angles around the Co—C and Co—N bonds and the dihedral angles between the mean planes of the cobaloxime and phenyl rings are listed in Table 3, in which the corresponding values of *R*-cn-tpp are also given. The conformations of the phosphine ligands of *R*-cn-depp and *R*-cn-dpep are very similar to that of *R*-cn-tpp. The rotation angle around the Co—C bond of *R*-cn-dpep has a similar value to those of *R*-cn-tpp and *R*-cn-tbp, whereas that of *R*-cn-depp is similar to those of *R*-cn-*S*-mba and *S*-cn-*S*-mba.

Bond distances of the two molecules are listed in Table 4. The Co—P distance of *R*-cn-depp is approximately the same as that of *R*-cn-tbp, 2·316 (2) Å. The Co—P bond of *R*-cn-dpep is significantly longer than that of *R*-cn-depp and is shorter than that of *R*-cn-tpp, 2·410 (3) Å. The difference in the Co—P distances of the phosphine complexes may be explained by the steric repulsion between the cobaloxime moiety and the phosphine ligand. The Co—C distances are similar to those of *R*-cn-tbp, 2·089 (6) Å, and *R*-cn-tpp, 2·08 (1) Å. Other distances are in good agreement with those of the related complexes.

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Neutron Diffraction Study at 37 K of Sodium Triaqua(ethylenediaminetetraacetato)samarate(III) Pentahydrate, $Na[Sm(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$*

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Abstract. $M_r = 605·7$, orthorhombic, $Fdd2$, $T = 37\,(2)$ K, $a = 19·416\,(10)$, $b = 35·315\,(15)$, $c = 12·014\,(6)$ Å, $V = 8238\,(7)$ Å^3, $Z = 16$, $D_x = 1·953$ g cm^{-3}; $T = 298\,(3)$ K, $a = 19·457\,(10)$, $b = 35·530\,(15)$, $c = 12·108\,(6)$ Å, $D_x = 1·922$, $D_m = 1·906$ g cm^{-3}, $\lambda = 1·300$ Å, $\mu = 165$ mm^{-1}, $F(000) = 1231 + 46i$ fm. $R = 0·059$ based on F^2 and $R_w = 0·080$ for 1795 independent reflections (including those with $F_o^2 \leq 0·0$) out of 1947 measured and 434 parameters. The refinement was partially anisotropic. All H atoms were located revealing an extensive H-bond network incorporating two water molecules in a disordered arrangement around the twofold axis.

Introduction. The neutron diffraction study of $NaSmA.8H_2O$ (A = edta) originally was undertaken in order to evaluate methods of phase determination based on multiwavelength data exploiting the anomalous scattering of ^{149}Sm for thermal neutrons. A preliminary report of the determination using room-temperature data obtained at three neutron wavelengths, including location of most of the H atoms, was given by Koetzle & Hamilton (1975). The structure is isomorphous with a number of lanthanide–edta complexes investigated by

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Hoard, Lee & Lind (1965) and Lee (1967). The authors reported the structures of $KLaA.8H_2O$ and $NaTbA.8H_2O$ by X-ray diffraction. A further X-ray determination of the isomorphous $NaDyA.8H_2O$ has been reported by Nassimbeni, Wright, van Niekerk & McCallum (1979). H atoms were not located in this X-ray work. Templeton, Templeton & Phizackerley (1980) and Templeton, Templeton, Phizackerley & Hodgson (1982) have reported measurements of X-ray anomalous scattering of synchrotron radiation near the L_{III} edges of Gd, Pr and Sm using the edta complexes.

The determination of the structure of $NaSmA.8H_2O$ with a new neutron data set obtained at low temperature is reported here and reveals in detail an extensive H-bonding network and disorder in the water structure in the crystal. A brief account of the low-temperature structure has been presented earlier (Engel & Koetzle, 1981). Measurements of a limited set of reflections were made at a number of neutron wavelengths and the scattering length of Sm was determined as a function of wavelength. This work is reported elsewhere (Engel & Koetzle, 1982, 1984).

Recently, Templeton, Templeton, Zalkin & Ruben (1982) have completed a refinement of the $NaSmA.8H_2O$ structure, together with those of the isomorphous Pr and Gd salts, based on room-temperature X-ray data.

Experimental. Crystals of $NaSmA.8H_2O$ were prepared by cooling a hot 2*M* NaCl solution containing 0·1 *M* $SmCl_3$ and edta and adjusted to pH 4·5 (Brunisholz, 1955). The samples used in the present work were taken from a batch that had been recrystallized from water and preserved in mother liquor for a number of years. The crystals deteriorated rapidly when viewed under a microscope light, possibly through heating and resultant loss of water, but were stable at room temperature under normal lighting. D_m was determined by flotation in $CHBr_3$–CCl_4 (Koetzle & Hamilton, 1975). A relatively large crystal with longest dimensions in directions **a**, **b** and **c** of 4·4, 1·7 and 2·1 mm, respectively, was chosen in order to obtain sufficient intensity, even though this meant that the absorption-correction factors would be large and thus also the residual absorption errors after correction.

The crystal was oriented with its longest dimension (*a*-axis direction) parallel to the rotation axis of the diffractometer in order to minimize the absorption effects in most areas of reciprocal space. The crystal was mounted on an Al pin and enclosed in a helium-filled Al can; the can was placed in a closed-cycle helium refrigerator* and mounted on an automated four-circle diffractometer (Dimmler, Greenlaw, Kelley, Potter, Rankowitz & Stubblefield, 1976; McMullan, Andrews, Koetzle, Reidinger, Thomas & Williams, 1976) at the Brookhaven High Flux Beam Reactor. The neutron beam was monochromated using the (002) face of Be at a take-off angle of 37°; neutron wavelength 1·300 Å (based on Al_2O_3, hexagonal $a = 4{\cdot}758$, $c = 12{\cdot}991$ Å). Lattice parameters obtained by least-squares analysis of the 2θ angles of 32 strong reflections. Intensities measured employing a $\theta/2\theta$ step-scan technique in two octants of reciprocal space (hkl and $hk\bar{l}$, c being the polar axis) for $2\theta < 50°$ and in one octant only (hkl) for $50° \leq 2\theta \leq 90°$. The reflections were generally weak due to the strong absorption by Sm and long counting times were used (5·5 s per step). The scan range $\Delta 2\theta$ was therefore kept to a minimum and varied to follow approximately the experimentally observed reflection widths. The function chosen was $\Delta 2\theta = 3{\cdot}750\,(1{\cdot}0 - 0{\cdot}428\tan\theta)°$ for $2\theta < 50°$ and $\Delta 2\theta = 2{\cdot}232\,(1{\cdot}0 + 0{\cdot}743\tan\theta)°$ for $50° \leq 2\theta \leq 90°$ giving a minimum of 3·0° at $2\theta = 50°$. The step size was adjusted to give approximately 60 steps in each scan. Three monitor reflections were measured periodically and found to show no systematic variation in intensity.

Data reduction and refinement. Background corrections were made using the program *PEAK* (Takusagawa, 1977) written for a PDP-11/40 computer with interactive graphics display (Bernstein *et al.*, 1974; Vector General Inc., 1973). Initially a linear background function was fitted by a least-squares procedure to the flat portion of each profile. Reflection profiles were displayed and where the net intensity was weak or the background unusual, the most suitable background line was estimated visually. For a number of reflections, spurious peaks occurred in the profile near 2θ values for Al, possibly due to the Al pin on which the crystal was mounted. Where possible the extra peak was excluded from the range of integration and where this was not possible the reflection was discarded.

Absorption corrections were carried out by a Gaussian integration procedure (Busing & Levy, 1957) yielding absorption factors between 0·095 and 0·184. Details of the calculation of the absorption coefficient of the crystal are given by Engel & Koetzle (1984). The crystal shape was described by 20 planes of the forms $\{1k1\}$ and $\{010\}$ and a fine grid of 3840 points was used. The crystal volume was calculated to be 7·50 mm³. Squared observed structure factors were obtained as $F_o^2 = I\sin 2\theta$.

Atomic coordinates from the room-temperature neutron diffraction study by Koetzle & Hamilton (1975) were used as initial values for a full-matrix least-squares refinement minimizing $\sum w(F_o^2 - k^2F_c^2)^2$ and using *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962). Weights were chosen as $w = 1/\sigma^2(F_o^2) = 1/[\sigma^2(I)\sin^2 2\theta]$ with $\sigma^2(I) = T + B + [0{\cdot}02(T - B)]^2$ where T and B are the total peak and background counts respectively.

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* Air Products and Chemicals Inc., DISPLEX® Model CS-202.

Initially the positive direction of the polar *c* axis corresponding to the atomic coordinates was identified by inspecting a number of *hkl*, $hk\bar{l}$ reflection pairs. The scale factor and the real and imaginary scattering lengths of Sm were allowed to vary throughout the refinement. The *z* coordinate (polar axis) of atom N(1) was fixed, N having the largest scattering length in the structure.

The following atomic nomenclature is used: water O atoms are labeled *W*(1)–*W*(8), the H atoms bound to *W*(1) are *U*(1) and *V*(1) *etc.*, the H atoms bound to C(1) are H(1) and *J*(1) *etc.* Isotropic refinement of 56 atoms, *i.e.* all atoms except *U*(8) and *V*(8) which were not located by Koetzle & Hamilton (1975), gave an unweighted residual based on F^2 of 0·135 (226 parameters).

Inspection of Fourier difference maps and trial refinements suggested a disordered structure for water molecules 4 and 8. Inclusion of two positions *A* and *B* with occupancy 0·5 for the six atoms of these two water molecules in an isotropic refinement yielded $R = 0{\cdot}092$ (64 atom sites and 258 parameters). Hamilton's *R*-ratio test (Hamilton, 1965; *International Tables for X-ray Crystallography*, 1974) shows this to be a very significant improvement to the model. Space-group symmetry requires that the occupancy of the disordered water molecules be 0·5 as they are hydrogen bonded in the model, and in all further refinements the occupancies of water molecules 4*A*, 4*B*, 8*A* and 8*B* were therefore fixed at that value.

The structure was then refined anisotropically. In order not to increase the number of parameters too drastically, 29 atoms were kept isotropic. These included the 14 atoms with the lowest isotropic temperature factors and the 12 atomic sites with occupancy 0·5. This refinement (434 parameters) reduced the residual to 0·066 and then to 0·063 after removal of eight suspect reflections.

Finally a Zachariasen (1967) isotropic extinction parameter was included in the refinement. The extinction correction, applied to F_c^2, is given by $y = (1 + 2\bar{T}F_c^2g/\bar{V}\sin2\theta)^{-1/2}$, where $\bar{T}$ is the effective mean pathlength approximated from the calculated absorption *A*, by $\bar{T} \simeq -\ln A/\mu$, and $\bar{V} = V^2/\lambda^3$. The smallest *y* value was calculated to be 0·784 for the reflection $19\bar{1}$ and the value of *g* was 0·68 (6) × 10^4. The refinement converged at a final *R* (on F^2) of 0·059.* The goodness-of-fit (*S*) is 2·48, and this somewhat high value may be a result of the disorder present or uncorrected systematic errors in the data.

Table 1. *Fractional atomic coordinates and isotropic temperature factors B* ($\text{Å}^2 \times 10^2$)

H and *J* are H atoms bonded to carbon, *W* are water O atoms and *U* and *V* are water H atoms. *A* and *B* signify alternate positions of water molecules with occupancy 0·5. The numbering in the first column refers to the nomenclature used by NWVM where this differs from that used in this paper (ETK). For those atoms refined anisotropically in the final cycles the temperature factor obtained in the last isotropic refinement is shown in parentheses for reference.

NWVM	ETK	*x*	*y*	*z*	*B*
Dy	Sm	8494 (44)	15520 (17)	0 (53)	0·09 (25)
	Na	14065 (39)	13273 (17)	31522 (51)	(1·23) (17)
	N(1)	5879 (13)	22884 (6)	579	0·43 (4)
	N(2)	15130 (14)	19325 (6)	−16078 (25)	0·54 (4)
O(2)	O(1)	- 2797 (23)	16931 (9)	7224 (32)	0·56 (7)
O(1)	O(2)	9827 (23)	18323 (9)	18354 (33)	0·51 (7)
	O(3)	20663 (23)	16936 (9)	3105 (32)	0·52 (7)
	O(4)	1941 (22)	16449 (9)	−16685 (31)	0·35 (6)
O(6)	O(5)	−9563 (24)	21130 (10)	15775 (37)	(1·01) (10)
O(5)	O(6)	10387 (23)	23315 (10)	29642 (33)	(0·92) (10)
	O(7)	31407 (24)	17623 (11)	−3008 (35)	(1·12) (10)
	O(8)	1160 (23)	17075 (9)	−35211 (34)	0·66 (6)
	C(1)	8070 (20)	24793 (8)	-9824 (31)	(0·60) (9)
	C(2)	15087 (20)	23417 (8)	−13536 (31)	(0·77) (9)
C(5)	C(3)	−1661 (21)	23415 (8)	2244 (30)	(0·96) (9)
C(6)	C(4)	−4825 (20)	20284 (9)	9066 (30)	(0·98) (9)
C(3)	C(5)	9471 (20)	24519 (8)	10288 (32)	0·54 (6)
C(4)	C(6)	9853 (19)	21843 (8)	20259 (31)	0·38 (6)
	C(7)	22368 (20)	18033 (8)	−16225 (29)	0·56 (6)
	C(8)	25080 (20)	17538 (9)	−4443 (30)	(1·00) (9)
	C(9)	11864 (20)	18568 (8)	−26862 (31)	0·66 (6)
	C(10)	4458 (19)	17307 (8)	−26282 (30)	0·40 (5)
O(10)	*W*(1)	13760 (23)	10943 (9)	−12587 (33)	0·58 (7)
O(11)	*W*(2)	13501 (21)	10620 (9)	12330 (33)	0·31 (6)
O(9)	*W*(3)	400 (22)	9787 (9)	−1187 (35)	0·42 (6)
W(1)	*W*(5)	6406 (23)	4147 (10)	10570 (35)	0·66 (7)
W(2)	*W*(6)	14883 (52)	9944 (14)	54746 (61)	(3·99) (19)
W(3)	*W*(7)	12015 (38)	18015 (14)	45431 (45)	(2·72) (14)
	H(1)	8192 (45)	27893 (16)	−8846 (53)	(1·27) (17)
	J(1)	4254 (43)	24191 (18)	16272 (55)	(1·72) (18)
	H(2)	16615 (45)	25042 (19)	−20727 (61)	(2·10) (19)
	J(2)	18769 (43)	23931 (18)	−6921 (58)	(1·57) (18)
	H(3)	−2817 (51)	26173 (18)	5659 (65)	(2·23) (21)
	J(3)	−4059 (47)	23240 (20)	−6090 (53)	(2·44) (21)
	H(5)	14963 (52)	25120 (22)	8080 (64)	(2·60) (22)
	J(5)	7135 (53)	27214 (18)	12889 (58)	(2·14) (20)
	H(7)	25658 (42)	19972 (19)	20868 (56)	(2·05) (19)
	J(7)	22770 (44)	15238 (18)	−20438 (53)	(1·56) (17)
	H(9)	12227 (44)	21028 (20)	−32310 (58)	(2·21) (21)
	J(9)	14538 (42)	16259 (19)	- 31001 (59)	(2·15) (20)
	U(1)	18178 (40)	9672 (18)	−11432 (57)	(1·67) (18)
	V(1)	11040 (42)	9452 (19)	- 17490 (56)	(1·69) (18)
	U(2)	18401 (40)	10002 (17)	10477 (59)	(1·93) (18)
	V(2)	11179 (41)	8153 (16)	12303 (55)	(1·47) (17)
	U(3)	−1109 (43)	9063 (18)	−8839 (56)	(1·49) (17)
	V(3)	2188 (48)	7455 (18)	2150 (59)	(2·03) (19)
	U(5)	4163 (42)	3582 (16)	17658 (55)	(1·80) (19)
	V(5)	9157 (42)	1967 (17)	8311 (57)	(1·44) (17)
	U(6)	12183 (59)	9194 (21)	60489 (75)	(3·19) (25)
	V(6)	15437 (60)	7879 (21)	49911 (73)	(2·73) (21)
	U(7)	8071 (68)	17544 (21)	50374 (64)	(2·75) (21)
	V(7)	10267 (66)	19874 (21)	40416 (64)	(2·97) (24)
W(4)	*W*(4*A*)	1796 (53)	11056 (25)	32125 (69)	0·99 (14)
	W(4*B*)	3445 (74)	11318 (32)	35981 (103)	2·77 (20)
W(5)	*W*(8*A*)	2514 (71)	3239 (28)	32715 (87)	2·26 (18)
	W(8*B*)	−1278 (69)	4181 (26)	28902 (83)	1·99 (17)
	U(4*A*)	808 (106)	8616 (57)	32120 (129)	2·62 (30)
	V(4*A*)	2470 (85)	12543 (34)	30646 (107)	1·28 (24)
	U(4*B*)	433 (111)	13290 (47)	36211 (143)	2·87 (33)
	V(4*B*)	5246 (167)	11436 (69)	42916 (238)	5·91 (57)
	U(8*A*)	7033 (110)	3295 (41)	35799 (133)	2·56 (29)
	V(8*A*)	−998 (129)	388 (60)	32432 (100)	2·73 (27)
	U(8*B*)	5377 (122)	4851 (47)	26621 (144)	3·15 (34)
	V(8*B*)	1319 (82)	6864 (42)	32356 (103)	1·30 (23)

Shifts in all positional parameters were less than their associated e.s.d.'s. Neutron scattering lengths used were (in fm) $b_{\text{Na}} = 3{\cdot}63$, $b_{\text{C}} = 6{\cdot}6484$, $b_{\text{N}} = 9{\cdot}36$, $b_{\text{O}} = 5{\cdot}803$ and $b_{\text{H}} = -3{\cdot}7409$ (Koester, 1977). The real and imaginary parts of the Sm scattering length were refined to the values $(b_o + b')_{\text{Sm}} = 0{\cdot}00\ (5)$ and $b''_{\text{Sm}} = 2{\cdot}90\ (6)$ fm.

Discussion. The fractional coordinates and isotropic temperature factors are listed in Table 1.

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* Lists of squared structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39507 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Lanthanide coordination

The X-ray crystal structures of three isomorphous nine-coordinate lanthanide edta complexes have been reported previously: K*LaA*.8H$_2$O (Hoard, Lee & Lind, 1965), NaTb*A*.8H$_2$O (Lee, 1967) and NaDy*A*.8H$_2$O* (Nassimbeni, Wright, van Niekerk & McCallum, 1979; NWVM hereafter). The structure of a ten-coordinate acid complex, HLa*A*.7H$_2$O, is given by Lind, Lee & Hoard (1965). NWVM have reported atomic coordinates which are very similar to ours, except that atom *W*(5) is transformed by $\frac{1}{4}+x$, $\frac{1}{4}-y$, $\frac{1}{4}+z$ relative to our corresponding *W*(8*A*) and *W*(8*B*). The atomic numbering is taken from Lee (1967) and this differs somewhat from that used later by NWVM. For reference the NWVM numbering is included in Table 1. The bond lengths in the Sm anion are shown in Fig. 1, while selected bond angles around the central ion are given in Table 2. Bonding parameters involving non-hydrogen atoms agree to within experimental error with those by Templeton, Templeton, Zalkin & Ruben (1982) in their recent room-temperature X-ray study of NaSm*A*.8H$_2$O.

NWVM describe the anion starting from a girdle of four O atoms around the central ion. These atoms labeled O(1)–O(4) are indeed closely coplanar (the standard deviation of the set of four from the plane is 0·14 Å). However, one of the N atoms [N(2)] is also moderately close to this plane (the standard deviation of the set of five atoms from a plane is 0·38 Å) and these five atoms form a rather uniform girdle round the central ion, as evidenced by the first five angles in Table 2 all being reasonably near 72°. The Sm ion is 0·52 (1) Å from the mean plane through the four O atoms. This value lies between those for La (0·60 Å) and Tb (0·49 Å) and Dy (0·48 Å), paralleling the trend in ionic radius. The distance of the central ion from the mean plane through five atoms is 0·82 Å (La), 0·72 (1) Å (Sm), 0·68 Å (Tb) and 0·69 Å (Dy).

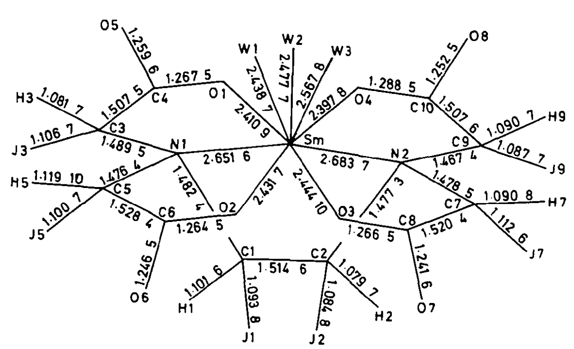

Fig. 1. Bond lengths (Å) in the anion with e.s.d.'s following the values. H and *J* are H atoms.

Table 2. *Selected bond angles* (°) *around the* Sm^{3+} *ion*

O(1)–Sm–O(2)	71·7 (2)	O(1)–Sm–*W*(3)	68·0 (2)
O(2)–Sm–O(3)	71·1 (2)	O(2)–Sm–*W*(2)	72·6 (2)
O(3)–Sm–N(2)	62·8 (2)	O(3)–Sm–*W*(1)	79·9 (3)
N(2)–Sm–O(4)	65·4 (2)	O(3)–Sm–*W*(2)	70·9 (2)
O(4)–Sm–O(1)	77·9 (3)	O(4)–Sm–*W*(1)	78·2 (2)
N(1)–Sm–O(1)	67·3 (2)	O(4)–Sm–*W*(3)	74·7 (2)
N(1)–Sm–O(2)	66·2 (2)	N(2)–Sm–*W*(1)	71·6 (2)
N(1)–Sm–O(3)	88·9 (2)	*W*(1)–Sm–*W*(2)	75·1 (2)
N(1)–Sm–N(2)	67·6 (2)	*W*(1)–Sm–*W*(3)	72·5 (2)
N(1)–Sm–O(4)	77·6 (2)	*W*(2)–Sm–*W*(3)	73·9 (2)

Table 3 summarizes the lanthanide coordination geometry in the Sm, Dy, La and Tb complexes. The Ln–*W*(3) distances are particularly long and would appear to identify this water molecule as the one which will be squeezed out of the coordination sphere as the radius of the central lanthanide ion is decreased resulting finally in eightfold coordination for the Yb complex determined by NWVM.

In the room-temperature Sm structure the four Sm–O coordination distances to edta are very similar with a mean of 2·401 Å and standard deviation 0·016 Å (Table 3). In the Dy structure (NWVM) the four reported Dy–O coordination lengths are scattered more widely with a mean of 2·391 Å and standard deviation 0·076 Å. This scatter is, however, probably due to the effect of anomalous scattering by Dy. In a polar crystal the anomalous atom appears to be shifted along the polar axis to compensate for this omission. Cruickshank & McDonald (1967) estimate the shift to be $dz = \delta/2\pi(\sin\theta/\lambda)_{\max}$, where $\delta = f''/f$, the ratio of the imaginary to real scattering power. Taking $f''_{\rm Dy} = 5{\cdot}4$ and $f_{\rm Dy} \approx 48$ (an average over the range of $\sin\theta/\lambda$) and $(\sin\theta/\lambda)_{\max} = 0{\cdot}53$ Å^{-1} we obtain $dz = 0{\cdot}034$ Å.

From the reported bond lengths, *d*, a corrected bond length d_c was calculated from $d_c^2 = d^2 - z^2 + (z + dz)^2$ where *z* is the coordinate (in Å) relative to Dy of the atom bonded to Dy (*c* being the polar axis). Table 3 compares the reported and corrected Dy–O bond lengths with the Sm–O bond lengths. A shift of $dz = +0{\cdot}08$ Å improves the correlation with the Sm–O bond lengths and reduces the standard deviation of the set of four Dy–O bond lengths from 0·076 to 0·025 Å (mean value now 2·378 Å). Further, the bond lengths, *d*, exhibit a distinct trend with *z* coordinate (*cf.* Table 3) which disappears for the bond lengths, d_c, after the shift. This together with the improved correlation between the two structures after the shift strongly suggests that the fractional *z* coordinate of Dy is in error and should not be zero as reported but 0·0066. Templeton, Templeton, Zalkin & Ruben (1982) have also pointed out this discrepancy. The shift does not significantly affect the values reported for the distance of the Dy^{3+} ion from the mean atom planes mentioned above, as these planes are nearly parallel to *c*.

The possibility of a similar effect was investigated for the La and Tb complexes, and the coordinates (Lee, 1967) were inspected for possible systematic errors in *z*. For

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* Recent X-ray work on the Dy and Ho salts indicates that these are actually monoclinic, with $\alpha \approx 89{\cdot}6°$ (Templeton, Templeton, Zalkin & Ruben, 1982).

Table 3. *Lanthanide coordination in the* Sm, Dy, La *and* Tb *edta complexes* (*distances in* Å)

For the Dy complex, *z* is the fractional coordinate of the atom bonded to Dy, *d*(Dy) the bond length reported by NWVM, and d_c(Dy) the bond length corrected by shifting the Dy atom 0·08 Å along the polar *c* axis. For the Tb complex d_c(Tb) is the bond length corrected by shifting the Tb atom +0·032 Å along *c*. ETK is the atomic nomenclature used in this work.

Nomenclature								
NWVM	ETK	*z*	*d*(Sm)	*d*(Dy)	d_c(Dy)	*d*(La)	*d*(Tb)	d_c(Tb)
O(2)	O(1)	0·0790	2·410 (9)	2·396 (15)	2·365	2·469 (14)	2·353 (11)	2·365
O(1)	O(2)	0·1862	2·431 (7)	2·464 (14)	2·391	2·525 (14)	2·366 (10)	2·396
	O(3)	0·0380	2·444 (10)	2·420 (14)	2·406	2·528 (12)	2·410 (10)	2·407
	O(4)	−0·1555	2·397 (8)	2·285 (15)	2·351	2·482 (15)	2·386 (10)	2·360
O(10)	*W*(1)	−0·1168	2·438 (8)	2·351 (16)	2·400	2·559 (14)	2·441 (10)	2·423
O(11)	*W*(2)	0·1260	2·477 (7)	2·483 (14)	2·435	2·584 (15)	2·449 (10)	2·469
O(9)	*W*(3)	−0·0090	2·567 (8)	2·553 (16)	2·558	2·626 (13)	2·552 (9)	2·551
	N(1)	0·0150	2·651 (7)	2·642 (16)	2·638	2·776 (15)	2·638 (11)	2·640
	N(2)	−0·1523	2·683 (7)	2·614 (17)	2·671	2·758 (14)	2·691 (11)	2·669
$\bar{d}\lvert$O(1–4)$\rvert$			2·421 (21)	2·391 (76)	2·378 (25)	2·501 (30)	2·377 (21)	2·382 (23)
$d\lvert(W1)-\bar{d}\rvert$			0·017	−0·040	0·022	0·058	0·064	0·040
$d\lvert(W2)-\bar{d}\rvert$			0·056	0·092	0·057	0·083	0·072	0·087
$d\lvert(W3)-\bar{d}\rvert$			0·146	0·162	0·179	0·125	0·175	0·169

Table 4. *Geometry of the water molecules and hydrogen-bonding parameters*

(*a*) Geometry of water molecules			(*b*) Hydrogen-bonding parameters		
	O–H (Å)	H–O–H (°)		O···H (Å)	O···H–O (°)
W(1)–*U*(1)	0·978 (10)	108·7 (7)	O(3)···$U(3^{\mathrm{i}})$	1·726 (8)	175·0 (7)
–*V*(1)	0·950 (9)		O(4)···$U(2^{\mathrm{ii}})$	1·755 (9)	174·0 (6)
W(2)–*U*(2)	1·001 (9)	104·0 (7)	O(5)···$V(6^{\mathrm{ii}})$	1·791 (9)	173·4 (12)
–*V*(2)	0·981 (7)		O(5)···$U(8A^{\mathrm{ii}})$	1·750 (21)	173·9 (15)
W(3)–*U*(3)	0·998 (8)	105·4 (6)	O(6)···$V(5^{\mathrm{iii}})$	1·726 (8)	175·3 (8)
–*V*(3)	0·980 (8)		O(6)···*V*(7)	1·776 (8)	158·0 (12)
W(5)–*U*(5)	0·977 (8)	109·0 (6)	O(7)···$V(1^{\mathrm{i}})$	1·715 (8)	169·9 (7)
–*V*(5)	0·976 (8)		O(7)···$U(6^{\mathrm{iv}})$	1·892 (11)	176·7 (9)
W(6)–*U*(6)	0·906 (13)	108·1 (10)	O(8)···$U(1^{\mathrm{ii}})$	1·675 (9)	173·3 (7)
–*V*(6)	0·939 (11)		*W*(5)···*V*(2)	1·704 (7)	171·0 (7)
W(7)–*U*(7)	0·983 (15)	102·8 (11)	*W*(5)···*V*(3)	1·749 (8)	164·6 (7)
–*V*(7)	0·954 (11)		*W*(6)···$V(4A^{\mathrm{i}})$	1·733 (18)	173·1 (13)
W(4*A*)–*U*(4*A*)	0·883 (25)	109·5 (19)	*W*(7)···$U(8B^{\mathrm{i}})$	1·817 (23)	168·6 (19)
–*V*(4*A*)	0·997 (20)		*W*(4*B*)···*V*(8*B*)	1·683 (19)	165·9 (15)
W(4*B*)–*U*(4*B*)	0·910 (27)	100·7 (23)	*W*(8*A*)···*U*(4*A*)	1·929 (23)	157·5 (21)
–*V*(4*B*)	0·905 (37)		*W*(8*A*)···*U*(5)	1·841 (12)	161·3 (8)
W(8*A*)–*U*(8*A*)	0·953 (30)	123·0 (15)	*W*(8*B*)···$V(8A^{\mathrm{v}})$	1·726 (23)	129·6 (19)
–*V*(8*A*)	1·216 (30)		*W*(8*B*)···*U*(5)	1·728 (13)	158·3 (7)
W(8*B*)–*U*(8*B*)	0·874 (33)	106·8 (16)			
–*V*(8*B*)	1·151 (17)				

Symmetry code: (i) $\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$; (ii) $-\frac{1}{4}+x, \frac{1}{4}-y, -\frac{1}{4}+z$; (iii) $\frac{1}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z$; (iv) $\frac{1}{4}+x, \frac{1}{4}-y, -\frac{3}{4}+z$; (v) $-x, -y, z$.

the Tb structure the correlation with the Sm and Dy structures is improved if the Tb^{3+} ion is shifted +0·032 Å along **c** (Table 3). No significant systematic error was observed for the La structure, as might be expected since f'' is considerably smaller for La than for Tb or Dy for Mo *K*α radiation.

Water structure

Table 4(*a*) shows the geometry of the water molecules. The covalent bond length furthest from the standard O–H value is 1·216 Å for *W*(8*A*)–*V*(8*A*). Molecule 8*A* also has the poorest H—O—H angle, at 123·0°. A reason for this inaccuracy may be that atom *V*(8*A*) lies close to the crystallographic twofold axis so that the two equivalent positions are only 0·47 Å apart. [*W*(4*A*) and *W*(4*B*) are 0·57 Å apart and *U*(4*A*) and *V*(8*B*) 0·63 Å apart.] If atom *V*(8*A*) were placed on the line joining *W*(8*A*) and the twofold axis and 1·0 Å from *W*(8*A*), the geometry of the water molecule 8*A* would be quite normal and the *W*(8*B*)···$V(8A^{\mathrm{v}})$–$W(8A^{\mathrm{v}})$ angle nearer 180°. However, the position reported is that obtained in the refinement.

The geometry of the disordered water molecules is generally poorer than that of the others. However, the fact that the refinement yielded generally acceptable molecular geometry with no atoms constrained, in spite of partial overlapping and reduced occupancy of some atoms, lends support to the proposed model for the disorder.

A virtually complete hydrogen-bonding network is found in the structure. Table 4(*b*) gives O···H distances and the corresponding O···H–O angles. All water O atoms accept hydrogen bonds, except *W*(4*A*) which is coordinated to Na, and *W*(1), *W*(2) and *W*(3) which are coordinated to Sm. All the water H atoms act as hydrogen-bond donors except *U*(7), *U*(4*B*) and *V*(4*B*). [*U*(7) is involved in a short contact of 2·198 (22) Å with O(8).]

Six of the eight acetate O atoms [all but O(1) and O(2)] accept hydrogen bonds from water molecules, there being nine such bonds in all. Six hydrogen bonds are formed by the H atoms of water molecules 1, 2 and 3 which are part of the anion. Further, atoms O(1), O(2), *W*(2) and *W*(3) are coordinated to Na^+ ions giving 19 bonds between an anion and its environment.

NWVM give eight short O···O distances between atoms belonging to the anion (involving at least one water O atom in each case) and suggest that these may be 'intramolecular' hydrogen bonds (their Table 5). The present neutron determination which provides H positions, however, shows that no such hydrogen bonds exist. All the 'intermolecular' hydrogen bonds proposed by NWVM are confirmed. [They suggest bond O(7)···O(2) but this is probably an error and should read O(7)··· *W*(2) in their notation.] One further bond is found here between water molecules 7 and 8*B*, namely *W*(7)··· *U*(8*B*).

NWVM also suggest the existence of 'intramolecular' hydrogen bonds for the eight-coordinate Yb complex (their Table 6). However, it seems unlikely that this complex will behave very differently from the nine-coordinate ones. The water molecules coordinated to the lanthanide ion would rather be expected to form 'intermolecular' hydrogen bonds here also.

Of crystallographic interest is the hydrogen bonding among the disordered water molecules near the twofold axis. Fig. 2 shows the bonding of molecules 4*A*, 4*B*, 8*A* and 8*B*, only one of the two chains of four hydrogen-bonded molecules shown being present in any one locality in the crystal. NWVM were not able to resolve the disordered structure with X-rays but an indication of the disorder is to be found in the high temperature factors they obtained for *W*(4) and *W*(5) (their notation).

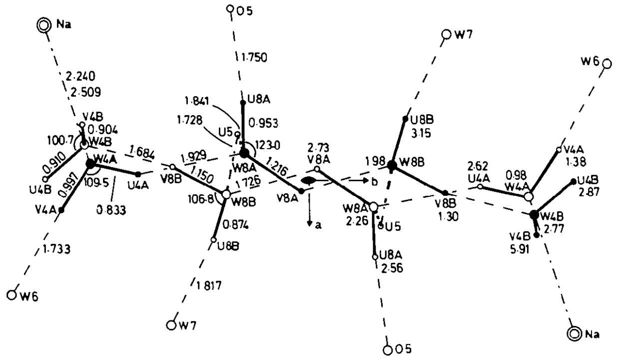

Fig. 2. Bonding of disordered water molecules around the twofold axis. Bond lengths (Å) and bond angles (°) appear on the left half of the diagram and isotropic temperature factors (*B* in $Å^2$) on the right. Only one of the two chains of four hydrogen-bonded molecules is present in any one locality in the crystal. Atoms belonging to one of the chains are shown black in the diagram. H atoms bonded to *WJ* are labelled *UJ* and *VJ*.

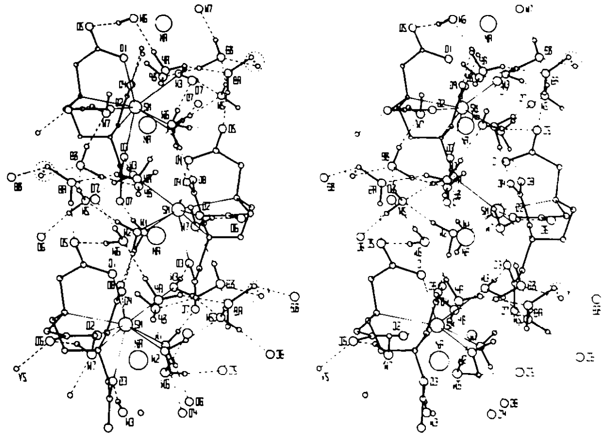

Fig. 3. Stereoview of three asymmetric units of the structure related by the diamond glide plane perpendicular to the *b* axis. The structure is viewed approximately down the *c* axis with the *b* axis to the right (De Wet, 1980).

Crystal packing

Anions related by the diamond glide plane perpendicular to the *b* axis are strongly bound together in chains as has been described by Lee (1967). The anions in each chain are linked through two coordination bonds to Na^+ ions and 6·5 hydrogen bonds [*cf.* symmetry operations (i) and (ii) in Table 4*b*]. In the chain Sm^{3+} and Na^+ ions are doubly bridged alternately by O(2) and *W*(2), and O(1) and *W*(3). A total of 6·5 hydrogen bonds are counted if a bond to an atom with occupancy 0·5 is given weight 0·5. Fig. 3 gives a stereoview approximately down the *c* axis of three asymmetric units related by this diamond glide.

Parallel chains related by unit translation in the **c** direction are stacked above one another to form a layer in the *xy* plane. They are only weakly linked together by a single hydrogen bond O(7)···*U*(6) [symmetry operation (iv) in Table 4*b*] and by the O(8)···*U*(7)[*x*,*y*,−1+*z*] interaction mentioned earlier. The layers of chains are, however, quite strongly linked by three hydrogen bonds per asymmetric unit to adjacent layers related by the twofold axis. These hydrogen bonds, O(6)···*V*(5), *V*(5)···O(6), *W*(8*B*)···*V*(8*A*) and *V*(8*A*)···*W*(8*B*), protrude to left and right of the chain in Fig. 3 [*cf.* symmetry operations (iii) and (v) in Table 4*b*]. The structure is thus well stabilized as the chains in adjacent layers criss-cross one another, the chains extending in the [101] and [$\bar{1}$01] directions respectively in alternate layers.

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Bis(phenylmethanethiolato)(2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene)iron(III) Hexafluorophosphate, $C_{28}H_{38}FeN_4S_2^+.PF_6^-$

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Abstract. M_r = 695·58, space group $P\bar{1}$, a = 12·385 (3), b = 12·483 (2), c = 12·155 (2) Å, α = 97·446 (12), β = 111·408 (12), γ = 63·960 (13)°, V = 1570·8 (5) Å^3, Z = 2, D_x = 1·471 (5) Mg m^{-3}, Nb-filtered Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 0·738 mm^{-1}, $F(000)$ = 722, $T \sim$ 290 K, R = 0·082, R_w = 0·053, S = 1·38 for 3622, 4040, 4040 reflections, 462 parameters. The average Fe—N(TIM) and Fe—S bond lengths are 1·928 (3) [6] (e.s.d. 0·003, scatter e.s.d. 0·006 of the average 1·928) and 2·288 (1) [2] Å. Comparison with other Fe(TIM) complexes seems to imply increased donation of electron density from the axial ligands (here sulfur) to Fe^{III}, and from Fe^{III} to the diimines of TIM. The two cations are both centrosymmetric, but have different axial ligand conformations, one fully extended, away from the TIM plane, and the other with the phenyls lying next to the TIM plane [Fe—S—C—C torsion angles 176·7 (3) and −80·2 (5)°; Fe—S—CH$_2$ 108·8 (2) and 114·4 (2)°].

Introduction. The crystal structures of two iron(II) complexes containing the macrocyclic ligand TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene), [Fe(TIM)(NCCH$_3$)(CO)].(PF$_6$)$_2$ (McCandlish, Santarsiero, Rose & Lingafelter, 1979) and [Fe(TIM)(NCCH$_3$)$_2$].(PF$_6$)$_2$ (Smith, Santarsiero & Lingafelter, 1979), and one iron(III) complex, [Fe(TIM)(SCN)$_2$].PF$_6$ (Stenkamp & Jensen, 1980), have been determined. Here we describe a second Fe^{III}–TIM structure, [Fe(TIM)(SCH$_2$C$_6$H$_5$)$_2$].PF$_6$.

Experimental. Crystals dark-brown cubes, 0·10 mm on edge, prepared by Dr E. O. Fey; Picker FACS-I diffractometer. Lattice constants by least-squares refinement of the orientation matrix from two settings, '$\pm 2\theta$', 27 reflections, $2\theta > 25°$. Intensity measurements: 4081 reflections, $\pm h + k \pm l$, $2\theta \leq 45°$, by 1·0° min^{-1} θ–2θ scans of 2θ width 1·6° plus α_1–α_2 angular dispersion, 20 s post-scan stationary-crystal–stationary-counter background counts fore and aft. 5 check reflections every 50 reflections, with no unusual variations, led to q = 0·0057 ('instability constant'), used in $1/w_{F^2} = (s + r^2b + q^2I^2)k^4/(\mathrm{Lp})^2$, $I = s - rb$, $F_o = k\sqrt{I/\mathrm{Lp}}$, k = 1·1781 (12). Form factors from Stewart, Davidson & Simpson (1965) for H, and from *International Tables for X-ray Crystallography* (1962)

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