

The Structure of $[\text{Li}(\text{H}_2\text{O})_4]_2\text{H}[\text{Co}_4\text{H}_{12}\text{I}_3\text{O}_{24}]\cdot 3\text{H}_2\text{O}$ – A Heteropoly Periodate Representative of a New Type of Heteropoly Salt

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Abstract

$[\text{Li}(\text{H}_2\text{O})_4]_2\text{H}[\text{Co}_4^{3+}\text{H}_{12}\text{I}_3^+\text{O}_{24}]\cdot 3\text{H}_2\text{O}$ is triclinic, space group $P\bar{1}$, with $a = 10.163$ (2), $b = 16.572$ (4), $c = 9.624$ (1) Å, $\alpha = 105.61$ (2), $\beta = 114.77$ (3), $\gamma = 90.32$ (2)°, $Z = 2$. Refinement gave a final R of 0.058. In each anion, one Co^{3+} is at the center of a planar hexagon, the six vertices of which locate three Co^{3+} and three I^+ arranged alternately around the hexagon. Two water molecules are bonded as ligands on the exterior coordination sites of each of the three peripheral Co atoms, and the Co and I atoms are joined by bridging O atoms. The complex anion is isomorphous with many hexaheteropoly molybdates and tungstates. The enantiomorphous anions are H-bonded into layers, between which lie the $\text{Li}(\text{H}_2\text{O})_4^+$ groups and partially disordered lattice water molecules.

Introduction

Only five elements (Mo, W, and V in their higher oxidation states, and Ta^V and Nb^V to a more limited extent) have been reported as functioning in heteropoly complexes in the role of *addenda* atoms [*i.e.* the positive valent element(s) present in high atomic proportions]. Thus, essentially all known heteropoly complexes contain several atoms of one or more of these few elements, although about 50 other elements (mainly non-metals and transition metals) function as hetero-atoms.

In an earlier paper (Baker, Lebioda, Grochowski & Mukherjee, 1980) the characteristics which an atom

must possess in order to function as a heteropoly *addendum* species were discussed. It was shown in a preliminary report on the determination of the structure of the $[\text{Co}_4^{3+}\text{H}_{12}\text{I}_3^+\text{O}_{24}]^{3-}$ heteropolyanion that I^{VII} has these qualities. That structure indicates that there should be a new category of heteropoly complexes made up of I^+O_6 octahedra sharing O atoms with lower-charged transition-metal atoms. Such heteropoly periodate species should form derivatives with organic ligands and should be susceptible to controlled condensations and co-condensations into large cross-linked or linear polymers *via* poly-functional ligands. The present paper reports the crystal structure of $[\text{Li}(\text{H}_2\text{O})_4]_2\text{H}[\text{Co}_4\text{H}_{12}\text{I}_3\text{O}_{24}]\cdot 3\text{H}_2\text{O}$.

This compound can probably be useful for obtaining heavy-atom derivatives of proteins. The rigid anion contains four Co atoms with high f'' (for Cu $K\alpha$) and three I atoms which should enable the position of the anion to be located from the difference Patterson map.

Experimental

The green crystalline free acid of the tris(orthoperiodato)tetracobaltate(III) anion, $\text{H}_3[\text{Co}_4\text{H}_{12}\text{I}_3\text{O}_{24}]\cdot 3\text{H}_2\text{O}$, was prepared and purified by the method previously described (Nyman & Plane, 1961; Williams & Nyman, 1967). Its purity was established by analyses for replaceable hydrogen, Co^{III} , I^{VII} and H_2O . Preliminary X-ray examination of crystals of the free acid showed that they were twinned. Similar examination of diffusion-grown crystals of the normal K and normal Na salts also showed twinned crystals. The dilithium monohydrogen acid salt, prepared by the following procedure, formed untwinned crystals.

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Solid LiNO_3 was dissolved in a saturated aqueous solution (1.5 M) of the free acid at room temperature. The resulting clear solution was heated for 4 h at 333 K and allowed to evaporate slowly at room temperature for two weeks. The green crystals were filtered, washed with a minimum of ice water, and air dried.

A parallelepiped crystal bounded by faces (001), (010), (110), with dimensions $0.17 \times 0.20 \times 0.03$ mm, was used to collect the intensity data on an Enraf-Nonius CAD-4 diffractometer. The cell parameters were obtained from the least-squares fit of the φ , χ , ω and 2θ values for 15 reflections. The intensities were measured up to $\theta = 27^\circ$ with graphite-monochromated $\text{Mo } K\alpha$ radiation. A θ - 2θ scan was used with a scan range varying as $0.80^\circ + 0.42^\circ \tan \theta$.

The intensities were corrected for Lorentz, polarization, and absorption factors ($\mu_{\text{Mo } K\alpha} = 5.42 \text{ mm}^{-1}$). From 5993 measured unique reflections, 5673 with $F > 3\sigma$ were used in further calculations.

Structure determination and refinement

The positions of the heavy atoms were obtained by the Patterson method. Fourier maps then revealed each anion's 24 O atoms and 8 water molecules per formula. Two cycles of the refinement reduced the R factor to 0.12, and the resulting Fourier map revealed the position of one Li atom. Anisotropic refinement gave an R factor of 0.074, and the resulting difference Fourier map showed the second Li atom and six peaks of height corresponding to about $6 \text{ e } \text{Å}^{-3}$ – assigned to disordered water molecules. For these water molecules, site-occupancy factors of 0.5 were used based on the heights of the electron density peaks. However, some of these molecules are probably disordered, as suggested by the shape of the electron density peaks and probability ellipsoids. In the further refinement, anisotropic temperature factors were used for all except Li atoms. Eleven reflections suffering from extinction were omitted in the last cycles of the refinement. The refinement converged at $R = 0.058$ and $R_g = 0.069$. The weights used were $w^{-1} = 4kLp[N + 4(LB + RB)]/[N - 2(LB + RB)]$, where N , LB and RB are respectively the counts of the peak, and left and right backgrounds. The calculations were carried out with programs *SHELX 76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1972). The figures were plotted using *ORTEP II* (Johnson, 1976). The final atomic coordinates and their standard deviations are given in Table 1.*

* Lists of structure factors, thermal parameters, bond angles (Table 2), and intermolecular distances (Table 3) are available from the authors on request and have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35437 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. The final atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses and isotropic thermal parameters

W denotes the O atom of a water molecule which is not coordinated to Co.

	x	y	z	$U (\text{Å}^2 \times 10^3)$
I(1)	2821 (1)	1155 (1)	2021 (1)	9
I(2)	5762 (1)	3634 (1)	1684 (1)	9
I(3)	300 (1)	2600 (1)	-2452 (1)	9
Co(1)	2950 (1)	2465 (1)	418 (1)	8
Co(2)	5414 (1)	2351 (1)	3134 (1)	9
Co(3)	318 (1)	1365 (1)	-764 (1)	9
Co(4)	3068 (1)	3706 (1)	-1063 (1)	10
O(1)	1695 (7)	2086 (4)	1203 (7)	12
O(2)	1650 (7)	1000 (4)	2938 (8)	18
O(3)	3872 (7)	303 (4)	2308 (8)	17
O(4)	4079 (7)	1610 (4)	1152 (7)	12
O(5)	1500 (7)	516 (4)	-99 (7)	13
O(6)	4087 (7)	2023 (4)	3853 (7)	11
O(7)	4446 (7)	4409 (4)	962 (8)	14
O(8)	4339 (7)	3198 (4)	2407 (7)	11
O(9)	6575 (7)	2677 (4)	2221 (7)	15
O(10)	6896 (7)	3775 (4)	716 (8)	18
O(11)	4205 (7)	2844 (3)	-378 (7)	10
O(12)	6824 (7)	4396 (4)	3576 (7)	14
O(13)	-751 (7)	3462 (4)	-2783 (8)	16
O(14)	-693 (7)	2258 (4)	-1393 (8)	15
O(15)	1546 (7)	1725 (4)	-1562 (7)	12
O(16)	1746 (7)	2933 (4)	-3012 (7)	13
O(17)	-668 (7)	1813 (4)	-4372 (7)	13
O(18)	1837 (7)	3340 (4)	-294 (8)	14
O(19)	6585 (7)	1478 (4)	3754 (8)	18
O(20)	6493 (7)	3159 (4)	5258 (7)	15
O(21)	-957 (7)	1122 (4)	189 (7)	16
O(22)	-981 (7)	561 (4)	-2792 (7)	15
O(23)	4232 (7)	3974 (4)	-2083 (8)	18
O(24)	1933 (7)	4625 (4)	-1460 (9)	21
W(1)	3576 (8)	7298 (4)	2262 (8)	25
W(2)	9882 (9)	3616 (5)	1683 (10)	37
W(3)	9878 (10)	4169 (5)	5025 (10)	39
W(4)	4056 (10)	9173 (5)	4058 (10)	38
W(5)	2830 (8)	3477 (5)	4625 (8)	26
W(6)	4032 (11)	8628 (5)	729 (10)	46
W(7)	6938 (9)	8556 (6)	3761 (9)	36
W(8)	9433 (9)	2252 (5)	3055 (9)	28
W(9)*	6837 (10)	-148 (11)	2058 (22)	32
W(10)*	6243 (23)	57 (10)	1301 (20)	34
W(11)*	4143 (19)	4841 (10)	4314 (19)	36
W(12)*	2783 (27)	4814 (13)	2862 (24)	60
W(13)*	1395 (30)	5040 (10)	1275 (31)	111
W(14)*	9096 (30)	-70 (15)	4196 (31)	83
Li(1)	4828 (24)	8347 (13)	2783 (26)	38
Li(2)	658 (23)	3345 (12)	3754 (25)	33

* Position with site-occupancy factor 0.5.

Description and discussion of the structure

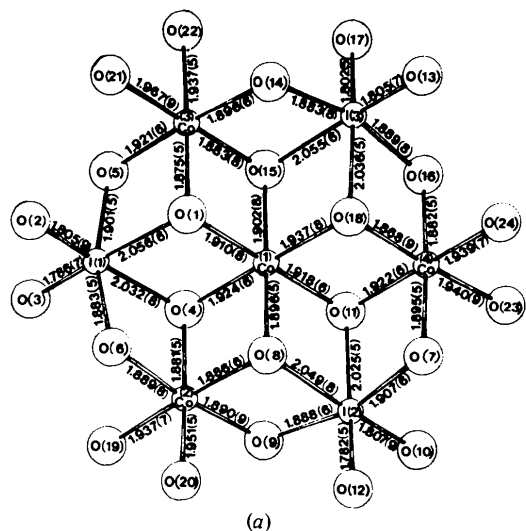
The crystal structure consists of complex heteropolyanions corresponding to the classical Anderson-type configuration. Fig. 1 shows the anion bond lengths and the distances from the plane of the heavy atoms. The polyanion has approximate symmetry 32 with

significant deviations from the ideal symmetry. The coordination octahedron of the central Co^{3+} ion is distorted, with the mean acute angle $\text{O}-\text{Co}-\text{O} = 83.5^\circ$. The angles within the anion are given in Table 2.* The bonds between $\text{Co}(2)$, $\text{Co}(3)$ and $\text{Co}(4)$ and their peripheral O atoms are longer than the other $\text{Co}-\text{O}$ bonds, which, taken with the chemical evidence (Ama, Hidaka & Shimura, 1973; Baker *et al.*, 1980), confirms that the protons of the anion are attached to these O atoms. In contrast, the bonds between I^{7+} and exterior unshared O atoms are significantly shorter than those between the I atoms and the inner-ring O atoms, showing that the I^{7+} are shifted outwards from the

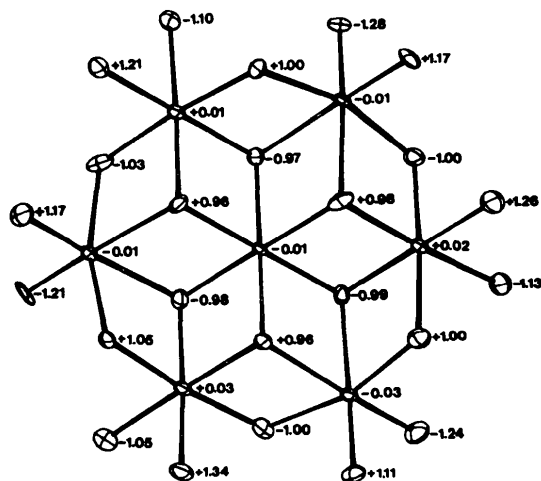
central positions of their IO_6 octahedra. The bonds between the I atoms and the peripheral O atoms, which are acceptors of strong interanion H bonds (Table 3),* are in the range 1.802–1.807 Å. The distances between I atoms and those O atoms which accept H bonds from the water molecules coordinated to Li, or from lattice water molecules, are 1.786 (7) and 1.782 (5) Å. These distances are much shorter than the 1.882 (4) Å found for $\text{I}-\text{O}(\text{hydroxyl})$ in the protonated form of the same anion (Sasaki, 1980). This suggests that in the present structure the acidic proton is not bound to the anion.

The equation of the best least-squares plane through the heavy atoms is $(-6.337)X + (+8.308)Y + (+6.240)Z = 0.448$. The deviations of the heavy atoms from this plane are all less than 0.03 Å. The distances of the O atoms from this plane are given in Fig. 1(b). They show that the anion is somewhat flattened in the central part. A similar effect observed for hexamolybdo-tellurate ion was attributed to the repulsion of the metal atoms (Evans, 1974). However, attractive forces between I^{7+} and peripheral O atoms are probably more important (Baker *et al.*, 1980).

* See deposition footnote.



(a)



(b)

Fig. 1. (a) Projection of the anion on the least-squares plane through the Co/I atoms, showing the atomic notation and the bond lengths (Å). (b) The distances (Å) of the O atoms from the Co/I plane. Standard deviations for these distances are smaller than 0.01 Å. The thermal ellipsoids are scaled to enclose 50% probability (ORTEP II; Johnson, 1976).

* See deposition footnote.

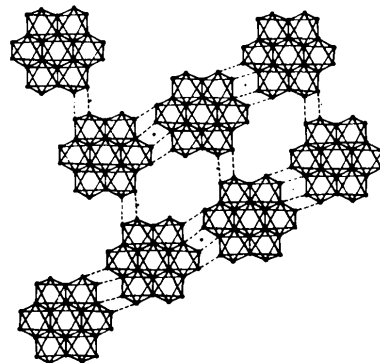


Fig. 2. Projection of the anion layer fragment on the $(\bar{1}11)$ plane. Interanion O–O distances shorter than 2.75 Å are marked by broken lines.

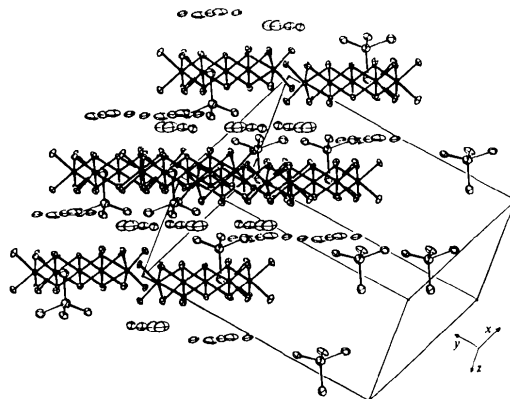


Fig. 3. The packing of the hetero-anions, hydrated lithium cations, and lattice waters in the structure of $[\text{Li}(\text{H}_2\text{O})_4]_2\text{H}[\text{Co}_4\text{H}_{12}\text{I}_3\text{O}_{24}] \cdot 3\text{H}_2\text{O}$.

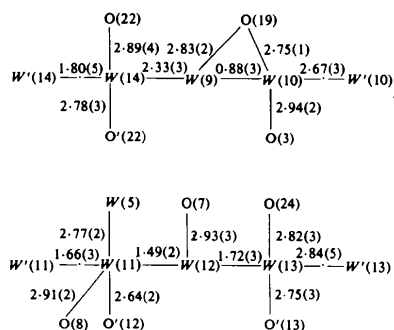


Fig. 4. Distances (Å) in the environments of the clusters of lattice water molecules. Those four water molecules which are equivalent by centers of inversion are denoted by W' .

The anions, which are linked by strong H bonds into two-dimensional nets, form layers parallel to $(\bar{1}11)$. The bonding scheme is illustrated in Fig. 2. There are two chains of hydrogen bonds between anions which are equivalent by the translations $a + c$. These O—H...O distances are short, 2.566 (8) and 2.588 (8) Å, which coincides with the fact that one O in each such bond is that of a water molecule coordinated to a Co^{3+} , the other O being closely bonded to I^{7+} . The second string is formed by two sets of four hydrogen bonds linking those anions which are related by centers of symmetry, along the $[110]$ direction. The anionic layers separate the $Li(H_2O)_4^+$ cations and lattice water molecules as shown in Fig. 3. Inspection of $W-Li-W$ angles shows that both the tetraaqualithium cations deviate from tetrahedral symmetry. As discussed above, the acidic

proton is not bonded to the anion and it is probably hydrated by the lattice water molecules. The distances between positions of disordered water molecules with partial site-occupancy factors are given in Fig. 4. The environment of $W(11)$ could correspond to that of an H_3O^+ ion, as there is a short distance of 2.64 (2) Å to the non-protonated $O'(12)$ and two further acceptors, $W(5)$ and $O(8)$, are available. None of the other positions is particularly suitable for a hydroxonium ion. They are either far from the anion or close to the water molecules coordinated to Co, which are poor H-bond acceptors.

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Etude Structurale d'une Phase Non Stoechiométrique Partiellement Désordonnée:



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Abstract

The crystal structure of the non-stoichiometric phase $Ba_{(4-z)}Zr_{(2+z/2)}F_{16}$ ($0 \leq z \leq 0.232$) has been solved and refined to a conventional $R = 0.041$ for 429 independent reflexions recorded on a four-circle automatic diffractometer. For the composition $z = 0.232$, the symmetry is tetragonal with $a = b = 5.637$ (2), $c = 10.423$ (4) Å and space group $P4/nmm$. The structure is a regular succession of two kinds of sheets: quite

perfect perovskite, and partly disordered anion-excess ReO_3 -type. A non-stoichiometric process based on the creation of cation vacancies within a constant anionic subcell is proposed.

Introduction

L'étude, toujours en cours, des divers systèmes AF_2-ZrF_4 ($A = Sr, Ba, Pb, Eu$) a révélé l'existence de

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