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Hexaammine, Tris(ethylenediamine), Glycinato, and L-Alaninato Complexes of a Triperiodatotetracobaltate(III) Condensed Anion

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Malaprade's triperiodatotetracobaltate(III) heteropoly condensed acid, $H_3[Co_4I_3O_{18}(OH_2)_6]\cdot nH_2O$, was characterized by examination of its coordination derivatives with ammonia, ethylenediamine, glycinato, or L-alaninato ligands. It was concluded that the ion of parent acid and its derivatives, $[Co_4I_3O_{18}X_6]^{n-}$ ($X_6=(OH_2)_6$, $(NH_3)_6$, en$_3$, $(OH_2)_4$(gly), or $(OH_2)_4$(L-ala)), commonly have a hexol-like arrangement of four cobalt(III) octahedra so that the whole skeletons are based on the Anderson structure. The hexol-like configuration is chiral, this being demonstrated by the separation of two diastereomers of $[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$ ion.

A dark green heteropoly condensed acid $H_3[Co_4I_3O_{24}H_{12}]\cdot nH_2O$ was first separated by Malaprade.[1] Nyman and Plane[2] proposed two possible structures, one being based on the so-called Anderson structure.[3] The Anderson structure consists of seven octahedra condensed by edge sharing into a flat aggregate of trigonal symmetry and includes some important examples such as $[TeMo_6O_{24}]^{6-}$,[4] and $[CrMo_6O_{18}(OH)_6]^{3-}$.[5] If this is the case for $H_3[Co_4I_3O_{24}H_{12}]$, the arrangement of four cobalt(III) octahedra in the green acid have a chiral configuration same as that in a hexol-cobalt(III) ion $[Co\{(\mu\text{-}OH)_2Co(NH_3)_4\}_3]^{6+}$, and accordingly the green acid should be optically resolved into enantiomers. Our attempts at optical resolution of this acid were unsuccessful but we obtained several coordination derivatives of the acid, and finally two diastereomers of $[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$ ion, which proves the chiral configuration of the skeleton of the starting acid. Details of preparation and electronic absorption and circular dichroism (CD) spectral studies are presented. These compounds may be new examples of a hybrid between ordinary metal complex and heteropoly condensed compound. So far only a few examples of this compound have been reported, such as $Na_5[CoNb_6O_{19}(OH_2)(en)]\cdot 17H_2O$[6] and $K_5[SiCoW_{11}O_{39}(NH_3)]\cdot 14H_2O$.[7]

Experimental

Preparation. 1) $H_3[Co_4I_3O_{24}H_{12}]\cdot nH_2O$: This was prepared by the method described in literature.[8] Previous authors reported $n=3$[8] or $n=6$,[2,9] but the following elemental analysis showed our samples to be an octahydrate with $n=8$. Found: H, 2.62; I, 32.56%. Calcd for $H_3[Co_4I_3O_{24}H_{12}]\cdot 8H_2O$: H, 2.69; I, 32.83%.

Sodium salt of this acid was also prepared. Found: H, 2.81; I, 29.28%. Calcd for $Na_3[Co_4I_3O_{24}H_{12}]\cdot 12H_2O$: H, 2.80; I, 29.33%.

2) $H_3[Co_4I_3O_{18}(en)_3]\cdot 5H_2O$: The starting acid $H_3[Co_4I_3O_{24}H_{12}]\cdot 8H_2O$ was reacted with 98% ethylenediamine at 55 °C for 3 hr. The reaction mixture was filtered and the resulting solid was washed with methanol. The crude product was dissolved in a minimum amount of water and the insoluble material was filtered off. To the filtrate was gradually added 15% perchloric acid and the complex deposited was purified by adding 15% perchloric acid to an alkaline solution (pH=about 12) of the complex. The reddish brown precipitate was filtered and washed with water, methanol and finally with acetone. Found: N, 7.20; C, 6.14; H, 3.18; I, 32.28%. Calcd for $H_3[Co_4I_3O_{18}(en)_3]\cdot 5H_2O$: N, 7.14; C, 6.12; H, 3.17; I, 32.32%.

3) $H_3[Co_4I_3O_{18}(NH_3)_6]\cdot 9.5H_2O$: This was derived from $H_3[Co_4I_3O_{24}H_{12}]\cdot 8H_2O$. Five grams of the starting acid was dried *in vacuo* overnight and was added in an excess of liquid ammonia at room temperature. The suspension was allowed to stand for 30 hr to complete the reaction. The solid phase gradually turned brown from green. Both the green starting compound and the reddish brown reaction product were sparingly soluble in liquid ammonia. The resulting solid was filtered and washed with a large amount of methanol. The crude product was dissolved in a minimum amount of water and the insoluble material was filtered off. An appropriate amount of methanol was added to the filtrate, a reddish brown precipitate being formed. This was recrystallized from a minimum amount of water by addition of methanol. When an aqueous solution of the complex was acidified, it precipitated immediately. Found: N, 7.10; H, 3.40%. Calcd for $H_3[Co_4I_3O_{18}(NH_3)_6]\cdot 9.5H_2O$: N, 7.12; H, 3.41%.

4) $(NH_4)_7H[Co_4I_3O_{18}(OH_2)_4(gly)]_2\cdot 14H_2O$: Two and a half grams of glycine was dissolved in a solution containing 5 g of $H_3[Co_4I_3O_{24}H_{12}]\cdot 8H_2O$ in 1.5 l of water. This solution was kept at 65 °C for 10 hr, during which the pH of the solution was about 2.8. After the solution had been cooled to room temperature and filtered, the filtrate was poured into a column (length *ca.* 0.5 m, diameter 3 cm) containing an anion exchanger, QAE-Sephadex A-25 chloride form. The dark green layer adsorbed at the top of the column was eluted with a solution of NaCl (5 g in 1 l of 1M acetic acid). It was confirmed from measurements of absorption spectra that the first eluted green band is the original aquo complex (sodium salt). The second eluted dark green species was adsorbed again on a column of QAE-Sephadex and eluted with NH_4Cl (100 g in 1 l of 1M acetic acid). When an appropriate amount of methanol was added to the eluate,

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[1] L. Malaprade, *Bull. Soc. Chim. Fr.*, **6**, 223 (1939).

[2] C. J. Nyman and R. A. Plane, *J. Amer. Chem. Soc.*, **83**, 2617 (1967).

[3] J. C. Anderson, *Nature*, **140**, 850 (1937).

[4] H. T. Evans, Jr., *J. Amer. Chem. Soc.*, **90**, 3275 (1968); **70**, 1291 (1948).

[5] A. Perloff, *Inorg. Chem.*, **9**, 2228 (1970).

[6] C. M. Flynn, Jr., and G. D. Stucky, *ibid.*, **8**, 178 (1969).

[7] L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, **92**, 3794 (1970).

[8] J. M. Williams and C. J. Nyman, "Inorganic Syntheses," **9**, 142 (1967).

[9] Y. Yoshino, T. Takeuchi, and H. Kinoshita, *Nippon Kagaku Zasshi*, **86**, 978 (1965).

the dark green complex was precipitated. This was recrystallized from a minimum amount of water by addition of NH_4Br and methanol. Found: N, 5.03; C, 1.92; H, 3.28; I, 30.07%. Calcd for $(NH_4)_7H[Co_4I_3O_{18}(OH_2)_4(gly)]_2\cdot 14H_2O$: N, 5.08; C, 1.94; H, 3.29; I, 30.69%.

5) $(NH_4)_2H_2[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]\cdot 9H_2O$: This was obtained by the same procedure as for 4), using 2.5 g of L-alanine instead of glycine. The L-alaninato complex was recrystallized from water by addition of methanol. The ammonium salt of the complex was less soluble than that of the glycinato complex. Found: N, 3.30; C, 2.65; H, 3.33; I, 29.79%. Calcd for $(NH_4)_2H_2[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]\cdot 9H_2O$: N, 3.32; C, 2.85; H, 3.35; I, 30.10%.

6) $(+)_{589}\text{-}Na_4[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]\cdot 8H_2O$ *and* $(-)_{589}\text{-}Na_4[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]\cdot 9H_2O$: For the separation of isomers of L-alaninato complex, the reaction mixture prepared in 5) was chromatographed by use of an eluent containing 3 g of NaCl in 1 l of 1M acetic acid and a column of 1.5 m length and 3 cm diameter. The first eluted band was the starting aquo complex (sodium salt) as in the case of the glycinato complex, and the second eluted band was broader than that of the glycinato complex. In this band, the species eluted faster showed a positive rotation at 589 nm and that eluted more slowly a negative one. These were sorbed separately on QAE-Sephadex columns, each adsorbed band being eluted again with a solution of NaCl (100 g in 1 l of 1M acetic acid). The sodium salts of L-alaninato isomers were obtained by adding methanol to each purified eluate and recrystallized from water by addition of methanol. Found: N, 0.79; C, 2.50; H, 2.36; I, 29.76%. Calcd for $(+)_{589}\text{-}Na_4[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]\cdot 8H_2O$: N, 1.08; C, 2.77; H, 2.32; I, 29.27%. Found: N, 0.92; C, 2.78; H, 2.48; I, 28.84%. Calcd for $(-)_{589}\text{-}Na_4[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]\cdot 9H_2O$: N, 1.06; C, 2.73; H, 2.45; I, 28.87%.

Measurements. The electronic absorption spectra were measured with Shimadzu QR-50 and Hitachi EPS-3T recording spectrophotometers. The CD spectra were recorded with a Roussel-Jouan dichrographe. All the measurements except for $[Co_4I_3O_{18}(en)_3]^{3-}$ were made in aqueous solutions at room temperature. The spectra of $[Co_4I_3O_{18}(en)_3]^{3-}$ were measured in 1/10M NaOH aqueous solution.

Results and Discussion

Nyman and Plane[2] proposed two possible structures for the dark green triperiodatotetracobaltate(III) heteropoly acid $H_3[Co_4I_3O_{30}H_{24}]\cdot nH_2O$ (Fig. 1), one chain and the other hexol-like, which have a notable difference in the number of water molecules coordinating to the cobalt(III) ions; *viz.*, 12 for the former and 6 for the latter. $[Co_4I_3O_{18}(NH_3)_6]^{3-}$ and $[Co_4I_3O_{18}(en)_3]^{3-}$ were derived from the reactions of the dark green acid with liquid ammonia and 98% ethylenediamine, respectively. This supports the view that the original dark green acid has structure (a) in Fig. 1. The formation of ethylenediamine complex indicates out that every two of the six water molecules take a *cis* position to each other. The dark green acid and its derivatives are thus assigned to have a hexol-like structure. One monoglycinato and two mono(L-alaninato) complexes resulted from the reactions of the dark green starting acid and glycine or L-alanine. The two L-alaninato isomers separated by column chromatographic method are assigned to a pair of diastereomers (Fig. 2) from their CD behaviors.

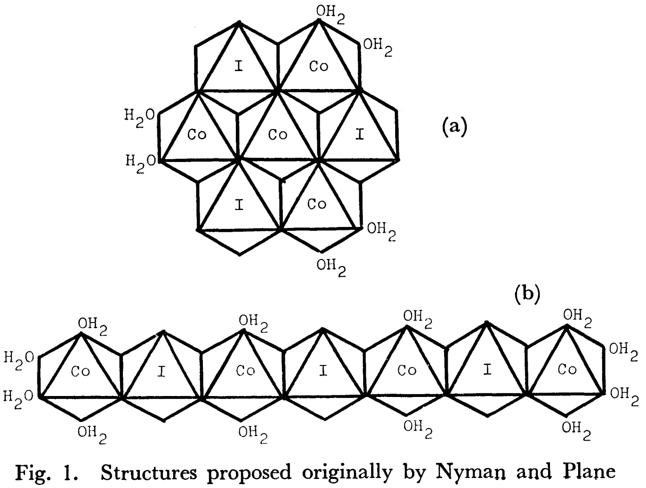

Fig. 1. Structures proposed originally by Nyman and Plane for the dark green parent complex.

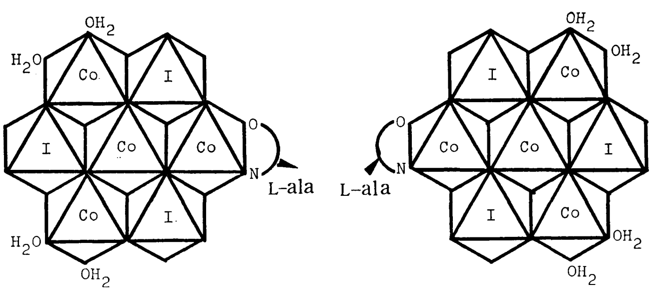

Fig. 2. Two diastereomers of the L-alaninato complex.

The absorption curves of the complexes are on the whole similar to each other (Figs. 3 and 4). Each complex shows three absorption bands in the region from visible to near-ultraviolet. Of these bands a shoulder at about 25—30×10^3 cm^{-1} is assigned to the "poly-nuclear band"[10–12] due to a charge-transfer transition in the group $Co\langle\substack{O\\O}\rangle Co$, from a comparison of the spectra of present complexes to those of $[(ox)_2Co(\mu\text{-}OH)_2Co(ox)_2]^{4-}$,[13] and $[Co_2Mo_{10}O_{34}(OH)_4]^{6-}$,[12,14]. This assignment is emphasized by the fact that the mono-nuclear complexes $[CoMo_6O_{24}H_6]^{3-}$,[12] and $[CoW_6O_{22}]^{5-}$,[15] did not have this kind of absorption band.

The first absorption band for the dark green parent complex $[Co_4I_3O_{18}(OH_2)_6]^{3-}$ appears at 16.8×10^3 cm^{-1} which agrees well with the behavior of several $[Co(O)_6]$ type complexes[12,16] (Table 1). The first bands of the

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10) Y. Inamura and Y. Kondo, *ibid.*, **74**, 627 (1953).

11) Y. Sasaki, J. Fujita, and K. Saito, This Bulletin, **42**, 146 (1969).

12) Y. Shimura, H. Ito, and R. Tsuchida, *Nippon Kagaku Zasshi*, **75**, 560 (1954).

13) Diffuse reflectance spectrum of $K_4[Co_2(OH)_2(ox)_4]\cdot 3H_2O$, measured by N. Matsuoka (Department of Chemistry, Faculty of Science, Osaka University), showed three absorption bands at 16.6, 24.1 and 30.6×10^3 cm^{-1}, the last one being the poly-nuclear band.

14) T. Ama, J. Hidaka, and Y. Shimura, This Bulletin, **43**, 2654 (1970).

15) M. Shibata, *Nippon Kagaku Zasshi*, **87**, 771 (1966).

16) N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 1868 (1967).

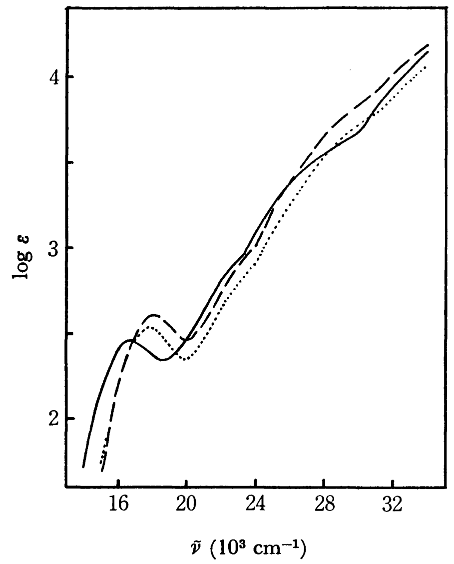

Fig. 3. Absorption curves of $[Co_4I_3O_{18}(OH_2)_6]^{3-}$ (———), $[Co_4I_3O_{18}(NH_3)_6]^{3-}$ (····) and $[Co_4I_3O_{18}(en)_3]^{3-}$ (-----).

ammine and ethylenediamine complexes shift to somewhat higher energy, *i.e.*, 17.7 and 18.0×10^3 cm^{-1}, respectively (Fig. 3). These positions may be reasonable, since the hexol-like complexes containing six ammonia or three ethylenediamine ligands have one $[Co(O)_6]$ and three *cis*-$[Co(O)_4(N)_2]$ type chromophores. A similar consideration is applicable to the first absorption bands of glycinato and L-alaninato complexes, which are contributed from three $[Co(O)_6]$ and one $[Co(O)_5(N)]$ type chromophores (Fig. 4 and Table 1). The second absorption bands appear at about 20—25×10^3 cm^{-1} as a vague shoulder on the strong poly-nuclear band in all of the present complexes.

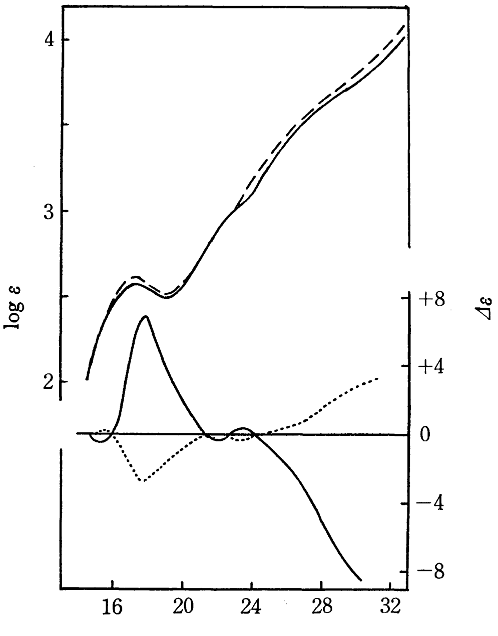

Fig. 4. Absorption and CD curves of $(+)_{589}$-$[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$ (——), absorption curve of $[Co_4I_3O_{18}(OH_2)_4(gly)]^{4-}$ (-----) and CD curve of $(-)_{589}$-$[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$ (····).

The CD curves of the two L-alaninato complexes are shown in Fig. 4. Roughly speaking two CD curves are antipodal to each other, indicating that the two complexes are a diastereomeric pair, ΔL and ΛL. Two CD bands with opposite signs to each other appear in the first absorption band region (14—21×10^3 cm^{-1}); that at lower energy is weak and the other at higher energy comparatively intense and broad. Broadening

TABLE 1. ABSORPTION MAXIMUM DATA FOR THE FIRST ABSORPTION BAND

Complex	$\tilde{\nu}_{max}$, 10^3 cm^{-1}	log ε_{max}	log ε(Co) a)
$[Co_4I_3O_{18}(OH_2)_6]^{3-}$	16.8	2.47	1.87
$[Co_4I_3O_{18}(NH_3)_6]^{3-}$	17.7	2.54	1.94
$[Co_4I_3O_{18}(en)_3]^{3-}$ in 1/10 M NaOH	18.0	2.60	2.00
$[Co_4I_3O_{18}(OH_2)_4(gly)]^{4-}$	17.2	2.62	2.02
$(+)_{589}$-$[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$	17.2	2.57	1.97
$(-)_{589}$-$[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$	17.2	2.57	1.97
$[CoMo_6O_{18}(OH)_6]^{3-}$, 12)	16.5	1.29	1.29
$(+)_{589}$-$[Co_2Mo_{10}O_{34}(OH)_4]^{6-}$, 14)	16.5	1.96	1.66
$[CoNb_6O_{19}(OH_2)(en)]^{5-}$, 6)	16.7	1.81	1.81

a) intensity calculated per one cobalt(III) ion.

TABLE 2. CD IN THE $[Co(O)_6]$ CHROMOPHORE BAND REGION

Complex	$\tilde{\nu}_{ext}$, 10^3 cm^{-1} (Δε)	$\tilde{\nu}_{ext}$, 10^3 cm^{-1} (Δε)	Ref.
$(+)_{589}$-$[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$	15.3 (−0.5)	17.8 a) (+6.9)	
$(-)_{589}$-$[Co_4I_3O_{18}(OH_2)_4(\text{L-ala})]^{4-}$	15.5 (+0.2)	17.6 a) (−2.7)	
$(-)_{589}$-$[Co_4(OH)_6(NH_3)_{12}]^{6+}$	14.7 (*ca.* −4) b)	16.5 (*ca.* +15) b)	17)
$(-)_{589}$-$[Co_4(OH)_6(en)_6]^{6+}$ (L$_I$-isomer)	14.6 (−5.0)	16.5 (+16.0)	18)
$(-)_{589}$-$[Co_4(OH)_6(\text{L-pn})_6]^{6+}$	14.3 (−1.1)	16.2 (+10.8)	19)
$(+)_{589}$-$[Co_4(OH)_6(\text{L-pn})_6]^{6+}$	14.5 (+1.3)	16.3 (−13.3)	19)
$(+)_{589}$-$[Co_2Mo_{10}O_{34}(OH)_4]^{6-}$	15.6 (−2.20)	17.1 (+1.35)	14)

a) Overlapped with the bands due to $[Co(O)_4(\text{L-ala})]$ chromophore.
b) Estimated from figure.

in the latter suggests a contiguity of two CD bands of the same sign. The CD bands in the second absorption band region ($21-25\times10^3$ cm^{-1}) are weak as compared with those in the first band region. The CD in the poly-nuclear band region is considerably strong.

As seen in Table 2, the CD behavior in the region of d-d absorption band due to the $[Co(O)_6]$ chromophore ($14-18\times10^3$ cm^{-1}) is quite similar to that observed for some hexol-cobalt(III) ions with ammonia,[17] ethylenediamine,[17,18] and L-propylenediamine[19] in the corresponding region. Thus, it is concluded that the complexes have the hexol-like Anderson structure. For the absolute configurations of hexol-cobalt(III) ions with ammonia, ethylenediamine or L-propylenediamine, Mason *et al.*[17] and Douglas *et al.*[19] gave reversed assignments, but Wentworth *et al.*[18] none. Since the one X-ray study of this type of compound is confined to the racemic ammine hexol,[20] we have not attempted to assign the absolute configurations of the L-alaninato diastereomers. Nevertheless, it is evident from Table 2 that the $(+)_{589}$-L-alaninato diastereomer has the same configuration as the $(-)_{589}$-isomers of the ammine-, ethylenediamine-, and L-propylenediamine-hexols.

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17) S. F. Mason and J. W. Wood, *Chem. Commun.*, **1967**, 209.

18) R. D. Kern and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1018 (1967).

19) I. Masuda and B. E. Douglas, *J. Coord. Chem.*, **1**, 189 (1971).

20) U. Thewalt, *Chem. Ber.*, **104**, 2657 (1971).