satellite positions from the equivalent positions in the diffraction patterns of the two parent phases is directly related to the stoichiometry of the compound. Both occupational and displacement modulation waves exhibit a strong block-wave character. Refinements were also performed with block-wave parameters for the occupational waves instead of the usual principal harmonics and found to be consistent with the latter.

The fundamental inability of an accurate recording of all harmonics needed for the correct characterization of the various block waves is one of the reasons that the refinement of the model against the observed intensity data does not lower the overall R factor below 0.09. It can be shown that for block-wave types, or more general piecewise constant functions, the intensities of satellites do not vanish rapidly with increasing order n [Janssen & Janner, 1987, equation (6)]. This causes the intensity due to the modulation to be spread over a large number of relatively weak reflections. These are normally measured with less accuracy than the strong main reflections, making the overall fit less accurate. Other reasons for the relatively large R factor, inherent to the two-dimensional character of the system, are the well-known presence of stacking faults in the structure and the very asymmetric shape of the crystal in conjunction with a high linear absorption coefficient of 510 cm^{-1}.

References

BÖTTCHER, P. (1988). Angew. Chem. 100, 781–794.

CANADELL, E., JOBIC, S., BREC, R., ROUXEL, J. & WHANGBO, M.-H. (1992). J. Solid State Chem. 99, 189–199.

CANADELL, E., MONCONDUIT, L., EVAIN, M., BREC, R., ROUXEL, J. & WHANGBO, M. (1993). Inorg. Chem. 32, 10–12.

EVAIN, M. (1992). U-FIT. A Program for the Least-Square Refinement of Cell Parameters and Modulation Vectors. IMN, Laboratoire de Chimie des Solides, 44072 Nantes CEDEX 03, France.

EVAIN, M., MONCONDUIT, L., VAN DER LEE, A., BREC, R., ROUXEL, J. & CANADELL, E. (1994). New J. Chem. In the press.

FUJIWARA, K. (1957). J. Phys. Soc. J. 12, 7–13.

HALL, S. R., FLACK, H. D. & STEWART, J. M. (1992). Editors. XTAL3.2 Reference Manual. Univs. of Western Australia, Australia, Geneva and Maryland, USA.

JANSSEN, T. & JANNER, A. (1987). Adv. Physics 36, 519–624.

JOBIC, S., BREC, R. & ROUXEL, J. (1992). J. Alloys Compd. 178, 253–283.

LI, J., BADDING, E. & DISALVO, F. J. (1992). J. Alloys Compd. 184, 257–263.

LI, J. & CARROLL, P. J. (1992). Mater. Res. Bull. 27, 1073–1081.

MAHY, J., VAN LANDUYT, J., AMELINCKX, S., BRONSEMA, K. D. & VAN SMAALEN, S. (1986). J. Phys. C, 19, 5049–5069.

MAR, A., JOBIC, S. & IBERS, J. A. (1992). J. Am. Chem. Soc. 114, 8963–8971.

MONCONDUIT, L., EVAIN, M., BOUCHER, F., BREC, R. & ROUXEL, J. (1992). Z. Anorg. Allg. Chem. 616, 1–6.

MONCONDUIT, L., EVAIN, M., BREC, R., ROUXEL, J. & CANADELL, E. (1993). C. R. Acad. Sci. 314, 25–34.

PETŘÍČEK, V. (1993). JANA93. Programs for Modulated and Composite Crystals. Institute of Physics, Praha, Czech Republic.

ROUXEL, J. (1993). Comments Inorg. Chem. 14, 207–228.

SCHUTTE, W. J. & DE BOER, J. L. (1988). Acta Cryst. B44, 486–494.

SMAALEN, S. VAN (1993). Unpublished. Lab. of Chemical Physics, Univ. of Groningen, The Netherlands.

VAN AALST, W., DEN HOLLANDER, J., PETERSE, W. J. A. M. & DE WOLFF, P. M. (1976). Acta Cryst. B32, 47–58.

VAN DER LEE, A., EVAIN, M., MONCONDUIT, L., BREC, R. & VAN SMAALEN, S. (1994). J. Phys. Condens. Matter. In the press.

VAN DER LEE, A., VAN SMAALEN, S., WIEGERS, G. A. & DE BOER, J. L. (1991). Phys. Rev. B, 43, 9420–9430.

VAN DER LEE, A., MANSUETTO, M., EVAIN, M., MONCONDUIT, L., BREC, R. & ROUXEL, J. (1994). J. Solid State Chem. In the press.

VAN DYCK, D., CONDE, C. & AMELINCKX, S. (1979). Phys. Status Solidi A, 56, 327–334.

YAMAMOTO, A. (1981). Acta Cryst. A37, 838–842.

Effect of Lanthanide Contraction on the Structures of the Decatungstolanthanoate Anions in K3Na4H2[LnW10O36].nH2O (Ln = Pr, Nd, Sm, Gd, Tb, Dy) Crystals

BY TOMOJI OZEKI AND TOSHIHIRO YAMASE

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Abstract

Structures of tripotassium tetrasodium dihydrogen decatungstolanthanoate crystals, $K_3Na_4H_2[LnW_{10}O_{36}]$.- nH_2O (Ln = Pr, Nd, Dy; n = 21–22), have been determined and compared with the structures of their isomorphous crystals with Ln = Sm, Gd and Tb. $K_3Na_4H_2[PrW_{10}O_{36}]$.$22H_2O$ crystallizes in monoclinic,

$P2_1/n$, $a = 30.049\,(4)$, $b = 16.055\,(2)$, $c = 11.462\,(2)$ Å, $\beta = 96.36\,(1)°$, $V = 5496\,(1)$ Å^3 and $R = 0.056$ for 7990 reflections. $K_3Na_4H_2[NdW_{10}O_{36}].22H_2O$ crystallizes in monoclinic, $P2_1/n$, $a = 30.057\,(5)$, $b = 16.051\,(4)$, $c = 11.468\,(2)$ Å, $\beta = 96.52\,(2)°$, $V = 5497\,(2)$ Å^3 and $R = 0.052$ for 6432 reflections. $K_3Na_4H_2[DyW_{10}O_{36}].21H_2O$ crystallizes in monoclinic, $P2_1/n$, $a = 29.816\,(6)$, $b = 16.097\,(4)$, $c = 11.443\,(2)$ Å, $\beta = 96.36\,(2)°$, $V = 5458\,(2)$ Å^3 and $R = 0.053$ for 6114 reflections. All six $[LnW_{10}O_{36}]^{9-}$ anions in these isomorphous crystals exhibit structural distortion from their ideal symmetry of D_{4d} in a way that the dihedral twofold symmetry is lost, which is most evident in that Ln—W distances are about 0.04 Å longer in one $[W_5O_{18}]^{6-}$ group than in the other. This distortion originates in the coordination of the K^+ cations to the O atoms of the central LnO_8 square antiprisms in the $[LnW_{10}O_{36}]^{9-}$ anions. The Ln—O distances in the six decatungstolanthanoate anions correlate with the ionic radii of the central lanthanide elements. Average Ln—O distances range from 2.48 Å in $[PrW_{10}O_{36}]^{9-}$ to 2.39 Å in $[DyW_{10}O_{36}]^{9-}$, accompanied with the variation in the Ln—W distances from 3.899 to 3.843 Å for one $[W_5O_{18}]^{6-}$ group and from 3.849 to 3.807 Å for the other group.

Introduction

In the course of our investigations on the structures of photoluminescent and electroluminescent polyoxo-tungstolanthanoates, tripotassium tetrasodium dihydrogen salts of $[LnW_{10}O_{36}]^{9-}$, where Ln = Sm, Gd and Tb, have been found to crystallize in isomorphous crystals, namely $K_3Na_4H_2[SmW_{10}O_{36}].22H_2O$ (3) (Ozeki & Yamase, 1993), $K_3Na_4H_2[GdW_{10}O_{36}].21H_2O$ (4) (Yamase & Ozeki, 1993) and $K_3Na_4H_2[TbW_{10}O_{36}].20H_2O$ (5) (Ozeki, Takahashi & Yamase, 1992). In each of these three crystals, distances from the central lanthanide atom to the W atoms were found to be different for the two $[W_5O_{18}]^{6-}$ units, while this type of distortion was not observed in the crystals of this family of polyoxoanions with the other combination of counter-cations, which include $Na_6H_2[CeW_{10}O_{36}].30H_2O$ (Iball, Low & Weakley, 1974), $Na_9[EuW_{10}O_{36}].32H_2O$ (Sugeta & Yamase, 1993), $NaSr_4[EuW_{10}O_{36}].34.5H_2O$ (Yamase, Ozeki & Ueda, 1993), $Na_6H_3[SmW_{10}O_{36}].28H_2O$ (Ozeki & Yamase, 1994) and $Na_{6.5}H_{2.5}[GdW_{10}O_{36}].34H_2O$ (Yamase, Ozeki & Tosaka, in preparation). Also, these isomorphous crystals showed a systematic change in their lattice constants and interatomic distances, correlating with the atomic number of their central lanthanide elements (62 for Sm, 64 for Gd and 65 for Tb). These variations originate in the systematic change in ionic radii of the lanthanide elements due to lanthanide contraction. In order to investigate the origin of the distortion of the $[LnW_{10}O_{36}]^{9-}$ anions in their tripotassium tetrasodium dihydrogen salts, and also to obtain a deeper understanding of the correlation between the ionic radii of the

central lanthanide elements and the interatomic distances by extending the examples to more of the lanthanide elements, isomorphous structures incorporating Pr, Nd and Dy, the atomic numbers of which are 59, 60 and 66, were investigated by X-ray diffraction and the detailed structural deviations were examined. Here we report the crystal structures of $K_3Na_4H_2[PrW_{10}O_{36}].22H_2O$, (1), $K_3Na_4H_2[NdW_{10}O_{36}].22H_2O$, (2), and $K_3Na_4H_2$-$[DyW_{10}O_{36}].21H_2O$, (6), and compare them with those of (3), (4) and (5).

Experimental

Preparations of the samples are as follows: a 10 ml aqueous solution of 2.5 mmol of the desired lanthanide element, as nitrate or acetate, was added to a 20 ml aqueous solution containing 25 mmol of $Na_2WO_4.2H_2O$, the pH of which was adjusted to 7 using CH_3COOH beforehand. Then, 7.5 mmol of KCl powder was added to the solution. After allowing the solution to evaporate at room temperature for more than a week, plate crystals of the title compounds were obtained. All the crystals, from (1) to (6), are very efflorescent and the X-ray diffraction experiments were carried out by sealing the crystals in glass capillaries.

Crystal data for compounds (1)–(6) are listed in Table 1. A summary of the experimental conditions for crystals (1), (2) and (6) is listed in Table 2. Fractional coordinates for the W and lanthanide atoms were taken from those in the isomorphous $K_3Na_4H_2[TbW_{10}O_{36}].20H_2O$ (5) crystal and coordinates for the other atoms were obtained from the difference Fourier syntheses. W, lanthanide, K and Na atoms were refined with anisotropic thermal parameters and O atoms were refined isotropically. Atomic parameters for (1), (2) and (6) are listed in Tables 3, 4 and 5, respectively.*

Results and discussion

Compounds (1)–(6) crystallize in isomorphous lattices with space group $P2_1/n$, $a = 29.772$–30.057, $b = 16.051$–16.164, $c = 11.443$–11.468 Å, $\beta = 96.01$–96.52°, $V = 5458$–5497 Å^3 and $Z = 4$. Fractional coordinates for the atoms are almost identical among these six crystals except for a few O atoms of the water molecules of crystallization, some of which are disordered. Fig. 1 shows the structure of the decatungstopraseodate anion with its proximate K^+ cations in crystal (1). The other five decatungstolanthanoate anions exhibit a similar structure. The $[LnW_{10}O_{36}]^{9-}$ anion is comprised of two $[W_5O_{18}]^{6-}$ groups and a central trivalent lanthanide

---

Table 1. *Crystal data for crystals* (1)–(6)

	(1)	(2)	(3)	(4)	(5)	(6)
Ln	Pr	Nd	Sm	Gd	Tb	Dy
(Atomic number)	(59)	(60)	(62)	(64)	(65)	(66)
Formula	$K_3Na_4H_2[PrW_{10}O_{36}]$.- $22H_2O$	$K_3Na_4H_2[NdW_{10}O_{36}]$.- $22H_2O$	$K_3Na_4H_2[SmW_{10}O_{36}]$.- $22H_2O$	$K_3Na_4H_2[GdW_{10}O_{36}]$.- $21H_2O$	$K_3Na_4H_2[TbW_{10}O_{36}]$.- $20H_2O$	$K_3Na_4H_2[DyW_{10}O_{36}]$.- $21H_2O$
Formula weight	3163.0	3166.3	3172.5	3161.3	3145.0	3166.6
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	30.049 (4)	30.057 (5)	29.894 (5)	29.920 (5)	29.772 (8)	29.816 (6)
b (Å)	16.055 (2)	16.051 (4)	16.072 (3)	16.103 (5)	16.164 (2)	16.097 (4)
c (Å)	11.462 (2)	11.468 (2)	11.446 (3)	11.449 (3)	11.443 (1)	11.443 (2)
β (°)	96.36 (1)	96.52 (2)	96.32 (2)	96.36 (1)	96.01 (2)	96.36 (2)
V (Å³)	5496 (1)	5497 (2)	5466 (3)	5482 (4)	5476 (2)	5458 (2)
Z	4	4	4	4	4	4
Crystal habit	Plate	Plate	Plate	Plate	Plate	Plate
Crystal color	Pale purple	Pale green	Colorless	Colorless	Colorless	Colorless

Table 2. *Experimental parameters for crystals* (1), (2) *and* (6)

	(1)	(2)	(6)
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	0.71069	0.71069
Crystal size (mm)	0.36 × 0.10 × 0.04	0.28 × 0.08 × 0.06	0.25 × 0.08 × 0.08
Temperature (K)	298	298	298
Scan method	$\omega/2\theta$	$\omega/2\theta$	ω/θ
Absorption correction		Empirical *via* ψ scan (North, Phillips & Mathews, 1968)	
Transmission factors	0.432–1.000	0.818–1.000	0.559–1.000
No. of measured reflections	13713	13713	13621
No. of independent reflections	13078	13078	12987
No. of observed reflections	7990	6432	6114
Criterion for observed	$I_{obs} > 3\sigma(I_{obs})$	$I_{obs} > 3\sigma(I_{obs})$	$I_{obs} > 3\sigma(I_{obs})$
θ_{max} (°)	27.5	27.5	27.5
Range of indices	$-39 \le h \le 38$ $0 \le k \le 20$ $0 \le l \le 14$	$-39 \le h \le 38$ $0 \le k \le 20$ $0 \le l \le 14$	$-38 \le h \le 38$ $0 \le k \le 20$ $0 \le l \le 14$
Final R, wR	0.056, 0.062	0.052, 0.041	0.053, 0.044
S	2.35	1.68	1.55
No. of parameters, reflections	395, 7990	395, 6432	391, 6114
Weighting scheme	$[\sigma^2(F) + (0.005F)^2]^{-1}$	$[\sigma^2(F) + (0.001F)^2]^{-1}$	$[\sigma^2(F) + (0.001F)^2]^{-1}$
$(\Delta/\sigma)_{max}$	0.01	0.02	0.01
$\Delta\rho_{max}$ (e Å⁻³)	4.01	3.03	3.50
$\Delta\rho_{min}$ (e Å⁻³)	−2.94	−2.80	−2.49
Program used for data reduction and refinement	*TEXSAN* (Molecular Structure Corporation, 1989)		

cation. Two square arrays of O atoms from two $[W_5O_{18}]^{6-}$ moieties, each of which is derived by the removal of a WO^{4+} group from a $[W_6O_{19}]^{2-}$ anion, sandwich the central lanthanide atom by twisting about 45° from each other to make the square antiprismatic coordination around the lanthanide atom. The whole anion has approximate point symmetry of D_{4d}, based

on which the W and O atoms in the anion are classified into two and six categories, respectively. The eight W atoms close to the central lanthanide atom will hereafter be referred to as belt W atoms and the other two W atoms will be called cap W atoms. O atoms can be classified as follows: I, terminal O atom attached to a cap W atom; II, terminal O atom attached to a belt W atom; III, O atom bridging a cap and a belt W atom; IV, O atom bridging two belt W atoms; V, O atom bridging a belt W and the central lanthanide atoms; VI, central O atom shared by one cap and four belt W atoms. The W—O bonds in the anion can be classified into seven categories as depicted in Fig. 1: (*a*) terminal bond between a cap W atom and an O atom of type I; (*b*) terminal bond between a belt W atom and an O atom of type II; (*c*) bond between a cap W atom and an O atom of type III; (*d*) bond between a belt W atom and an O atom of type III; (*e*) bond between a belt W atom and an O atom of type IV; (*f*) bond between a belt W atom and an O atom of type V; (*g*) bond between a cap W atom and an O atom of type VI; (*h*) bond between a belt W atom and an O atom of type VI. Unlike the other salts in this series of compounds, where the dihedral twofold axes were observed either crystallographically (Iball, Low & Weakley, 1974) or approximately (Sugeta & Yamase, 1993; Yamase, Ozeki & Ueda, 1993; Ozeki & Yamase, 1994; Yamase, Ozeki & Tosaka, in preparation), the dihedral twofold symmetry of the anions is lost in all crystals (1)-(6) with the degradation of their approximate point symmetry from D_{4d} to C_{4v}. Thus, the two $[W_5O_{18}]^{6-}$ units are not equivalent. The fragment incorporating W0-W4 will be referred to as fragment A and the other as B.

Interatomic distances in the six anions are averaged based on the categories described above and summarized in Table 6. In all six $[LnW_{10}O_{36}]^{9-}$ anions investigated, the Ln—W_{belt} distances were found to be asymmetric for the W atoms in fragments A and B, while the Ln—O

Table 3. *Fractional coordinates and equivalent iso-tropic or isotropic thermal parameters* (Å^2) *for the atoms in the* $K_3Na_4H_2[PrW_{10}O_{36}].22H_2O$ *crystal*

W, Pr, K and Na atoms were refined anisotropically.

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
W0	0.58796 (4)	0.20502 (7)	0.4597 (1)	0.0247
W1	0.66467 (4)	0.08688 (6)	0.61770 (10)	0.0220
W2	0.67196 (4)	0.28931 (6)	0.63579 (10)	0.0212
W3	0.67170 (4)	0.30274 (6)	0.35171 (9)	0.0204
W4	0.66500 (4)	0.09966 (6)	0.33337 (10)	0.0211
W5	0.95661 (4)	0.17415 (7)	0.58256 (9)	0.0214
W6	0.87392 (4)	0.17276 (6)	0.75382 (9)	0.0195
W7	0.87443 (4)	0.03347 (6)	0.54382 (10)	0.0194
W8	0.87806 (4)	0.18206 (7)	0.35009 (9)	0.0196
W9	0.87794 (4)	0.32208 (6)	0.55977 (10)	0.0203
Pr	0.77335 (5)	0.18321 (9)	0.5141 (1)	0.0174
K1	0.7813 (3)	-0.0038 (4)	0.7423 (6)	0.0469
K2	0.7958 (4)	0.3737 (4)	0.2857 (6)	0.0388
K3	0.9228 (2)	-0.0680 (4)	0.2901 (6)	0.0354
Na1	0.2588 (4)	0.2069 (6)	0.4841 (9)	0.0364
Na2	0.6220 (4)	0.1851 (8)	0.905 (1)	0.0495
Na3	0.7506 (4)	0.0760 (6)	0.0275 (10)	0.0338
Na4	0.9975 (5)	0.0643 (9)	0.122 (1)	0.0506
O1	0.5299 (8)	0.211 (1)	0.448 (2)	0.051 (6)
O2	0.6000 (7)	0.116 (1)	0.570 (2)	0.035 (5)
O3	0.6046 (7)	0.280 (1)	0.591 (2)	0.034 (5)
O4	0.6046 (6)	0.290 (1)	0.358 (1)	0.024 (4)
O5	0.5991 (6)	0.127 (1)	0.343 (2)	0.027 (4)
O6	0.6572 (7)	0.006 (1)	0.709 (2)	0.033 (5)
O7	0.6689 (7)	0.362 (1)	0.747 (2)	0.032 (5)
O8	0.6663 (6)	0.383 (1)	0.249 (2)	0.027 (4)
O9	0.6570 (6)	0.028 (1)	0.221 (2)	0.027 (4)
O10	0.6648 (6)	0.185 (1)	0.716 (2)	0.028 (4)
O11	0.6693 (6)	0.3625 (10)	0.500 (1)	0.022 (4)
O12	0.6636 (6)	0.204 (1)	0.253 (2)	0.026 (4)
O13	0.6573 (6)	0.028 (1)	0.469 (2)	0.029 (4)
O14	0.6643 (6)	0.1966 (9)	0.483 (1)	0.019 (4)
O15	0.7239 (6)	0.0927 (10)	0.617 (1)	0.022 (4)
O16	0.7309 (6)	0.2717 (10)	0.634 (2)	0.023 (4)
O17	0.7305 (6)	0.286 (1)	0.376 (2)	0.026 (4)
O18	0.7239 (7)	0.104 (1)	0.363 (2)	0.030 (5)
O19	0.8144 (6)	0.171 (1)	0.712 (2)	0.029 (4)
O20	0.8154 (6)	0.0467 (10)	0.526 (1)	0.022 (4)
O21	0.8184 (6)	0.1886 (10)	0.349 (1)	0.021 (4)
O22	0.8178 (6)	0.3117 (10)	0.536 (1)	0.020 (4)
O23	0.8806 (6)	0.166 (1)	0.908 (2)	0.027 (4)
O24	0.8829 (6)	-0.071 (1)	0.535 (2)	0.027 (4)
O25	0.8873 (6)	0.187 (1)	0.199 (2)	0.031 (4)
O26	0.8865 (7)	0.426 (1)	0.572 (2)	0.038 (5)
O27	0.8772 (5)	0.0553 (9)	0.711 (1)	0.014 (4)
O28	0.8803 (5)	0.0660 (9)	0.384 (1)	0.014 (4)
O29	0.8829 (5)	0.2996 (9)	0.397 (1)	0.015 (3)
O30	0.8792 (6)	0.2893 (10)	0.721 (2)	0.023 (4)
O31	0.8783 (7)	0.176 (1)	0.555 (2)	0.042 (5)
O32	0.9391 (6)	0.1691 (9)	0.735 (1)	0.018 (4)
O33	0.9406 (6)	0.062 (1)	0.565 (2)	0.026 (4)
O34	0.9435 (6)	0.1800 (10)	0.418 (1)	0.021 (4)
O35	0.9425 (7)	0.289 (1)	0.583 (2)	0.032 (5)
O36	1.0141 (6)	0.172 (1)	0.600 (2)	0.029 (4)
O37	0.7494 (6)	0.1703 (10)	0.868 (1)	0.022 (4)
O38	0.2535 (7)	0.071 (1)	0.553 (2)	0.039 (5)
O39	0.7534 (7)	0.203 (1)	0.147 (2)	0.034 (5)
O40	0.7666 (7)	0.009 (1)	0.208 (2)	0.038 (5)
O41	0.2616 (8)	0.057 (1)	0.065 (2)	0.054 (6)
O42	0.0767 (7)	0.052 (1)	0.115 (2)	0.033 (5)
O43	0.0027 (7)	0.094 (1)	0.900 (2)	0.043 (6)
O44	0.6684 (8)	0.075 (1)	0.992 (2)	0.046 (6)
O45	0.2850 (7)	0.143 (1)	0.315 (2)	0.044 (6)
O46	0.9954 (7)	0.049 (1)	0.324 (2)	0.041 (5)
O47	0.9189 (7)	0.035 (1)	0.102 (2)	0.043 (6)
O48	0.1754 (7)	0.211 (1)	0.490 (2)	0.041 (5)
O49	0.8213 (7)	0.039 (1)	0.968 (2)	0.040 (5)
O50	0.0751 (8)	0.213 (1)	0.312 (2)	0.055 (7)

Table 3 (*cont.*)

	x	y	z	U_{eq}/U_{iso}
O51	0.5797 (8)	0.204 (1)	0.083 (2)	0.058 (7)
O52	0.3341 (8)	0.190 (1)	0.580 (2)	0.053 (6)
O53	0.969 (1)	0.218 (2)	0.092 (3)	0.12 (1)
O54	0.4954 (9)	0.205 (2)	0.814 (2)	0.072 (8)
O55	0.573 (1)	0.076 (2)	0.823 (3)	0.11 (1)
O56	0.430 (2)	0.063 (3)	0.776 (5)	0.21 (2)
O57	0.509 (2)	0.081 (3)	0.049 (5)	0.25 (3)
O58	0.464 (2)	0.124 (3)	0.322 (5)	0.23 (3)

Table 4. *Fractional coordinates and equivalent iso-tropic or isotropic thermal parameters* (Å^2) *for the atoms in the* $K_3Na_4H_2[NdW_{10}O_{36}].22H_2O$ *crystal*

W, Nd, K and Na atoms were refined anisotropically.

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
W0	0.58832 (4)	0.20472 (8)	0.4599 (1)	0.0247
W1	0.66503 (4)	0.08679 (8)	0.6189 (1)	0.0215
W2	0.67245 (4)	0.28941 (8)	0.6356 (1)	0.0208
W3	0.67201 (4)	0.30218 (8)	0.35173 (10)	0.0201
W4	0.66530 (4)	0.09901 (7)	0.3347 (1)	0.0202
W5	0.95630 (4)	0.17366 (8)	0.58347 (10)	0.0211
W6	0.87373 (4)	0.17265 (8)	0.75455 (9)	0.0194
W7	0.87406 (4)	0.03285 (7)	0.5457 (1)	0.0190
W8	0.87751 (3)	0.18087 (8)	0.35102 (9)	0.0196
W9	0.87751 (4)	0.32148 (8)	0.5598 (1)	0.0198
Nd	0.77332 (5)	0.1828 (1)	0.5151 (1)	0.0174
K1	0.7807 (3)	-0.0035 (5)	0.7433 (7)	0.0536
K2	0.7950 (2)	0.3734 (4)	0.2856 (6)	0.0372
K3	0.9225 (2)	-0.0681 (5)	0.2919 (7)	0.0410
Na1	0.2580 (4)	0.2072 (7)	0.483 (1)	0.0355
Na2	0.6214 (4)	0.1849 (9)	0.913 (1)	0.0466
Na3	0.7505 (4)	0.0761 (8)	0.026 (1)	0.0329
Na4	0.9970 (4)	0.0665 (10)	0.122 (1)	0.0515
O1	0.5301 (7)	0.212 (1)	0.443 (2)	0.043 (6)
O2	0.6007 (6)	0.114 (1)	0.565 (2)	0.032 (5)
O3	0.6050 (6)	0.283 (1)	0.587 (2)	0.027 (5)
O4	0.6058 (6)	0.290 (1)	0.362 (1)	0.025 (5)
O5	0.5999 (6)	0.124 (1)	0.349 (2)	0.024 (5)
O6	0.6590 (6)	0.007 (1)	0.715 (2)	0.034 (5)
O7	0.6701 (7)	0.363 (1)	0.750 (2)	0.039 (6)
O8	0.6679 (6)	0.384 (1)	0.251 (2)	0.030 (5)
O9	0.6585 (6)	0.028 (1)	0.220 (2)	0.031 (5)
O10	0.6650 (6)	0.183 (1)	0.716 (1)	0.026 (4)
O11	0.6704 (6)	0.361 (1)	0.498 (2)	0.026 (5)
O12	0.6647 (6)	0.203 (1)	0.252 (1)	0.025 (5)
O13	0.6590 (6)	0.030 (1)	0.470 (2)	0.023 (4)
O14	0.6640 (5)	0.195 (1)	0.485 (1)	0.020 (4)
O15	0.7240 (6)	0.091 (1)	0.619 (1)	0.017 (4)
O16	0.7313 (5)	0.273 (1)	0.634 (1)	0.014 (4)
O17	0.7310 (6)	0.284 (1)	0.381 (1)	0.019 (4)
O18	0.7249 (6)	0.102 (1)	0.365 (2)	0.021 (4)
O19	0.8136 (5)	0.171 (1)	0.712 (1)	0.020 (4)
O20	0.8146 (6)	0.049 (1)	0.526 (2)	0.022 (5)
O21	0.8166 (5)	0.185 (1)	0.347 (1)	0.027 (5)
O22	0.8164 (6)	0.311 (1)	0.539 (1)	0.023 (4)
O23	0.8805 (6)	0.169 (1)	0.909 (1)	0.027 (5)
O24	0.8814 (6)	-0.072 (1)	0.539 (2)	0.023 (5)
O25	0.8859 (5)	0.185 (1)	0.202 (1)	0.023 (4)
O26	0.8851 (6)	0.427 (1)	0.567 (2)	0.027 (5)
O27	0.8770 (6)	0.052 (1)	0.712 (2)	0.019 (4)
O28	0.8789 (6)	0.063 (1)	0.384 (2)	0.027 (5)
O29	0.8836 (5)	0.300 (1)	0.395 (1)	0.018 (4)
O30	0.8788 (6)	0.290 (1)	0.726 (2)	0.026 (5)
O31	0.8783 (5)	0.175 (1)	0.556 (1)	0.014 (4)
O32	0.9397 (5)	0.168 (1)	0.740 (1)	0.018 (4)
O33	0.9414 (6)	0.060 (1)	0.570 (1)	0.017 (4)
O34	0.9446 (5)	0.179 (1)	0.416 (1)	0.017 (4)
O35	0.9426 (6)	0.290 (1)	0.582 (1)	0.023 (4)
O36	1.0137 (6)	0.174 (1)	0.598 (1)	0.027 (5)
O37	0.7488 (5)	0.170 (1)	0.868 (1)	0.023 (4)

Table 4 (cont.)

	x	y	z	U_{eq}/U_{iso}
O38	0.2544 (6)	0.071 (1)	0.548 (2)	0.029 (5)
O39	0.7546 (6)	0.201 (1)	0.152 (2)	0.029 (5)
O40	0.7679 (7)	0.008 (1)	0.208 (2)	0.038 (6)
O41	0.2618 (7)	0.058 (1)	0.057 (2)	0.049 (7)
O42	0.0766 (6)	0.049 (1)	0.113 (2)	0.034 (5)
O43	0.0037 (7)	0.095 (1)	0.903 (2)	0.049 (6)
O44	0.6702 (7)	0.076 (1)	0.988 (2)	0.034 (5)
O45	0.2851 (7)	0.143 (1)	0.317 (2)	0.053 (7)
O46	0.9952 (6)	0.048 (1)	0.322 (2)	0.024 (5)
O47	0.9201 (7)	0.034 (1)	0.092 (2)	0.041 (6)
O48	0.1770 (7)	0.210 (1)	0.492 (2)	0.037 (5)
O49	0.8201 (7)	0.039 (1)	0.967 (2)	0.047 (6)
O50	0.0750 (7)	0.211 (1)	0.316 (2)	0.046 (6)
O51	0.5800 (7)	0.207 (2)	0.084 (2)	0.057 (7)
O52	0.3348 (7)	0.188 (2)	0.583 (2)	0.058 (7)
O53	0.966 (1)	0.216 (2)	0.089 (3)	0.12 (1)
O54	0.4950 (8)	0.205 (2)	0.819 (2)	0.062 (7)
O55	0.5733 (9)	0.072 (2)	0.830 (2)	0.077 (9)
O56	0.428 (1)	0.063 (2)	0.792 (3)	0.14 (2)
O57	0.499 (1)	0.056 (2)	0.850 (3)	0.12 (1)
O58	0.460 (1)	0.123 (3)	0.334 (4)	0.20 (2)

Table 5. Fractional coordinates and equivalent isotropic or isotropic thermal parameters (Å^2) for the atoms in the $K_3Na_4H_2[DyW_{10}O_{36}].21H_2O$ crystal

W, Dy, K and Na atoms were refined anisotropically.

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
W0	0.58770 (4)	0.20391 (9)	0.4595 (1)	0.0228
W1	0.66525 (5)	0.08732 (8)	0.6184 (1)	0.0196
W2	0.67230 (4)	0.28847 (8)	0.6349 (1)	0.0185
W3	0.67198 (4)	0.30084 (8)	0.3516 (1)	0.0180
W4	0.66576 (5)	0.09909 (8)	0.3348 (1)	0.0188
W5	0.95575 (4)	0.17359 (8)	0.5807 (1)	0.0199
W6	0.87265 (4)	0.17299 (8)	0.75208 (10)	0.0182
W7	0.87286 (5)	0.03421 (7)	0.5438 (1)	0.0175
W8	0.87629 (4)	0.18090 (8)	0.34942 (10)	0.0179
W9	0.87664 (4)	0.32059 (8)	0.5578 (1)	0.0183
Dy	0.77255 (5)	0.18305 (9)	0.5145 (1)	0.0155
K1	0.7789 (3)	−0.0036 (5)	0.7428 (7)	0.0435
K2	0.7939 (3)	0.3740 (5)	0.2851 (7)	0.0367
K3	0.9228 (2)	−0.0686 (4)	0.2922 (6)	0.0291
Na1	0.2580 (5)	0.2071 (8)	0.480 (1)	0.0344
Na2	0.6219 (4)	0.1850 (9)	0.910 (1)	0.0413
Na3	0.7516 (5)	0.0758 (8)	0.030 (1)	0.0325
Na4	0.9978 (6)	0.065 (1)	0.124 (1)	0.0558
O1	0.5288 (7)	0.210 (1)	0.441 (2)	0.034 (6)
O2	0.6001 (8)	0.115 (1)	0.567 (2)	0.034 (6)
O3	0.6060 (7)	0.280 (1)	0.590 (2)	0.024 (5)
O4	0.6043 (7)	0.289 (1)	0.361 (2)	0.027 (5)
O5	0.5991 (8)	0.124 (1)	0.345 (2)	0.032 (6)
O6	0.6618 (8)	0.010 (1)	0.718 (2)	0.037 (6)
O7	0.6707 (8)	0.362 (1)	0.746 (2)	0.032 (6)
O8	0.6681 (7)	0.383 (1)	0.250 (2)	0.021 (5)
O9	0.6587 (7)	0.029 (1)	0.220 (2)	0.019 (5)
O10	0.6650 (6)	0.183 (1)	0.716 (2)	0.022 (5)
O11	0.6706 (7)	0.363 (1)	0.500 (2)	0.019 (5)
O12	0.6654 (7)	0.203 (1)	0.247 (2)	0.025 (5)
O13	0.6591 (7)	0.028 (1)	0.469 (2)	0.021 (5)
O14	0.6624 (6)	0.195 (1)	0.483 (1)	0.013 (4)
O15	0.7245 (6)	0.095 (1)	0.617 (2)	0.015 (4)
O16	0.7313 (6)	0.269 (1)	0.632 (2)	0.013 (4)
O17	0.7317 (7)	0.283 (1)	0.385 (2)	0.016 (5)
O18	0.7251 (7)	0.106 (1)	0.371 (2)	0.020 (5)
O19	0.8127 (6)	0.170 (1)	0.704 (2)	0.021 (5)
O20	0.8115 (7)	0.052 (1)	0.523 (2)	0.017 (5)
O21	0.8162 (6)	0.186 (1)	0.352 (2)	0.023 (5)
O22	0.8160 (6)	0.309 (1)	0.537 (1)	0.017 (4)
O23	0.8781 (7)	0.171 (1)	0.904 (2)	0.033 (6)
O24	0.8790 (7)	−0.073 (1)	0.534 (2)	0.020 (5)

Table 5 (cont.)

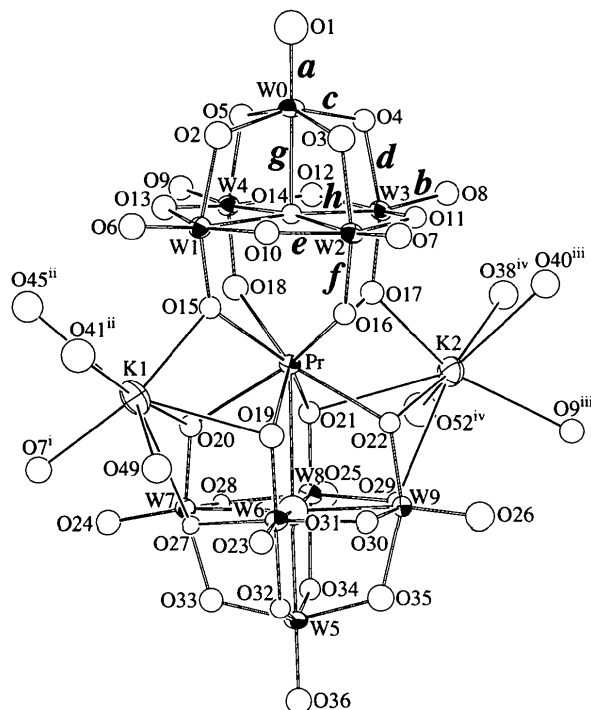|	x	y	z	U_{eq}/U_{iso}
O25	0.8836 (8)	0.184 (2)	0.201 (2)	0.043 (6)
O26	0.8834 (7)	0.428 (1)	0.562 (2)	0.028 (5)
O27	0.8773 (7)	0.054 (1)	0.709 (2)	0.022 (5)
O28	0.8784 (7)	0.063 (1)	0.383 (2)	0.019 (5)
O29	0.8813 (7)	0.298 (1)	0.393 (2)	0.025 (5)
O30	0.8785 (7)	0.291 (1)	0.721 (2)	0.025 (5)
O31	0.8783 (7)	0.175 (1)	0.554 (2)	0.020 (4)
O32	0.9390 (7)	0.169 (1)	0.740 (2)	0.029 (5)
O33	0.9422 (7)	0.058 (1)	0.568 (2)	0.022 (5)
O34	0.9425 (6)	0.177 (1)	0.413 (1)	0.018 (4)
O35	0.9424 (7)	0.290 (1)	0.581 (2)	0.021 (5)
O36	1.0136 (7)	0.173 (1)	0.598 (2)	0.033 (6)
O37	0.7487 (7)	0.167 (1)	0.867 (2)	0.026 (5)
O38	0.2538 (7)	0.069 (1)	0.542 (2)	0.021 (5)
O39	0.7543 (7)	0.203 (1)	0.150 (2)	0.030 (5)
O40	0.7692 (8)	0.010 (1)	0.211 (2)	0.041 (7)
O41	0.2611 (8)	0.057 (1)	0.053 (2)	0.035 (6)
O42	0.0780 (8)	0.047 (1)	0.115 (2)	0.035 (6)
O43	0.0034 (9)	0.094 (2)	0.898 (2)	0.044 (7)
O44	0.6698 (8)	0.075 (1)	0.986 (2)	0.039 (6)
O45	0.2848 (8)	0.141 (1)	0.314 (2)	0.042 (7)
O46	0.9958 (7)	0.046 (1)	0.322 (2)	0.028 (5)
O47	0.9200 (8)	0.035 (2)	0.097 (2)	0.043 (7)
O48	0.1758 (9)	0.211 (2)	0.492 (2)	0.047 (7)
O49	0.8208 (8)	0.034 (2)	0.966 (2)	0.045 (7)
O50	0.0719 (10)	0.209 (2)	0.316 (2)	0.071 (9)
O51	0.5789 (9)	0.207 (2)	0.085 (2)	0.062 (8)
O52	0.3333 (8)	0.184 (2)	0.578 (2)	0.050 (7)
O53	0.967 (1)	0.213 (3)	0.094 (3)	0.14 (2)
O54	0.4949 (9)	0.205 (2)	0.821 (2)	0.066 (9)
O55	0.574 (1)	0.069 (2)	0.829 (3)	0.11 (1)
O56	0.495 (2)	0.050 (3)	0.850 (4)	0.17 (2)
O57	0.455 (2)	0.124 (3)	0.340 (4)	0.17 (2)

Fig. 1. ORTEP (Johnson, 1976) drawing of the $[PrW_{10}O_{36}]^{9-}$ anion with its proximate K^+ cations and their coordination spheres. Symmetry codes are as follows: (i) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (ii) $1 - x, -y, 1 - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

distances do not show any distinguishable differences between the two fragments. The average Ln—W_{belt} distance for the W_{belt} atoms in fragment A is 0.04 Å longer than that in fragment B in each of the six structures. The distances from the central lanthanide atom to the least-squares planes defined by the four belt W atoms of the two $[W_5O_{18}]^{6-}$ groups are also different for fragments A and B, where they range from 3.142 to 3.079 Å for fragment A and from 3.071 to 3.027 Å for fragment B. W_{belt}—W_{belt} distances in fragment A are 0.014- 0.018 Å shorter than those in fragment B. The differences in the W_{cap}—W_{belt} distances in the two fragments are within 0.01 Å. This reduction of symmetry originates in the coordination of the two K^+ cations, namely K1 and K2, to the $[LnW_{10}O_{36}]^{9-}$ anion in the vicinity of the central lanthanide atom. As shown in Fig. 1, each K^+ cation has contacts to an O atom of type V in fragment A and two O atoms of type V and an O atom of type IV in fragment B. Consequently, two basal squares of the LnO_8 square antiprism become unequivalent. All four O atoms of type V in fragment B coordinate to the K^+ cations and, therefore, are somewhat extracted outside the polyoxoanion because of the electrostatic attraction between the O and K atoms, while only two in A are pulled outward. As a result, the average O—O distances in the square in B are 0.05-0.07 Å longer than those found in A. Thus, the central lanthanide atom is shifted to

the square in B rather than that in A. In contrast, in other salts of the decatungstolanthanoate anions (Iball, Low & Weakley, 1974; Sugeta & Yamase, 1993; Yamase, Ozeki & Ueda, 1993; Ozeki & Yamase, 1994; Yamase, Ozeki & Tosaka, in preparation) where no cations coordinate to the O atoms of the central LnO_8 square antiprism in the decatungstolanthanoate anions, no distortion of this kind was observed, presumably because the three adjacent O atoms of the central LnO_8 square antiprism can be readily coordinated to K^+ compared with the other cations such as Na^+ and Sr^{2+}. As shown here, the counter-cations in these crystals deform not only the crystal structures but also the molecular structures of the polyoxometalate anions and, in this particular case, the coordination of the central lanthanide atoms, which may influence the luminescence properties of the polyoxometalate solids.

Table 6 also shows the correlations between atomic numbers of the central lanthanide elements and interatomic distances in these decatungstolanthanoate anions. As shown in Fig. 2, the average Ln—O distances change
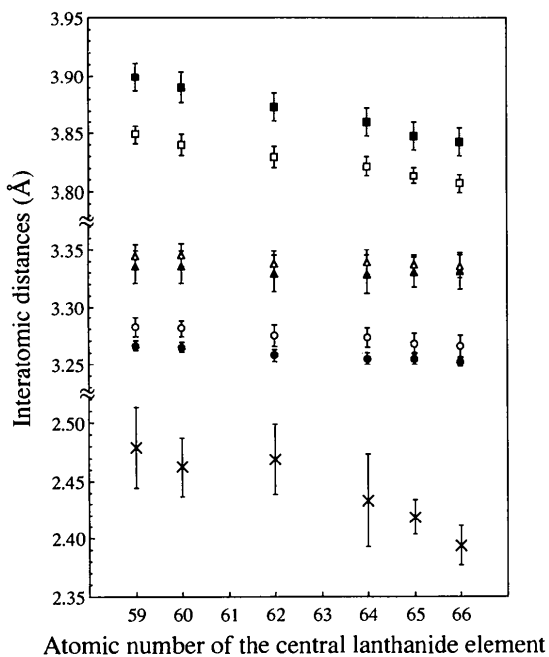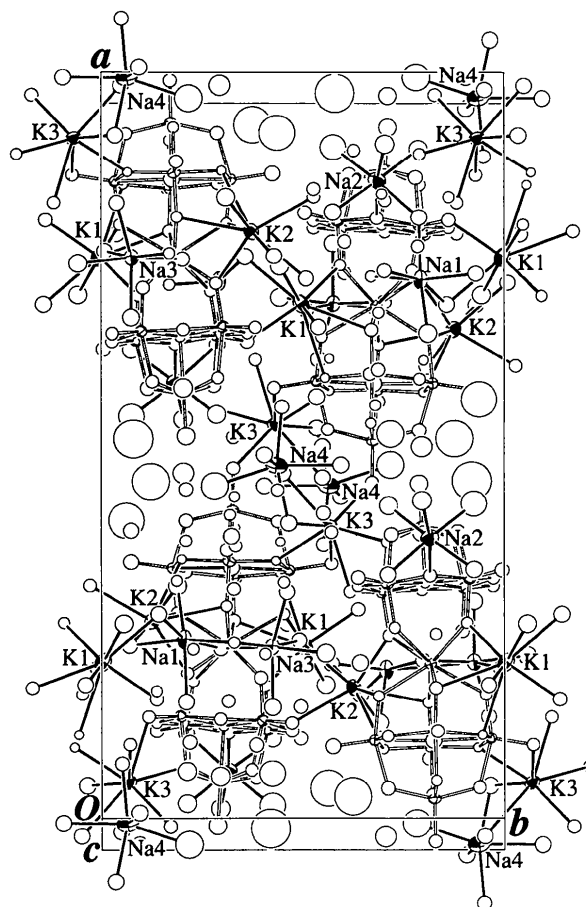

Fig. 2. Correlations between the atomic number of the central lanthanide elements and the averaged interatomic distances in the $[LnW_{10}O_{36}]^{9-}$ anions: (×) Ln—O, (■) Ln—W_{belt} in fragment A, (□) Ln—W_{belt} in fragment B, (●) W_{belt}—W_{belt} in fragment A, (○) W_{belt}—W_{belt} in fragment B, (▲) W_{cap}—W_{belt} in fragment A, (△) W_{cap}—W_{belt} in fragment B.

Fig. 3. Packing diagram of the unit cell of $K_3Na_4H_2[PrW_{10}O_{36}].22H_2O$ viewed along the c^* axis. K^+—O and Na^+—O contacts are shown as solid spokes.

Table 6. *Averaged interatomic distances* (Å) *in the* $[LnW_{10}O_{36}]^{9-}$ *anions in crystals* (1)–(6)

Bond type	Fragment	Lanthanide (Ln)					
		Pr	Nd	Sm	Gd	Tb	Dy
$Ln—O_V$	A	2.48 (4)	2.48 (2)	2.47 (2)	2.43 (4)	2.42 (1)	2.40 (2)
	B	2.47 (3)	2.45 (2)	2.47 (4)	2.44 (4)	2.41 (2)	2.39 (2)
$W_{cap}—O_I(a)$	A	1.74 (2)	1.74 (2)	1.69 (2)	1.75 (2)	1.71 (2)	1.75 (2)
	B	1.72 (2)	1.72 (2)	1.72 (2)	1.76 (2)	1.71 (2)	1.71 (2)
$W_{belt}—O_{II}(b)$	A	1.73 (2)	1.74 (2)	1.73 (2)	1.76 (2)	1.74 (1)	1.73 (2)
	B	1.73 (4)	1.73 (2)	1.75 (2)	1.76 (3)	1.74 (1)	1.73 (2)
$W_{cap}—O_{III}(c)$	A	1.92 (2)	1.90 (3)	1.93 (3)	1.93 (4)	1.92 (2)	1.91 (3)
	B	1.88 (1)	1.91 (1)	1.94 (2)	1.96 (2)	1.92 (2)	1.92 (1)
$W_{belt}—O_{III}(d)$	A	2.03 (1)	2.02 (1)	1.97 (3)	1.96 (5)	2.03 (1)	2.02 (2)
	B	2.01 (2)	2.04 (3)	2.00 (5)	1.97 (5)	2.01 (1)	2.03 (3)
$W_{belt}—O_{IV}(e)$	A	1.94 (2)	1.93 (2)	1.95 (3)	1.97 (3)	1.95 (2)	1.95 (2)
	B	1.93 (2)	1.95 (3)	1.93 (4)	1.95 (3)	1.94 (2)	1.94 (2)
$W_{belt}—O_V(f)$	A	1.78 (1)	1.78 (1)	1.76 (1)	1.79 (1)	1.77 (1)	1.79 (1)
	B	1.79 (1)	1.82 (1)	1.75 (2)	1.76 (2)	1.80 (1)	1.81 (2)
$W_{cap}—O_{VI}(g)$	A	2.29 (2)	2.26 (2)	2.23 (2)	2.26 (2)	2.24 (1)	2.22 (2)
	B	2.34 (2)	2.33 (2)	2.32 (2)	2.30 (2)	2.28 (1)	2.29 (2)
$W_{belt}—O_{VI}(h)$	A	2.31 (2)	2.31 (2)	2.31 (3)	2.31 (5)	2.31 (1)	2.31 (1)
	B	2.32 (2)	2.32 (3)	2.32 (2)	2.32 (3)	2.31 (2)	2.31 (3)
$Ln—W_{belt}$	A	3.899 (12)	3.889 (13)	3.872 (12)	3.860 (12)	3.848 (12)	3.843 (12)
	B	3.849 (9)	3.841 (10)	3.829 (9)	3.822 (8)	3.814 (7)	3.807 (8)
$W_{belt}—W_{belt}$	A	3.266 (4)	3.265 (4)	3.258 (5)	3.255 (4)	3.255 (5)	3.252 (4)
	B	3.282 (8)	3.281 (7)	3.275 (9)	3.273 (8)	3.269 (9)	3.266 (8)
$W_{cap}—W_{belt}$	A	3.335 (14)	3.335 (14)	3.329 (16)	3.328 (17)	3.330 (13)	3.330 (16)
	B	3.343 (10)	3.344 (10)	3.338 (12)	3.339 (11)	3.337 (8)	3.335 (11)
$O_V—O_V$	A	2.92 (2)	2.92 (1)	2.90 (3)	2.86 (4)	2.86 (3)	2.83 (1)
	B	2.98 (7)	2.97 (5)	2.95 (3)	2.92 (4)	2.92 (3)	2.90 (5)
W0—W5		11.022 (2)	11.001 (2)	10.967 (3)	10.948 (3)	10.927 (3)	10.919 (3)

from 2.48 to 2.39 Å in accordance with the change in atomic numbers of the central lanthanide elements, which range from 59 to 66. This variation originates in the change of ionic radii of the central lanthanide elements as a result of the lanthanide contraction. The variation of the ionic radii of the lanthanide cations from 1.013 Å for Pr^{3+} to 0.908 Å for Dy^{3+} is reflected in the Ln—O distances. This change induces the change in Ln—W_{belt} distances, which range from 3.899 to 3.843 Å in fragment A and from 3.849 to 3.807 Å in fragment B. The W_{belt}—W_{belt} distances show a similar but not so significant correlation. They range from 3.266 to 3.252 Å in fragment A and from 3.282 to 3.266 Å in fragment B. The W_{cap}—W_{belt} distances show no systematic variations over the six anions. This change in Ln—W and W—W distances results in the contraction of the apical lengths of the $[LnW_{10}O_{36}]^{9-}$ anions, which is exemplified by the distances between the W0 and W5 atoms ranging from 11.022 Å for Pr^{3+} to 10.919 Å for Dy^{3+}. This change in size of the decatungstolanthanoate anion influences the cell constants of these crystals. The length of the a axis was found to be contracted, correlating to the

atomic number of the central lanthanide elements, while the lengths of axes b and c do not show any significant correlations. As shown in the packing diagram in Fig. 3, the a axis is parallel to the apical direction of the $[LnW_{10}O_{36}]^{9-}$ anion, the length of which correlates with the atomic number of the central lanthanide elements.

References

IBALL, J., LOW, J. N. & WEAKLEY, T. J. R. (1974). *J. Chem. Soc. Dalton Trans.* pp. 2021-2024.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A24, 351-359.

OZEKI, T., TAKAHASHI, M. & YAMASE, T. (1992). *Acta Cryst.* C48, 1370-1374.

OZEKI, T. & YAMASE, T. (1993). *Acta Cryst.* C49, 1574-1577.

OZEKI, T. & YAMASE, T. (1994). *Acta Cryst.* C50. In the press.

SUGETA, M. & YAMASE, T. (1993). *Bull. Chem. Soc. Jpn*, 66, 444-449.

YAMASE, T. & OZEKI, T. (1993). *Acta Cryst.* C49, 1577-1580.

YAMASE, T., OZEKI, T. & UEDA, K. (1993). *Acta Cryst.* C49, 1572-1574.