felsche, 1982). A rhombohedral variation of the perovskite structure type is demonstrated by the low-temperature form