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Determination of the Absolute Configuration of Sodium $(-)_{589}$-Bis(*N*-methyliminodiacetato)cobaltate(III) Trihydrate

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Abstract. $\mathrm{Na^{+}.(-)_{589}\text{-}[Co(C_5H_7NO_4)_2]^{-}.3H_2O}$, M_r = 426.2, orthorhombic, $P2_12_12_1$, a = 11.071 (3), b = 16.606 (6), c = 8.761 (2) Å, V = 1610.7 (9) Å^3, Z = 4, D_m = 1.74, D_x = 1.76 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 11.12 cm^{-1}, $F(000)$ = 879.92, T = 294 (1) K, R = 0.0426 for 1755 observed unique reflections. The bis(*N*-methyliminodiacetato)cobaltate(III) ion, $\mathrm{[Co(mida)_2]^-}$, has an unsymmetrical facial configuration. The absolute configuration of $(-)_{589}$-$\mathrm{[Co(mida)_2]^-}$ has been determined to be $\Lambda\Lambda\Delta$. The *cis*-$\mathrm{N_2O_4}$ octahedron around the $\mathrm{Co^{III}}$ ion is largely distorted because of the steric compression between the two adjacent *N*-methyl groups. Hydrogen bonds may form between the O atom of the carboxylate groups of the ligand and the water molecules. The Na ion is octahedrally surrounded by six O atoms, one each from three water molecules and three ligand carbonyl groups.

Introduction. An octahedral cobalt(III) complex with two terdentate *N*-methyliminodiacetato (mida) ligands, having three geometrical isomers, symmetrical-facial (*s-fac*), unsymmetrical-facial (*u-fac*) and meridional (*mer*), has been investigated for spectroscopic properties, stereochemistry and reactivity such as isomerization, racemization, epimerization *etc.* (Koine, Tanigaki, Hidaka & Shimura, 1980; Uehara, Kyuno & Tsuchiya, 1970; Cooke, 1966; Hidaka, Shimura & Tsuchida, 1962). Of the three isomers, only the crystal structure of *u-fac*-$\mathrm{[Co(mida)_2]^-}$ has been determined as a racemate (Kushi, Ideno, Yasui & Yoneda, 1983). Later, Ama, Kawaguchi & Yasui (1981) succeeded in the separation of the $(-)_{589}$-*u-fac* isomer; they have assigned its absolute configuration as $\Lambda\Lambda\Delta$ by comparison of the CD spectrum in the visible region with that of $(-)_{546}$-*u-fac*-$\mathrm{[Co(ida)_2]^-}$ (ida = iminodiacetato) whose absolute configuration has been determined as $\Lambda\Lambda\Delta$ (Ama, Kawaguchi & Yasui, 1981; Yasui, Kawaguchi, Koine & Ama, 1983). In the present study, a crystal of $\mathrm{Na^{+}.(-)_{589}}$-*u-fac*-$\mathrm{[Co(mida)_2]^{-}.3H_2O}$ has been subjected to X-ray crystal analysis in order to establish the absolute configuration and structural details of the complex ion.

Experimental. The crystal used for data collection was kindly supplied by Professor Yasui of Kochi University (Ama, Kawaguchi & Yasui, 1981). Blue needle crystals; 0.1 × 0.1 × 0.2 mm; Rigaku AFC four-circle diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; ω–2θ scan. No systematic absences indicated the Laue symmetry *mmm* and the correct space group $P2_12_12_1$ was confirmed from subsequent analysis. Cell parameters were determined from setting angles of 25 reflections with $8 < 2\theta < 30°$. The values of $|F|$ and $\sigma(|F|)$ were corrected for Lorentz and polarization effects, but no absorption correction was made. The intensities of three standard reflections did not show any systematic variation during data collection; 3510 unique reflections were measured with $4 < 2\theta < 70°$; 1755 reflections with $|F_o|/\sigma(|F|) > 3.0$ were used in refinement. Data collected: h, k, l; h 0 − 17, k 0 − 26, l 0 − 14. Structure was solved by the heavy-atom technique by the use of Patterson and electron-density syntheses. Refinement was performed by a full-matrix least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = a/(\sigma^2|F| + b|F|^2)$, where final a and b values were 0.7844 and 0.001. Anisotropic thermal parameters were refined for all non-H atoms. The H atoms were not located. Final R = 0.0426, wR = 0.0431, S = 1.1293, $(\Delta/\sigma)_{\max}$ = 0.016, $(\Delta\rho)_{\max}$ = 0.56, $(\Delta\rho)_{\min}$ = −0.38. All the calculations were performed with the *SHELX76* (Sheldrick, 1976) set of programs that use analytical approximation for atomic scattering factors and anomalous-dispersion corrections for all non-H atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The absolute configuration was determined using Hamilton's R-value significance test for the two isomers ($\Delta\Delta\Lambda$ and $\Lambda\Lambda\Delta$) (Hamilton, 1965). Refinement of $+h+k+l$ reflections for the $\Delta\Delta\Lambda$ (R = 0.0539) and $\Lambda\Lambda\Delta$ (R = 0.0426) isomers rejected the former at

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Table 1. *Final atomic coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* (Å² × 10⁴) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Co	5899 (1)	2596 (0)	2282 (1)	176 (3)
O(1)	6118 (4)	3425 (2)	3724 (4)	253 (21)
O(2)	7060 (4)	1950 (2)	3319 (5)	280 (22)
N(1)	4735 (4)	2111 (3)	3748 (6)	196 (22)
O(3)	5680 (4)	1787 (2)	842 (5)	275 (21)
O(4)	7202 (3)	3021 (2)	1114 (5)	247 (20)
N(2)	4920 (4)	3303 (3)	918 (6)	186 (22)
C(1)	5286 (6)	1298 (4)	4095 (9)	336 (36)
C(2)	7024 (5)	3719 (3)	547 (7)	226 (28)
O(5)	7808 (4)	4135 (2)	−68 (5)	314 (23)
C(3)	4788 (6)	2869 (3)	−579 (6)	247 (29)
C(4)	6645 (6)	1366 (4)	4116 (8)	285 (33)
O(6)	7256 (5)	859 (3)	4765 (7)	530 (32)
C(5)	4745 (6)	2620 (4)	5153 (7)	305 (31)
O(7)	5714 (5)	3784 (2)	6114 (5)	355 (25)
O(8)	5295 (5)	1593 (3)	−1628 (5)	400 (27)
C(6)	5564 (5)	3322 (3)	5026 (6)	230 (29)
C(7)	5297 (6)	2025 (3)	−499 (7)	273 (30)
C(8)	5731 (5)	4028 (3)	688 (7)	243 (28)
C(9)	3729 (6)	3637 (4)	1417 (9)	361 (35)
C(10)	3453 (5)	1937 (4)	3278 (9)	355 (36)
Na	9419 (2)	4769 (1)	1430 (3)	300 (12)
O*W*(1)	5779 (5)	103 (3)	823 (6)	442 (26)
O*W*(2)	6135 (4)	−177 (3)	7055 (6)	446 (27)
O*W*(3)	8086 (4)	4538 (3)	3461 (6)	428 (28)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Complex ion			
Co—O(2)	1.905 (4)	Co—O(4)	1.904 (4)
Co—N(1)	1.990 (5)	Co—N(2)	1.995 (5)
Co—O(1)	1.884 (3)	Co—O(3)	1.859 (4)
O(1)—C(6)	1.306 (6)	O(3)—C(7)	1.310 (7)
C(6)—O(7)	1.235 (7)	C(7)—O(8)	1.222 (7)
C(6)—C(5)	1.481 (8)	C(7)—C(3)	1.512 (7)
C(5)—N(1)	1.493 (8)	C(3)—N(2)	1.504 (7)
N(1)—C(10)	1.506 (7)	N(2)—C(9)	1.496 (8)
N(1)—C(1)	1.512 (8)	N(2)—C(8)	1.515 (7)
C(1)—C(4)	1.509 (9)	C(8)—C(2)	1.526 (8)
C(4)—O(6)	1.221 (9)	C(2)—O(5)	1.233 (7)
C(4)—O(2)	1.280 (8)	C(2)—O(4)	1.276 (6)
N(1)—Co—O(2)	84.3 (2)	N(2)—Co—O(4)	82.6 (2)
N(1)—Co—N(2)	105.8 (2)	O(2)—Co—O(4)	87.4 (2)
O(2)—Co—O(3)	90.3 (2)	N(2)—Co—O(3)	87.0 (2)
N(1)—Co—O(3)	93.5 (2)	O(4)—Co—O(3)	90.1 (2)
O(2)—Co—O(1)	90.3 (2)	N(2)—Co—O(1)	92.4 (2)
N(1)—Co—O(1)	86.9 (2)	O(4)—Co—O(1)	89.6 (2)
O(2)—Co—N(2)	169.6 (2)	O(4)—Co—N(1)	170.9 (2)
O(1)—Co—O(3)	179.4 (2)	Co—N(1)—C(10)	120.8 (4)
Co—N(2)—C(9)	121.5 (4)		
Possible hydrogen bonds			
O*W*(1)···O(3)	2.799 (6)	O*W*(3)···O(1)	2.866 (6)
O*W*(1^{i})···O(6)	2.854 (8)	O*W*(3^{ii})···O(5)	2.738 (6)
O*W*(2)···O(6)	2.920 (8)		

Symmetry code: (i) $\frac{3}{2}-x, -y, \frac{1}{2}+z$; (ii) $\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$.

greater than the 99.5% confidence level. The absolute configuration *ΛΛΔ* for $(-)_{589}$-[Co(mida)$_2$]$^-$ is consistent with that estimated from the CD spectral study (Yasui, Kawaguchi, Koine & Ama, 1983). The final atomic positional and equivalent isotropic thermal parameters are given in Table 1.* The molecular plots were produced by the program *ORTEP*II (Johnson, 1976).

Discussion. A perspective view of the Co^{III}-containing moiety, with atomic labels, is shown in Fig. 1. Selected bond distances and angles around the Co^{III} ion are given in Table 2.

The cobalt(III) ion is surrounded by four O and two N atoms from two mida ligands to form a distorted octahedral structure. The bond lengths and angles between the Co atom and two *N*-methylimino N atoms for the present complex are larger than the values [1.946 (4) Å for N(1), 1.937 (4) Å for N(2), 98.5 (2)°] for the corresponding octahedral *u-fac*-[Co(ida)$_2$]$^-$ complex (Corradi, Palmieri, Nardelli, Pellinghelli & Tani, 1973). This deviation from octahedral symmetry is caused by the intramolecular steric compression between the two methyl groups of the mida ligands. The non-bonded short contact between the two adjacent methyl groups [C(9)···C(10)] is 3.274 (10) Å, which is much shorter than the value [3.440(7) Å] previously reported for the racemate (Kushi, Ideno, Yasui & Yoneda, 1983).

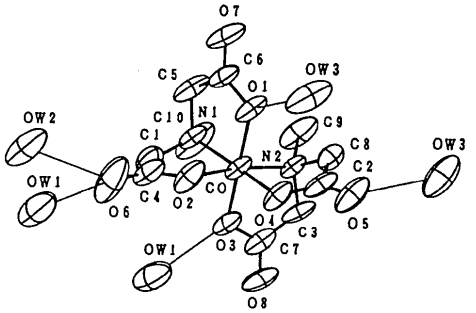

Fig. 1. Perspective view of $(-)_{589}$-*u-fac*-[Co(mida)$_2$]$^-$.

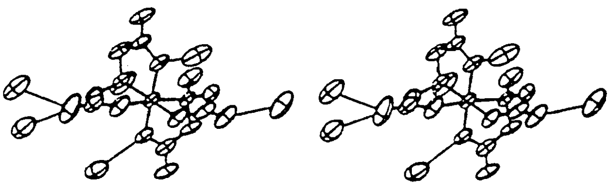

Fig. 2. Stereoview of $(-)_{589}$-*u-fac*-[Co(mida)$_2$]$^-$.

Hydrogen bonds may form between O atoms [O(1), O(3), O(5), O(6)] of the mida carboxylic groups and water molecules (Fig. 1 and Table 2). The sodium cation is octahedrally surrounded by six O atoms arising from three water molecules [O*W*(1),

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* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles of sodium-ion coordination have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55575 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1006]

O*W*(2) and O*W*(3)], two O atoms [O(7) and O(8)] of carbonyl ligands which do not participate in hydrogen bonding with the water molecules, and the carbonyl O(5) atom hydrogen bonded with atom O*W*(3) (Fig. 2 and Table 2).

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Structure of Bis(tetramethylammonium) Hexachlororhenate(IV)

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Abstract. Bis(tetramethylammonium) hexachlororhenate(IV), $[N(CH_3)_4]_2[ReCl_6]$, $M_r = 547.2$, cubic, $Fm3m$, $a = 12.760\,(2)$ Å, $V = 2077.5\,(6)$ Å^3, $Z = 4$, $D_x = 1.7505\,(6)$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 75.0$ cm^{-1}, $F(000) = 1052$. The structure was solved by Patterson and difference Fourier methods and refined to an R value of 0.0669 against 176 unique reflections collected at room temperature. Structural parameters are discussed and compared with those derived from other hexachlororhenate complexes.

Introduction. The low-temperature laser-excited luminescence spectra of the related series of compounds A_2ReCl_6 [$A = K$, Rb, Cs, $N(CH_3)_4$, $N(C_2H_5)_4$] have been reported and discussed (Bettinelli, Flint & Ingletto, 1991). The well resolved spectra have been assigned to the $\Gamma_7(^2T_{29}) \rightarrow \Gamma_8(^4A_{29})$ transition in several defect sites of essentially octahedral geometry. The emitting traps have been identified as $ReCl_6^{2-}$ ions at elongated lattice sites near interstitial sites or dislocations.

Single-crystal X-ray data (Grundy & Brown, 1970; Sperka & Mautner, 1988) showed that the alkali-metal salts K_2ReCl_6 and Cs_2ReCl_6 are cubic (space group $Fm3m$) and that the regular $ReCl_6^{2-}$ ions occupy sites of perfect octahedral symmetry. The luminescence spectra of K_2ReCl_6, Rb_2ReCl_6 and Cs_2ReCl_6 are characterized by vanishingly small electronic origins and strong vibronic origins, indicating that the defect sites maintain the inversion symmetry of the regular sites. $[N(C_2H_5)_4]_2ReCl_6$ has been shown by single-crystal X-ray diffraction (Bettinelli, Di Sipio, Valle, Aschieri & Ingletto, 1989) to be isostructural with $[N(C_2H_5)_4]_2SnCl_6$ (monoclinic, space group $C2/c$) with $ReCl_6^{2-}$ sites of C_1 symmetry, only slightly distorted from O_h. The luminescence spectra of this compound are dominated by pure

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