Letters to the Editor

Crystal Structures of (*R*)- and (*S*)-Methionato-(*SSSR*)-[(2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]cobalt(III) Dipерchlorate Monohydrate¹

Kimiko KOBAYASHI, Sei TSUBOYAMA, Naoyuki TABATA, Kaoru TSUBOYAMA
and (the late) Tosio SAKURAI

The Institute of Physical and Chemical Research, Wako, Saitama 351-01, Japan

The title compounds (2 and 3) were prepared and characterized in connection with study of optical resolution of amino acids by using *cis*-*SSSR*-{bromo[dibromoaqua]-[(2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane (=TETA)]}cobalt(III) (1).¹ In order to elucidate the stereochemistry of the diastereomeric complexes, the crystal structures have been determined by X-ray analysis.

Two red cubic crystals having size of 0.45×0.43×0.40 and 0.45×0.43×0.40 mm³ were used for the data col-

lection with graphite-monochromatized Mo K α radiation. No absorption correction was applied ($\mu=0.83$ and 0.84 mm⁻¹). Table 1 summarizes the crystal and experimental data. The absolute configurations were

Table 1 Crystal and experimental data of 2 and 3

Formula: C ₂₁ H ₄₈ Cl ₂ CoN ₅ O ₁₁ S, C ₂₁ H ₄₈ Cl ₂ CoN ₅ O ₁₁ S
Formula weight=708.53, 708.53
Crystal system: orthorhombic, orthorhombic
Space group: <i>P</i> 2 ₁ 2 ₁ 2 ₁ , <i>P</i> 2 ₁ 2 ₁ 2 ₁ <i>Z</i> = 4, 4
<i>a</i> =15.677(3), 15.486(3) Å
<i>b</i> =17.036(4), 17.015(4)
<i>c</i> =11.878(3), 11.954(2)
<i>V</i> =3172(1), 3150(1) Å ³
<i>D_x</i> =1.484, 1.494 <i>D_m</i> =1.490, 1.491
<i>R</i> =0.080, 0.060
No. of reflections used=3072, 3210
Measurement: Rigaku AFC-4
Program system: UNICS III
Structure determination: MULTAN 78
Refinement: block-diagonal least-squares

The data of 3 are placed after those of 2 in each row.

Fig. 2 Perspective view of the structures of 2 (a) and 3 (b). Only the hydrogen atoms at the asymmetric nitrogens, and the chiral centers in methionine are attached for clarity.

Fig. 1 Chemical structure.

Table 2 Atomic coordinates ($\times 10^4$) of non-hydrogen atoms

(a) Complex 2				
Atom	x	y	z	$B_{eq}/\text{\AA}$
Co	885(1)	705(1)	625(1)	2.72(4)
N(1)	100(5)	-74(4)	1246(7)	3.1(2)
C(2)	-683(6)	-156(6)	511(11)	4.1(3)
C(3)	-777(6)	568(6)	-228(9)	3.8(3)
N(4)	105(5)	795(5)	-626(7)	3.2(2)
C(5)	193(7)	1593(6)	-1143(9)	3.7(3)
C(6)	1138(6)	1770(6)	-1124(8)	3.4(2)
N(7)	1464(5)	1640(5)	47(7)	2.9(2)
C(8)	1307(6)	2337(6)	809(9)	3.4(3)
C(9)	893(7)	2051(5)	1903(8)	3.2(2)
N(10)	254(5)	1458(4)	1548(7)	3.0(2)
C(11)	-292(7)	1051(6)	2443(9)	3.7(3)
C(12)	-71(7)	180(6)	2419(10)	4.1(3)
C(21)	-628(9)	-920(7)	-181(11)	5.3(4)
C(22)	-700(12)	-1625(10)	467(15)	9.0(6)
C(51)	-185(9)	1630(8)	-2343(11)	5.5(4)
C(52)	-135(15)	2461(10)	-2772(15)	9.8(7)
C(81)	2134(7)	2797(7)	1022(10)	4.3(3)
C(82)	2021(9)	3548(7)	1605(13)	6.0(4)
C(111)	-179(9)	1403(7)	3616(11)	5.1(4)
C(112)	-744(11)	953(8)	4492(11)	7.0(5)
N(13)	1650(5)	-34(5)	-173(8)	3.8(2)
C(14)	2489(7)	-40(8)	424(12)	4.9(3)
C(15)	2345(6)	202(6)	1656(10)	3.9(3)
O(16)	1678(4)	547(4)	1846(6)	3.7(2)
C(141)	3020(8)	-803(9)	254(13)	6.5(4)
C(142)	2668(12)	-1523(12)	924(19)	11.1(8)
S	1726(4)	-1943(3)	255(5)	9.3(2)
C(144)	2268(11)	-2059(16)	-959(23)	14.0(11)
O(151)	2917(5)	73(6)	2359(7)	5.4(2)
Cl(1)	-1081(2)	3390(2)	1145(3)	5.8(1)
O(1)	-1927(7)	3616(6)	1241(10)	8.2(4)
O(2)	-675(8)	3468(6)	2235(10)	9.4(4)
O(3)	-1039(7)	2597(5)	761(11)	8.3(4)
O(4)	-725(10)	3883(10)	345(12)	13.6(6)
Cl(2)	1926(2)	4329(3)	-1700(3)	6.9(1)
O(5)	1253(9)	3870(8)	-1505(15)	13.7(6)
O(6)	2369(11)	4471(16)	-770(15)	21.9(12)
O(7)	1577(14)	4991(10)	-2137(17)	18.1(9)
O(8)	2379(13)	4274(16)	-2551(20)	23.4(12)
O(W)	364(6)	-303(6)	-2468(8)	6.5(3)

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} (a_i \cdot a_j).$$

(b) Complex 3

Atom	x	y	z	$B_{eq}/\text{\AA}$
Co	800(1)	790(1)	5578(1)	2.12(5)
N(1)	47(4)	-16(3)	6215(5)	2.3(1)
C(2)	-736(5)	-134(4)	5481(7)	2.9(2)
C(3)	-882(5)	600(4)	4772(6)	2.9(2)
N(4)	-8(4)	857(4)	4348(5)	2.5(1)
C(5)	27(5)	1675(5)	3869(7)	3.1(2)
C(6)	989(5)	1867(5)	3841(6)	3.0(2)
N(7)	1346(4)	1734(3)	4997(5)	2.6(1)
C(8)	1196(5)	2435(4)	5755(7)	2.7(2)
C(9)	753(5)	2142(4)	6828(6)	2.9(2)
N(10)	135(4)	1520(3)	6494(5)	2.4(1)
C(11)	-404(5)	1110(4)	7382(6)	2.6(2)
C(12)	-139(5)	257(4)	7382(7)	2.8(2)
C(21)	-627(6)	-885(5)	4799(7)	3.7(2)
C(22)	-608(7)	-1622(5)	5468(9)	5.2(3)
C(51)	-378(7)	1726(6)	2706(8)	4.7(3)
C(52)	-476(8)	2586(7)	2346(10)	6.2(3)
C(81)	2047(6)	2859(6)	5990(8)	4.1(2)
C(82)	1921(8)	3597(6)	6642(10)	6.2(3)
C(111)	-335(6)	1481(6)	8546(7)	4.0(2)
C(112)	-875(8)	1015(5)	9401(8)	5.3(3)
N(13)	1567(4)	52(4)	4784(5)	2.7(2)
C(14)	2101(5)	-369(5)	5651(8)	3.5(2)
C(15)	2233(5)	193(5)	6618(7)	3.0(2)
O(16)	1640(3)	703(3)	6737(4)	3.1(1)
C(141)	2938(5)	-733(5)	5197(8)	4.3(2)
C(142)	2755(7)	-1433(6)	4429(10)	5.3(3)
S	2087(2)	-2190(2)	5014(3)	5.8(1)
C(144)	2620(8)	-2428(8)	6309(11)	6.6(4)
O(151)	2826(4)	104(4)	7283(5)	4.7(2)
Cl(1)	3810(1)	1489(1)	3896(2)	4.2(1)
O(1)	4082(6)	1360(5)	2770(7)	7.5(3)
O(2)	3800(6)	2307(4)	4115(8)	7.8(3)
O(3)	4425(7)	1110(8)	4566(10)	12.2(5)
O(4)	2998(5)	1190(5)	4057(10)	9.0(4)
Cl(2)	1859(2)	4390(2)	3309(2)	4.7(1)
O(5)	1172(8)	3912(7)	3402(12)	13.8(5)
O(6)	2269(8)	4626(11)	4229(11)	17.0(7)
O(7)	1385(13)	5046(10)	2953(17)	21.0(9)
O(8)	2321(10)	4318(13)	2409(15)	22.1(9)
O(W)	-5451(4)	200(4)	7576(6)	5.3(2)

Table 3 Selected bond lengths ($\text{\AA}$), and bond and torsion angles ($^\circ$) for complexes 2 and 3

		2	3			2	3
Co	-N(1)	1.954(8)	1.953(6)	Co	-N(4)	1.931(8)	1.933(6)
Co	-N(7)	1.957(8)	1.944(6)	Co	-N(10)	1.956(7)	1.950(6)
Co	-N(13)	1.980(9)	1.972(6)	Co	-O(16)	1.930(7)	1.906(5)
N(1)	-C(2)	1.51(1)	1.51(1)	N(1)	-C(12)	1.48(2)	1.50(1)
C(2)	-C(3)	1.52(2)	1.53(1)	C(3)	-N(4)	1.51(1)	1.51(1)
N(4)	-C(5)	1.50(1)	1.51(1)	C(5)	-C(6)	1.51(1)	1.53(1)
C(6)	-N(7)	1.50(1)	1.51(1)	N(7)	-C(8)	1.51(1)	1.52(1)
C(8)	-C(9)	1.53(1)	1.54(1)	C(9)	-N(10)	1.48(1)	1.48(1)
N(10)	-C(11)	1.53(1)	1.52(1)	C(11)	-C(12)	1.52(2)	1.51(1)
N(13)	-C(14)	1.50(2)	1.51(1)	C(14)	-C(15)	1.54(2)	1.52(1)
C(14)	-C(141)	1.56(2)	1.54(1)	C(15)	-O(151)	1.24(1)	1.22(1)
C(15)	-O(16)	1.22(1)	1.27(2)	C(141)	-O(142)	1.44(2)	1.53(1)
C(142)	-S	1.82(2)	1.79(1)	S	-C(144)	1.69(3)	1.80(1)

N(1)	-Co	-N(4)	87.2(5)	87.3(3)	N(1)	-Co	-N(7)	167.8(5)	168.2(3)
N(1)	-Co	-N(10)	84.6(5)	85.0(2)	N(1)	-Co	-N(13)	98.0(5)	95.8(3)
N(1)	-Co	-O(16)	90.3(4)	94.1(2)	N(4)	-Co	-N(7)	87.2(4)	87.8(3)
N(4)	-Co	-N(10)	93.9(4)	92.8(3)	N(4)	-Co	-N(13)	92.9(4)	93.5(3)
N(4)	-Co	-O(16)	175.3(4)	177.0(2)	N(7)	-Co	-N(10)	85.0(5)	84.5(3)
N(7)	-Co	-N(13)	93.2(5)	95.3(3)	N(7)	-Co	-O(16)	96.0(4)	91.5(3)
N(10)	-Co	-N(13)	172.9(4)	173.7(3)	N(10)	-Co	-O(16)	89.8(4)	90.1(3)
N(13)	-Co	-O(16)	83.6(4)	83.6(2)					

				2	3
O(16)	-Co	-N(13)	-C(14)	-19.8(9)	23.0(6)
Co	-N(13)	-C(14)	-C(15)	24.3(12)	-32.4(8)
N(13)	-C(14)	C(15)	-O(16)	-18.1(16)	29.0(11)
C(14)	-C(15)	-O(16)	-Co	1.9(15)	-10.6(11)
C(15)	-O(16)	-Co	N(13)	10.6(9)	-7.7(7)

Fig. 3 The three possible $[\text{Co}^{\text{III}}(\text{methionine})\text{TETA}]^{+}$ linkage isomers.

assigned from the known configurations of the ligand. Hydrogen-atom coordinates were calculated assuming ideal geometry and were included in the refinement with isotropic temperature factors. The anisotropic temperature factors for all non-H atoms were applied. The atomic parameters are given in Table 2. The chemical and molecular structures of 2 and 3 are shown in Figs. 1 and 2.

The structures of 2 and 3 are quite similar to each other except for methionine moiety. The coordination around the cobalt atom is approximately octahedral, and

the metal is surrounded by four N atoms of TETA, and the amino-N and carboxyl-O of methionine with *cis* β_1 mode. This coordination form was also found in the other [Co^{III} (amino acid) (TETA)] complexes.^{2,3} The conformations of the chelate rings formed by *R*- and *S*-methionines are distinctly different from each other, and are expressed as δ and λ conformations respectively (see the torsion angles in Table 3).

Since methionine is a potential tridentate ligand, three kinds of coordination forms: A, B and C are possible for the metal (Fig. 3). The A form with the five membered chelate ring was found in the present complexes; the B form was found in other [Pt^{II}(*S*)- and (*RS*)-methionine]Cl₂ and [Pd^{II}(*RS*)-methionine]Cl₂ complexes.^{4,5}

Attempts to resolve racemic methionine using **1** as resolving agent were unsuccessful owing to the marked similarity of the physical properties of **2** and **3**.

References

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