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Molecular and Crystal Structure of *cis*-[Co^{III}(3-hydroxyimino-2,4-pentanedionato)$_2$(pyridine)$_2$] ClO$_4$

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The crystal structure of cis-*[Co^{III}(3-hydroxyimino-2,4-pentanedionato)$_2$(pyridine)$_2$] ClO$_4$ has been determined by X-ray analysis. The brown hexagonal tabular crystals are orthorhombic and the space group* Pna2$_1$. *The unit cell dimensions are* a = *17.11(1),* b = *10.62(2),* c = *13.65(1) Å; Z = 4. The structure was deduced by the heavy atom method and refined by the block-diagonal least-squares method to a final* R *value of 0.090 for 1812 observed reflections. The structure consists of the complex cation with a* cis *geometry and the perchlorate anion. The cobalt atom has an octahedral coordination with the two Co–N(pyridine) bond distances of 1.99 and 1.99 Å, and the two Co–N (hydroxyiminato) bond distances of 1.88 and 1.90 Å, and the two Co–O bond distances of 1.88 and 1.88 Å. Each of the planes of pyridine rings in the complex cation is almost perpendicular to each of the corresponding equatorial planes. The axial pyridine plane does not exactly bisect O–Co–N angle on the equatorial plane: it rotates about the axis of Co–N (pyridine) in the range of 6° to 24° from the bisector of O–Co–N angle toward the Co–O bond.*

Introduction

Stable cobalt(III) complexes of α-hydroxyimino ketones (mOH), R–C(=O)–C(=NOH)R′, with the formula Co^{III}(mo)$_3$ can be prepared with ease in case of R or R′ being an aromatic group, but with difficulty in case of both R and R′ being aliphatic groups. In spite of the instability of the aliphatic α-hydroxyimino ketone cobalt(III) complexes, the authors have recently succeeded in obtaining the crystalline cobalt(III) complexes of a series of aliphatic α-hydroxyimino ketones having the formula [Co(mo)$_2$(py)$_2$]ClO$_4$, where py is pyridine, by adding pyridine to a solution of α-hydroxyimino ketone and Co(ClO$_4$)$_2$6H$_2$O and by stirring the mixture in air at room temperature [1]. The PMR spectral investigation shows that the proton resonances of the R′ alkyl groups bound to the hydroxyimino group are shifted toward higher fields upon complex formation. This upfield shift for the R′ proton resonances can be attributed to the ring-current effect of the coordinated pyridine. Consequently, we have proposed the limiting structure for [Co(mo)$_2$(py)$_2$]ClO$_4$ in which the pyridine plane faces the R′ group. Unfortunately, however, the absolute configuration of the complexes cannot be determined from the results of PMR and IR. It is interesting to determine the absolute configuration of [Co(mo)$_2$(py)$_2$]ClO$_4$.

[Co(3-hydroxyimino-2,4-pentanedionato)$_2$(py)$_2$]·ClO$_4$ gives crystals suitable for X-ray study in a series of [Co(mo)$_2$(py)$_2$]ClO$_4$. In this paper, the crystal structure analysis of bis(3-hydroxyimino-2,4-pentanedionato)dipyridinecobalt(III)perchlorate was undertaken to determine the coordination of –C(=O)–C(–N=O)– group to the central cobalt atom and compare it with that of *trans*-bis(2,4-pentanedionato) dipyridinecobalt(II) [2] or *trans*-bis(2,4-pentanedionato)dipyridinenickel(II) [3], as has been determined to be *trans* form by Elder.

Experimental

The brown hexagonal tabular crystals of *cis*-[Co^{III}(3-hydroxyimino-2,4-pentanedionato)$_2$(pyridi-

TABLE I(a). Atomic Coordinates with their Standard Deviations in Parentheses.

	x	y	z
Co	0.8299(1)	0.7819(2)	0.5000(2)
Cl	0.7190(3)	0.7830(4)	0.8677(4)
N(1)	0.7395(7)	0.8582(13)	0.5514(9)
O(1)	0.7701(6)	0.6342(8)	0.5149(7)
O(3)	0.7359(7)	0.9726(12)	0.5657(10)
C(1)	0.6787(10)	0.7815(17)	0.5680(12)
C(3)	0.6991(7)	0.6552(17)	0.5431(11)
C(5)	0.6473(12)	0.5438(20)	0.5438(17)
C(7)	0.6013(10)	0.8208(19)	0.6115(12)
C(9)	0.5929(11)	0.9529(21)	0.6603(16)
O(5)	0.5499(7)	0.7430(15)	0.6064(10)
N(2)	0.8732(7)	0.7795(12)	0.6285(9)
O(2)	0.8823(5)	0.9371(9)	0.4920(9)
O(4)	0.8679(7)	0.6854(10)	0.6794(8)
C(2)	0.9036(9)	0.8918(15)	0.6558(11)
C(4)	0.9079(8)	0.9768(15)	0.5747(12)
C(6)	0.9414(11)	1.1046(16)	0.5765(16)
C(8)	0.9374(10)	0.9200(21)	0.7563(12)
C(10)	0.9551(14)	0.8189(23)	0.8249(15)
O(6)	0.9440(10)	1.0277(14)	0.7785(10)
N(11)	0.7879(7)	0.8018(12)	0.3650(10)
C(11)	0.7685(9)	0.9136(14)	0.3330(11)
C(21)	0.7378(11)	0.9337(19)	0.2386(13)
C(31)	0.7273(11)	0.8291(19)	0.1805(15)
C(41)	0.7454(11)	0.7060(18)	0.2147(14)
C(51)	0.7755(10)	0.6979(15)	0.3088(11)
N(12)	0.9220(6)	0.6873(11)	0.4494(9)
C(12)	0.9305(9)	0.5626(15)	0.4720(12)
C(22)	0.9929(11)	0.4945(18)	0.4381(17)
C(32)	1.0457(10)	0.5528(19)	0.3718(16)
C(42)	1.0386(13)	0.6777(21)	0.3521(15)
C(52)	0.9738(8)	0.7448(15)	0.3883(12)
O(15)	0.6636(12)	0.8278(18)	0.9357(15)
O(25)	0.6798(13)	0.7058(17)	0.7980(13)
O(35)	0.7757(10)	0.7121(17)	0.9160(15)
O(45)	0.7536(11)	0.8865(17)	0.8196(13)

TABLE I(b). Anisotropic Thermal Parameters ($\times 10^4$) of the Form: exp $-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$, and Their Standard Deviations.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	21.9(5)	52.7(13)	35.0(8)	−5.8(19)	4.5(19)	−12.4(32)
Cl	54(2)	83(4)	55(2)	9(6)	−4(4)	−5(6)
N(1)	24(5)	86(13)	35(7)	−40(14)	6(10)	−1(17)
O(1)	33(4)	50(8)	26(6)	−28(9)	−15(9)	28(13)
O(3)	43(5)	98(13)	72(9)	18(15)	0(12)	−27(20)
C(1)	35(7)	101(18)	39(9)	77(21)	5(14)	28(24)
C(3)	7(4)	139(21)	36(8)	−41(15)	−10(10)	74(23)
C(5)	41(8)	127(24)	90(17)	−55(24)	−3(20)	33(34)
C(7)	27(6)	149(25)	40(10)	−5(21)	−11(14)	42(27)
C(9)	30(7)	156(28)	80(15)	42(24)	37(18)	−59(37)
O(5)	27(4)	169(19)	81(10)	−61(16)	6(11)	4(24)
N(2)	31(5)	58(12)	37(7)	−22(14)	8(10)	44(17)
O(2)	26(3)	64(9)	50(7)	−32(9)	10(10)	0(18)

(continued on facing page)

TABLE I(b). *(continued)*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(4)	38(5)	77(12)	38(6)	–3(12)	0(10)	24(15)
C(2)	27(6)	73(16)	38(9)	10(16)	35(12)	42(21)
C(4)	11(4)	84(16)	50(10)	–30(15)	9(11)	–51(23)
C(6)	41(8)	66(16)	79(14)	–38(20)	5(18)	40(27)
C(8)	33(7)	182(29)	28(9)	–71(25)	–17(14)	–66(28)
C(10)	63(11)	160(29)	59(13)	31(30)	–78(21)	63(33)
O(6)	106(10)	122(17)	46(8)	–84(23)	–52(16)	–71(20)
N(11)	22(4)	85(14)	39(7)	31(13)	–15(10)	–0(18)
C(11)	21(5)	68(14)	40(9)	38(15)	–21(12)	–18(20)
C(21)	42(8)	120(23)	40(11)	–19(22)	–13(16)	55(26)
C(31)	33(7)	135(24)	60(12)	–20(24)	15(16)	–53(33)
C(41)	45(8)	83(18)	54(11)	6(20)	–20(15)	2(25)
C(51)	44(7)	59(15)	33(8)	–7(18)	–7(14)	–9(19)
N(12)	10(3)	69(12)	43(7)	–14(11)	–3(9)	–19(16)
C(12)	22(5)	70(15)	57(12)	–27(15)	–11(12)	3(20)
C(22)	34(7)	78(17)	89(15)	52(19)	22(18)	–61(29)
C(32)	24(6)	120(22)	92(16)	–1(20)	–1(17)	–99(34)
C(42)	51(9)	160(28)	49(12)	–22(28)	–12(18)	8(32)
C(52)	14(4)	86(16)	51(10)	–7(14)	21(12)	–52(22)
O(15)	96(12)	210(27)	114(15)	86(30)	1(24)	–102(35)
O(25)	110(12)	161(22)	87(13)	17(29)	–59(21)	–6(28)
O(35)	62(8)	179(23)	133(16)	18(24)	–31(20)	100(34)
O(45)	80(10)	163(22)	103(14)	–24(25)	2(19)	46(29)

ne)$_2$]ClO$_4$(*cis*-[Co(hipd)$_2$(py)$_2$]ClO$_4$) were obtained by slow evaporation of an aqueous ethanol solution. Intensity data were measured by the θ–2θ scan technique on a Rigaku four-circle diffractometer with graphite-monochromated Mo$K\alpha$ radiation. The size of the crystal used was 0.15 × 0.10 × 0.05 mm. The scan speed and scan width in ω were 2° min^{-1} and $(1.4 + 0.35\ \tan\theta)°$, respectively. Of 2349 independent reflections collected up to $\sin\theta/\lambda = 0.6$ Å^{-1}, 1812 reflections with $|F_o| \geqslant 3\sigma(|F_o|)$ were used in the subsequent calculation. The corrections were made for Lorentz and polarization effects, but not for absorption.

Crystal Data

$C_{20}ClH_{22}N_4O_{10}Co$, F.W. = 572.8, orthorhombic, space group $Pna2_1$, a = 17.11(1), b = 10.62(2), c = 13.65(1) Å, V = 2481 Å^3, D_m = 1.55 (flotation), D_x = 1.56 g cm^{-3}, Z = 4, μ = 8.49 cm^{-1} (Mo$K\alpha$).

Structure Determination and Refinement

The systematic absence $0kl$, $k + l = 2n + 1$ and $h0l$, $h = 2n + 1$ indicated the space group, $Pnam$ or $Pna2_1$. A three-dimensional Patterson map clearly indicated space group $Pna2_1$, which was confirmed by the following successful structure analysis.

The structure was determined by the heavy-atom method. The coordinates of the cobalt atom were found from a three-dimensional Patterson synthesis and those of all other non-hydrogen atoms were from the subsequent Fourier synthesis. Several cycles of block-diagonal least-squares refinement, using isotropic thermal parameters, brought the R value to 0.118. After further several cycles of block-diagonal least-squares refinement with anisotropic temperature factors was carried out, R dropped to 0.095. At this stage, the geometrical structure of the present complex cation was found to be *cis*-configuration. There are two kinds of optical isomers in this *cis*-configuration of the cation. Using the anomalous scattering and the Bijvoet difference of the reflections, the determination of the absolute structure of the present crystal can be expected, because the crystal is polar in the c-axis direction. In order to determine the absolute configuration, 1451 intensity data in the first quadrant were collected by the θ–2θ scan technique on a Rigaku four-circle diffractometer with Ni-filtered Cu$K\alpha$ radiation. If the representative atomic coordinates of Λ-cation, which had been adopted so far, are assumed as (x, y, z), those of Δ-cation should be expressed as (x, y, $\bar{z}$), with reference to the same crystal axes [4]. Applying anomalous dispersion corrections for Co, Cl, O, N and C atoms, the atomic parameters of Δ-cation and atomic parameters of Λ-cation were refined by a block diagonal least-squares method. The resultant R factors of 0.081 and 0.100 were obtained for Δ- and Λ-cations respectively. The hypothesis that the absolute configuration is of the Λ-cation was rejected at the 0.005 level by Hamilton's R value

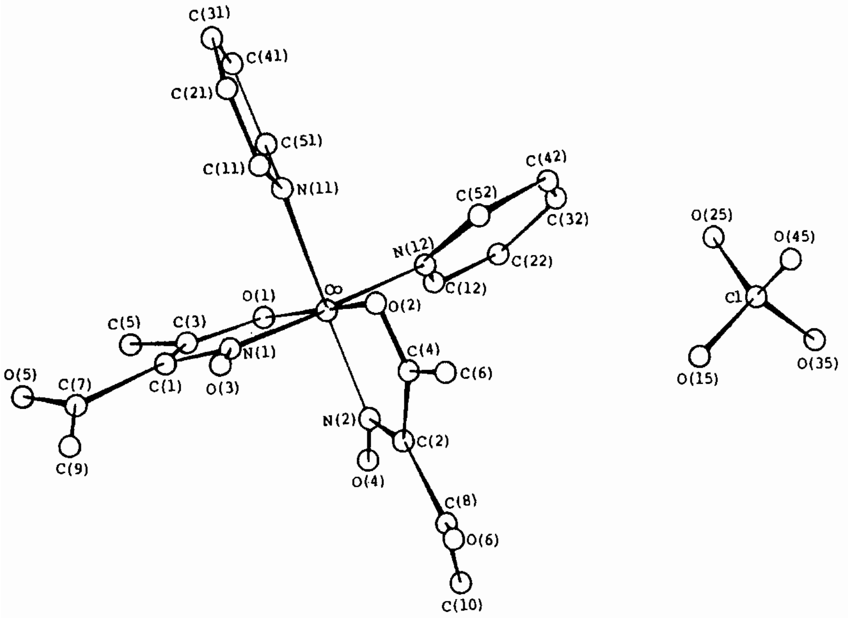

Fig. 1. The geometry and atom numbering scheme of the Co(hipd)$_2$(py)$_2$ cation and the perchlorate anion. Among the hydroxyiminato and pyridine groups, each moiety with odd-numbering atoms was designated as Mox1 and Py1 respectively, and each one with even-numbering atoms as Mox2 and Py2 respectively.

significance test [5]. In addition, the bond distances and angles of Δ-cation indicated more reasonable values than those of Λ-cation. The final R value was 0.090 (for Mo$K\alpha$). The function minimized was $\Sigma w(F_o - |F_c|)^2$, with w = 1.0 for all reflections. All the atomic scattering factors and anomalous scattering factors were taken from 'International Tables for X-Ray Crystallography' [6]. The computations were carried out on an ACOS-S700 computer at Crystallographic Research Center, Institute for Protein Research Laboratory, Osaka University, with 'The Universal Crystallographic Computing System-Osaka (1979)' [7]. The final positional and thermal parameters are listed in Table I. A list of structure factors multiplied by 10 is available from the Editor.

Description of Structure and Discussion

The geometry and atom numbering of the Co(hipd)$_2$(py)$_2$ cation and the perchlorate anion are illustrated in Fig. 1. The intramolecular bond lengths and angles with their associated e.s.d.s are given in Tables II and III respectively. Table IV lists the distances of selected atoms from least-squares planes, and their dihedral angles. Hereafter, the four independent ligands coordinating to the central cobalt atom will be designated as Mox1 and Mox2 for hydroxyimino ketone moieties, and as Py1 and Py2 for pyridine groups.

TABLE II. Bond Lengths (Å) with their Estimated Standard Deviations in Parentheses.

Co–O(1)	1.88(1)	Co–O(2)	1.88(1)
Co–N(1)	1.88(1)	Co–N(2)	1.90(1)
O(1)–C(3)	1.29(2)	O(2)–C(4)	1.28(2)
N(1)–C(1)	1.34(2)	N(2)–C(2)	1.35(2)
C(1)–C(3)	1.43(2)	C(2)–C(4)	1.43(2)
N(1)–O(3)	1.23(2)	N(2)–O(4)	1.22(2)
C(3)–C(5)	1.48(3)	C(4)–C(6)	1.47(3)
C(1)–C(7)	1.51(3)	C(2)–C(8)	1.52(3)
C(7)–C(9)	1.56(3)	C(8)–C(10)	1.46(3)
C(7)–O(5)	1.21(2)	C(8)–O(6)	1.19(3)
Co–N(11)	1.99(1)	Co–N(12)	1.99(1)
N(11)–C(11)	1.31(2)	N(12)–C(12)	1.37(2)
C(11)–C(21)	1.41(2)	C(12)–C(22)	1.37(3)
C(21)–C(31)	1.38(3)	C(22)–C(32)	1.42(3)
C(31)–C(41)	1.42(3)	C(32)–C(42)	1.36(3)
C(41)–C(51)	1.39(3)	C(42)–C(52)	1.41(3)
C(51)–N(11)	1.36(2)	C(52)–N(12)	1.36(2)
Cl–O(15)	1.41(2)		
Cl–O(25)	1.42(2)		
Cl–O(35)	1.39(2)		
Cl–O(45)	1.41(2)		

Environment of the Cobalt Atom

The ligands Mox1, Mox2, Py1 and Py2 coordinating to the cobalt atom do not adopt *trans* geometry but *cis* geometry. That was entirely

TABLE III. Bond Angles (°) with their Estimated Standard Deviations in Parentheses.

O(1)–Co–O(2)	174.6(5)	O(2)–Co–N(1)	92.0(6)
O(1)–Co–N(1)	82.6(5)	O(2)–Co–N(2)	83.1(6)
O(1)–Co–N(2)	95.7(5)	O(2)–Co–N(11)	91.4(6)
O(1)–Co–N(11)	89.5(5)	O(2)–Co–N(12)	92.6(5)
O(1)–Co–N(12)	92.7(5)	N(2)–Co–N(11)	174.5(6)
N(1)–Co–N(2)	89.0(6)	N(2)–Co–N(12)	90.2(5)
N(1)–Co–N(11)	90.1(6)	N(11)–Co–N(12)	91.0(5)
N(1)–Co–N(12)	175.2(6)		
Co–O(1)–C(3)	113(1)	Co–O(2)–C(4)	113(1)
Co–N(1)–C(1)	116(1)	Co–N(2)–C(2)	113(1)
Co–N(1)–O(3)	121(1)	Co–N(2)–O(4)	120(1)
O(3)–N(1)–C(1)	122(1)	O(4)–N(2)–C(2)	126(1)
N(1)–C(1)–C(3)	110(1)	N(2)–C(2)–C(4)	111(1)
N(1)–C(1)–C(7)	125(1)	N(2)–C(2)–C(8)	124(1)
C(3)–C(1)–C(7)	124(1)	C(4)–C(2)–C(8)	124(1)
C(1)–C(3)–O(1)	117(1)	C(2)–C(4)–O(2)	117(1)
C(1)–C(3)–C(5)	127(2)	C(2)–C(4)–C(6)	126(1)
O(1)–C(3)–C(5)	115(1)	O(2)–C(4)–C(6)	117(1)
C(1)–C(7)–O(5)	115(2)	C(2)–C(8)–O(6)	117(2)
C(1)–C(7)–C(9)	120(1)	C(2)–C(8)–C(10)	121(2)
O(5)–C(7)–C(9)	125(2)	O(6)–C(8)–C(10)	122(2)
Co–N(11)–C(11)	120(1)	Co–N(12)–C(12)	119(1)
Co–N(11)–C(51)	119(1)	Co–N(12)–C(52)	120(1)
C(11)–N(11)–C(51)	120(1)	C(12)–N(12)–C(52)	120(1)
N(11)–C(11)–C(21)	122(1)	N(12)–C(12)–C(22)	121(1)
C(11)–C(21)–C(31)	117(2)	C(12)–C(22)–C(32)	118(2)
C(21)–C(31)–C(41)	121(2)	C(22)–C(32)–C(42)	119(2)
C(31)–C(41)–C(51)	116(2)	C(32)–C(42)–C(52)	119(2)
C(41)–C(51)–N(11)	122(1)	C(42)–C(52)–N(12)	120(1)
O(15)–Cl–O(25)	108(1)	O(25)–Cl–O(35)	109(1)
O(15)–Cl–O(35)	110(1)	O(25)–Cl–O(45)	109(1)
O(15)–Cl–O(45)	109(1)	O(35)–Cl–O(45)	110(1)

TABLE IV. Some Best Planes through Sets of Atoms and Distances (Å) of Atoms from those Planes.

Plane	Defined by atoms	Distances of specified atoms from the plane
(1)	O(1), O(2), N(1), N(12)	O(1) –0.00, O(2) –0.00, N(1) 0.00, N(12) 0.00, Co –0.00
(2)	O(1), O(2), N(2), N(11)	O(1) 0.03, O(2) 0.03, N(2) –0.02, N(11) –0.03, Co –0.05
(3)	N(1), N(2), N(11), N(12)	N(1) –0.08, N(2) 0.11, N(11) 0.06, N(12) –0.08, Co –0.00
(4)	Co, O(1), N(1)	Co 0, O(1) 0, N(1) 0
(5)	Co, O(2), N(2)	Co 0, O(2) 0, N(2) 0
(6)	O(1), N(1), C(1), C(3)	O(1) 0.01, N(1) –0.01, C(1) 0.01, C(3) –0.01
(7)	O(2), N(2), C(2), C(4)	O(2) –0.00, N(2) 0.00, C(2) –0.00, C(4) 0.00
(8)	C(7), C(9), O(5)	C(7) 0, C(9) 0, O(5) 0
(9)	C(8), C(10), O(6)	C(8) 0, C(10) 0, O(6) 0

Dihedral angles (°) between planes

(4)–(6)	4
(5)–(7)	12
(6)–(8)	14
(7)–(9)	20

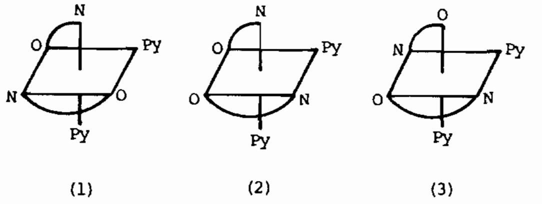

Fig. 2. The *cis* isomers of the cation.

unexpected before the structure analysis. In the octahedral ion about the cobalt atom, three kinds of *cis*-isomer are possible (Fig. 2). The isomer(1) corresponds to the present case. The N(1), O(2), N(12), O(1) and Co atoms lie on the same plane within experimental accuracy. The bond Co–N(11) is almost perpendicular to this plane, while the bond Co–N(2) makes an angle of 83° with it. Two Co–N (pyridine) distances (1.99, 1.99 Å) are comparable to those (2.04 Å) observed in O-methyl–(Co–C)carboxymethyl(bisdimethylglyoximato)pyridinato-cobalt [8], and (2.013 Å) observed in (*p*-methylphenyl)-1-ethyldioxybis(dimethylglyoximato)pyridinecobalt(III) [9]. The Co–N(hydroxyiminato) (1.88, 1.90 Å) and Co–O (1.88 Å) distances are in good agreement with the mean Co(III)–N and Co(III)–O distances in octahedral cobalt(III) complexes [10].

Geometry of the Cation

The projected line of the axial pyridine ring Py1 or Py2 on each corresponding equatorial plane is designated as LPy1 or LPy2. The line LPy1 is inclined by 11° away from the bisector of the O(2)–Co–N(1) angle toward the Co–O(2) bond, and also by 6° away from the bisector of the O(1)–Co–N(12) angle toward the Co–O(1) bond. Similarly the line LPy2 is inclined by 21° away from the bisector of the O(2)–Co–N(11) angle toward the Co–O(2) bond, and also by 24° away from the bisector of the O(1)–Co–N(2) angle toward the Co–O(1) bond. The axial Py1 or the axial Py2 does not exactly bisect the O–Co–N angle on the each equatorial plane, but is deviated from the bisector at angles more than 6°. Such deviation angle seems to be caused by interionic forces rather than the steric interaction within the cation as shown in Fig. 3.

On the other hand, in such molecular complexes as *trans*-bis(2,4-pentanedionato)dipyridinecobalt(II) and O-methyl–(Co–C)carboxymethyl(bisdimethylglyoximato) pyridinato-cobalt, each of the axial

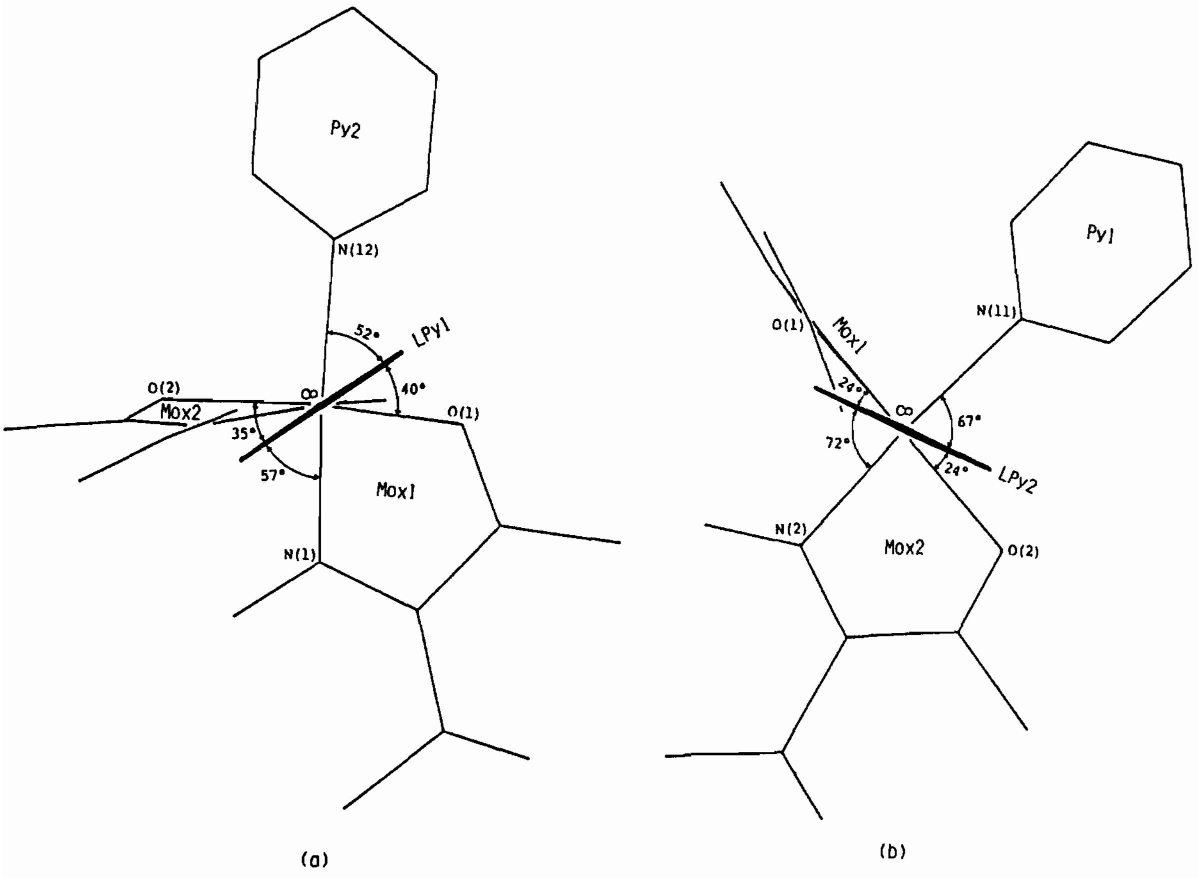

Fig. 3. Projections of the cation along (a) Co–N(11) and (b) Co–N(12).

pyridine planes bisects exactly the O–Co–O angle on the corresponding equatorial plane. In another complex of (*p*-methylphenyl)-1-ethyldioxybis-(dimethylglyoximato)pyridine-cobalt(III), the axial pyridine plane does not exactly bisect the N–Co–N angle on the equatorial plane; the deviation angle of 4.5° was reported to be caused mainly by the intermolecular interaction.

The hydroxyiminato rings Mox1 and Mox2 are at *cis* positions and bent in the direction getting near to each other. The hydroxyiminato ring Mox1 or Mox2 adopts an envelope conformation; the plane through N(1), Co, O(1) atoms makes an angle of 4° with the plane through N(1), C(1), C(3), O(1) atoms of the hydroxyiminato ring Mox1, while the plane through N(2), Co, O(2) atoms makes an angle of 12° with the plane through N(2), C(2), C(4), O(2) atoms of the hydroxyiminato ring Mox2. Such a difference between the dihedral angles of the hydroxyiminato rings Mox1 and Mox2 may be caused by the difference between the intermolecular forces (Fig. 3). The plane of the acetyl group C(9)C(7)O(5) branched from the hydroxyiminato ring Mox1 twists about C(1)–C(7) bond by 15° so that its methyl group, C(9), may go away from the pyridine ring Py1. On the contrary, the plane of another acetyl group twists about C(2)–C(8) bond by 20° so that its methyl group, C(10), may get near to the pyridine ring Py2. Of the hydroxyiminato rings the average distances of C–N, C–C and C–O bonds are 1.345, 1.43 and 1.285 Å respectively and they are comparable to those in 1:1 pyridine adduct of

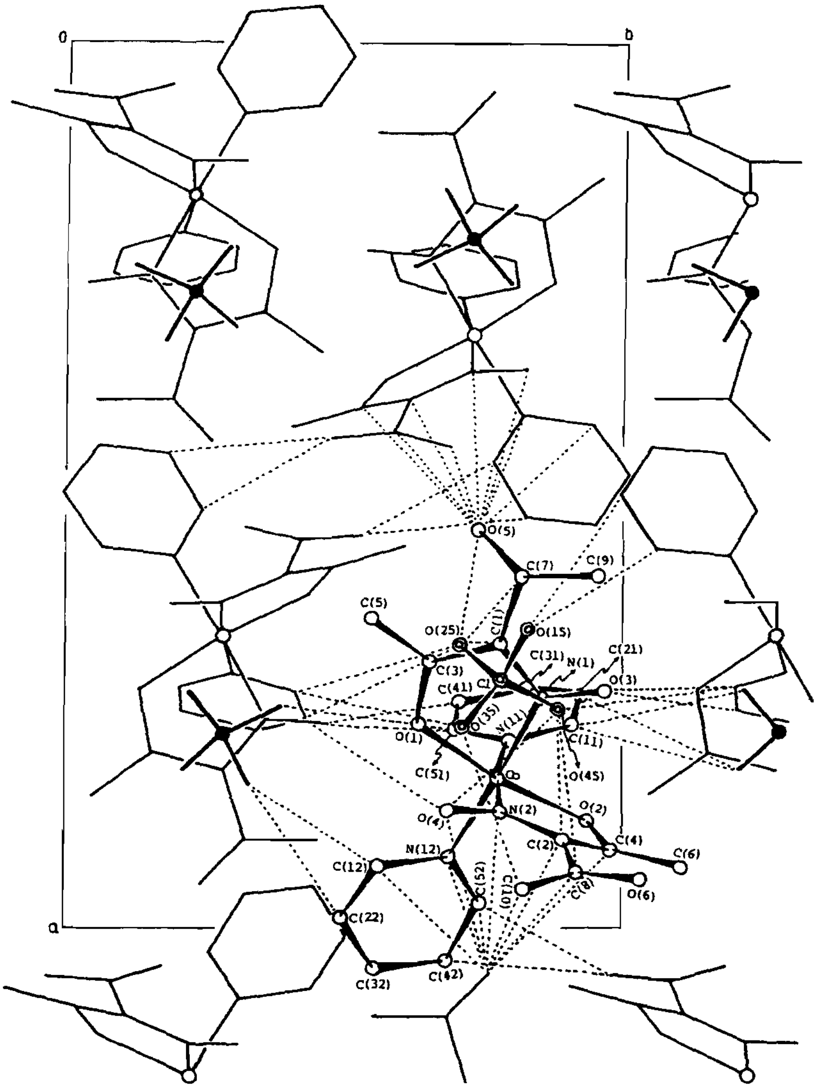

Fig. 4. The crystal structures of $Co(hipd)_2(py)_2ClO_4$. Broken lines denote intermolecular distances shorter than 3.5 Å. (a). c axis projection. *See overleaf for 4(b).*

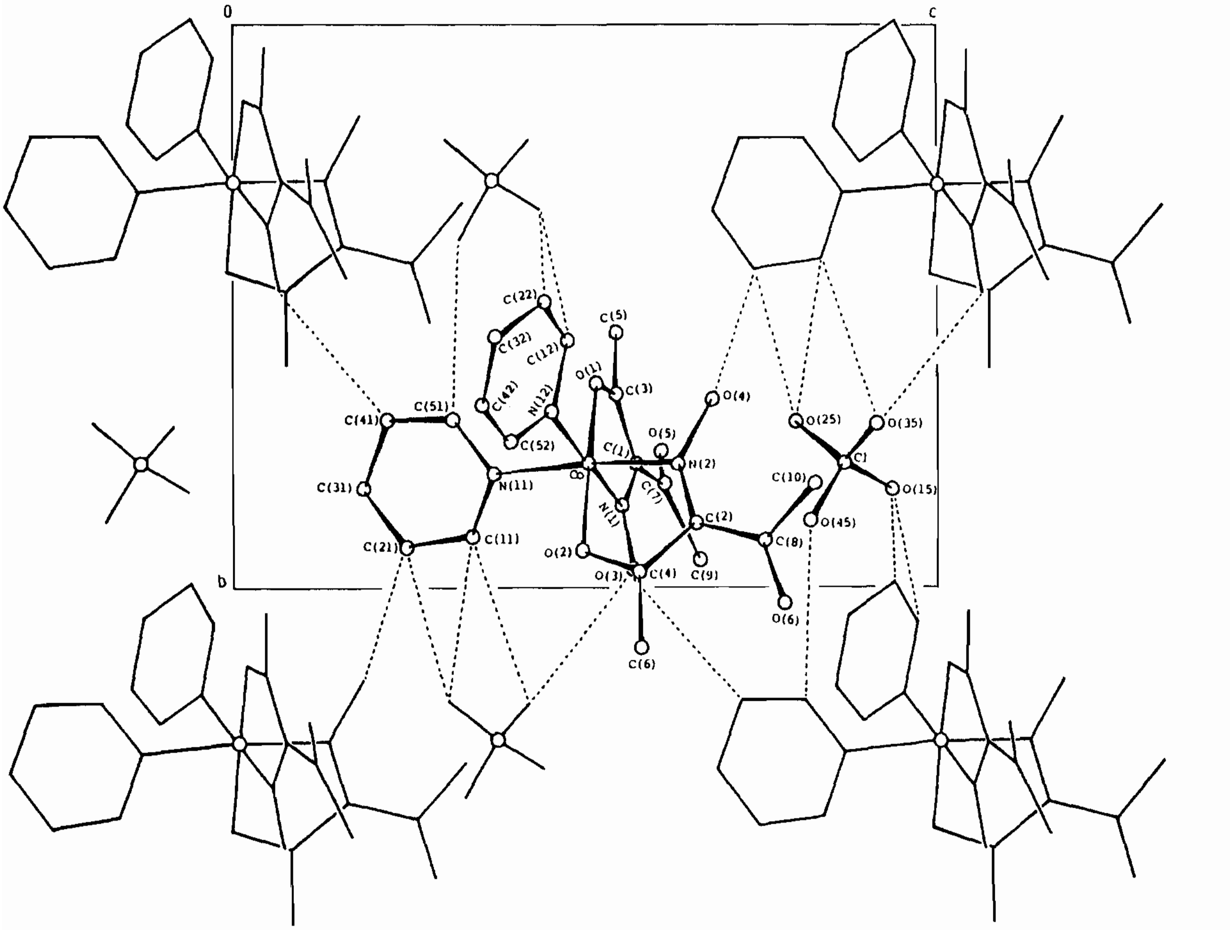

Fig. 4. The crystal structures of Co(hipd)$_2$(py)$_2$ClO$_4$. Broken lines denote intermolecular distances shorter than 3.5 Å. (b). *a* axis projection. Two complex cations and two perchlorate anions in the unit cell are omitted for clarity.

TABLE V. Selected Non-Bonding Contacts (Å) Shorter than 3.5 Å.

O(15)···C(12)^{ii}	3.01	O(3)··· C(41)^{ii}	3.22
O(15)···C(22)^{ii}	3.21	O(4)···C(21)^{iii}	3.33
O(25)···C(11)^{iii}	3.26	O(5)···N(2)^{i}	3.04
O(25)···C(21)^{iii}	3.31	O(5)···C(2)^{i}	2.96
O(25)···C(1)	3.24	O(5)···C(4)^{i}	3.40
O(25)···C(7)	3.13	O(5)···O(4)^{i}	3.35
O(25)···O(5)	3.45	O(5)···C(8)^{i}	3.30
O(35)···C(11)^{iii}	3.45	O(5)···C(10)^{i}	3.46
O(35)···C(10)	3.50	O(5)···N(12)^{i}	3.15
O(35)···O(3)^{iii}	3.27	O(5)···C(12)^{i}	3.43
O(45)···C(51)^{ii}	3.35	O(5)···C(52)^{i}	3.25
O(45)···C(2)	3.40	O(6)···C(42)^{iv}	3.30
O(45)···C(8)	3.28	O(6)···C(52)^{iv}	3.17
O(45)···O(4)	3.47		

The symmetry code is the following:

i	−1/2 + x	3/2 − y	z
ii	3/2 − x	1/2 + y	1/2 + z
iii	3/2 − x	−1/2 + y	1/2 + z
iv	2 − x	2 − y	1/2 + z

(4-methyl-1-quinone-2-oximato)copper(II) [11]. The shortening of C–C bonds in Mox1 or Mox2 may be related with the delocalization of π-electrons in the hydroxyiminato rings. Of the four N–C bonds in the pyridine rings, only the N(11)–C(11) bond distance (1.31 Å) is significantly shorter than the others.

The perchlorate ion is approximately regular-tetrahedral; the value of O–Cl–O angles ranges from 108° to 110° and the distance of Cl–O bonds ranges from 1.39 Å to 1.42 Å.

Crystal Structure

The crystal structure is shown in Fig. 4. Some shorter contacts than 3.5 Å were found between a cation and an anion, or between a cation and the neighbor cation (Table V).

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