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Acta Cryst. (1996). C**52**, 2191–2193

Bis(nitrato-*O*,*O*′)bis{2-[2-(2-thienyl)-ethynyl]pyridine-*N*}cobalt(II)

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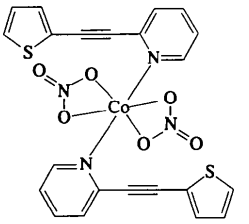
(*Received 18 December 1995; accepted 17 April 1996*)

Abstract

The title compound, $[Co(NO_3)_2(C_{11}H_7NS)_2]$, has two-fold axial symmetry. The central cobalt ion is coordinated by four O atoms of two nitrate anions and two N atoms of two 2-[2-(2-thienyl)ethynyl]pyridine ligands in a distorted octahedral geometry. The non-coordinating thiophene moiety is disordered over two overlapping orientations. Short bifurcated C—H···O interactions link the molecules into an infinite chain parallel to the *c* axis.

Comment

The structure of the 1-(2-pyridyl)-2-(2-thienyl)ethyne–cobalt complex, (I), was investigated as part of a study on new modes of coordination of ligands connected by rigid groups such as acetylenes (Neenan & Driessen, 1996; Neenan, Driessen, Haasnoot & Reedijk, 1996).



(I)

The cobalt ion in (I) is coordinated by two nitrate ions and two pyridyl N atoms and is located on a crystallographic twofold rotation axis. The triple bond of the acetylene moiety and the thiophene S atom do not participate in the coordination. The coordination sphere of cobalt is octahedral, with a severe distortion due to the small bite angle of the nitrate anions. Although nitrate ions do not often coordinate with cobalt, nine $Co(NO_3)_2$ fragments out of 83 structures containing both cobalt(II) and at least one nitrate ion are reported in the Cambridge Structural Database (Allen & Kennard, 1993). All of these display the nitrate ions in the '*cis*' orientation observed in the present structure. The observed distances in the coordination sphere of the Co atom are in agreement with the values reported in the literature. Uneven Co—O bond lengths have been reported for other complexes and are often associated with a strong distortion of the octahedral geometry towards a tetrahedral one (*e.g.* Han & Parkin, 1991). Each pyridine ring is virtually coplanar with one nitrate anion, as is indicated by the angle between the least-squares planes of 3.3 (3)°. The angle between the least-squares planes through the thiophene and pyridine rings (in the same ligand molecule) is 6.1 (8)°. A view of (I) is shown in Fig. 1.

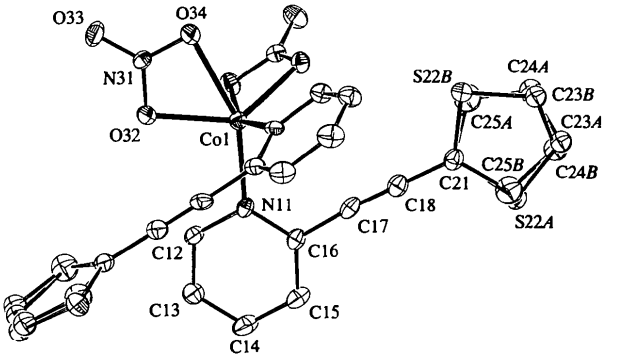


Fig. 1. Atomic displacement parameter plot (30% probability level) of the title compound, with the atomic labelling scheme, showing the disorder in the thiophene ring. Labels with suffix *A* denote the major disorder component.

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The thiophene ring is disordered over two orientations in the ratio 0.580:0.420(7), related approximately by reflection in a plane perpendicular to that of the ligand. This kind of disorder is not uncommon in ligands containing thiophene and pyridine rings and has been reported previously by Giordano & Rasmussen (1975) in the case of a single C—C bond between the rings and by Barrow, Milburn, Zeng, Sarkar & Talwar (1994) in the case of a double acetylene bridge between the rings.

The molecules are linked by C—H···O interactions into infinite chains in the **c** direction (Fig. 2). The C12—H12 group beside the pyridyl N atom displays short contacts with both the O32 [H···O 2.458 (8) Å and C—H···O 124.5 (6)°] and O34(x, $1-y$, $\frac{1}{2}+z$) [H···O 2.579 (7) Å and C—H···O 125.6 (6)°] atoms, *i.e.* both coordinating O atoms of the nitrate ion (see Table 2). The sum of the intermolecular angles involving H12 as the central atom is 359.5 (9)°, which is in accordance with a bifurcated geometry. The non-coordinating O atom of the nitrate anion has no contacts significantly shorter than the sum of the van der Waals radii.

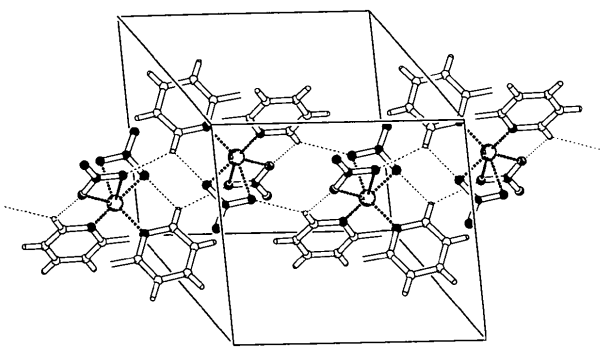

Fig. 2. C—H···O interactions link the molecules in an infinite chain parallel to the c axis. The thienylethyne moieties have been omitted for clarity.

Experimental

Dissolution of 1-(2-pyridyl)-2-(2-thienyl)ethyne (300 mg, 1.62 mmol) in ethanol (5 ml), followed by addition of $Co(NO_3)_2.6H_2O$ (238 mg, 81 mmol) dissolved in acetone (5 ml), yielded deep-purple crystals of the title compound after 24 h at room temperature.

Crystal data

$[Co(NO_3)_2(C_{11}H_7NS)_2]$
M_r = 553.44
Monoclinic
$C2/c$
a = 21.2695 (10) Å
b = 10.376 (2) Å
c = 12.054 (2) Å
β = 117.297 (10)°
V = 2364.0 (6) Å^3
Z = 4
D_x = 1.555 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 15 reflections
θ = 9.92–12.17°
μ = 0.95 mm^{-1}
T = 180 K
Block-shaped
0.4 × 0.2 × 0.1 mm
Deep purple

Data collection

Enraf–Nonius CAD-4-T diffractometer (rotating anode)
ω–2θ scans
Absorption correction: empirical, refined from ΔF (*PLATON*; Spek, 1995*b*)
T_{min} = 0.36, T_{max} = 1.00
4160 measured reflections
2090 independent reflections
1369 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.1149
θ_{max} = 24.99°
$h = 0 \rightarrow 25$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 12$
1 standard reflection
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
R = 0.0697
wR = 0.1725
S = 0.970
2090 reflections
163 parameters
H atoms riding with U(H) = 1.2U_{eq}(C)
$w = 1/[\sigma^2(F_o^2) + (0.0865P)^2]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.668 e Å^{-3}
$\Delta\rho_{min}$ = −0.617 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	1/2	0.40138 (11)	1/4	0.0275 (3)
S22A†	0.2377 (3)	0.0576 (7)	−0.1487 (5)	0.0413 (12)
S22B‡	0.3220 (6)	0.2457 (10)	−0.1819 (8)	0.049 (2)
O32	0.5813 (2)	0.4848 (4)	0.4041 (4)	0.0347 (12)
O33	0.6430 (2)	0.6514 (5)	0.4030 (4)	0.0473 (16)
O34	0.5669 (2)	0.5618 (4)	0.2303 (4)	0.0385 (14)
N11	0.4650 (2)	0.2774 (4)	0.3438 (4)	0.0279 (14)
N31	0.5986 (2)	0.5694 (4)	0.3471 (4)	0.0291 (16)
C12	0.4952 (3)	0.2868 (6)	0.4689 (5)	0.0332 (17)
C13	0.4784 (3)	0.2052 (6)	0.5402 (6)	0.0406 (19)
C14	0.4291 (3)	0.1122 (6)	0.4854 (7)	0.049 (2)
C15	0.3969 (3)	0.1005 (6)	0.3563 (6)	0.046 (2)
C16	0.4154 (3)	0.1853 (5)	0.2896 (5)	0.0320 (17)
C17	0.3808 (3)	0.1804 (6)	0.1543 (6)	0.0361 (19)
C18	0.3463 (3)	0.1726 (6)	0.0448 (6)	0.0365 (19)
C21	0.3049 (3)	0.1634 (6)	−0.0853 (6)	0.0349 (17)
C23A†	0.2189 (8)	0.0974 (17)	−0.2957 (14)	0.038 (4)
C23B‡	0.2572 (12)	0.176 (2)	−0.308 (2)	0.038 (4)
C24A†	0.2568 (10)	0.1957 (16)	−0.3024 (17)	0.046 (5)
C24B‡	0.2167 (12)	0.097 (3)	−0.275 (2)	0.046 (5)
C25A†	0.3114 (17)	0.237 (3)	−0.183 (3)	0.063 (10)
C25B‡	0.245 (2)	0.077 (4)	−0.144 (3)	0.063 (10)

† Occupancy of 0.580(7). ‡ Occupancy of 0.420(7).

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

Co1—O32	2.060 (4)	N11—C16	1.349 (7)
Co1—O34	2.272 (5)	N11—C12	1.344 (7)
Co1—N11	2.064 (4)	C16—C17	1.450 (8)
S22A—C21	1.682 (10)	C17—C18	1.183 (9)
S22A—C23A	1.679 (16)	C18—C21	1.406 (9)
S22B—C21	1.614 (13)	C21—C25A	1.46 (3)
O32—N31	1.269 (6)	C23A—C24A	1.33 (3)
O33—N31	1.219 (7)	C24A—C25A	1.44 (4)
O34—N31	1.254 (6)		
O32—Co1—O34	58.63 (16)	O32^i—Co1—N11^i	97.61 (17)
O32—Co1—N11	97.61 (17)	O34^i—Co1—N11^i	156.13 (16)
O32—Co1—O32^i	130.31 (17)	Co1—O32—N31	97.7 (3)

O32—Co1—O34^{i}	84.54 (17)	Co1—O34—N31	88.2 (3)
O32—Co1—N11^{i}	113.04 (18)	Co1—N11—C12	117.5 (4)
O34—Co1—N11	156.13 (16)	Co1—N11—C16	125.1 (4)
O32^{i}—Co1—O34	84.54 (17)	C12—N11—C16	117.4 (5)
O34—Co1—O34^{i}	85.78 (17)	O32—N31—O34	115.1 (4)
O34—Co1—N11^{i}	89.93 (17)	O33—N31—O34	123.1 (5)
O32^{i}—Co1—N11	113.04 (18)	O32—N31—O33	121.8 (4)
O34^{i}—Co1—N11	89.93 (17)	N11—C12—C13	122.2 (6)
N11—Co1—N11^{i}	102.88 (18)	N11—C16—C17	116.8 (5)
O32^{i}—Co1—O34^{i}	58.63 (16)	N11—C16—C15	122.9 (5)

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

Reflections were measured with a scan angle of $\Delta\omega = (0.80 + 0.35\tan\theta)°$, and horizontal and vertical apertures of 3.00 and 4.00 mm, respectively. Only 27% of the intensity data were above the $2.5\sigma(I)$ level in the $\theta = 25°$ region. Due to the irregular shape of the crystal (which was cut from a larger aggregate), no satisfactory description of the crystal could be obtained for use in a numerical absorption correction procedure. An empirical absorption correction was therefore applied. The thiophene ring proved to be disordered over two orientations. The site-occupation factor of the major disorder component refined to 0.580 (7). Mild restraints were applied to the bond lengths and 1,3 distances in both disorder components. All non-H atoms were refined with anisotropic displacement parameters, except for the disordered C atoms, which were refined isotropically. The displacement parameters of the C atoms in both disorder components were constrainted to the same value. The relatively high R values are related to the weak scattering that is most probably a consequence of the disorder in the thiophene ring.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990), *PLUTON* (Spek, 1995*a*). Software used to prepare material for publication: *PLATON*.

This work was supported in part (ALS) by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Scientific Research (NWO). Financial support of the European Union, allowing regular exchange of preliminary results with several European colleagues, under contract ERBCHRXCT920090, is greatfully acknowledged. The authors thank the Netherlands Organization for the Advancement of Research (NWO) for a visiting grant for TXN.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2193–2196

Bis[1,2-bis(diphenylphosphino)ethane-*P*,*P*′]-chloroosmium(II) Hexafluorophosphate Dichloromethane Solvate

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(*Received 28 March 1996; accepted 14 May 1996*)

Abstract

The cation molecule of the title compound, $[OsCl(C_{26}H_{24}P_2)_2]PF_6.1.5CH_2Cl_2$, has a distorted trigonal-bipyramidal structure. Despite strong steric repulsion between the PPh_2 groups, the Os—P bonds in the equatorial plane are short [2.2416 (12) and 2.2587 (13) Å] and the P—Os—P angle is only 94.24 (5)°.

Comment

The title compound, (1), was synthesized in order to provide the starting material in the preparation of the dihydrogen complex *trans*-$[Os(H_2)Cl(dppe)_2]PF_6$, (3) [where dppe is 1,2-bis(diphenylphosphino)ethane; see scheme below]. The X-ray and neutron diffraction studies of (3) are discussed elsewhere (Maltby *et al.*, 1996). An X-ray study of the five-coordinate compound