Jezowska-Trzebiatowska, B. & Sobota, P. (1972). *J. Organomet. Chem.* **46**, 339–343.
Komiya, S., Akita, M., Yoza, A., Kasuga, N., Fukuoka, A. & Kai, Y. (1993). *J. Chem. Soc. Chem. Commun.* pp. 787–788.
Leigh, G. J. (1992). *Acc. Chem. Res.* **25**, 177–181.
Lowe, D. J. & Thorneley, R. N. F. (1984). *Biochem. J.* **224**, 877–886.
Rehder, D., Woitha, C., Priebsch, W. & Gailus, H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 364–365.
Richards, R. L. (1991). *Biology and Biochemistry of Nitrogen Fixation*, edited by M. J. Dilworth & A. R. Glenn, p. 58. Oxford: Elsevier.
Richards, R. L. (1996). *Coord. Chem. Rev.* **154**, 83–97.
Sacco, A. & Aresta, M. (1968). *J. Chem. Soc. Chem. Commun.* pp. 1223–1224.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1990). *SHELXTL/PC.* Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1998). C**54**, 46–47

trans-Bis(acetylacetonato-*O*,*O*′)(3-methylpyridine-*N*)nitrocobalt(III)

Hiroki Miyazaki, Masanobu Tsuchimoto and Shigeru Ohba

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223, Japan. E-mail: ohba@chem.keio.ac.jp

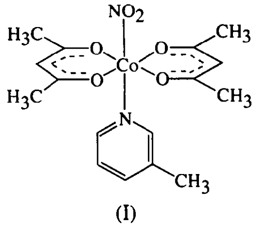
(*Received 25 July 1997; accepted 26 September 1997*)

Abstract

The crystal structure determination of the title compound, [Co($C_5H_7O_2$)$_2$(NO_2)(C_6H_7N)], shows that the coordination geometry around the Co^{III} atom is slightly distorted octahedral, with a Co—NO_2 bond distance of 1.905 (3) Å. The crystal is photostable, which may be due to the narrow cavity around the nitro group.

Comment

Solid-state photochemical nitro–nitrito linkage isomerization has been investigated in single crystals of [Co(NH_3)$_5$(NO_2)]Cl_2 (Kubota & Ohba, 1992) and in [Co(NH_3)$_5$(NO_2)]Br_2 powder (Masciocchi *et al.*, 1994). Johnson & Martin (1969) reported the solid-state photochemical reaction of [Co(acac)$_2$(py)(NO_2)], based on IR spectra (acac is the acetylacetonate ion and py is pyridine). Recrystallization of the pyridine complex failed in the present study. When the pyridine ligand was replaced by 2-, 3- or 4-methylpyridine, only the 3-methylpyridine complex, (I), gave good crystals. However, the IR spectra showed no change before and after irradiation of the KBr disk with Xe light.



(I)

The Co atom and the 3-methylpyridine ligand lie on the mirror plane which bisects the nitro O—N—O bond angle. The dimensions of the reaction cavity of NO_2 were calculated (Kubota & Ohba, 1992), from which it was ascertained that there is no room in the crystal to allow isomerization from the nitro (Co—NO_2) to the nitrito (Co—ONO) form. The intermolecular contacts with the nitro O atom near the NO_2 plane are 2.405 (2) Å for O4···H11*A*—C11 ($\frac{3}{2}-x$, $y+\frac{1}{2}$, $z+\frac{1}{2}$) and 2.687 (2) Å for O4···H16—C16 ($x+\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{3}{2}-z$).

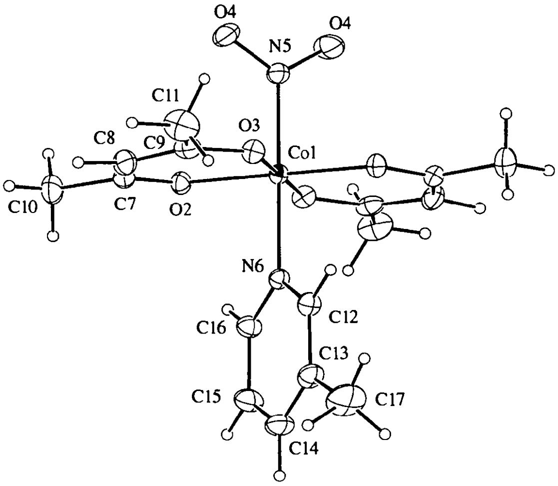


Fig. 1. The molecular structure of (I) with displacement ellipsoids at the 20% probability level. H atoms are represented by circles of radius 0.1 Å.

Experimental

The compound was prepared according to the method of Boucher & Bailar (1965) from Na[Co(acac)$_2$(NO_2)$_2$] and 3-methylpyridine. Crystals were grown from an acetonitrile solution.

Crystal data

$[Co(C_5H_7O_2)_2(NO_2)-(C_6H_7N)]$
$M_r = 396.29$
Orthorhombic
Pnma
$a = 13.451$ (3) Å
$b = 14.746$ (3) Å
$c = 9.402$ (3) Å
$V = 1864.9$ (8) Å^3
$Z = 4$
$D_x = 1.411$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 14.3–15.0°$
$\mu = 0.953$ mm^{-1}
$T = 299$ K
Needle
0.9 × 0.1 × 0.1 mm
Dark red

Data collection

Rigaku AFC-5 diffractometer
ω scans
Absorption correction: by integration (Coppens, Leiserowitz & Rabinovich, 1965)
$T_{min} = 0.885$, $T_{max} = 0.926$
2815 measured reflections
2815 independent reflections

1955 reflections with $|F_o| > 3\sigma(|F_o|)$
$\theta_{max} = 30.0°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.048$
$wR = 0.041$
$S = 1.20$
1955 reflections
140 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{max} = 0.047$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ 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)*

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

	x	y	z	U_{eq}
Co1	0.62470 (3)	1/4	0.60300 (4)	0.0308 (1)
O2	0.5457 (1)	0.1646 (1)	0.6993 (2)	0.0402 (5)
O3	0.7033 (1)	0.1645 (1)	0.5063 (2)	0.0410 (5)
O4	0.7464 (2)	0.3215 (1)	0.8068 (2)	0.0783 (8)
N5	0.7172 (2)	1/4	0.7565 (3)	0.0418 (9)
N6	0.5268 (2)	1/4	0.4427 (2)	0.0335 (8)
C7	0.5519 (2)	0.0790 (2)	0.6811 (2)	0.0468 (8)
C8	0.6191 (2)	0.0359 (1)	0.5935 (3)	0.0538 (8)
C9	0.6923 (2)	0.0789 (2)	0.5159 (3)	0.0464 (8)
C10	0.4775 (3)	0.0256 (2)	0.7670 (3)	0.071 (1)
C11	0.7671 (3)	0.0249 (2)	0.4336 (4)	0.081 (1)
C12	0.5560 (2)	1/4	0.3060 (3)	0.043 (1)
C13	0.4913 (3)	1/4	0.1932 (4)	0.053 (1)
C14	0.3913 (3)	1/4	0.2238 (4)	0.059 (1)
C15	0.3600 (3)	1/4	0.3616 (4)	0.060 (1)
C16	0.4294 (2)	1/4	0.4698 (4)	0.045 (1)
C17	0.5314 (5)	1/4	0.0411 (5)	0.097 (3)

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

Co1—O2	1.880 (2)	Co1—N6	2.001 (3)
Co1—O3	1.880 (2)	O4—N5	1.220 (3)
Co1—N5	1.905 (3)		
O2—Co1—O2^i	84.1 (1)	O3—Co1—N5	89.9 (1)
O2—Co1—O3	95.8 (1)	O3—Co1—N6	90.3 (2)
O2—Co1—O3^i	179.8 (1)	N5—Co1—N6	179.6 (2)
O2—Co1—N5	90.2 (1)	Co1—N5—O4	120.2 (2)
O2—Co1—N6	89.5 (2)	O4—N5—O4^i	119.5 (3)

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

Positions of all H atoms were calculated geometrically and restrained to maintain the C—H distance at 0.96 Å.

Data collection: *AFC/MSC Diffractometer Control Software* (Rigaku Corporation, 1993). Cell refinement: *AFC/MSC Diffractometer Control Software*. Data reduction: local programs. Program(s) used to solve structure: *CRYSTAN-GM* (Edwards *et al.*, 1996). Program(s) used to refine structure: *CRYSTAN-GM*. Molecular graphics: *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1185). Services for accessing these data are described at the back of the journal.

References

Boucher, L. J. & Bailar, J. C. Jr (1965). *Inorg. Nucl. Chem.* **27**, 1093–1099.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1996). *CRYSTAN-GM*. Version 6.3. *Computer Program for the Solution and Refinement of Crystal Structures*. MacScience, Japan.

Johnson, D. A. & Martin, J. E. (1969). *Inorg. Chem.* **8**, 2509–2511.

Kubota, M. & Ohba, S. (1992). *Acta Cryst.* B**48**, 627–632.

Masciocchi, N., Kolyshev, A., Dulepov, V., Boldyreva, E. & Sironi, A. (1994). *Inorg. Chem.* **33**, 2579–2585.

Rigaku Corporation (1993). *AFC/MSC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.

Acta Cryst. (1998). C**54**, 47–49

Structure of the Chromium(III) Salt $[Cp^*_2Cr]^+[Cp^*CrCl_3]^-$

SIMON ALDRIDGE, MAOYU SHANG AND THOMAS P. FEHLNER

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA. E-mail: thomas.p.fehlner.1@nd.edu

(*Received 8 May 1997; accepted 19 August 1997*)

Abstract

The title compound, bis(η^5-pentamethylcyclopentadienyl)chromium(III) trichloro(η^5-pentamethylcyclopentadienyl)chromium(III), $[Cr(C_{10}H_{15})_2][CrCl_3(C_{10}H_{15})]$, is a salt consisting of discrete anionic $[\{\eta^5\text{-}C_5(CH_3)_5\}CrCl_3]^-$ and cationic $[\{\eta^5\text{-}C_5(CH_3)_5\}_2Cr]^+$ chromium(III) species. The anion adopts a 'three-legged piano-stool' structure, whereas the cation displays a