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Structure of an *N*-Iminopyridine Complex of Methylcobaloxime, Bis(dimethylglyoximato)(*N*-iminopyridine)methylcobalt

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The structure of bis(dimethylglyoximato)(*N*-iminopyridine)methylcobalt, $CH_3Co(Hdmg)_2(HNNC_5H_5)$, has been determined by using X-ray diffraction techniques. The *N*-iminopyridine coordinates to cobalt through the imino nitrogen atom which has sp^2 character. The N–N bond distance in the Co–N(1)–N(2) system is 1.350 (9) Å and the bonding around the N(1) is planar. The bond distance Co–N(1) is 2.038 (6) Å and Co–CH_3 is 2.006 (8) Å. The pyridine ring is nearly perpendicular (82.6°) to the equatorial plane of dimethylglyoximes. The title complex crystallized in space group $P2/c$ with a = 11.479 (2) Å, b = 9.234 (2) Å, c = 17.105 (5) Å, β = 90.26 (2)°, and Z = 4. On the basis of 2237 ($|F_o| \geq 3\sigma$) unique reflections, the structure was refined by block-diagonal, least-squares methods to R_F = 0.076.

Introduction

Complexes with the ligands having N–N bonding have been extensively studied partly because of the relation to the intermediate stages of the reduction of coordinated dinitrogen.[1-3] Pyridinium imines are isoelectronic with pyridinium ylides and their complexes have been reported,[4,5] but little chemistry of unsubstituted *N*-iminopyridine, $C_5H_5N^+-N^-H$, as a ligand is known. As probably the first complex of the ligand, the title complex has been prepared by the method employed for the preparation of the pyridinium phenacylide complexes of methylcobaloxime.[6] The reactivity of the coordinated *N*-iminopyridine toward 1,3-dipolarophiles suggested that the imino nitrogen was in the similar hybridization state to that of the free *N*-iminopyridine.[7] We have carried out the present X-ray study to determine whether the coordinated nitrogen has a planar bonding character (sp^2) or a tetrahedral bonding character with a lone pair (sp^3).

Experimental Section

Preparation of $CH_3Co(Hdmg)_2(HNNC_5H_5)$. The complex was prepared by the treatment of $CH_3Co(Hdmg)_2\{S(CH_3)_2\}$[8] with an ethanol solution containing *N*-iminopyridine which was formed in situ by the reaction of pyridine and hydroxylamine-*O*-sulfonic acid followed by K_2CO_3 treatment.[9] The complex was purified from CH_2Cl_2–hexane. Infrared spectra indicate ν(NH) at 3270 cm^{-1} (KBr) and ^1H NMR spectra show Co methyl at δ 0.63 and dmg methyl at δ 2.04.

Crystal Preparation. Crystals were grown in CH_2Cl_2/ether solution at 5 °C. They were stable toward X-ray irradiation in air during the data collection.

Crystallographic Data. Weissenberg photographs indicated that the crystals were monoclinic belonging to a space group of either $P2/c$ or Pc from systematic absences: $h0l$, $l = 2n + 1$. Accurate unit cell dimensions were determined by a least-squares analysis of the angular positions of 18 strong reflections determined by a Rigaku four-circle automated diffractometer. The intensities were measured by the diffractometer in ω–2θ scan mode and corrected for Lorentz and polarization effects. The intensities of three standard reflections measured every 50 reflections during the data collection did not vary by more than 3%.

Table I. Summary of Crystallographic Data

compd: $Co(C_4H_7N_2O_2)_2(CH_3)(HNNC_5H_5)$	cryst size: 0.40 × 0.20 × 0.09 mm
formula: $C_{14}H_{23}CoN_6O_4$	D_m = 1.45 g cm^{-3}
fw: 398.3	D_x = 1.46 g cm^{-3}
space group: $P2/c$	μ = 10.11 cm^{-1} (Mo Kα)
a = 11.479 (2) Å	Mo Kα radiatn: λ 0.710 69
b = 9.234 (2) Å	scan speed: 2.0°/min
c = 17.105 (5) Å	bkgd counting: 10 s
β = 90.26 (2)°	2θ limit: 3–60°
V = 1813 Å^3	unique data: $I_o > 3\sigma(I_o)$ 2237
Z = 4	R_F = 0.076

Solution and Refinement of the Structure. The structure was solved by the usual heavy-atom method. The position of the cobalt atom was determined from a Patterson synthesis, and all the nonhydrogen atoms were located by the subsequent Fourier syntheses. The positions of the atoms were refined by the block-diagonal least-squares method with anisotropic temperature factors. A difference-Fourier synthesis at the stage of R = 0.090 revealed the positions of the imino hydrogen, pyridine hydrogens, oxime hydrogens, cobalt methyl hydrogens, and three dmg methyl hydrogens. Further refinements including the above 14 hydrogens and the calculated positions (l(C–H) = 1.08 Å; B = 3 Å^2) of six of nine remaining dmg hydrogens, using isotropic temperature factors for the hydrogen atoms, reduced the final $R = \sum||F_o| - |F_c||/\sum|F_o|$ to 0.076. The space group $P2/c$ was chosen from the test of R-factor ratio described by Hamilton.[10]

Atomic scattering factors were taken from ref 11, that of cobalt being corrected for the real and imaginary parts of anomalous dispersion. A weighting scheme with w = 1 for $|F_o| \geq 15.2$ on an absolute scale and w = 0.5 in other cases was employed. The calculation was performed on the HITAC 8700/8800 computer at the computer center of the University of Tokyo, using a local version of the UNICS programs.[12]

The final positional and thermal parameters of the refined atoms are given in Tables II and III. A listing of observed and calculated structure factors is available.

Results

Description of the Structure. The structure of $CH_3Co(Hdmg)_2(HNNC_5H_5)$ consists of discrete monomeric molecules in the unit cell. A molecular structure together with the labeling scheme is shown in Figure 1, and the bonding around the imino nitrogen N(1) is shown in Figure 2.

The four nitrogen atoms of dimethylglyoxime are coplanar within 0.003 Å and the cobalt atom is almost on this plane

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Table II. Fractional Coordinates[a]

atom	x	y	z
Co	2902 (1)	1770 (1)	961 (1)
C(1)	2968 (8)	1763 (13)	2133 (5)
N(1)	2960 (6)	1538 (8)	−223 (4)
N(2)	2603 (5)	2351 (7)	−835 (4)
C(22)	1878 (7)	3503 (9)	−738 (5)
C(23)	1487 (8)	4321 (10)	−1357 (6)
C(24)	1846 (10)	3985 (12)	−2115 (6)
C(25)	2568 (8)	2796 (11)	−2209 (5)
C(26)	2947 (7)	1996 (10)	−1584 (5)
N(3)	2492 (6)	−200 (8)	1008 (4)
N(4)	1268 (6)	2000 (8)	1035 (4)
N(5)	3322 (6)	3735 (7)	987 (4)
N(6)	4538 (6)	1540 (7)	952 (4)
O(3)	3268 (5)	−1279 (6)	970 (4)
O(4)	760 (5)	3301 (8)	1089 (4)
O(5)	2509 (5)	4830 (7)	1060 (4)
O(6)	5053 (5)	243 (7)	956 (4)
C(3)	1375 (8)	−500 (10)	1024 (5)
C(4)	671 (8)	805 (11)	1066 (6)
C(5)	4423 (7)	4025 (9)	984 (5)
C(6)	5141 (7)	2735 (10)	939 (5)
C(7)	927 (10)	−2025 (12)	1006 (7)
C(8)	−645 (8)	827 (14)	1181 (7)
C(9)	4888 (10)	5551 (11)	1067 (6)
C(10)	6447 (7)	2768 (12)	858 (6)
H(1)	359 (8)	74 (10)	−37 (5)
H(2)	401 (9)	−86 (11)	99 (6)
H(3)	169 (10)	440 (14)	92 (7)
H(22)	159 (6)	369 (8)	−20 (4)
H(23)	91 (7)	513 (10)	−136 (5)
H(24)	161 (8)	469 (11)	−254 (5)
H(25)	313 (10)	252 (13)	−268 (7)
H(26)	353 (7)	123 (9)	−162 (5)
H(11)	357 (7)	224 (10)	232 (5)
H(12)	230 (10)	246 (13)	231 (7)
H(13)	263 (11)	86 (14)	240 (7)
H(71)	46 (8)	−227 (11)	66 (6)
H(81)	−84 (8)	30 (10)	85 (5)
H(101)	674 (9)	256 (13)	118 (6)

[a] The values in the table are multiplied by 10^4 for nonhydrogen atoms and by 10^3 for hydrogen atoms.

Table III. Anisotropic Temperature Factors (× 10^3) with Esd's in Parentheses

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	25 (1)	27 (1)	29 (1)	−2 (1)	3 (1)	0 (1)
C(1)	64 (6)	63 (6)	29 (4)	−9 (6)	3 (4)	4 (5)
N(1)	46 (4)	39 (4)	29 (3)	8 (3)	−5 (3)	3 (3)
N(2)	29 (3)	32 (4)	33 (4)	−8 (3)	−4 (3)	3 (3)
C(22)	33 (4)	36 (5)	39 (5)	−2 (4)	0 (3)	4 (4)
C(23)	45 (5)	45 (6)	49 (6)	−6 (4)	−5 (4)	9 (5)
C(24)	73 (7)	52 (6)	44 (6)	−7 (6)	−5 (5)	17 (5)
C(25)	52 (6)	63 (7)	39 (5)	−5 (5)	−3 (4)	9 (5)
C(26)	43 (5)	40 (6)	30 (4)	−2 (4)	7 (3)	−3 (4)
N(3)	44 (4)	32 (4)	36 (4)	6 (3)	10 (3)	6 (3)
N(4)	33 (4)	39 (4)	42 (4)	3 (3)	3 (3)	1 (3)
N(5)	44 (4)	28 (3)	32 (4)	−5 (3)	2 (3)	−2 (3)
N(6)	35 (4)	33 (4)	35 (4)	2 (3)	0 (3)	4 (3)
O(3)	49 (4)	30 (3)	60 (4)	−2 (3)	1 (3)	2 (3)
O(4)	40 (3)	52 (4)	64 (4)	17 (3)	6 (3)	−1 (4)
O(5)	44 (4)	37 (4)	65 (4)	12 (3)	5 (3)	−6 (3)
O(6)	35 (3)	36 (3)	54 (4)	9 (3)	2 (3)	3 (3)
C(3)	41 (5)	43 (5)	41 (5)	−9 (4)	−1 (4)	11 (4)
C(4)	39 (5)	58 (6)	46 (6)	−14 (5)	6 (4)	2 (5)
C(5)	41 (5)	35 (5)	35 (5)	−4 (4)	3 (4)	−4 (4)
C(6)	35 (4)	45 (5)	29 (4)	−6 (4)	−2 (3)	4 (4)
C(7)	76 (8)	51 (7)	85 (8)	−36 (6)	−19 (6)	14 (6)
C(8)	28 (5)	96 (9)	91 (9)	−19 (6)	12 (5)	−9 (7)
C(9)	80 (8)	40 (6)	64 (7)	−21 (6)	−5 (6)	−8 (5)
C(10)	27 (4)	82 (8)	51 (6)	−9 (5)	−4 (4)	6 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2(as)^2 + \ldots + 2U_{12}hk(as)(bs) + \ldots)]$, where *as*, *bs*, and *cs* are the reciprocal lattice constants.

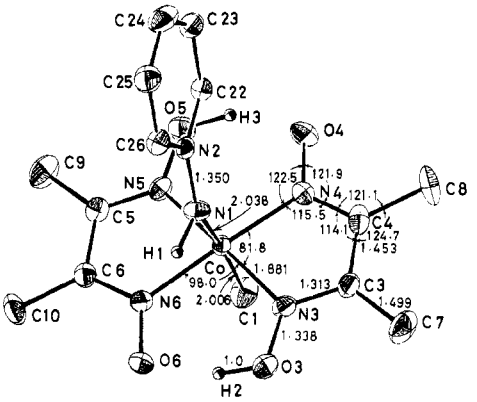


Figure 1. Drawing of a molecule of $CH_3Co(Hdmg)_2(HNNC_5H_5)$. The vibrational ellipsoids have been drawn at the 30% probability level except for the hydrogen atoms which have been drawn artificially small.

Table IV. Bond Distances (Å) in $CH_3Co(Hdmg)_2(HNNC_5H_5)$

Co-C(1)	2.006 (8)	N(3)-C(3)	1.31 (1)
Co-N(1)	2.038 (6)	N(4)-C(4)	1.30 (1)
Co-N(3)	1.881 (7)	N(5)-C(5)	1.29 (1)
Co-N(4)	1.893 (7)	N(6)-C(6)	1.30 (1)
Co-N(5)	1.878 (7)	C(3)-C(7)	1.50 (1)
Co-N(6)	1.890 (6)	C(4)-C(8)	1.52 (1)
N(1)-N(2)	1.350 (9)	C(5)-C(9)	1.51 (1)
N(2)-C(22)	1.36 (1)	C(6)-C(10)	1.51 (1)
C(22)-C(23)	1.37 (1)	C(3)-C(4)	1.45 (1)
C(23)-C(24)	1.39 (1)	C(5)-C(6)	1.45 (1)
C(24)-C(25)	1.38 (2)	[O(3)-O(6)]	2.485 (8)
C(25)-C(26)	1.37 (1)	[O(4)-O(5)]	2.455 (9)
C(26)-N(2)	1.38 (1)	N(1)-H(1)	1.07 (9)
N(3)-O(3)	1.34 (1)	O(3)-H(2)	0.9 (1)
N(4)-O(4)	1.34 (1)	O(5)-H(3)	1.0 (1)
N(5)-O(5)	1.38 (1)		
N(6)-O(6)	1.34 (1)		

Table V. Bond Angles (Deg) in $CH_3Co(Hdmg)_2(HNNC_5H_5)$

C(1)-Co-N(1)	172.6 (3)	N(3)-C(3)-C(4)	111.7 (8)
Co-N(1)-N(2)	134.5 (5)	N(4)-C(4)-C(3)	114.1 (8)
Co-N(1)-H(1)	110 (5)	N(5)-C(5)-C(6)	112.8 (8)
N(2)-N(1)-H(1)	114 (5)	N(6)-C(6)-C(5)	113.1 (7)
N(3)-Co-N(4)	81.8 (3)	N(3)-C(3)-C(7)	122.2 (8)
N(4)-Co-N(5)	98.3 (3)	N(4)-C(4)-C(8)	121.1 (9)
N(5)-Co-N(6)	81.6 (3)	N(5)-C(5)-C(9)	122.5 (8)
N(6)-Co-N(3)	98.1 (3)	N(6)-C(6)-C(10)	123.2 (8)
Co-N(3)-C(3)	116.8 (6)	C(7)-C(3)-C(4)	126.1 (8)
Co-N(4)-C(4)	115.5 (6)	C(8)-C(4)-C(3)	124.7 (9)
Co-N(5)-C(5)	116.8 (6)	C(9)-C(5)-C(6)	124.7 (8)
Co-N(6)-C(6)	115.7 (6)	C(10)-C(6)-C(5)	123.7 (8)
Co-N(3)-O(3)	123.5 (5)	N(2)-C(22)-C(23)	122.3 (8)
Co-N(4)-O(4)	122.5 (5)	C(22)-C(23)-C(24)	119.8 (9)
Co-N(5)-O(5)	122.4 (5)	C(23)-C(24)-C(25)	117.5 (9)
Co-N(6)-O(6)	122.8 (5)	C(24)-C(25)-C(26)	121.7 (9)
O(3)-N(3)-C(3)	119.6 (7)	C(25)-C(26)-N(2)	120.4 (8)
O(4)-N(4)-C(4)	121.9 (7)	C(26)-N(2)-C(22)	118.4 (7)
O(5)-N(5)-C(5)	120.7 (7)	N(3)-O(3)-H(2)	107 (6)
O(6)-N(6)-C(6)	121.6 (7)	N(5)-O(5)-H(3)	108 (6)

with slight displacement of 0.059 Å. The cobalt–nitrogen bond distances are 1.878 (7)–1.893 (7) Å (average 1.886 Å). The dihedral angle of the two least-squares planes of the dmg ligands is 2.3°, and those between the dmg planes and the equatorial coordination planes are 2.7° and 3.3°.

The pyridine ring is nearly planar and the dihedral angle between its plane and the equatorial plane is 82.6°. The imino nitrogen N(1) and hydrogen H(1) are nearly on the pyridine plane, and the N(2)–N(1) bond distance is 1.350 (9) Å. The imino nitrogen N(1) is displaced by only 0.1 Å from the plane passing Co, N(2), and H(1).

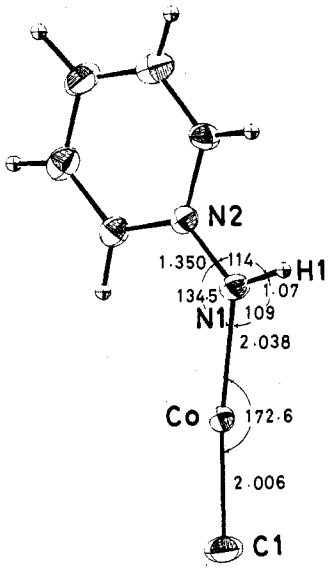


Figure 2. Bonding around the imino nitrogen atom.

Table VI. Least-Squares Planes[a] and Atomic Deviation Therefrom and Dihedral Angles for $CH_3Co(Hdmg)_2(HNNC_5H_5)$

Planes and Deviations (Å)

(A) $-0.0377X - 0.0000Y - 0.9993Z + 1.8270 = 0$[b]

N(3)*	−0.0034	O(4)	−0.0666	C(6)	0.0000
N(4)*	0.0034	O(5)	−0.0928	C(7)	0.0671
N(5)*	−0.0034	O(6)	−0.0255	C(8)	−0.1638
N(6)*	0.0034	C(3)	0.0176	C(9)	−0.2087
Co	0.0585	C(4)	−0.0241	C(10)	0.0811
O(3)	0.0272	C(5)	−0.0467		

(B) $-0.0790X + 0.0233Y - 0.9966Z + 1.8848 = 0$

N(3)*	−0.0632	C(4)*	0.0245	Co	0.0214
N(4)*	0.0492	C(7)*	0.0423	O(3)	−0.0928
C(3)*	0.0044	C(8)*	−0.0517	O(4)	0.0315

(C) $-0.0554X + 0.0553Y - 0.9969Z + 1.7778 = 0$

N(5)*	0.0747	C(6)*	−0.0104	Co	0.0446
N(6)*	−0.0557	C(9)*	−0.0695	O(5)	0.0581
C(5)*	0.0237	C(10)*	0.0454	O(6)	−0.1614

(D) $-0.7938X - 0.6000Y - 0.0996Z + 3.5322 = 0$

N(2)*	−0.0050	C(24)*	−0.0097	N(1)	0.0197
C(22)*	0.0014	C(25)*	0.0063	Co	−0.2510
C(23)*	0.0060	C(26)*	0.0011	H(1)	−0.0904

(E) $-0.7897X - 0.6131Y - 0.0223Z + 3.6638 = 0$

Co*	H(1)*	
N(2)*	N(1)	0.1172

(F) $-0.8889X - 0.4579Y + 0.01552Z + 3.6778 = 0$

Co*	N(2)*	
N(1)*	H(1)	−0.3140

Dihedral Angles (Deg)

A/B	2.7	A/C	3.3	B/C	2.3	A/D	82.6

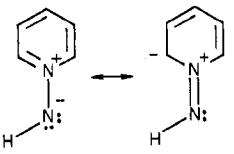
[a] Atoms used in calculating the plane are marked with an asterisk. [b] Cartesian (orthonormalized Å) coordinates.

The Co–CH_3 and Co–N(1) bond distances are 2.006 (8) and 2.038 (6) Å, respectively. The bond angle C(1)–Co–N(1) is 172.6 (3)°.

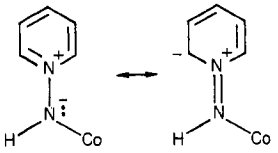
Discussion

The results show that the cobaloxime system is very similar to those of other methylcobaloxime complexes,[6,13-16] and its detailed description and discussion are omitted.

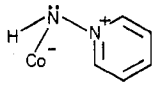
N-Iminopyridine is a 1,3-dipole



and when it coordinates to cobalt through the imino nitrogen, two possibilities arise. Namely, it can coordinate to cobalt retaining the sp^2 character of the imino nitrogen, **1**. Alternatively, the formal charge on the imino nitrogen is shifted to cobalt and the nitrogen becomes sp^3 hybridized with a lone pair to one of the tetrahedral directions, **2**.



1



2

The X-ray analysis indicates that the bonding around the imino nitrogen N(1) is almost planar, and the bond distance N(1)–N(2) (1.350 Å) has the value of a conjugated N=N bond. The Co–N(1) distance 2.038 Å is even shorter than those of methylcobaloxime complexes with pyridine (2.068 Å) or *N*-methylimidazole (2.058 Å) in which sp^2 hybridized nitrogen atoms coordinate to cobalt.[15] If the imino nitrogen is sp^3 hybridized, a longer bond distance is expected.[17] Consequently, we conclude that the *N*-iminopyridine coordinates to cobalt through the imino nitrogen which retains its sp^2 character.

The Co–CH_3 bond distance (2.006 Å) suggests that the bond lengthening effect (trans influence) of *N*-iminopyridine ligand is weaker than that of a keto-stabilized pyridinium ylide, $C_5H_5N^+C^-HCOPh$, which gives the Co–CH_3 bond distance of 2.04 Å, when it is coordinated to the methylcobaloxime system.[6]

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Registry No. $CH_3Co(Hdmg)_2(HNNC_5H_5)$, 73746-87-9; $CH_3Co(Hdmg)_2\{S(CH_3)_2\}$, 25482-40-0.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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