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Tris(tellurato)cobaltate(III) and Tris(ethylenediamine)tris(tellurato)-tetracobaltate(III) Complexes[1]

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(Received April 24, 1986)

Synopsis. Alkali metal salts of two new telluratocobaltate(III) complexes, $[Co(TeO_6H_4)_3]^{3-}$ and $[Co_4Te_3O_{18}(en)_3]^{6-}$, have been prepared. The latter heteropoly type complex and the related periodate analogue $[Co_4I_3O_{18}(en)_3]^{3-}$ have been optically resolved.

Only a limited number of telluratocobalt(III) complexes have been known such as $[Co(TeO_6H_4)(en)_2]Cl\cdot 3H_2O$[2] and $K_3[Co(TeO_6H_4)_2(OH)_2]$.[3,4] We report here two new entries, $K_3[Co(TeO_6H_4)_3]\cdot 2H_2O$ and $Na_3H_3[Co_4Te_3O_{18}(en)_3]\cdot 6H_2O$, of which the former belongs to a trischelate type and the latter to a hexol-like heteropoly type[5] as seen in Fig. 1.

Experimental

$K_3[Co(TeO_6H_4)_3]\cdot 4H_2O$. To a solution of 0.84 g (3.1 mmol) of *cis*-$K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$[6] in 20 cm^3 of water was added a solution of 2.5 g (11 mmol) of $Te(OH)_6$ in 20 cm^3 of water with mechanical stirring. After the evolution of carbon dioxide ceased, a solution of 1.12 g (20 mmol) of potassium hydroxide in 20 cm^3 of water was added gradually, and the mixture was stirred for a few hours at about 75 °C. The resulting solution was kept in a refrigerator overnight and filtered to remove a pale green precipitate of unknown nature. The filtrate was kept in a refrigerator for week. Then the dark green product was washed with methanol, ethanol, and acetone, and dried in a desiccator over silica gel. Found: H, 1.80; Co, 6.0; K, 12.4; Te, 40.8%. Calcd for $H_{20}O_{22}CoK_3Te_3$: H, 2.16; Co, 6.3; K, 12.6; Te, 41.1%.

$Na_3H_3[Co_4Te_3O_{18}(en)_3]\cdot 6H_2O$. A solution of 2.3 g (10 mmol) of $Te(OH)_6$ in 15 cm^3 of water was added to a mixed solution of 2.6 g (9.4 mmol) of *trans*(NH_3)-$[CoCl_2(NH_3)_2(en)]Cl\cdot H_2O$[7] and 1.0 g (3.0 mmol) of *cis*-$[Co(NH_3)_4(H_2O)_2](SO_4)_{1.5}\cdot 1.5H_2O$ in 30 cm^3 of water. A solution of 2.4 g (60 mmol) of sodium hydroxide in 20 cm^3 of water was added gradually to the mixture with mechanical stirring, and the stirring was continued at about 60 °C until the evolution of ammonia ceased. After cooling to room temperature an appropriate amount of ethanol was added gradually and the resulting solution was kept in a refrigerator overnight. The greenish brown product deposited was separated by a centrifuge, recrystallized twice from a 0.001 mol dm^{-3} sodium hydroxide solution by adding a small amount of ethanol, and washed with methanol and acetone several times. Found: C, 5.76; H, 3.54; N, 6.60; Co, 17.6; Te, 29.0%. Calcd for $C_6H_{39}N_6O_{24}Co_4Na_3Te_3$: C, 5.69; H, 3.10; N, 6.63; Co, 18.6; Te, 30.2%.

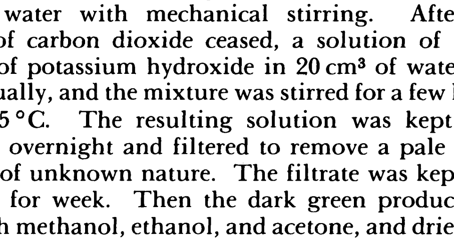

Fig. 1. Schematic structure of (a) Δ-$[Co(TeO_6H_4)_3]^{3-}$ and (b) $\Delta\Lambda'(\Lambda'')_3$-$[Co_4M^{(x)}{}_3O_{18}(en)_3]^{(24-3x)-}$ ($M^{(x)}=$ Te^{VI} or I^{VII}). For the notation of absolute configuration, see the text.

$Na_3[Co_4I_3O_{18}(en)_3]\cdot 11H_2O$. This periodate complex was prepared in the same way as for the corresponding tellurate one by using H_5IO_6 instead of $Te(OH)_6$ at 80 °C. Found: C, 5.11; H, 3.26; N, 6.27%. Calcd for $C_6H_{46}N_6O_{29}Co_4I_3Na_3$: C, 5.33; H, 3.43; N, 6.22%. The visible-UV absorption spectrum was identical to that of the known free acid $H_3[Co_4I_3O_{18}(en)_3]\cdot 5H_2O$[8] which was prepared from $H_3[Co_4I_3O_{18}(H_2O)_6]\cdot 8H_2O$.[8,9]

Optical Resolution of $[Co_4M^{(x)}{}_3O_{18}(en)_3]^{(24-3x)-}$ ($M^{(x)}=Te^{VI}$ and I^{VII}). A solution of 0.02 g of the resolving agent Λ-$(+)_{589}$-$[Co(en)_3]Br_3\cdot H_2O$ in 30 cm^3 of water was added by portions with vigorous stirring to a solution of 0.1 g of $Na_3H_3[Co_4Te_3O_{18}(en)_3]\cdot 6H_2O$ dissolved in 100 cm^3 of a 0.001 mol dm^{-3} sodium hydroxide solution. The mixture was concentrated to about 40 cm^3 at 5—15 °C in air. The greenish brown less-soluble diastereomer deposited was separated by a centrifuge and washed with water-methanol (1:3). The diastereomer was stirred in a 0.001 mol dm^{-3} sodium hydroxide solution with a cation exchanger SP-Sephadex C-25 (Na$^+$ form) while being cooled in an ice-bath. The solution was filtered to remove the Sephadex, and CD (circular dichroism) of the filtrate was measured. $\Delta\varepsilon_{589}=+0.31$ cm^{-1} mol^{-1} dm^3.

The corresponding periodate complex was resolved similarly using a solution of 0.12 g of $H_3[Co_4I_3O_{18}(en)_3]\cdot 5H_2O$ in 150 cm^3 of a sodium hydroxide solution (pH 12) and a solution of 0.012 g of Λ-$(+)_{589}$-$[Co(en)_3]Br_3\cdot H_2O$ in 25 cm^3 of water. The enantiomer obtained from the less-soluble diastereomer has $\Delta\varepsilon_{589}=-0.68$ cm^{-1} mol^{-1} dm^3. An attempt was made to resolve the $[Co(TeO_6H_4)_3]^{3-}$ complex by a similar way, but only slight CD intensity was observed in the visible region.

Measurements. A Shimadzu UV-200 spectrophotometer and a JASCO MOE-1 spectropolarimeter were used for the absorption and CD measurements, respectively, of aqueous solutions at room temperature.

Results and Discussion

The absorption spectrum of $[Co(TeO_6H_4)_3]^{3-}$ ion was measured in a cooled 0.1 mol dm^{-3} potassium hydroxide solution (Fig. 2). The first spin-allowed d–d absorption band is located at 16500 cm^{-1} and the position of tellurate ligand $TeO_6H_4{}^{2-}$ is determined in the spectrochemical series of oxygen chelate ligands: acetylacetonate(1−) 16900>oxalate(2−) 16570>tellurate(2−) 16500>malonate(2−) 16460>nitrate(1−) 16400>carbonate(2−) 15500 (values in the series mean the wavenumbers of the first d–d absorption bands of trischelate complexes). The strong absorption band at 27500 cm^{-1} [$\log(\varepsilon$/cm^{-1} mol^{-1} dm$^3)=3.18$] is assigned to a ligand-to-metal charge transfer transition

Table 1. CD and Absorption Data[a] in the First d-d Transition Region

Complex	$\sigma_{\mathrm{ext}}(\Delta\varepsilon)$	$\sigma_{\mathrm{max}}(\log \varepsilon)$	Chromophore
$[Co(TeO_6H_4)_3]^{3-}$		16.5(1.82)	CoO_6
$(+)^{CD}_{589}$-$[Co_4Te_3O_{18}(en)_3]^{6-}$	15.0(−0.65)		CoO_6
	17.0(+3.01)	17.7(2.47)	CoO_4N_2
	19.7(−0.24)		CoO_4N_2
$(-)^{CD}_{589}$-$[Co_4I_3O_{18}(en)_3]^{3-}$	15.9(+0.37)		CoO_6
	17.8(−1.12)	18.2(2.61)	CoO_4N_2

a) Energies of CD extrema, σ_{ext}, and absorption maxima, σ_{max}, are given in 10^3 cm^{-1}, and the intensities $\Delta\varepsilon$ and ε in cm^{-1} mol^{-1} dm^3.

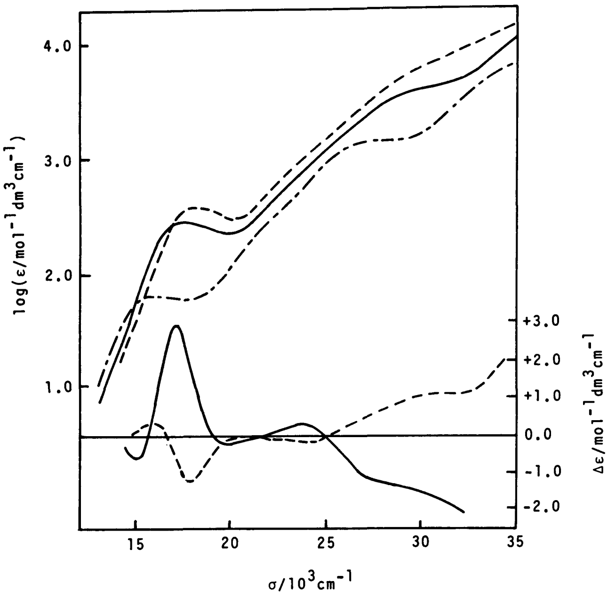

Fig. 2. Absorption and CD spectra of $(+)^{CD}_{589}$-$[Co_4Te_3O_{18}(en)_3]^{6-}$ (——) and $(-)^{CD}_{589}$-$[Co_4I_3O_{18}(en)_3]^{3-}$ (----), absorption spectrum of $[Co(TeO_6H_4)_3]^{3-}$ being also shown (—·—).

$e_g(Co) \leftarrow p_\pi(O)$ concerning the bridging oxo ligands.[10]

The tris(ethylenediamine)tris(tellurato)tetracobaltate(III) complex has a composition quite similar to that of the known periodate complex[8] $[Co_4I_3O_{18}(en)_3]^{3-}$. The parent aqua ion $[Co_4I_3O_{18}(H_2O)_6]^{3-}$ had been established in full detail from X-ray crystallography by two independent groups of workers.[11,12] A less characterized aqua derivative of the tellurato heteropoly compound had also been reported briefly.[3,4] For the present preparation of the heteropoly type tris(ethylenediamine) complexes, it was essential to use a mixed solution of two kinds of cobalt(III) complexes, one containing ethylenediamine and the other not.

$$\begin{aligned}&3[CoCl_2(NH_3)_2(en)]Cl + [Co(NH_3)_4(H_2O)_2](SO_4)_{1.5}\\&+ 3Te(OH)_6 + 15NaOH \longrightarrow Na_3H_3[Co_4Te_3O_{18}(en)_3]\\&+ 9NaCl + 1.5Na_2SO_4 + 10NH_3 + 17H_2O\end{aligned}$$

When only one kind of complex $[CoCl_2(NH_3)_2(en)]Cl$ was used, the main products containing tellurate ligands were a brown hexanuclear and a blue pentanuclear condensate of chain structure.[10] On the other hand, by using another kind of cobalt(III) complex $[Co(NH_3)_4(H_2O)_2](SO_4)_{1.5}$, the tris(tellurato)cobalt(III) complex was obtained.

The $(+)^{CD}_{589}$-tellurato and $(-)^{CD}_{589}$-periodato heteropoly complexes show the similar CD patterns, the signs of the corresponding CD bands being opposite (Fig. 2 and Table 1). The enantiomer shown in Fig. 1 has the absolute configuration Δ concerning the $Co(MO_6)_3$ moiety, while Λ' the $Co(CoO_4en)_3$ moiety. In addition, the same enantiomer has three Λ'' peripheral chromophores $Co(en)(MO_6)_2$ (M=Te or I). Thus the total absolute configuration of this isomer should be represented by $\Delta\Lambda'(\Lambda'')_3$. From the well-known criterion that the Λ isomer of a trischelate cobalt(III) complex has a sign (+) for the main CD band in the first d-d absorption region,[13] the $(+)^{CD}_{589}$-$[Co_4Te_3O_{18}(en)_3]^{6-}$ isomer with a main positive CD band in the CoO_4N_2 chromophore region (Table 1) is assigned to be $\Delta\Lambda'(\Lambda'')_3$ configuration and the $(-)^{CD}_{589}$-$[Co_4I_3O_{18}(en)_3]^{3-}$ isomer to the $\Lambda\Delta'(\Delta'')_3$ configuration. Unfortunately, the optical resolution of trischelate type complex $[Co(TeO_6H_4)_3]^{3-}$ was achieved only partially, and the quantitative CD curve was not obtained.

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