  Bull. Chem. Soc. Jpn., 55, 2113—2117 (1982)

The Crystal Structure of $Na_2H_2[Co_4I_3O_{18}(OH_2)_6]$-$[Co_4I_3O_{16}(OH)_2(OH_2)_6]\cdot 22H_2O$

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(Received December 4, 1981)

The title compound has the analytical formula of $Co_4H_{36}I_3NaO_{35}$ and is seemingly well formulated as $NaH_2[Co_4I_3O_{18}(OH_2)_6]\cdot 11H_2O$. But the structure determination revealed that the crystals contain non-protonated $[Co_4I_3O_{18}(OH_2)_6]^{3-}$ and doubly protonated $[Co_4I_3O_{16}(OH)_2(OH_2)_6]^{-}$. The anion itself has a new variation of the Anderson structure. The almost identical three pK's of the acid, $H_3[Co_4I_3O_{18}(OH_2)_6]$, explain the formation of the present crystals by co-precipitation of two forms of the anion with different degrees of protonation. Crystals are monoclinic, space group P2/c, with $a=15.172(2)$, $b=10.874(1)$, $c=19.436(3)$ Å, $\beta=116.58(1)°$, $U=2867.6(5)$ Å^3, and $Z=2$. The final R factor was 0.036 for 7010 independent reflections.

The periodate anion has been reported to form complex anions with various transition metal cations.[1,2] The Co^{III} and I^{VII} form a highly condensed anion, $[Co_4I_3O_{18}]^{3-}$, as reported by Malaprade.[3]

On the basis of spectroscopic and stereochemical data, Ama, Hidaka, and Shimura proposed the Anderson structure for this anion, consisting of seven octahedra condensed into a flat arrangement of D_{3d} symmetry by edge-sharing.[4] Two types of the Anderson structure are known: the first one has been found in $[TeMo_6O_{24}]^{6-}$,[5] and $[IMo_6O_{24}]^{5-}$,[6] which has no constitutional water, while the second one has been reported in the cases of $[CrMo_6O_{24}H_6]^{3-}$,[7] and $[CoMo_6O_{24}H_6]^{3-}$,[8] having six non-acidic protons per molecule. Our present study has confirmed that this (tetracobaltato)triperiodate anion belongs to a new type of the Anderson structure which has twelve non-acidic protons.

Experimental

At the beginning, our aim was to prepare the free acid form of the title compound from $Na_3[Co(CO_3)_3]\cdot 3H_2O$, $HClO_4$ and $NaIO_4$. The method reported by Williams and Nyman[9] was used, but crystals of the compound having the analytical formula of $Co_8H_{72}I_6Na_2O_{70}$ were obtained and used for the present study.

Data Collection. Preliminary Weissenberg photographs showed that the crystal system is monoclinic. A systematic absence $h0l$, $l=2n+1$, indicated the space group to be either Pc or P2/c; P2/c was assumed and confirmed by the successful structure analysis.

The intensities of the reflections were measured with a Rigaku automatic four-circle diffractometer (graphite monochromator, Mo $K\alpha$ radiation, ω-2θ scan mode) up to $2\theta=60°$. The crystal used here was a parallelepiped with dimensions $0.45\times 0.1\times 0.2$ mm^3. Independent 7010 reflections, $|F_o|\geq 3\sigma(|F_o|)$, were adopted for the structure determination. The crystal data are: $Co_8H_{72}I_6Na_2O_{70}$, FW=2471.88, monoclinic, space group P2/c, $a=15.172(2)$, $b=10.874(1)$, $c=19.436(3)$ Å, $\beta=116.58(1)°$, $U=2867.6(5)$ Å^3, $Z=2$, $D_x=2.864$ g cm^{-3}, μ for Mo $K\alpha$ ($\lambda=0.71069$ Å)$=57.85$ cm^{-1}.

Structure Determination and Refinement

The structure was solved by the heavy-atom method. All the non-hydrogen atoms were refined by the block-diagonal least-squares method using anisotropic temperature factors. Almost all of the hydrogens attached to anions 1 and 2 have been located on the difference Fourier maps and treated isotropically in the refinements. One hydrogen atom of an aqua ligand bound to a cobalt atom, the cationic proton, and all of the hydrogens of the water molecules were not found. The eleven waters of crystallization are in general positions and one of them, Aq(11), are distributed in two sites, Aq(11a) and Aq(11b), by the ratio of 0.45 and 0.55. This ratio was estimated from the peak heights in the difference Fourier maps and fixed in the structure refinements. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=1/[\sigma(|F_o|)^2+c^2|F_o|^2]$. The parameter c was estimatedto be 0.02 from the fluctuations of the intensities of the standard reflections during the data collection and $\sigma(|F_o|)$ was found from counting statistics. The final R values are $R=0.035$ and $R_w=0.036$, where $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=\Sigma w||F_o|-|F_c||/\Sigma w|F_o|$. The atomic scattering factors and the corrections of anomalous dispersion were taken from International Tables for X-Ray Crystallography.[10] All the calculations were performed on a HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo with a local version of UNICS.[11] The atomic fractional coordinates and the averaged bond distances and angles are listed in Tables 1 and 2. The F_o-F_c tables and anisotropic thermal parameters are kept at the office of this Bulletin as Document No. 8230.

Description of the Structure and Discussion

Structure of Polyanion. There are two forms of the anion, which are different not only crystallographically but also in the degree of the protonation. We describe the common features of the structures of both forms in this section.

The structure of the polyanion is shown in Fig. 1. The anion has principally the Anderson structure, as found in several heteropolymolybdates.[5-8] But in the present (tetracobaltato)triperiodate anion, the six peripheral sites are occupied by Co and I alternatively and there is a Co at the central heteroatom site. In general, the Anderson polyanion has three types of

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TABLE 1. FRACTIONAL COORDINATES
($\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogen atoms)

Atom	x	y	z	Atom	x	y	z
Co*(a1)	0	2405(1)	2500	O_t(6b)	4407(3)	7049(3)	4002(2)
I(1)	0	5176(1)	2500	O_t(7a)	6126(3)	3053(3)	4882(2)
Co(2)	1647(1)	3715(1)	2545(1)	O_t(7b)	4332(3)	2066(3)	4046(2)
I(3)	1726(1)	1015(1)	2519(1)	O_t(8)	4186(3)	688(3)	2654(2)
Co(4)	0	−188(1)	2500	Na	1236(2)	2575(2)	5304(1)
Co*(a2)	5000	4500(1)	2500	Aq(1)	2236(3)	5747(5)	1016(3)
I(5)	5000	7264(1)	2500	Aq(2)	4951(4)	568(4)	5652(3)
Co(6)	5186(1)	5811(1)	3819(1)	Aq(3)	2379(4)	2759(4)	7659(3)
I(7)	5218(1)	3125(1)	3902(1)	Aq(4)	2408(4)	1183(5)	6093(3)
Co(8)	5000	1887(1)	2500	Aq(5)	2208(4)	2722(5)	4615(3)
O_c(12)	859(2)	3697(3)	3067(2)	Aq(6)	1991(4)	5949(6)	4792(4)
O_c(23)	804(2)	2424(3)	1972(2)	Aq(7)	590(5)	2483(5)	6179(4)
O_c(34)	853(2)	1101(3)	3064(2)	Aq(8)	−41(6)	4004(7)	431(4)
O_c(56)	4351(2)	5785(3)	2752(2)	Aq(9)	437(8)	775(10)	4634(4)
O_c(67)	5832(2)	4500(3)	3583(2)	Aq(10)	2941(6)	366(8)	4706(5)
O_c(78)	4343(2)	3180(3)	2741(2)	Aq(11)	1834(16)	1483(16)	220(11)
O_b(12)	765(3)	4948(3)	1967(2)	Aq(12)	1311(10)	2336(11)	540(9)
O_b(23)	2457(2)	2376(3)	3115(2)	H(2a)	295(8)	472(10)	332(7)
O_b(34)	729(3)	−104(3)	1926(2)	H(2a′)	233(8)	581(9)	286(7)
O_b(56)	5855(3)	7017(3)	3553(2)	H(2b)	238(10)	478(12)	175(8)
O_b(67)	4506(2)	4481(3)	4018(2)	H(2b′)	289(10)	328(12)	203(8)
O_b(78)	5825(2)	1942(3)	3571(2)	H(4)	84(9)	−216(10)	314(7)
O_t(1)	791(3)	6243(3)	3217(2)	H(6a)	655(8)	661(10)	507(7)
O_t(2a)	2523(3)	4946(3)	3229(2)	H(6a′)	599(8)	596(9)	530(6)
O_t(2b)	2311(3)	3767(3)	1892(2)	H(6b)	447(8)	761(9)	403(6)
O_t(3a)	2535(3)	−93(4)	3224(3)	H(6b′)	422(6)	693(8)	431(5)
O_t(3b)	2265(3)	998(4)	1859(3)	H(7b)	374(7)	217(8)	373(6)
O_t(4)	913(3)	−1399(3)	3184(3)	H(8)	347(10)	86(12)	228(8)
O_t(5)	4152(3)	8314(3)	2599(2)	H(8′)	416(10)	0(12)	261(8)
O_t(6a)	6171(3)	5825(3)	4886(2)				

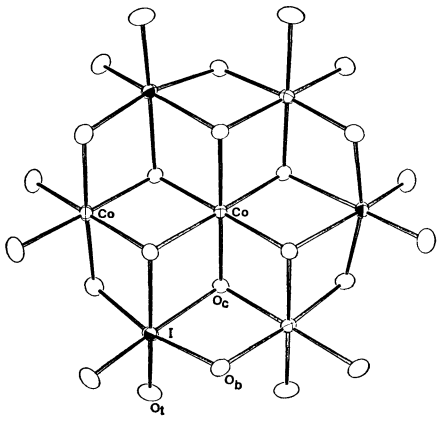

Fig. 1. Structure of $[Co_4I_3O_{18}(OH_2)_6]^{3-}$ "Anderson polyanion" (anion 1) viewed vertical to the hexagonal Co_4I_3 pseudo-plane.
The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).[17] All the terminal oxygen atoms attached to Co are those of water molecules. The terminal oxygens attached to I are not protonated. In the anion 2 two of them are protonated.

oxygen atoms, denoted as O_t, O_b, and O_c. O_t represents the terminal oxygen bonding to one peripheral metal atom, O_b the one bridging between two peripheral metal atoms, and O_c the one coordinating to the central atom and two peripheral atoms. In this (tetracobaltato)triperiodate anion, however, there are two different O_t atoms. Half of them are the terminal oxygen atoms of Co, which are actually aqua ligands. Others are those of I which attract a proton in acidic media or form hydrogen bonds with the aqua ligands coordinated to Co atom.

The alternate arrangement of Co and I atoms at the peripheral metal sites causes the reduction of symmetry of the ion from $D_{3d}(\bar{3}m)$ of the Anderson structure to $D_3(32)$. The Co_3I_3 framework is not regularly hexagonal, while Mo_6 in $[IMo_6O_{24}]^{5-}$ is.[6]

It should be noted that there are only a few examples of structure determination of the Co^{III}–OH_2 distances. The only reliable example of Co^{III}–OH_2 distance is 1.954(1) Å, in $[Co(OH_2)(NH_3)_5]^{3+}$.[12] Our present study provides six crystallographically independent Co^{III}–OH_2 distances, 1.912—1.947(10) Å.

Crystal Structure. The crystal structure is shown in Fig. 2. The crystal contains two symmetrically independent Anderson polyanions. The first anion, referred to as anion 1, is not protonated and lies on the crystallographic two-fold axis at $x=0$, $z=1/4$ or 3/4 with the Co_4I_3 pseudo-plane almost parallel to

TABLE 2. AVERAGED BOND DISTANCES AND ANGLES IN $[Co_4I_3O_{18}(OH_2)_6]^{3-}$ (ANION 1) AND $[Co_4I_3O_{16}(OH)_2(OH_2)_6]^{1-}$ (ANION 2)
(Estimated standard deviation is given in parentheses)

a) Bond distances l/Å

Atoms	$[Co_4I_3O_{18}(OH_2)_6]^{3-}$		$[Co_4I_3O_{16}(OH)_2(OH_2)_6]^{1-}$	
	Averaged distance	Distribution	Averaged distance	Distribution
Co*-Co	2.835(1)	2.820—2.843	2.837(1)	2.834—2.834
Co*-I	3.011(1)	3.010—3.014	2.998(1)	2.995—3.005
Co-I	2.927(1)	2.913—2.940	2.921(1)	2.915—2.925
Co*-O_c	1.905(4)	1.897—1.916	1.909(4)	1.896—1.922
Co-O_c	1.887(4)	1.882—1.890	1.894(4)	1.883—1.900
I-O_c	2.038(4)	2.026—2.053	2.034(4)	2.002—2.056
Co-O_b	1.891(4)	1.873—1.908	1.890(4)	1.868—1.913
I-O_b	1.888(4)	1.880—1.900	1.882(4)	1.857—1.902
Co-O_t	1.942(5)	1.935—1.947	1.930(5)	1.912—1.944
I-O_t	1.808(5)	1.796—1.824	1.789(5)	1.783—1.794
I-OH	—	—	1.885(5)	1.885

b) Bond angles ϕ/° ("anti" means two O atoms transverse to Co_4I_3 plane; "syn" means two on the same side)

Atoms	$[Co_4I_3O_{18}(OH_2)_6]^{3-}$		$[Co_4I_3O_{16}(OH)_2(OH_2)_6]^{1-}$	
	Averaged angle	Distribution	Averaged angle	Distribution
Co-Co*-I	60.0(1)	59.9—60.2	60.0(1)	59.8—60.2
Co-I-Co	114.0(1)	113.9—114.3	114.5(1)	114.4—114.6
I-Co-I	126.0(1)	125.6—126.6	125.5(1)	125.1—125.6
O_c-Co*-O_c (anti)	83.2(2)	82.3—84.5	83.6(2)	83.0—85.1
O_c-Co*-O_c (syn)	96.8(2)	96.0—97.6	96.4(2)	95.8—97.0
O_c-Co-O_c (anti)	83.7(2)	83.4—84.1	83.9(2)	83.6—84.5
O_c-I-O_c (anti)	77.2(2)	76.8—77.3	77.9(2)	77.1—78.4
O_b-Co-O_b (anti)	175.1(2)	174.3—175.5	175.3(2)	174.7—176.3
O_b-I-O_b (anti)	165.2(2)	164.9—165.3	166.1(2)	163.7—167.2
O_t-Co-O_t (anti)	92.5(2)	91.6—94.3	92.6(2)	92.0—93.7
O_t-I-O_t (anti)	99.4(2)	99.2—99.6	100.9(2)	100.9
O_t-I-OH (anti)	—	—	94.5(2)	94.5

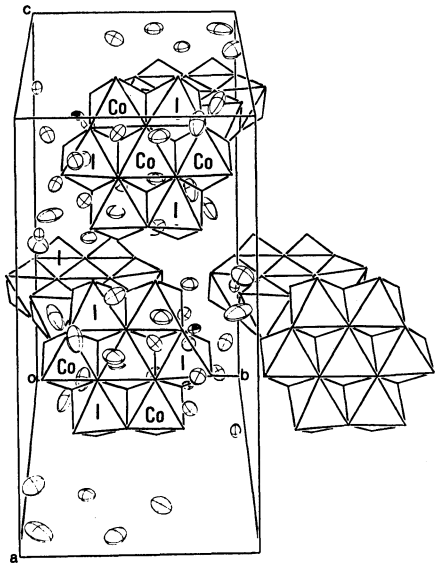

Fig. 2. Crystal structure viewed from the a*-axis. The shaded ellipsoids represent Na^+ ions and other ellipsoids are water molecules of crystallizations. Anions are shown with polyhedral models. The almost regular hexagonal shaped anions are the anion 1 and other are the anion 2.

the (001) plane. The second one, anion 2, contains two more protons and is on the diad axis at $x=1/2$, $z=1/4$ or 3/4 and almost parallel to the (100) plane. In Table 1, Co*(a1) and Co*(a2) mean the central Co atoms of anions 1 and 2 respectively and M(i), where M=Co or I, belongs to anion 1 for $1\leq i\leq 4$ and to anion 2 for $5\leq i\leq 8$.

Sodium Cation. The Na^+ ions do not interact with the polyanions directly. The Na^+ ion is coordinated by six water molecules of crystallization and forms an almost regular octahedral $[Na(OH_2)_6]^+$ ion, as is shown in Fig. 3. The distances of Na–O are 2.28—2.40(2) Å.

Anion-Anion Hydrogen Bond. As can be seen in Fig. 2, anion 1 is very close to its neighbour translated along the b-axis. Anion 2 is also in the same situation. This is because the O_t atoms of Co are aqua ligands, while those of I are oxygen atoms and inter-anionic hydrogen bonds are formed among them. As a result, 2 anions form a two-dimensional network (denoted 2D-net hereafter) parallel to the (100) plane shown in Fig. 4. These 2D-nets stack along the a-axis and the 1 anions link two 2D-nets with hydrogen bonds (Fig. 5). These inter-anionic hydrogen bonds are summarized in Table 3.

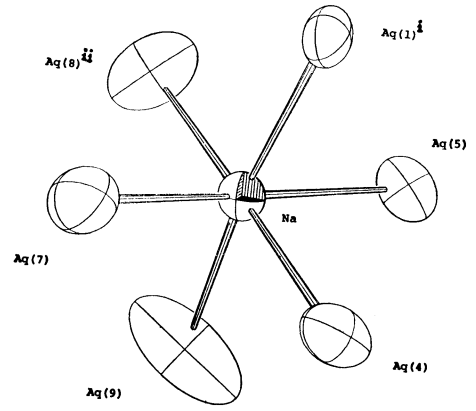

Fig. 3. The structure of the $[Na(OH_2)_6]^+$ cation.
Superscripts represent symmetry operations (i: $-x$, y, $1/2-z$; ii: x, $1-y$, $1/2+z$).

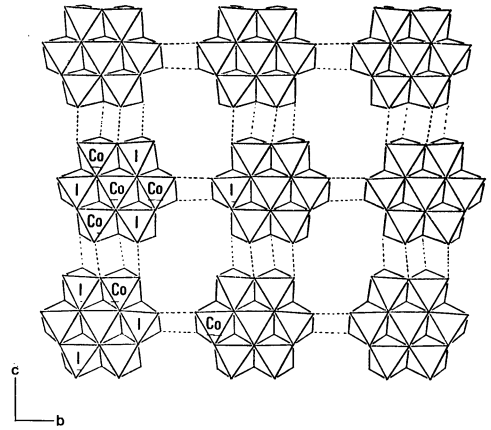

Fig. 4. The two-dimensional network (2D-net) of the anion 2 viewed from the a*-axis.
Dashed lines are inter-anionic hydrogen bonds.

TABLE 3. INTER-ANIONIC HYDROGEN BONDS

	H-donor	H-acceptor	Distance(l/Å)
Anion 1—Anion 1	O_t(4)	O_t(1)^i	2.548(7)
Anion 1—Anion 2	O_t(2a)	O_b(67)	2.709(6)
	O_t(2b)	O_c(78)	2.839(6)
	O_t(7b)	O_b(23)	2.610(6)
	O_t(8)	O_t(3b)	2.625(7)
Anion 2—Anion 2	O_t(6a)	O_b(67)^{ii}	2.758(6)
	O_t(6b)	O_t(7a)^{ii}	2.626(7)
	O_t(8)	O_t(5)^i	2.565(7)

i: x, $-1+y$, z
ii: $1-x$, $1-y$, $1-z$

Protonation of the Anions. One of the terminal oxygen atoms of I(7) in anion 2 is protonated. This oxygen, O_t(7b) is very close to O_b(23), a bridging oxygen atoms of the anion 1, with the distance of 2.61(1) Å. This short distance indicates that there is a strong hydrogen bond between O_t(7b) and O_b(23). Moreover, the I(7)–O_t(7b) distance is 1.885(5) Å, which agrees with the I–OH length, 1.89(2) Å, in H_5IO_6.[13] This value is significantly larger than the other I–O_t distances, 1.783—1.824(5) Å, in the anions

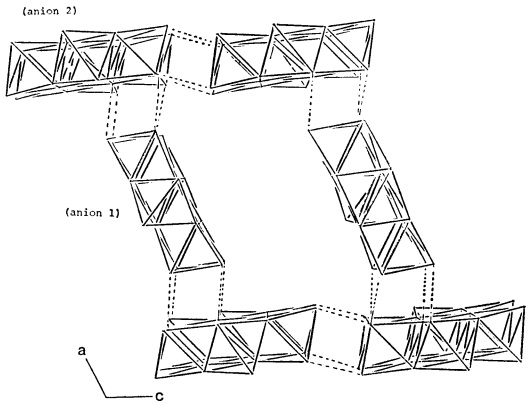

Fig. 5. Stacking scheme of the 2D-nets viewed from the b-axis.
The anion 1 acts as a girder between two 2D-nets.
Dashed lines represent inter-anionic hydrogen bonds.

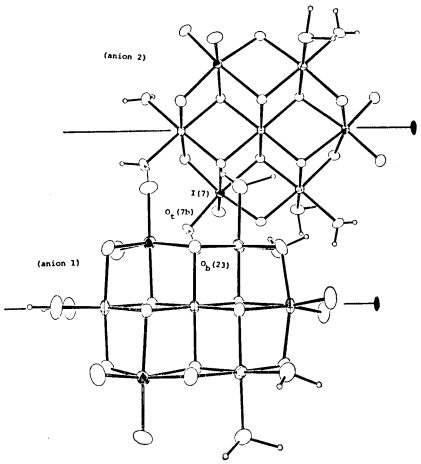

Fig. 6. Interaction of anions 1 and 2.
The protonated atom of anion 2 and the related atoms are shown. Small circles are hydrogen atoms included in the structure refinement. Fine lines are inter-anionic hydrogen bonds.

1 and 2. The minimum I–O_t length, 1.783(8) Å, is found in I(7)–O_t(7a), where O_t(7a) is the geminate O_t atom of O_t(7b). This short I(7)–O_t(7a) distance must be caused by the loose I(7)–O (7b) bond. In the difference Fourier maps, there is a peak with the height of ≈ 0.7 e/Å^3 at about 0.9 Å from O_t(7b) toward O_b(32). From these facts, we have concluded that O_t(7b) has a proton. There is no evidence for further protonation to the both polyanions. The anion 2 has a crystallographic 2-fold axis, so anion 2 is doubly protonated and should be formulated as $[Co_4I_3O_{16}(OH)_2(OH_2)_6]^{1-}$, while anion 1 is written as $[Co_4I_3O_{18}(OH_2)_6]^{3-}$. Figure 6 shows the interactions between anions 1 and 2. It has been reported that the acid is tri-basic, with virtually identical pK's (≈ 1.5).[14] Equilibrium calculations show that at the pH of 1.5, the concentrations of the four species: H_3X, H_2X^-, HX^{2-}, and X^{3-} ($X=Co_4I_3O_{18}(OH_2)_6^{3-}$) are equal in the solution.

The formation of the present crystals can be understood as the coprecipitation of H_2X^- and X^{3-}

anions; the one proton not found in this study must be present as an oxonium ion.

It is noteworthy that anion 2 is protonated at a terminal oxygen atom. There are several polyanions known to be protonated, but in most cases, the protonated sites are doubly or triply coordinated oxygen atoms, *e.g.* $[CrMo_6O_{24}H_6]^{3-}$.[7] The only exception is $[Mo_8O_{28}H_2]^{6-}$ anion, which has protonated terminal oxygen atoms.[15]

The bond distances and angles of the polyanions, except for the protonated sites, are the same as those of the Li salt determined by Lebioda, Ciechanowicz-Rutkowska, Baker, and Grochowski (1980).[16]

The authors thank Professor L. C. W. Baker for sending us his structure of the Li salt of the (tetracobaltato)triperiodate prior to the publication.

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