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The Molecular Structure of (+)$_{589}$-β_2-(3-Methyl-2-iminobutanoato) ((2*S*,10*S*)-4,8-diazaundecane-2,10-diamine)cobalt(III) Perchlorate: α-Imino Acidato Complex

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Synopsis. The crystal structure of (+)$_{589}$-β_2-(3-methyl-2-iminobutanoato)((2*S*,10*S*)-4,8-diazaundecane-2,10-diamine)cobalt(III) perchlorate has been determined by the single-crystal X-ray diffraction method. The complex ion adopts Λ-β_2 configuration, and it has the Co–N(imine) bond length of 1.90 Å, which is shorter than the Co–N(amine) bond lengths. The chelate ring of the 2-imino carboxylato is planar.

α-Imino acids (2-imino carboxylic acids) chelated to a metal ion are stable in an aqueous solution, while free α-imino acids are subject to be hydrolyzed. The syntheses and properties of cobalt(III) complexes of α-imino acids have been reported.[1–3] It reacts with nucleophile on its α-carbon, while it reacts with electrophile on its β-carbon and imino nitrogen. These facts make this ligand a useful building block for the synthesis of α-amino acid derivatives.

Recently, we obtained α-imino acidato Co(III) complexes by the dehydrogenation of the corresponding α-amino acidato complexes: The reaction of the [Co(α-amino acidato)(tetraamine)](ClO_4)$_2$ complex with potassium permanganate gave a dehydrogenated product [Co(α-imino acidato)(tetraamine)](ClO_4)$_2$.[2] Asymmetric addition of a nucleophile to the imino carbon atom of α-imino acidate ligand can be expected, when optically active tetraamine ligand is employed. Since the tetraamine ligand seems to have a significant influence on the stereoselectivity, the structure of the complex is important, but the structure of the simple α-imino acidato complex has not yet been determined, as far as we know.[4] In this paper, we wish to report the X-ray structure determination of the molecular structure of (+)$_{598}$-β_2-[Co(oval)(2,10-Me$_2$-2,3,2-tet)](ClO_4)$_2$.[5]

Experimental

(+)$_{598}$-β_2-[Co(oval)(2,10-Me$_2$-2,3,2-tet)](ClO_4)$_2$ was prepared in a manner similar to that described previously.[3] Red crystals were obtained by crystallization from an aqueous solution. Found: C, 30.03; H, 5.78; N, 12.23%. Calcd for $C_{14}H_{32}Cl_2CoN_5O_{10}$: C, 30.01; H, 5.76; N, 12.50%.

The crystal used in the data collection was a red needle with the approximate dimentions of 0.1X0.05X0.05 mm^3. The diffraction data were measured on a Rigakudenki AFC-5R diffractometer using Mo $K\alpha$ radiation monochromated by graphite (λ 0.7107 Å). Within the range of $2\theta<60°$, 1729 independent reflections with $|F_o|\geqq 2.5\sigma(F_o)$ were obtained. The intensities were corrected for Lorentz and polarization effects.

Crystal data for $C_{14}H_{32}Cl_2CoN_5O_{10}$: *F.W.*=560.3; Orthorhombic; $P2_12_12_1$; a=14.743(4), b=15.165(3), c=10.568(2) Å; V=2362.7(10) Å^3; Z=4; D_m=1.565 g cm^{-3}; D_x=1.575 g cm^{-3}; μ=10.07 cm^{-1}.

The structure was solved by the heavy-atom method and refined by a full-matrix least-squares method with anisotropic temperature factors for non-H atoms (for hydrogen atoms isotropically). The final discrepancy factors were $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.062$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.060$ with a weighting scheme, $1/w=a|F_o|^2+b|F_o|+c$, were a, b, and c were calculated automatically. The absolute configuration of the whole complex ion was determined by the known absolute configuration of the asymmetric carbon atoms. All the hydrogen atoms except those of the terminal methyl groups of the isopropyl group were located and refined. The atomic scattering factors and the corrections for anomalous dispersion of Co, Cl, O, N, and C were taken from the literature.[6] Final positional and thermal parameters for non-hydrogen atoms are listed in Table 1.[7]

All the calculations were carried out on a HITAC M200H computer at the Computer Center of the Institute for Molecular Science and a HITAC M280H computer at the Computer Center of the University of Tokyo with Universal Program System UNICS-III.[8]

Results and Discussion

The observed structure of the complex ion (+)$_{589}$-[Co(oval)(2,10-Me$_2$-2,3,2-tet)]$^{2+}$ is shown in Fig. 1. The

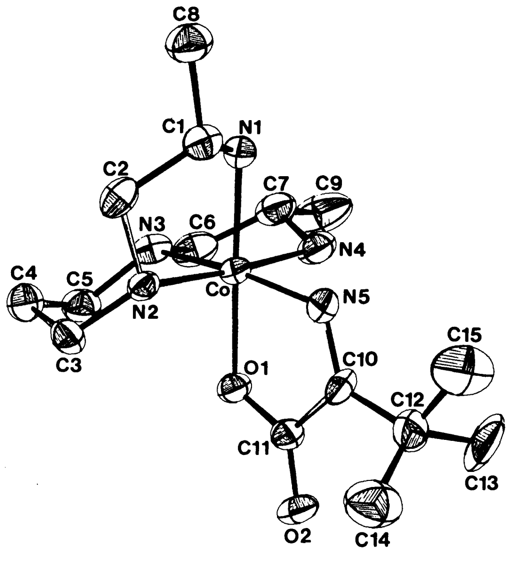

Fig. 1. An ORTEP[9] drawing of the complex cation Λ-β_2-[Co(oval)(2,10-Me$_2$-2,3,2-tet)]$^{2+}$. Ellipsoids enclose 30% probability. Hydrogen atoms are omitted for clarity.

Table 1. Fractional Positional Parameters ($\times 10^4$) and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	$B_{eq}/\text{Å}^2$
Co	213(1)	3365(1)	3102(2)	3.6
Cl(1)	2907(2)	1166(2)	3062(4)	4.9
Cl(2)	2086(4)	3885(3)	6475(6)	8.8
N(1)	382(7)	4522(6)	3830(10)	4.6
N(2)	−1106(6)	3600(5)	3279(9)	3.6
N(3)	208(8)	3796(6)	1345(9)	4.4
N(4)	1541(7)	3228(7)	2852(12)	5.3
N(5)	262(8)	2799(6)	4710(9)	4.5
O(1)	−5(6)	2184(4)	2519(7)	4.0
O(2)	−131(6)	799(4)	3226(9)	5.1
C(1)	−436(9)	4779(8)	4522(12)	4.7
C(2)	−1232(9)	4537(8)	3674(13)	4.5
C(3)	−1703(7)	3348(9)	2223(12)	4.5
C(4)	−1456(12)	3759(10)	1000(13)	6.2
C(5)	−514(10)	3472(9)	491(13)	5.1
C(6)	1089(11)	3578(9)	765(15)	5.7
C(7)	1831(9)	3707(8)	1713(16)	5.6
C(8)	−431(11)	5748(9)	4966(14)	6.2
C(9)	2754(12)	3428(11)	1191(22)	9.8
C(10)	135(10)	1955(7)	4705(13)	5.2
C(11)	−19(7)	1594(7)	3399(11)	4.1
C(12)	149(11)	1377(9)	5884(15)	6.7
C(13)	1038(18)	930(18)	5938(35)	10.1
C(14)	−737(20)	890(18)	6020(28)	9.6
C(15)	383(36)	1848(22)	7037(26)	14.4
O(Cl1)1	2209(8)	1379(7)	2253(14)	10.0
O(Cl1)2	2952(8)	288(6)	3373(15)	10.0
O(Cl1)3	3046(14)	1726(10)	4053(13)	12.9
O(Cl1)4	3685(14)	1367(15)	2424(20)	17.6
O(Cl2)1	2308(14)	3104(11)	6008(21)	15.7
O(Cl2)2	2597(11)	4157(9)	7495(14)	11.7
O(Cl2)3	1189(12)	3875(15)	6773(20)	15.8
O(Cl2)4	2109(13)	4462(10)	5477(19)	15.4

Table 2. Selected Bond Distances (*l*/Å) with Their Estimated Standard Deviations in Parentheses

Co-N(1)	1.933(10)	C(5)-N(3)	1.48(2)
Co-N(2)	1.986(10)	N(3)-C(6)	1.47(2)
Co-N(3)	1.969(10)	C(6)-C(7)	1.50(2)
Co-N(4)	1.985(11)	C(7)-C(9)	1.53(2)
Co-N(5)	1.905(10)	C(7)-N(4)	1.47(2)
Co-O(1)	1.922(7)	N(5)-C(10)	1.29(1)
		C(10)-C(11)	1.50(2)
N(1)-C(1)	1.46(2)	C(10)-C(12)	1.52(2)
C(1)-C(2)	1.52(2)	C(12)-C(13)	1.48(3)
C(1)-C(8)	1.54(2)	C(12)-C(14)	1.51(3)
C(2)-N(2)	1.49(1)	C(12)-C(15)	1.45(3)
N(2)-C(3)	1.47(2)	C(11)-O(1)	1.29(1)
C(3)-C(4)	1.48(2)	C(11)-O(2)	1.23(1)
C(4)-C(5)	1.55(2)		

tetraamine ligand and the α-imino acidato are coordinated to a cobalt ion in the cis-β_2 geometry.[10] The absolute configuration of the complex ion deduced from the known absolute configuration of the asymmetric carbon atoms of the tetraamine ligand is Λ. The geomtry around metal ion showed no change during the oxidation reaction. The electronic and circular dichroism (CD) spectra are shown in Fig. 2. The CD spectrum in a neutral solution showed a positive Cotton effect corresponding to the first absorption band, which is consistent with the absolute configuration. The solution showed characteristic

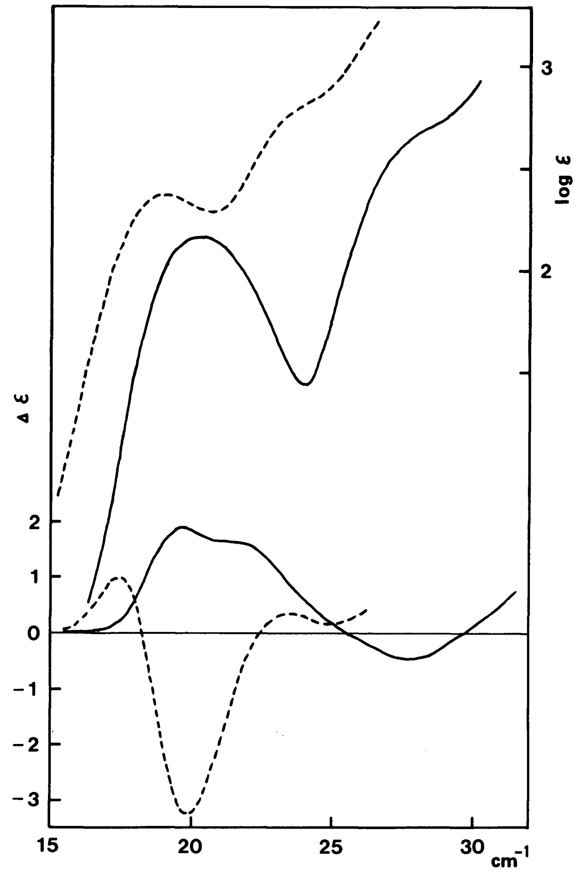

Fig. 2. Electronic absorption and circular dichroism spectra of Λ-β_2-[Co(oval)(2,10-Me_2-2,3,2-tet)]$(ClO_4)_2$: (a) in H_2O(——); (b) in N/10 NaOH (---).

Table 3. Selected Bond Angles (ϕ/°) with Their Estimated Standard Deviations

N(1)-Co-N(2)	85.7(4)	C(10)-C(11)-O(1)	114.0(9)
N(2)-Co-N(3)	91.5(4)	N(5)-C(10)-C(12)	124.4(12)
N(3)-Co-N(4)	85.0(5)	C(11)-C(10)-C(12)	122.9(10)
N(5)-Co-O(1)	82.7(4)	C(10)-C(11)-O(2)	120.9(10)
		O(1)-C(11)-O(2)	125.1(11)
Co-N(5)-C(10)	115.9(9)	C(10)-C(12)-C(13)	107.9(18)
Co-O(1)-C(11)	114.7(7)	C(10)-C(12)-C(14)	110.3(16)
N(5)-C(10)-C(11)	112.7(11)	C(10)-C(12)-C(15)	114.0(16)

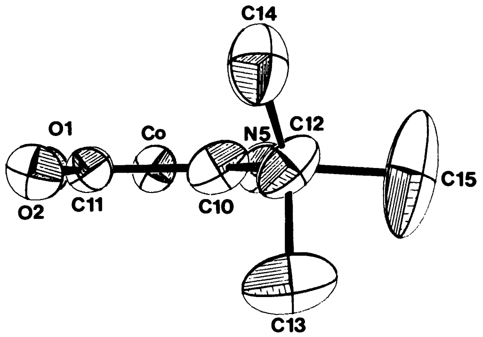

Fig. 3. An ORTEP9) drawing of the α-imino acidato ligand. Ellipsoids enclose 30% probability.

changes of the electronic and CD spectra on basification because of the dissociation of the imino proton.3)

Selected bond lengths and bond angles are given in Table 2 and 3, respectively. The bond length between the imino nitrogen atom and cobalt atom, Co–N(5) is 1.90(1) Å, which is shorter than the average of other Co–N bond lengths (1.97 Å). This value is similar to the Co–N(imine) bond lengths of the α-imino acidato Co(III) complex reported previously.4) The bond angle N(5)–Co–O(1) (82.7(4)°) is smaller than that of α-amino acidato chelate ring, and, therefore, is more strained. The bond length C(10)–N(5) (1.29(1) Å) is consistent with that expected for a C=N bond.4)

The chelate ring of the α-imino acidate moiety is planar as expected (Fig. 3). The deviations from the least-squares plane through the five atoms are within 0.0030 Å.11)

The isopropyl group appeared to be a *t*-butyl group, due to disordering in the crystal. Its conformation was gauche to the carboxylato group.

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11) The equation of the least-squares plane through the chelate ring of the α-imino acidato is $0.9841X-0.1395Y-0.1100Z+0.7619=0$, and the deviations from the plane are as follows: Co, −0.011; N(5), 0.0026; O(1), −0.0002; C(10), −0.0030; C(11), 0.0018 Å.