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Acta Cryst. (1979). **B35**, 2702–2704

Structure of *cis*-Bis(2,2'-bipyridine)dimethylcobalt(III) Tetraethylaluminate

BY SANSHIRO KOMIYA,* TAKAKAZU YAMAMOTO* AND AKIO YAMAMOTO

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

AND AKIO TAKENAKA AND YOSHIO SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

(Received 11 May 1979; accepted 10 July 1979)

Abstract. [Co(CH₃)₂(C₁₀H₈N₂)₂][Al(C₂H₅)₄], C₂₂H₂₂CoN₄⁺.C₈H₂₀Al⁻, monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 14.010 (1), *b* = 19.462 (2), *c* = 11.081 (1), Å, β = 99.15 (1)°, at room temperature; *D*_x = 1.19₂, *D*_m = 1.21 Mg m⁻³ (floatation). The crystal contains bis(2,2'-bipyridine)dimethylcobalt cations and tetraethylaluminium anions. The cation has an octahedral coordination, the two methyl groups lying at *cis* positions. The Co–N coordination distance shows the significant *trans* influence of the methyl group.

Introduction. A series of dialkylbis(2,2'-bipyridine)cobalt(III) cations have been prepared (Komiya, Bundo, Yamamoto & Yamamoto, 1979; Yamamoto, Bundo & Yamamoto, 1977). To confirm the *cis* configuration, an X-ray analysis of bis(2,2'-bipyridine)dimethylcobalt(III) tetraethylaluminate, [Co(bpy)₂(CH₃)₂]⁺[Al(C₂H₅)₄]⁻, has been performed.

Red prisms of the complex, suitable for X-ray diffraction studies, were obtained from a THF–diethyl ether–hexane solution. They are stable in dry air for at least 1 month, but they slowly decompose with moisture. The diffraction experiment was undertaken with a crystal 0.05 × 0.06 × 0.06 mm sealed in an N₂-filled capillary.

Intensity data were collected on a Rigaku automated four-circle diffractometer using graphite-monochromated Mo *K*α radiation (λ = 0.71069 Å). The ω–2θ scan mode was employed with a scan width of 1.5°

(in ω) plus α₁–α₂ divergence at a scan speed of 8° (in 2θ) min⁻¹. Intensities of four monitored reflexions gradually decreased by up to 15% throughout the experiment. Out of 5250 independent reflexions in the range 2 < 2θ < 50°, 1326 weak reflexions with counts less than the background were considered as zero-reflexions. Intensities were corrected for Lorentz and polarization factors but not for absorption effects. The standard deviation for each reflexion was estimated by σ²(*F*) = σ_p² + *qF*_o², where σ_p is from counting statistics and *q* is 9.38 × 10⁻⁴, derived from the variation of the monitored reflexions (McCandlish, Stout & Andrews, 1975).

The structure was solved by the heavy-atom method and atomic parameters were refined by block-diagonal least squares with the weight 1/σ(*F*). All the H atoms in the cation were found on a difference map, but they were not included in the least-squares calculations. The zero-reflexions were included in the least-squares calculation by assuming *F*_o = *F*_{lim} where *F*_{lim} was 5.76, an observational threshold value, but those for which |*F*_o| < *F*_{lim} were omitted. The final *R* value was 0.106 [*R*_c = 0.090 for *F*_o > 3σ(*F*)]. The final atomic parameters are listed in Table 1.† Atomic scattering factors

† Lists of structure factors, thermal parameters, bond lengths, and the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34608 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Authors to whom correspondence should be addressed.

used were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The crystal structure consists of $[\text{Co}(\text{bpy})_2(\text{CH}_3)_2]^+$ and $[\text{Al}(\text{C}_2\text{H}_5)_4]^-$ ions, as shown in Fig. 1. No unusual contacts between them are observed. Fig. 2 shows the molecular structure of the cationic dimethyl-

Table 1. Fractional coordinates ($\times 10^4$) with their standard deviations in parentheses

	x	y	z
Co	2595 (1)	1103 (0)	4135 (1)
Al	7682 (3)	1158 (1)	1222 (3)
N(1)	3658 (3)	1177 (2)	5595 (4)
N(2)	2936 (4)	138 (3)	4287 (5)
N(3)	1583 (3)	1031 (3)	5254 (4)
N(4)	2250 (4)	2061 (2)	4158 (4)
C(1)	1537 (5)	971 (4)	2703 (6)
C(2)	3530 (5)	1231 (3)	2970 (6)
C(3)	4022 (5)	1751 (3)	6178 (6)
C(4)	4740 (5)	1724 (4)	7213 (6)
C(5)	5086 (5)	1087 (4)	7692 (7)
C(6)	4715 (5)	504 (4)	7058 (7)
C(7)	4003 (4)	567 (3)	6011 (5)
C(8)	3598 (4)	-19 (3)	5297 (6)
C(9)	3845 (5)	-701 (4)	5591 (7)
C(10)	3431 (6)	-1232 (4)	4784 (8)
C(11)	2794 (6)	-1061 (4)	3751 (8)
C(12)	2538 (5)	-375 (3)	3479 (7)
C(13)	1290 (5)	470 (4)	5806 (6)
C(14)	549 (5)	502 (4)	6499 (7)
C(15)	103 (5)	1098 (4)	6615 (7)
C(16)	392 (5)	1705 (4)	6079 (6)
C(17)	1147 (4)	1638 (3)	5406 (5)
C(18)	1542 (4)	2234 (3)	4807 (5)
C(19)	1221 (5)	2911 (3)	4929 (6)
C(20)	1672 (6)	3436 (4)	4347 (7)
C(21)	2402 (5)	3277 (4)	3639 (7)
C(22)	2693 (5)	2590 (3)	3597 (6)
C(23)	7224 (6)	185 (4)	1284 (7)
C(24)	6557 (6)	-69 (4)	131 (8)
C(25)	8512 (7)	1420 (5)	2828 (10)
C(26)	8832 (9)	2164 (5)	2949 (12)
C(27)	6664 (14)	1827 (6)	497 (18)
C(28)	5797 (12)	1773 (7)	984 (18)
C(29)	8602 (15)	1207 (8)	-287 (16)
C(30)	9083 (13)	744 (10)	-206 (14)

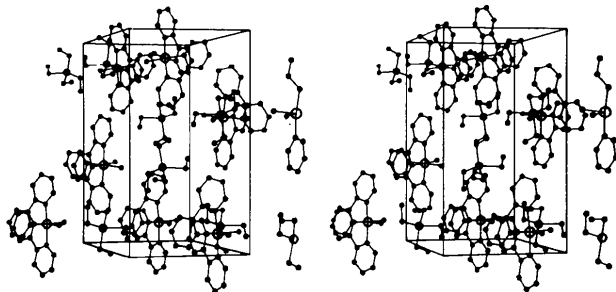


Fig. 1. Stereoscopic drawing of the molecular packing. For the origin at the lower rear right-hand corner, c is to the left, b is up and a is out of the paper.

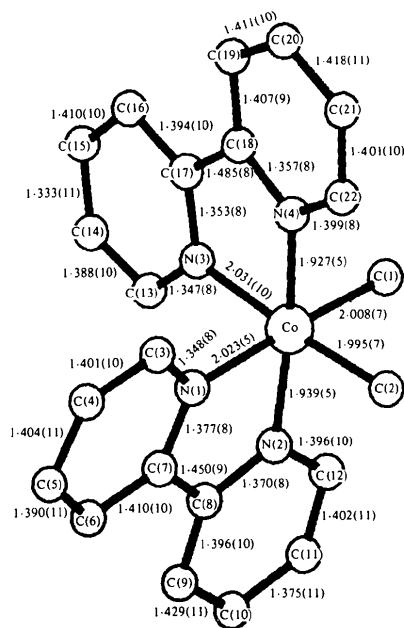


Fig. 2. The molecular structure of $[\text{Co}(\text{bpy})_2(\text{CH}_3)_2]^+$ with bond distances (Å).

cobalt moiety with bond distances. Bond angles are listed in Table 2. The Co atom has a distorted octahedral coordination and the methyl groups occupy the *cis* positions of the octahedron, as expected from an NMR study (Komiya, Bundo, Yamamoto & Yamamoto, 1979). This is a sterically favourable configuration, because of large repulsions between the two 2,2'-bipyridine ligands in *trans* coordination.

The Co-N(2) and Co-N(4) coordination distances are close to the normal $\text{Co}^{\text{III}}-\text{N}$ lengths, *ca* 1.9 Å (Kime & Ibers, 1969). However, the lengths of the Co-N bonds which are *trans* to the methyl groups are significantly longer than the normal Co-N value, the average difference being 0.094 Å. Although the *trans* influence in octahedral Co^{III} complexes is well known in alkyl cobaloximes, the present structure is a prominent example in which the strong *trans* influence of the methyl group appears in a discrete molecule. The Co-C bond lengths observed are comparable to the known values of 1.93–2.02 Å found in Co^{III} alkyl complexes having macrocyclic ligands (Bigotto, Zangrando & Randaccio, 1976).

All the pyridyl rings are reasonably planar, but the two pyridyl rings of the 2,2'-bipyridine ligands are twisted with dihedral angles of 4.3 (2) and 4.5 (2)°. $\text{N}(1)-\text{C}(7)-\text{C}(8) = 115.0 (5)^\circ$ and $\text{N}(2)-\text{C}(8)-\text{C}(7) = 115.2 (5)^\circ$ are smaller than $\text{C}(6)-\text{C}(7)-\text{C}(8) = 123.1 (6)^\circ$ and $\text{C}(7)-\text{C}(8)-\text{C}(9) = 123.9 (6)^\circ$, respectively, indicating the steric requirement for the coordination of a 2,2'-bipyridine ligand to Co. A similar constraint was observed for another bpy. The structural features including the bond lengths are similar to

Table 2. Bond angles ($^{\circ}$) with their standard deviations in parentheses

N(1)—Co—N(2)	81.9 (2)	N(1)—C(3)—C(4)	122.0 (6)
N(1)—Co—N(3)	90.7 (2)	C(3)—C(4)—C(5)	129.1 (7)
N(1)—Co—N(4)	94.3 (2)	C(4)—C(5)—C(6)	116.8 (7)
N(1)—Co—C(1)	176.7 (2)	C(5)—C(6)—C(7)	120.2 (7)
N(1)—Co—C(2)	91.9 (2)	N(1)—C(7)—C(6)	122.0 (6)
N(2)—Co—N(3)	93.8 (2)	N(1)—C(7)—C(8)	115.0 (5)
N(2)—Co—N(4)	174.2 (2)	C(6)—C(7)—C(8)	123.1 (6)
N(2)—Co—C(1)	94.9 (3)	N(2)—C(8)—C(7)	115.2 (5)
N(2)—Co—C(2)	89.9 (3)	N(2)—C(8)—C(9)	120.9 (6)
N(3)—Co—N(4)	81.8 (2)	C(7)—C(8)—C(9)	123.9 (6)
N(3)—Co—C(1)	88.6 (2)	C(8)—C(9)—C(10)	118.7 (7)
N(3)—Co—C(2)	175.7 (3)	C(9)—C(10)—C(11)	119.4 (8)
N(4)—Co—C(1)	88.8 (3)	C(10)—C(11)—C(12)	121.3 (8)
N(4)—Co—C(2)	94.6 (3)	N(2)—C(12)—C(11)	118.7 (7)
C(1)—Co—C(2)	89.0 (3)	N(3)—C(13)—C(14)	121.6 (6)
C(23)—Al—C(25)	110.4 (4)	C(13)—C(14)—C(15)	119.7 (7)
C(23)—Al—C(27)	114.6 (6)	C(14)—C(15)—C(16)	121.2 (8)
C(23)—Al—C(29)	106.7 (6)	C(15)—C(16)—C(17)	116.2 (7)
C(25)—Al—C(27)	117.4 (7)	N(3)—C(17)—C(16)	122.9 (6)
C(25)—Al—C(29)	108.8 (7)	N(3)—C(17)—C(18)	114.7 (5)
C(27)—Al—C(29)	97.4 (8)	C(16)—C(17)—C(18)	122.4 (6)
Co—N(1)—C(3)	128.0 (4)	N(4)—C(18)—C(17)	113.6 (5)
Co—N(1)—C(7)	113.1 (4)	N(4)—C(18)—C(19)	123.7 (6)
C(3)—N(1)—C(7)	118.8 (5)	C(17)—C(18)—C(19)	122.7 (6)
Co—N(2)—C(8)	114.4 (4)	C(18)—C(19)—C(20)	117.5 (7)
Co—N(2)—C(12)	124.7 (5)	C(19)—C(20)—C(21)	120.7 (7)
C(8)—N(2)—C(12)	120.9 (6)	C(20)—C(21)—C(22)	117.7 (7)
Co—N(3)—C(13)	128.7 (4)	N(4)—C(22)—C(21)	122.4 (6)
Co—N(3)—C(17)	112.9 (4)	Al—C(23)—C(24)	115.5 (6)
C(13)—N(3)—C(17)	118.4 (5)	Al—C(25)—C(26)	115.9 (8)
Co—N(4)—C(18)	116.9 (4)	Al—C(27)—C(28)	113.6 (14)
Co—N(4)—C(22)	125.2 (4)	Al—C(29)—C(30)	108.3 (17)
C(18)—N(4)—C(22)	117.9 (5)		

those of $[\text{Co}(2,2'\text{-bipyridine})_2\text{NO}_3](\text{NO}_3)(\text{OH})\cdot 4\text{H}_2\text{O}$ (Reimann, Zocchi, Mighell & Santoro, 1971).

The $[\text{Al}(\text{C}_2\text{H}_5)_4]^-$ ion is nearly tetrahedral. However, one of the four Al—C bond distances, 2.269 (18) Å [accompanied by an unusually short C—C bond, 1.12 (3) Å], is considerably longer than the others,

2.002 (18)—2.031 (11) Å, which are nearly equal to those found in $\text{Li}[\text{Al}(\text{C}_2\text{H}_5)_4]$ (Gerteis, Dickerson & Brown, 1964). The other C—C bond lengths range from 1.54 (2) to 1.41 (3) Å. Such unusual bond lengths are probably due to the degradation of the anion in the crystal used; such anions are usually highly reactive (Mole & Jeffery, 1972).

Figs. 1 and 2 were drawn by *TSD: XTAL* which is an interactive modelling program system for computer graphics (Takenaka & Sasada, 1978).

We wish to thank Kato Kagaku Shinkokai for financial support.

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Acta Cryst. (1979). **B35**, 2704–2707

trans-Dichlorobis(2,4-dimethylthiazole)copper(II)

BY DIANE P. GAVEL AND DEREK J. HODGSON*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, USA

(Received 23 March 1979; accepted 13 July 1979)

Abstract. $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{CuN}_2\text{S}_2$, $\text{Cu}(\text{C}_4\text{H}_7\text{NS})_2\text{Cl}_2$, monoclinic, $C2/c$, $a = 12.320$ (13), $b = 8.760$ (7), $c = 14.592$ (11) Å, $\beta = 105.81$ (6) $^{\circ}$, $U = 1515.2$ Å 3 , $Z = 4$, $D_c = 1.580$, D_m (floatation in benzene/bromoform) = 1.60 (2) Mg m $^{-3}$. The complex is square planar and monomeric, with Cu—N and Cu—Cl bond lengths of 1.985 (4) and 2.261 (2) Å, respectively. There is

approximate 75/25 disorder of the dimethylthiazole ring, involving ring atoms S and C(5).

Introduction. The complex was prepared by an analogous method to that used previously for the synthesis of the thiazole analog (Estes, Gavel, Hatfield & Hodgson, 1978). To a warm solution of 6 mmol 2,4-dimethylthiazole (Pfaltz and Bauer, Inc., Stamford, Connecticut) in 1 ml of absolute ethanol was added 3

* Author to whom correspondence should be addressed.