Heteropolytungstate Complexes of the Lanthanoid Elements. Part III.[1] Crystal Structure of Sodium Decatungstocerate(IV)–Water (1/30)

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Crystals of the title compound are monoclinic, space group $C2/c$, $a = 18.14(1)$, $b = 18.62(1)$, $c = 18.51(1)$ Å, $\beta = 95.9(5)°$, $Z = 4$. The heavy atoms were located by direct methods and the oxygen and sodium atoms by difference Fourier analyses, with block-diagonal least-squares refinement to R 0.083 for 2781 independent reflections measured on a diffractometer. The analysis confirms that the heteropolyanion is a heterodecatungstate, and not an octatungstate as originally reported. The cerium atom, on a two-fold crystal axis, takes two penta-tungstate ligands, $W_5O_{18}H^{5-}$, each of which is derived from a $W_6O_{19}^{2-}$ anion by the loss of one tungsten atom and its apical oxygen and consists of five WO_6 octahedra sharing edges. The eight oxygen atoms about the cerium define a square antiprism. The sodium cations have distorted octahedral co-ordination.

THE first heteropolytungstate compounds containing lanthanoid heteroatoms to be reported were the tungsto-cerate(IV) and tungstocerate(III) salts prepared by Ripan and Todorut,[2] containing anions formulated as $Ce^{n+}W_8O_{28}^{(8-n)-}$. Salts of heteropolyanions believed to be of this formula type with tetravalent uranium,[3] thorium,[4] titanium,[5] zirconium,[5] and hafnium [5] as heteroatoms were subsequently reported. Peacock and Weakley [6] confirmed the existence of the tungstocerates and prepared salts of analogous anions containing tri-valent lanthanum, praseodymium, etc., as heteroatoms. However, they concluded on the basis of chemical analysis and crystal isomorphism, together with the density and unit-cell parameters of sodium tungstocerate(IV), that these anions were all heterodecatungstates, $Ln^{n+}W_{10}O_{35+x}H_{2x}^{(10-n)-}$. A reinvestigation of the uranium[7] and thorium [8] complexes indicated that they also were of this type. A single-crystal X-ray structural analysis of $Na_6Ce^{IV}W_{10}O_{35+x}H_{2x},(31-x)H_2O$ has now enabled location of all non-hydrogen anions in the anion, whose formula proves to be $Ce^{IV}W_{10}O_{36}H_2^{6-}$.

EXPERIMENTAL

Roughly equidimensional multifaceted yellow crystals of $Na_6CeW_{10}O_{36}H_2,30H_2O$, some resembling truncated square pyramids, were supplied prepared as described previously.[6]

Crystal Data.—$H_{62}CeNa_6O_{66}W_{10}$, $M = 3235$, Monoclinic, $a = 18.14(1)$, $b = 18.62(1)$, $c = 18.51(1)$ Å, $\beta = 95.9(5)°$, $U = 6214$ Å³, $D_c = 3.46$, $Z = 4$, $D_m = 3.51$ g cm⁻³, $F(000) = 4856$. Cu-K_α ($\lambda = 1.5418$ Å, $\mu = 40.6$ mm⁻¹; unit-cell measurements) and Mo-K_α ($\lambda = 0.7107$ Å, $\mu = 20.3$ mm⁻¹; unit-cell and intensity measurements) radiation. From the systematic absences, the space group was Cc or $C2/c$; the intensity statistics indicated the centrosymmetric space group $C2/c$, and the structure was determined on this basis.

Intensity data were collected by use of a Hilger and Watts linear diffractometer with balanced filters, from crystals mounted on the b axis (data collected up to k 12) and on the c axis (data collected up to l 9). This gave 3887 intensities

whose values were acceptable having regard to the back-ground measurements. No corrections were made for absorption.

Structure Analysis.—The intensities were placed on a common scale and converted to structure factors in the usual way. By use of the direct method programs NOR-MAL and MULTAN (supplied by Dr. P. Main, York University) eight sets of signed E values were obtained for all values of $|E| > 2.10$. The set with the highest figure of merit (1.001) was used in the calculation of an E map. The starting reflections for this set are shown in Table 1.

TABLE 1

Reflection	Sign	E	
5,9,7	+	3.82	} Origin-defining
4,6,$\overline{17}$	+	2.90	} reflections
16,8,$\overline{14}$	±	4.04	} Variable
2,4,8	±	2.91	} reflections
3,3,6	±	2.77	}

A Fourier search of the E map, using programs supplied by Dr. W. D. S. Motherwell (Cambridge University) indi-cated the positions of six large peaks, one of which lay on a crystallographic two-fold axis. The latter peak was assigned to cerium, since the space group $C2/c$ with $Z = 4$ implies that the asymmetric unit contains 0.5 Ce + 5 W, and that the cerium must be either at a crystallographic centre of symmetry or on a two-fold axis. The interatomic distances at this stage (Ce–W $ca.$ 3.8, W–W $ca.$ 3.3 Å) were acceptable if the distorted WO_6 octahedra, which were expected to be present, shared edges, as later proved to be the case. This set of atoms, together with the set related to it by the two-fold axis, is shown in Figure 1, and the final interatomic distances within the set are given in Table 2. A structure-factor calculation using the 2781 strongest reflections and based on the cerium and tungsten atoms with an overall temperature factor B of 1.5 Å² gave a residual index, R, of 0.20. Block-diagonal least-squares refinement of the atomic co-ordinates and individual isotropic tempera-ture factors reduced R to 0.144, at which point a three-dimensional difference-Fourier synthesis revealed the presence of eighteen oxygen atoms in the half-anion, con-ferring octahedral co-ordination on each tungsten, four being

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in addition bonded to the cerium. These atoms were included in the refinement with isotropic temperature factors. Four cycles reduced R to 0·114, at which point the cerium and tungsten atoms were refined with anisotropic temperature factors. When R had fallen to 0·100 a second difference-Fourier synthesis revealed further peaks. Some of
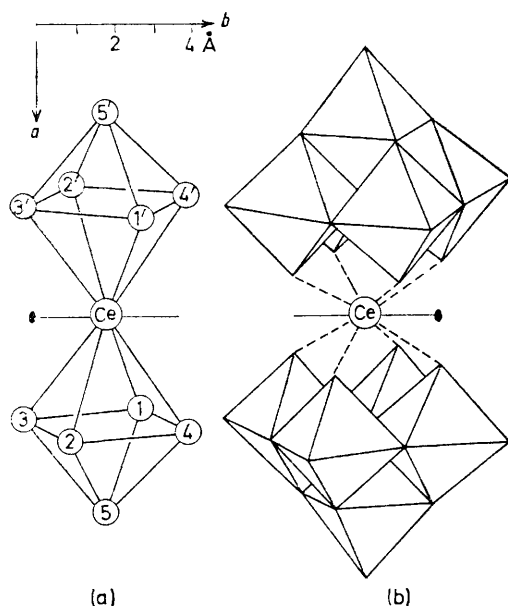

FIGURE 1 (a) The heavy-atom framework of the heteropoly-anion, viewed normal to (001) plane. (b) Linked-octahedron representation of the anion on the same scale

these were evidently spurious, as they were impossibly close to atoms already located. The remainder were firmly identified on the basis of their co-ordination environments as four sodium ions (two of which lay on a two-fold crystal

TABLE 2

Distances (Å) between heavy atoms within the asymmetric unit (half-anion). All σ 0·003 Å. See also Figure 1

Ce–W(1)	3·797	W(1)–W(3)	3·303	W(1)–W(5)	3·333
Ce–W(2)	3·788	W(1)–W(4)	3·259	W(2)–W(5)	3·327
Ce–W(3)	3·784	W(2)–W(3)	3·254	W(3)–W(5)	3·304
Ce–W(4)	3·791	W(2)–W(4)	3·275	W(4)–W(5)	3·314

axis) and twelve oxygen atoms of water molecules per asymmetric unit. These atoms were included in the subsequent refinement with isotropic temperature factors. The weighting scheme was $w = 1/\{1 + [(|F_0| - F^*)/G^*]^2\}$ where $F^* = 250$ and $G^* = 150$. The refinement was terminated when the shifts in the atomic parameters had become smaller than their standard deviations, R now being 0·083. Observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 21089 (8 pp.).*

DISCUSSION

Atomic co-ordinates are given in Table 3, and the heavy-atom framework of the anion and a representation of the anion as an assembly of linked WO_6 octahedra are

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shown in Figure 1. The mean planes Ce–W(1)–W(5)–W(2) and Ce–W(3)–W(5)–W(4) intersect at an angle of 90·6°, and the mean planes Ce–W(1)–W(5)–W(2) and Ce–W(1′)–W(5′)–W(2′) at an angle of 46·6°. Although the point-symmetry of the anion in the crystal is only C_2, there is evidently a local pseudo-four-fold axis [through W(5) and W(5′)] and it appears that the anion would have point-symmetry D_{4d} in the absence of crystal forces.

TABLE 3

(a) Atomic co-ordinates and isotropic temperature parameters with estimated standard deviations in parentheses

	x/a	y/b	z/c	$B_{iso}/Å^2$
Ce	−0·5000(0)	0·2564(2)	−0·2500(0)	
W(1)	−0·3786(1)	0·3064(1)	−0·3976(1)	
W(2)	−0·3055(1)	0·2077(1)	−0·1707(1)	
W(3)	−0·3568(1)	0·1423(1)	−0·3311(1)	
W(4)	−0·3261(1)	0·3706(1)	−0·2367(1)	
W(5)	−0·2164(1)	0·2561(1)	−0·3115(1)	
O(1)	−0·3364(15)	0·2520(18)	−0·2837(16)	0·4(4)
O(2)	−0·4656(21)	0·2993(22)	−0·3628(22)	2·1(7)
O(3)	−0·2690(17)	0·2986(19)	−0·3968(18)	1·0(5)
O(4)	−0·2485(18)	0·1645(18)	−0·3450(18)	1·1(6)
O(5)	−0·1237(20)	0·2539(23)	−0·3327(22)	1·9(7)
O(6)	−0·2103(16)	0·2162(16)	−0·2175(16)	0·4(4)
O(7)	−0·4492(21)	0·1548(22)	−0·3053(22)	1·9(7)
O(8)	−0·3782(18)	0·2079(19)	−0·4138(19)	1·3(6)
O(9)	−0·2240(20)	0·3477(21)	−0·2682(20)	1·7(6)
O(10)	−0·2948(19)	0·3091(20)	−0·1522(20)	1·5(6)
O(11)	−0·3625(18)	0·0601(18)	−0·3717(18)	0·9(5)
O(12)	−0·4022(21)	0·2130(23)	−0·1657(22)	2·0(7)
O(13)	−0·4197(20)	0·3576(21)	−0·2225(21)	1·8(6)
O(14)	−0·3973(20)	0·3452(20)	−0·4817(19)	1·5(6)
O(15)	−0·3174(19)	0·1203(20)	−0·2264(19)	1·3(6)
O(16)	−0·3090(22)	0·4547(24)	−0·2015(23)	2·3(7)
O(17)	−0·2700(22)	0·1692(22)	−0·0846(22)	2·1(7)
O(18)	−0·3500(19)	0·3927(20)	−0·3378(20)	1·4(6)
O(19)	−0·1133(23)	0·4232(24)	−0·1966(23)	2·4(8)
O(20)	−0·4441(24)	0·0396(25)	−0·1782(24)	2·6(8)
O(21)	−0·1792(25)	0·3689(26)	−0·4770(25)	3·0(9)
O(22)	−0·2000(26)	0·3809(27)	−0·0457(26)	3·3(9)
O(23)	−0·4944(26)	0·4741(25)	−0·1607(27)	2·9(9)
O(24)	−0·1867(27)	0·0461(27)	−0·4147(26)	3·2(9)
O(25)	−0·1345(32)	0·0790(31)	−0·2205(31)	4·4(11)
O(26)	−0·0713(28)	0·0416(29)	−0·0327(29)	3·8(10)
O(27)	−0·0242(24)	0·1474(25)	−0·3525(24)	2·6(8)
O(28)	−0·2401(45)	0·0049(46)	−0·1044(43)	7·5(19)
O(29)	−0·4261(33)	0·0215(33)	−0·0281(33)	4·8(13)
O(30)	−0·0470(45)	0·3779(45)	−0·3801(44)	7·8(19)
Na(1)	−0·3031(15)	0·0077(16)	−0·4860(15)	3·2(5)
Na(2)	−0·0558(13)	0·0530(14)	−0·4416(13)	2·5(4)
Na(3)	0·0000(0)	0·0704(21)	−0·2500(0)	2·8(7)
Na(4)	0·0000(0)	0·4379(29)	−0·2500(0)	5·1(10)

(b) Anisotropic temperature parameters ($\times 10^5$),* with estimated standard deviations in parentheses

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ce	71(9)	124(11)	97(10)	0(0)	1(16)	0(0)
W(1)	75(5)	96(5)	75(5)	7(9)	8(8)	40(11)
W(2)	68(5)	106(6)	81(6)	11(10)	−17(8)	10(11)
W(3)	68(5)	76(5)	103(5)	−7(9)	26(8)	−8(11)
W(4)	72(5)	78(5)	102(5)	−20(9)	−3(8)	−20(11)
W(5)	53(4)	101(6)	117(6)	3(10)	10(8)	11(11)

* In the form $T = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

The orientation of two of the anions in the unit cell is slightly different to that of the other two (Figure 2), but the local four-fold axes are all parallel to one another and to (010), and all make the same small angle (12·1°) with (001). The shortest distances between oxygen atoms in different anions are 3·81 and 3·89 Å.

The polytungstate portion of the half-anion is derived

from the compact hexatungstate $W_6O_{19}{}^{2-}$, which was shown [9] to be isostructural with hexaniobate,[10] by removal of one tungsten atom and its unshared oxygen. Four oxygen atoms formerly bonded to the missing tungsten atom are now bonded to the cerium atom. The union of two pentatungstate moieties with the elimination of four oxygen atoms would give the decatungstate
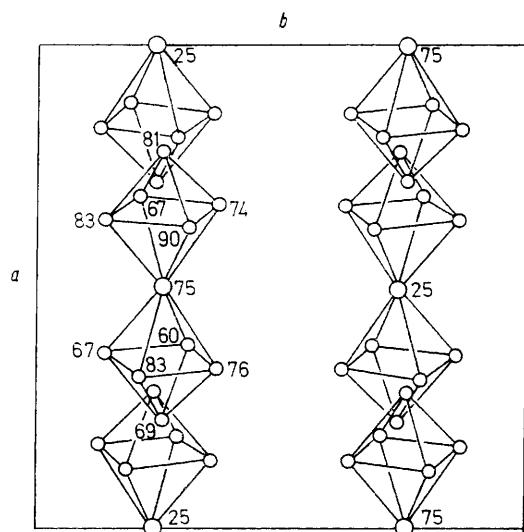

FIGURE 2   Orientation of the four anions in the unit cell; c-axis projection. Large circles, cerium; small circles, tungsten. Heights given as $100z$

anion, $W_{10}O_{32}{}^{4-}$, of Fuchs *et al.*[11]   The tungsten–tungsten distances (Table 2) are similar to those in hexatungstate.[9]   Precise tungsten–oxygen distances in the latter anion were not reported.   In Table 4, to be read in conjunction with Figure 3, we give the mean values of the

TABLE 4

Ranges of tungsten–oxygen and cerium–oxygen bond lengths (Å) and mean values

Bond type *	No. of bonds	Range	Mean
a	1	1·76(4)	
b	4	1·70(3)—1·80(4)	1·73(4)
c	4	1·88(3)—1·93(3)	1·90(3)
d	4	1·99(3)—2·05(3)	2·02(3)
e	8	1·86(4)—2·03(3)	1·95(4)
f	4	1·76(4)—1·80(4)	1·78(4)
g	1	2·29(3)	
h	4	2·24(3)—2·39(3)	2·32(3)
j	4	2·38(4)—2·40(4)	2·38(4)
k	1	3·09(4)	

* See Figure 3.

lengths of those bonds which are presumed to be equivalent in the free anion, as was done for other hetero- and iso-polyanions in a recent review,[12] and also the ranges of lengths for each bond type.   The expected dependence

of lengths of bonds to oxygen on the co-ordination number of the oxygen is observed (*cf.* tabulated parameters in ref. 12).

In the majority of heteropolyanions of known structure the ' ligand ' attached to the heteroatom consists of a continuous polymetallate sheath. The decatungstocerate anion, like dodecaniobomanganate(IV),[13] $Mn(Nb_6O_{19})_2{}^{12-}$, is an exception in that two discrete polymetallate ligands are present, but whereas the hexaniobate ligand in the latter complex is a well-characterised isopolyanion both in crystalline salts and in solution,[14] the pentatungstate anion $W_5O_{18}H^{5-}$ has not hitherto been identified. The charge distribution in free $W_5O_{18}H^{5-}$ would be uneven, however (four adjacent oxygens that would otherwise be co-ordinated to cerium would all bear formal negative charges) so probably this isopolyanion can only be stabilised through co-ordination. The analytical cation : cerium ratio and the 36 oxygen atoms in the anion together require the presence of two non-acidic hydrogen atoms. The present study gave no indication of their position. The failure [6] to distinguish by thermal analysis between the one molecule of ' water of constitution ' and the thirty molecules of lattice water may be due both to the number of the latter and to the onset of hydrolytic attack on the anion in the broad temperature range over which the crystal loses water. This anion and its isomorphs are certainly very susceptible to hydrolytic attack in solution.

The two sets of four oxygen atoms bonded to the cerium define a square antiprism. The oxygen–oxygen distances in the CeO_8 group for atoms in the same and in
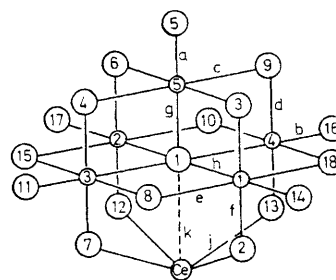

FIGURE 3   Numbering of atoms in the half-anion.   Large circles, oxygen; small circles, tungsten. Letters identify different classes of bonds; *cf.* Table 4

different half-anions are similar (means 2·87 and 2·94 Å). There is no room for additional co-ordination of water molecules. The cerium–oxygen bond lengths (mean 2·38 Å) are similar to those in CeO_2 (2·34 Å; cubic co-ordination) and are appreciably shorter, as expected, than the bond lengths for twelve-co-ordinate cerium [15] in $CeMo_{12}O_{42}{}^{8-}$ (2·51 Å). The second-nearest oxygen atoms [(1) and (1′)] are too far from the cerium (3·09 Å) for effective bonding.

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In some salts of heteropolyanions [*e.g.* Na_3CrMo_6-$O_{24}H_6,8H_2O$ (ref. 16), $Na_6P_2Mo_5O_{23},13H_2O$ (ref. 17), and $Na_3PMo_9O_{34}H_6,13H_2O$ (ref. 18)] the cations play a prominent role in linking together the anions, but in

TABLE 5

Bond lengths (Å) in NaO_6 groups; all σ 0·05 Å

Na(1)			Na(2)		
O(11)	(anion)	2·66	O(24)	(H₂O)	2·48
O(24)	(H₂O)	2·48	O(27)	(H₂O)	2·44
O(28)	(H₂O)	2·61	O(26′)	(H₂O)	2·42
O(29)	(H₂O)	2·35	O(26)(4)	(H₂O)	2·44
O(21′)(2′)	(H₂O)	2·41	O(23′)(3′)	(H₂O)	2·49
O(22′)(3′)	(H₂O)	2·43	O(14′)(2′)	(anion)	2·47
Na(3)			Na(4)		
O(25)	(H₂O)	2·56	O(19)	(H₂O)	2·39
O(27)	(H₂O)	2·38	O(30)	(H₂O)	2·71
O(25′)	(H₂O)	2·56	O(20)(3)	(H₂O)	2·47
O(27′)	(H₂O)	2·38	O(19′)	(H₂O)	2·39
O(23)(3)	(H₂O)	2·43	O(30′)	(H₂O)	2·71
O(23′)(3′)	(H₂O)	2·43	O(20′)(3′)	(H₂O)	2·49

Symbols (2), (2′), *etc.*, refer to atoms in other asymmetric units. Corresponding primed and unprimed units are related by two-fold axes.

$Na_6CeW_{10}O_{36}H_2,30H_2O$ two of the four structurally distinct sodium atoms are present as $Na(H_2O)_6{}^+$, the other

two being bonded to just one terminal oxygen atom of an anion and five water molecules each. Bond lengths in the NaO_6 octahedra are listed in Table 5. The remaining terminal oxygen atoms, however, and most (possibly all) of the other oxygen atoms on the outside of the anion, participate in hydrogen bonds to water molecules, with lengths ranging from 2·66 to 2·96 Å. Three of the fifteen water molecules which analysis indicates are present per asymmetric unit could not be located. It is possible that the water molecules not co-ordinated to sodium or forming hydrogen bonds to the anion are disordered. In certain other types of heteropolyanion salts, particularly salts of $XW_{12}O_{40}{}^{n-}$ and $XMo_{12}O_{40}{}^{n-}$ and structurally related anions, both the cation and lattice water sites may be disordered; in some X-ray studies few [19] or none [20] of the last two species could be located, although there was evidently considerable electron density in the interanionic spaces.

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