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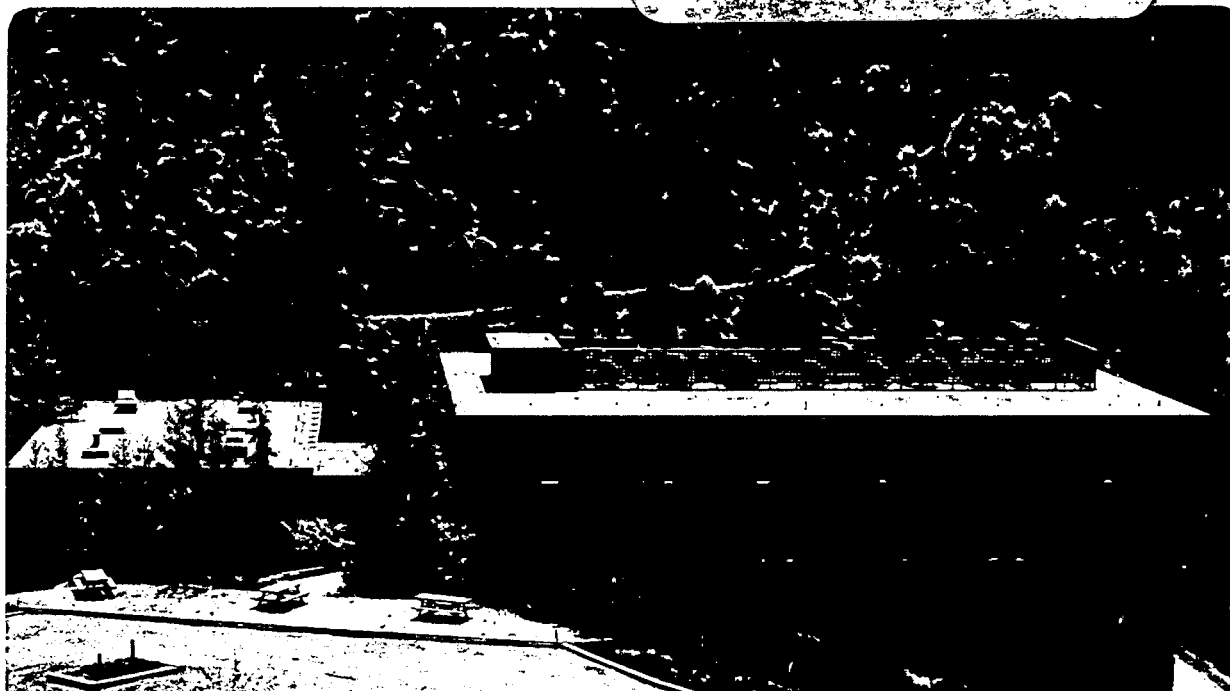
Materials & Molecular Research Division

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L.K. Templeton, D.H. Templeton, and A. Zalkin
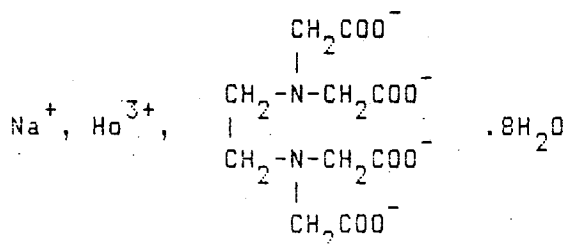
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DISCLAIMER

Structure of Monoclinic Sodium Holmium Ethylenediaminetetraacetate Octahydrate: Disorder Induced by Radiation

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Abstract. $NaHo(C_{10}H_{12}N_2O_8) \cdot 8H_2O$, $M_r = 620.3$, monoclinic, $Fd11$, $a = 19.333(3)$, $b = 35.366(6)$, $c = 12.106(2)$ Å, $\alpha = 90.40(10)°$, $V = 8277.0$ Å^3, $Z = 16$ [conventional setting: Cc, $a = 12.106(2)$, $b = 19.333(3)$, $c = 18.650(3)$ Å, $\beta = 108.54(10)°$, $Z = 8$], $D_x = 1.991$ g cm^{-3}, Mo Kα, $\lambda(\alpha_1) = 0.70930$ Å, $\mu = 39.7$ cm^{-1}, $F(000) = 4924$, $T = 294$ K, $R = 0.026$ for 4843 reflections. The atomic positions are very similar to those in the analogous compounds of lighter rare-earth elements which crystallize in the orthorhombic space group $Fdd2$. The monoclinic symmetry comes from ordering of water molecules in alternate sites which are occupied randomly in the orthorhombic structure. Exposure to X-rays induces disorder which makes the crystals more nearly orthorhombic. The dysprosium compound of the same composition is isomorphous with $a = 19.358(3)$, $b = 35.408(3)$, $c = 12.103(5)$, $\alpha = 90.34(3)°$.

Introduction. Crystal structure parameters were desired for the title salt,

$$Na^+, Ho^{3+}, \quad \begin{array}{c} CH_2COO^- \\ | \\ CH_2-N-CH_2COO^- \\ | \\ CH_2-N-CH_2COO^- \\ | \\ CH_2COO^- \end{array} \quad \cdot 8H_2O$$

so that it could be used to measure anomalous scattering terms for holmium

at various wavelengths (Chapuis, Templeton & Templeton, 1984) by analysis of

diffraction intensities.   We had expected the crystals to have the

orthorhombic structure with space group Fdd2 which has been reported for the

analogous salts of Pr, Nd, Sm, Gd, Tb, Dy and Er (Hoard, Lee & Lind, 1965;

Koetzle & Hamilton, 1975; Nassimbeni, Wright, van Niekerk & McCallum, 1979;

Templeton, Templeton, Zalkin & Ruben, 1982).   Indeed, the diffraction

patterns are very similar to those of the orthorhombic crystals, but close

inspection reveals monoclinic symmetry with twice as large an asymmetric

unit.   We describe the structure in space group Fd11 (an unconventional

setting of Cc) because that gives cell dimensions and atomic coordinates

which are nearly the same as for Fdd2.   We find the same monoclinic

structure for crystals of the dysprosium compound, contrary to the findings

of Nassimbeni, et al. (1979).   A recent neutron-diffraction study by Engel,

Takusagawa & Koetzle (1984) of the orthorhombic samarium compound

found disorder of water molecules among two sets of sites.   The monoclinic

symmetry involves an ordering of the occupancy of these same sites.

Experimental.   The compound was made from Ho_2O_3 (Research Chemical

Corporation) dissolved in HCl and mixed with a hot solution of

$Na_2H_2(edta).2H_2O$ (Aldrich Chemical Company); pH adjusted to about 5 with

NaOH; slow evaporation, then recrystallization from water yielded crystals,

many of which were twinned in a manner to nearly superimpose the reflections

which are equivalent in orthorhombic symmetry (Dy compound made in the same

way).   Cell dimensions from 24 reflections in θ range 57 to 60° measured

with CuKα and CAD-4 diffractometer.   Another crystal 0.15 x 0.24 x 0.25 mm,

15 faces, Picker FACS-I diffractometer, cell dimensions from 12 reflections

in θ range 20 to 22°, analytical absorption correction 1.42 < A < 1.71,

max. (sinθ)/λ = 0.60, hkℓ range 0 to 12, -42 to 42, -14 to 14; 10% intensity decay correction based on average of the changes of 400 (14%), 5$\bar{5}$5 (2%), and 0$\bar{4}$4 (13%); 4977 unique reflections; 91 with I < σ and 43 others with (sinθ)/λ < 0.11 given zero weight; refinement started with known structure of Sm salt duplicated for monoclinic symmetry, refined on F; 24 hydrogen atoms included in refinement with each thermal parameter equal to that of adjacent carbon atom and with distance restraints C-H = 1.00(5), H-H = 1.63(10), C'-H = 2.06(10), N'-H = 2.04(10) Å (C' and N' next atoms in chain), water hydrogen atoms omitted; 330 parameters including f'' for Ho and anisotropic thermal parameters for Ho and water oxygen atoms, but not counting those of H atoms; R = 0.026, wR = 0.034, S = 1.1, w = [σ(F)]$^{-2}$, p = 0.05 in calc. of σ(F^2), max. (shift/σ) = 0.16, max. correction for extinction 6% of F, atomic f for Ho^{3+}, Na$^+$, O$^{0.5-}$ (interpolated), and neutral O, N, C, and H from International Tables (1974), local unpublished programs. Atomic parameters are listed in Table 1. For this setting the equivalent positions are: x, y, z; 1/4 - x, 1/4 + y, 1/4 + z; plus the translations of the F lattice. The origin of this doubly-polar space group was defined by placing the center of gravity of the two Ho atoms at (x, 1/4, 0) in order to reduce covariance terms and to improve convergence (Templeton, 1960). The correct absolute polarity is confirmed by the refinement of f'' for Ho to the positive value 4.92(10) e/atom. Cell dimensions for Dy compound from 13 reflections, CAD-4, MoKα.*

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*Tables of structure factors, anisotropic thermal parameters, H-atomic coordinates, and bond distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP   (pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structure consists of two formula units at positions which are related approximately by a transformation (1/2 - x, 1/2 - y, z) which corresponds to a 2-fold axis in the c direction. Deletion of this symmetry element from Fdd2 lowers the space group to Fd11. For most of the atoms this relation is accurate to better than 0.2 Å, and the structure is hardly different from that found for the orthorhombic compounds of the lighter rare-earth elements. The only major difference is in the locations and hydrogen bonding of a few of the water molecules. The above transformation fails by 0.46 Å for the W(7)-W(15) pair, 0.91 Å for W(4)-W(12) and 1.07 Å for W(8)-W(16). The last two pairs correspond to those which are distributed randomly in alternate sites in the samarium structure, and designated as 4B, 4A and 8B, 8A, respectively, by Engel, Takusagawa & Koetzle (1984) in their neutron-diffraction study. In that work 18 hydrogen bonds were identified. Taking account of the half-occupancy of some sites, these become 28 distinct bonds in the monoclinic symmetry. We find exactly the same bonds, on the basis of oxygen-atom positions, plus one more: W(4)-W(14) = 2.75(2) Å. In the samarium salt the corresponding distance was found to be 3.04 Å, but a hydrogen atom (designated as "U(4B)") is pointed in about the right direction for such a bond. The network of bonds near the c axis, where the higher symmetry breaks down, is shown in Fig. 1. Water molecules W(8) and W(16), which are equivalent in Fdd2, form hydrogen bonds to W(15) and O(5), atoms which are not equivalent even in chemical state. This unsymmetrical bonding pulls them and their neighbors away from locations which conform to the higher symmetry. The only other lack of Fdd2 symmetry in the topology of the bonds is in the chain W(12)-H...W(16)-H...W(8)-H...W(4), if the hydrogen atoms are assigned according to ther neutron-diffraction study; an extra hydrogen atom on W(4) is not involved in a bond.

Hydrogen-bond O-O distances (supplementary material) range from 2.64 Å to 2.85 Å, except W(8)-W(4) = 2.88(2) and W(12)-W(16) = 2.98(1) Å. These two bonds join the atoms which are most involved in the order-disorder transition discussed below, and these distances may be affected by it.

Exposure to X-rays causes the unit-cell angle α to become more nearly equal to 90°, with insignificant changes in axial lengths. As noted above, the diffraction intensities tend to decrease, but not uniformly. At the end of the data collection α was 90.28°. For another crystal, after much exposure to X-rays, α was 90.11°. Values of 90.49(1)° and 90.45(2)° were measured for two other fresh crystals. We attribute these changes to the introduction of disorder in the hydrogen bonding, with an approach to the symmetry of the Fdd2 structure. Since our specimen suffered some damage in the course of the experiment, the results include the effects of some of this disorder, for example in the highly anisotropic thermal parameters for some of the water molecules.

Cell dimensions of the dysprosium compound (abstract) show that it is also monoclinic. Numerous cell determinations of crystals of the Pr, Sm and Gd compounds gave angles very close to 90° and no indication of monoclinic symmetry. It is possible that different methods of crystallization would produce ordered specimens of these materials, or that the monoclinic structure occurs in salts which have not been studied carefully, particularly those of terbium and erbium.

Distances from each holmium atom to its nine neighbors, listed in Table 2, are similar to those reported for the orthorhombic crystals (Templeton, Templeton, Zalkin & Ruben, 1982), but slightly smaller because of the lanthanide contraction of ionic radius; on the average they are 0.027 Å less than in the gadolinium salt. Bond distances within the edta moiety (supplementary material) are normal; the average values for the

various chemical types of bond (N-C = 1.482(5), C-O = 1.252(4), C-C = 1.505(5) (ethylenediamine) and 1.510(7) Å (acetate)) agree within 0.006 Å with averages from the Pr, Sm and Gd structures (Templeton, et al., 1982).

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Table 1. Atomic parameters for NaHo(edta).8-hydrate

$$B_{eq} = \Sigma(B_{ij}a_i^* a_j^* a_i a_j)/3, \text{ Å}^2.$$

	x	y	z	B (*or B_{eq})	
Ho(1)	.08268(2)	.15544(1)	-.00108(1)	1.55(1)	*
Ho(2)	.41843(2)	.34456	.00108	1.57(1)	*
W(1)	.1345(3)	.1100(2)	-.1220(4)	2.3(2)	*
W(2)	.1308(3)	.10709(14)	.1208(4)	2.1(2)	*
W(3)	.0014(4)	.09946(13)	-.0121(4)	2.6(2)	*
W(4)	.0289(7)	.1245(4)	.3801(14)	14.1(7)	*
W(5)	.0615(4)	.0409(2)	.1002(5)	3.9(2)	*
W(6)	.1438(6)	.0988(2)	.5612(9)	7.5(3)	*
W(7)	.1354(9)	.1830(3)	.4503(7)	11.6(5)	*
W(8)	-.0072(6)	.0509(3)	.2942(8)	9.7(4)	*
W(9)	.3656(4)	.38783(14)	-.1232(4)	2.6(2)	*
W(10)	.3694(4)	.39352(14)	.1195(4)	2.4(2)	*
W(11)	.4962(4)	.40195(13)	-.0141(4)	2.5(2)	*
W(12)	.4824(5)	.3903(3)	.3226(9)	7.7(4)	*
W(13)	.4374(4)	.4615(2)	.1033(5)	3.7(2)	*
W(14)	.3476(6)	.4025(2)	.5656(9)	7.8(4)	*
W(15)	.3851(5)	.3232(2)	.4567(5)	6.0(3)	*
W(16)	.4832(6)	.4746(3)	.3226(9)	8.5(4)	*
Na(1)	.1393(2)	.13492(9)	.3115(3)	3.84(7)	
N(1)	.0553(5)	.2273(2)	.0058(5)	2.0(1)	
N(2)	.1482(4)	.1922(2)	-.1603(5)	1.9(1)	
O(1)	-.0276(3)	.16832(14)	.0724(4)	2.51(9)	
O(2)	.0967(3)	.18267(13)	.1789(4)	2.12(9)	
O(3)	.2013(3)	.16792(13)	.0299(4)	2.30(9)	
O(4)	.0174(3)	.16333(13)	-.1622(4)	1.95(9)	

O(5)	-.1011(4)	.2088(2)	.1479(6)	4.5(1)
O(6)	.1072(4)	.2319(2)	.2897(5)	3.3(1)
O(7)	.3100(5)	.1760(2)	-.0271(5)	3.7(1)
O(8)	.0059(4)	.1708(2)	-.3444(5)	3.0(1)
C(1)	.0756(5)	.2464(2)	-.1000(7)	2.4(2)
C(2)	.1462(5)	.2337(2)	-.1359(6)	2.3(1)
C(3)	-.0181(6)	.2327(2)	.0212(7)	3.2(2)
C(4)	-.0504(5)	.2007(2)	.0866(6)	2.6(1)
C(5)	.0951(6)	.2441(2)	.1007(7)	2.6(2)
C(6)	.0992(5)	.2169(2)	.1979(6)	2.0(1)
C(7)	.2220(6)	.1798(2)	-.1623(6)	2.5(1)
C(8)	.2470(6)	.1743(2)	-.0446(6)	2.3(1)
C(9)	.1142(5)	.1832(2)	-.2663(7)	2.7(2)
C(10)	.0406(5)	.1723(2)	-.2570(6)	2.1(1)
Na(2)	.3656(2)	.36895(9)	.3133(3)	3.60(7)
N(3)	.4472(5)	.2724(2)	.0095(5)	2.0(1)
N(4)	.3529(4)	.3056(2)	-.1567(4)	1.8(1)
O(9)	.5293(3)	.33353(13)	.0733(4)	2.53(9)
O(10)	.4052(3)	.31877(13)	.1810(4)	2.11(9)
O(11)	.2991(3)	.33121(13)	.0332(4)	2.42(9)
O(12)	.4829(3)	.33606(13)	-.1604(4)	1.99(9)
O(13)	.6037(5)	.2941(2)	.1490(7)	5.3(2)
O(14)	.3965(3)	.2701(2)	.2957(4)	2.9(1)
O(15)	.1916(5)	.3210(2)	-.0227(5)	3.5(1)
O(16)	.4931(4)	.3282(2)	-.3434(4)	3.0(1)
C(11)	.4271(5)	.2523(2)	-.0945(6)	2.1(1)
C(12)	.3557(5)	.2645(2)	-.1301(6)	2.2(1)
C(13)	.5218(6)	.2689(2)	.0244(7)	3.1(2)

C(14)	.5534(6)	.3009(2)	.0879(6)	2.7(1)
C(15)	.4100(6)	.2560(2)	.1055(7)	2.5(2)
C(16)	.4031(5)	.2844(2)	.2017(6)	2.0(1)
C(17)	.2798(6)	.3173(2)	-.1562(6)	2.5(1)
C(18)	.2543(6)	.3232(2)	-.0399(6)	2.2(1)
C(19)	.3869(5)	.3131(2)	-.2625(6)	2.6(1)
C(20)	.4606(5)	.3264(2)	-.2550(5)	1.6(1)

Table 2.   Neighbor distances for holmium, Å

Atoms	Distance	Atoms	Distance
Ho(1)-O(1)	2.353(6)	Ho(2)-O(9)	2.348(6)
-O(2)	2.391(5)	-O(10)	2.381(5)
-O(3)	2.365(7)	-O(11)	2.387(7)
-O(4)	2.341(5)	-O(12)	2.335(5)
-W(1)	2.387(5)	-W(9)	2.383(5)
-W(2)	2.449(5)	-W(10)	2.432(5)
-W(3)	2.531(6)	-W(11)	2.533(6)
-N(1)	2.597(6)	-N(3)	2.613(6)
-N(2)	2.655(6)	-N(4)	2.667(6)
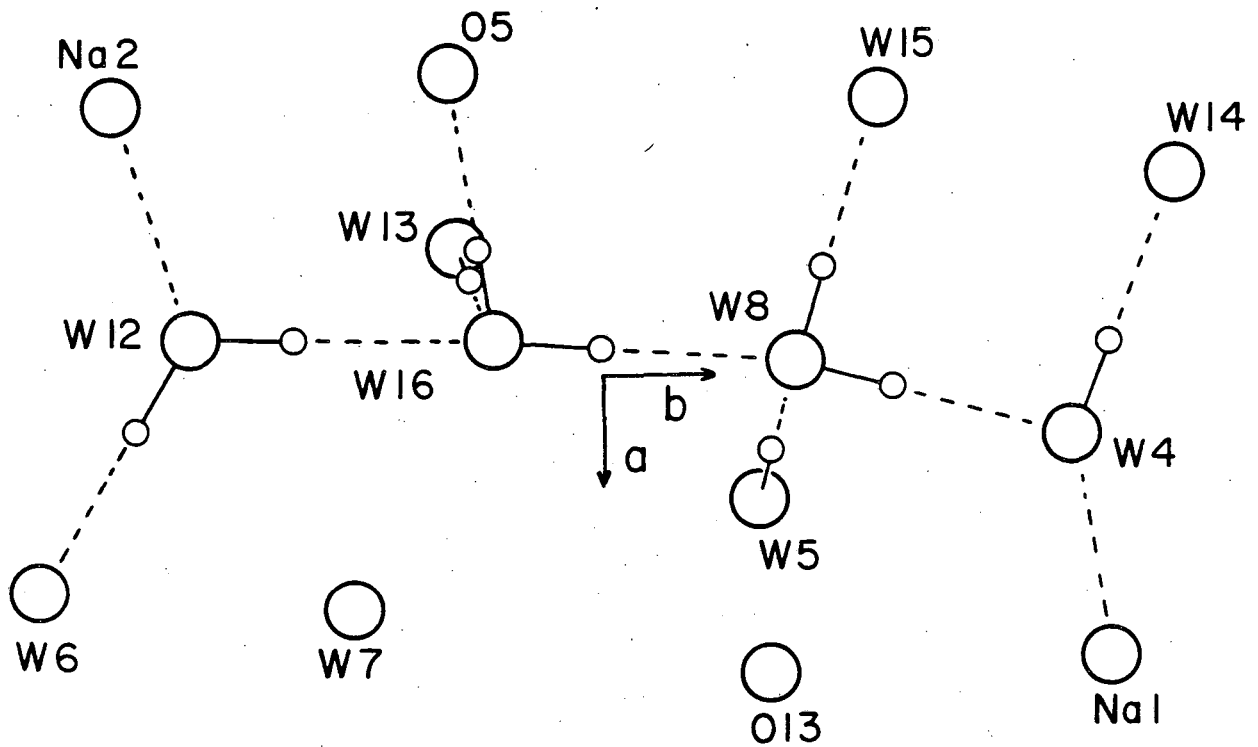
[Figure caption]

Fig. 1. Hydrogen bonding near the c axis. Hydrogen atoms are shown at
calculated positions. In the model for the radiation-induced disorder, some
of the bonds to O(5) and W(15) are broken, new bonds are formed to W(7) and
O(13), and the average structure approaches orthorhombic symmetry with a
two-fold axis at the center of the figure.

Supplementary Table 1. Anisotropic thermal parameters.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ho(1)	1.94(3)	1.37(1)	1.34(1)	.00(1)	-.17(1)	-.019(8)
Ho(2)	2.04(3)	1.40(1)	1.28(1)	-.05(1)	.17(1)	-.035(8)
W(1)	1.5(4)	3.1(2)	2.5(2)	.6(2)	-.0(2)	-.4(2)
W(2)	1.5(4)	2.4(2)	2.2(2)	.5(2)	-.7(2)	.2(2)
W(3)	3.4(5)	1.8(2)	2.5(2)	-.1(2)	-.6(2)	-.1(2)
W(4)	7.4(10)	14.0(9)	21.0(14)	3.2(8)	7.1(9)	10.3(10)
W(5)	5.0(5)	2.6(2)	4.1(3)	.2(3)	-.8(3)	.1(2)
W(6)	8.5(7)	5.3(4)	8.8(6)	-1.6(4)	3.1(5)	-1.4(4)
W(7)	24.6(13)	6.4(5)	3.7(4)	5.7(7)	-2.3(6)	-1.0(3)
W(8)	12.1(10)	10.6(7)	6.5(5)	-3.7(6)	3.8(5)	-.7(5)
W(9)	3.0(5)	2.6(2)	2.2(2)	.2(2)	.2(2)	.4(2)
W(10)	3.0(5)	2.1(2)	2.1(2)	.5(2)	-.1(2)	-.4(2)
W(11)	3.4(5)	2.0(2)	2.2(2)	-.2(2)	.5(2)	.1(2)
W(12)	4.9(6)	6.8(5)	11.4(7)	.2(4)	-1.9(5)	-2.0(5)
W(13)	4.3(5)	2.8(2)	4.0(3)	.1(2)	.4(3)	-.0(2)
W(14)	11.3(8)	3.9(4)	8.0(5)	-1.0(4)	-3.1(5)	.8(3)
W(15)	10.7(7)	4.1(3)	3.1(3)	1.2(4)	.6(3)	-.5(2)
W(16)	10.3(9)	7.4(5)	7.9(5)	-.5(5)	-.7(5)	1.4(4)

Supplementary Table 2 Hydrogen parameters.

	x	y	z	B, $Å^2$
H(1)	.083(4)	.274(1)	-.090(6)	2.433
H(2)	.047(3)	.237(2)	-.160(4)	2.433
H(3)	.164(3)	.248(2)	-.202(4)	2.2626
H(4)	.190(3)	.240(2)	-.089(5)	2.2626
H(5)	-.041(4)	.231(2)	-.049(4)	3.2083
H(6)	-.032(4)	.257(1)	.055(6)	3.2083
H(7)	.071(4)	.268(1)	.125(6)	2.5841
H(8)	.144(3)	.250(2)	.083(6)	2.5841
H(9)	.247(3)	.202(2)	-.198(5)	2.4826
H(10)	.234(4)	.156(1)	-.193(5)	2.4826
H(11)	.145(3)	.165(2)	-.296(6)	2.6762
H(12)	.113(4)	.205(2)	-.315(5)	2.6762
H(13)	.428(4)	.225(1)	-.077(5)	2.1464
H(14)	.452(3)	.261(2)	-.161(4)	2.1464
H(15)	.341(3)	.249(2)	-.197(4)	2.2147
H(16)	.318(3)	.258(2)	-.077(5)	2.2147
H(17)	.549(3)	.271(2)	-.039(5)	3.0535
H(18)	.538(4)	.247(1)	.066(6)	3.0535
H(19)	.445(3)	.237(2)	.135(5)	2.4762
H(20)	.362(3)	.252(2)	.083(5)	2.4762
H(21)	.251(3)	.296(2)	-.185(5)	2.5142
H(22)	.269(4)	.342(1)	-.190(5)	2.5142
H(23)	.361(3)	.331(2)	-.297(5)	2.6229
H(24)	.387(4)	.289(1)	-.308(5)	2.6229

Supplementary Table 3.   Bond distances in edta groups, Å

Atoms	Distance	Atoms	Distance
N(1)-C(1)	1.50(1)	N(3)-C(11)	1.49(1)
-C(3)	1.44(1)	-C(13)	1.46(1)
-C(5)	1.50(1)	-C(15)	1.49(1)
N(2)-C(2)	1.50(1)	N(4)-C(12)	1.49(1)
-C(7)	1.49(1)	-C(17)	1.47(1)
-C(9)	1.48(1)	-C(19)	1.46(1)
mean N-C = 1.482			
C(4)-O(1)	1.24(1)	C(14)-O(9)	1.26(1)
-O(5)	1.26(1)	-O(13)	1.25(1)
C(6)-O(2)	1.23(1)	C(16)-O(10)	1.24(1)
-O(6)	1.24(1)	-O(14)	1.25(1)
C(8)-O(3)	1.28(1)	C(18)-O(11)	1.27(1)
-O(7)	1.24(1)	-O(15)	1.23(1)
C(10)-O(4)	1.28(1)	C(20)-O(12)	1.27(1)
-O(8)	1.25(1)	-O(16)	1.24(1)
mean C-O = 1.252			
C(1)-C(2)	1.50(1)	C(11)-C(12)	1.51(1)
mean C-C (ethylenediamine) = 1.505			
C(3)-C(4)	1.52(1)	C(13)-C(14)	1.49(1)
C(5)-C(6)	1.53(1)	C(15)-C(16)	1.54(1)
C(7)-C(8)	1.52(1)	C(17)-C(18)	1.50(1)
C(9)-C(10)	1.48(1)	C(19)-C(20)	1.50(1)
Mean C-C (acetate) = 1.510			

Supplementary Table 4.   Hydrogen-bond distances, Å

Atoms	Distance	Atoms	Distance
W(1)-O(15)	2.715(9)	W(9)-O(7)	2.718(9)
-O(16)	2.644(9)	-O(8)	2.646(9)
W(2)-W(5)	2.708(8)	W(10)-W(13)	2.748(8)
-O(12)	2.764(9)	-O(4)	2.763(9)
W(3)-W(5)	2.745(8)	W(11)-W(13)	2.775(8)
-O(11)	2.736(7)	-O(3)	2.755(7)
W(4)-W(14)	2.754(18)	W(12)-W(6)	2.809(14)
---		-W(16)	2.982(14)
W(5)-O(6)	2.708(9)	W(13)-O(14)	2.728(9)
-W(8)	2.719(11)	-W(16)	2.833(12)
W(6)-O(13)	2.748(12)	W(14)-O(5)	2.854(11)
-O(15)	2.788(12)	-O(7)	2.735(12)
W(7)-O(6)	2.667(11)	W(15)-O(14)	2.706(8)
W(8)-W(4)	2.880(22)	W(16)-W(8)	2.729(15)
-W(15)	2.805(17)	-O(5)	2.770(14)