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The Monoclinic Perovskites Sr_2CaUO_6 and Ba_2SrUO_6. A Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. Sr_2CaUO_6, $M_r = 549\cdot35$, monoclinic, $P2_1/n$. At $T = 295$ K, $a = 5\cdot9377\ (2)$, $b = 6\cdot0734\ (2)$, $c = 8\cdot4563\ (3)$ Å, $\beta = 90\cdot14\ (1)°$, $V = 304\cdot95\ (3)$ Å^3, $Z = 2$, $D_x = 5\cdot983\ (1)$ Mg m^{-3}, $\mu R = 0\cdot12$ [$\lambda = 2\cdot5791\ (4)$ Å, $R_{wp} = 6\cdot36\%$]. Ba_2SrUO_6, $M_r = 696\cdot33$, monoclinic, $P2_1/n$. At $T = 295$ K, $a = 6\cdot2501\ (4)$, $b = 6\cdot2697\ (4)$, $c = 8\cdot8355\ (6)$ Å, $\beta = 89\cdot760\ (8)°$, $V = 346\cdot22\ (2)$ Å^3, $Z = 2$, $D_x = 6\cdot680\ (1)$ Mg m^{-3}, $\mu R = 0\cdot17$ [$\lambda = 2\cdot5791\ (4)$ Å, $R_{wp} = 6\cdot40\%$]. The structures have been refined by Rietveld analysis of neutron powder diffraction data recorded at room temperature for 147 (Sr_2CaUO_6) and 168 (Ba_2SrUO_6) reflections. The structures are of a monoclinic $GdFeO_3$-type perovskite. The octahedra ions are in complete order.

Introduction. In a research program to investigate perovskites or related structures as a host lattice for nuclear waste we investigated the monoclinic perovskites $A_2BB'O_6$ with A = Ba, Sr, Ca, B = Sr, Ca and B' = W, U.

Sleight & Ward (1962) first reported Sr_2CaUO_6 to be an orthorhombic perovskite and Rudorf & Pfitzer (1954) described Ba_2SrUO_6 as cubic. Kemmler-Sack & Seemann (1975) also reported Sr_2CaUO_6 and Ba_2SrUO_6 but they did not describe their structures. The structure of Sr_2CaUO_6 attracted our special attention because we observed twinning in this compound with high-resolution electron microscopy (Groen, Zandbergen & IJdo, 1987). Charvillat, Band & Besse (1970) report Ba_2SrUO_5 and Sr_2CaUO_5 with lattice parameters close to the lattice parameters reported here for Ba_2SrUO_6 and Sr_2CaUO_6.

Experimental. AR starting materials $BaCO_3$, $SrCO_3$, $CaCO_3$ and UO_2 were thoroughly mixed in agate mortars in the appropriate ratios. The mixtures were heated to 1373 K for a total of 7 d in air; the samples were cooled to 295 K for regrinding several times. X-ray powder diffraction patterns were obtained with a Philips PW 1050 diffractometer. No other phases were observed in the diffraction pattern. Systematic absences are $h0l$, $h+l = 2n+1$ and $0k0$, $k = 2n+1$ suggesting space group $P2_1/n$. This result is in accordance with electron diffraction data (Siemens Elmiskop 102 electron microscope, double tilt, lift cartridge, 100 kV). Since no single crystals were available Rietveld's (1969) method was used for refinement of neutron powder diffraction data on the powder diffractometer at the Petten High-Flux Reactor; $5 < 2\theta < 163°$ in steps of $0\cdot1°$; neutrons at 295 K from (111) planes of a Cu crystal; pyrolytic graphite with a total thickness of 120 mm as a second-order filter; Soller slits, horizontal divergence $0\cdot5°$, placed between the reactor and the monochromator and in front each of the four ^{3}He counters; sample holder ($\varnothing = 14\cdot46$ mm) consisted of a V tube, closed with Cu plugs fitted with O rings. No precautions to avoid preferred orientation. Maximum absorption correction for Sr_2CaUO_6 is 5%, $\mu R = 0\cdot12$ and maximum absorption correction for Ba_2SrUO_6 is 5%, $\mu R = 0\cdot17$ (Weber, 1967). Background determined by extrapolation between those parts in the diagram containing no contribution from reflections. Statistically expected value of $R_{wp} = 4\cdot20\%$ (Sr_2CaUO_6) and $4\cdot21\%$ (Ba_2SrUO_6).

The structure of Ca_3UO_6 (van Duivenboden & IJdo, 1986) was used as a trial model: Ba, Sr, O(1), O(2), O(3) at (x, y, z); Ca, Sr at ($\frac{1}{2}$,0,0); U at (0,$\frac{1}{2}$,0) for Ba_2SrUO_6 and Sr_2CaUO_6 respectively.

28 parameters in the refinement: a scale factor, three half-width parameters defining the Gaussian-like shape of the reflections, the counter zero error, the unit-cell parameters, the atomic positional parameters, the isotropic thermal parameters and an asymmetry parameter.

Coherent scattering lengths: Ba 5·25, Sr 7·02, Ca 4·90, U 8·42 and O 5·805 fm (Koester, Rauch, Herkens & Schroeder, 1981). The Rietveld program minimizes the function $\chi^2 = \sum_i w_i[y_i(\text{obs.}) - (1/c) \times y_i(\text{calc.})]^2$, where y_i(obs.) and y_i(calc.) are the observed and the calculated data points, w_i is the statistical weight [$1/y_i$(obs.)] allotted to each data point and c is the scale factor. The R factor $R_{wp} = 100[\sum_i w_i \times |y_i(\text{obs.}) - (1/c)y_i(\text{calc.})|^2/\sum_i w_i|y_i(\text{obs.})|^2]^{1/2}$, was calculated. $\Delta/\sigma < 0\cdot3$ in final cycle. E.s.d.'s calculated according to the original Rietveld formulation. Largest correlation matrix element for structural parameters is 0·72 for Sr_2CaUO_6 and 0·64 for Ba_2SrUO_6.

Discussion. Atomic parameters are given in Table 1 and selected atomic distances in Table 2. The agree-

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ments between the observed and calculated profiles of the data are shown in Fig. 1.* The projections of the structures along the *c* axes are shown in Fig. 2.

The structures A_2BUO_6 can be described in each case as a perovskite with nearly regular BO_6 (B = Ca and Sr) and UO_6 octahedra. Each UO_6 octahedron shares corners with six BO_6 octahedra and *vice versa*. The A atoms (A = Sr and Ba) are in bicapped trigonal prisms between the octahedra as can be seen in Fig. 3. An impression of the structures is given in Fig. 4. The UO_6 octahedra are smaller than the BO_6 octahedra. All octahedra are rotated around a fourfold axis parallel to [001] and a twofold axis parallel to [110] of the aristotype (Megaw, 1973). As a result of these rotations the coordination numbers of Ba and Sr are changed from 12 in the aristotype to 8 in the present structure. The mean Ba—O, Sr—O and U—O distances in Ba_2SrUO_6 are 2·91, 2·462 (4) and 2·099 (4) Å respectively [calculated from the Shannon (1976) radii of 2·80, 2·54 and 2·11 Å respectively]. The mean Sr—O, Ca—O and U—O distances in Sr_2CaUO_6 are 2·73, 2·338 (4), 2·079 (4) Å respectively [calculated from the Shannon (1976) radii of 2·63, 2·38 and 2·11 Å respectively].

In Ba_2SrUO_6 the Ba—O distance is too large and the Sr—O distance too short compared with distances calculated from the Shannon (1976) radii. In Sr_2CaUO_6 the Sr—O distance is also too large compared with the distance calculated from the Shannon (1976) radii.

The formulae for the calculation of the rotations of the UO_6 and the BO_6 octahedra around the fourfold axis (parallel to the *c* axis) and the twofold axis (parallel to the *b* axis) are obtained by Groen, van Berkel & IJdo (1986). In Table 3 the rotation angles for the octahedra calculated from the atomic positional parameters are given.

Table 1. *Fractional atomic coordinates and thermal parameters of* Sr_2CaUO_6 *and* Ba_2SrUO_6 *at* 295 K

	x	y	z	B(Å^2)
Sr_2CaUO_6				
Sr	0·5101 (5)	0·5459 (3)	0·2476 (9)	0·63 (5)
Ca	0·5	0	0	0·6 (1)
U	0	0·5	0	0·4 (1)
O1	0·1853 (7)	0·2193 (8)	−0·0572 (6)	0·7 (1)
O2	0·2818 (7)	0·6878 (8)	−0·0479 (6)	0·4 (1)
O3	0·3993 (5)	0·9598 (4)	0·2657 (8)	0·5 (1)
Ba_2SrUO_6				
Ba	0·508 (1)	0·5307 (5)	0·245 (1)	0·82 (7)
Sr	0·5	0	0	0·3 (1)
U	0	0·5	0	0·5 (1)
O1	0·192 (1)	0·233 (1)	−0·0495 (7)	0·8 (2)
O2	0·269 (1)	0·6861 (9)	−0·0432 (9)	1·2 (2)
O3	0·420 (1)	0·9773 (8)	0·2720 (6)	0·8 (2)

Table 2. *Atomic distances* (Å) *at* 295 K

Sr_2CaUO_6		Ba_2SrUO_6	
Sr—O_8 bicapped prism		Ba—O_8 bicapped prism	
Sr—O1	2·528 (7)	Ba—O1	2·715 (9)
	2·813 (6)		2·944 (9)
	3·054 (8)		3·22 (1)
Sr—O2	2·968 (8)	Ba—O2	3·11 (1)
	2·863 (7)		3·06 (1)
	2·531 (7)		2·64 (1)
Sr—O3	2·603 (3)	Ba—O3	2·863 (6)
	2·489 (4)		2·701 (9)
Ca—O_6 octahedra		Sr—O_6 octahedra	
Ca—O1	2·344 (4)	Sr—O1	2·457 (6)
Ca—O2	2·331 (5)	Sr—O2	2·471 (6)
Ca—O3	2·339 (7)	Sr—O3	2·457 (5)
U—O_6 octahedra		U—O_6 octahedra	
U—O1	2·087 (5)	U—O1	2·105 (6)
U—O2	2·066 (4)	U—O2	2·081 (6)
U—O3	2·083 (7)	U—O3	2·083 (5)

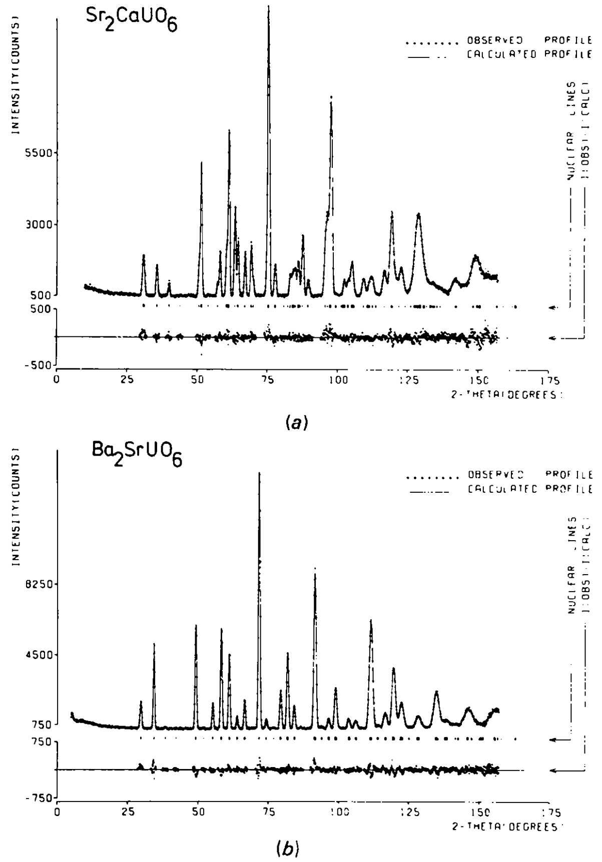

Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of (*a*) Sr_2CaUO_6 and (*b*) Ba_2SrUO_6 at 293 K.

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* A list of numerical values corresponding to the data in Fig. 1 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43688 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The same structure type is found for Nd_2MgTiO_6 (Groen, van Berkel & IJdo, 1986) and Ca_3UO_6 (van Duivenboden & IJdo, 1986). Ringwood (1978) stated that in Synroc the uranium is present in the zirconolith phase. There is however a possibility that uranium is also present in perovskite-like phases such as Ca_3UO_6, Sr_2CaUO_6 or Ba_2SrUO_6.

It is to be noted that some of the fission products in nuclear waste form perovskites with Sr at two different crystallographic positions. Charvillat, Band & Besse (1970) report the compounds A_2BUO_5 (A = Ba, Sr; B = Ba, Sr, Ca and Cd). The small differences in lattice parameters between Sr_2CaUO_5 [$a = 5{\cdot}971\,(5)$, $b = 6{\cdot}079$, $c = 8{\cdot}518\,(5)$ Å, *Pbnm*], Ba_2SrUO_5 [$a = 8{\cdot}852\,(2)$ Å, reported as a cubic compound (*Fm*3*m*)] and also Sr_3UO_5 [$a = 6{\cdot}037\,(5)$, $b = 6{\cdot}194\,(5)$, $c = 9{\cdot}644\,(5)$ Å, *Pbnm*] compared with the lattice parameters reported above and for Sr_3UO_6 [$a = 5{\cdot}959\,(4)$, $b = 6{\cdot}1795\,(22)$, $c = 8{\cdot}5535\,(38)$ Å, $\beta = 90{\cdot}14\,(4)°$] (Loopstra & Rietveld, 1969) suggest that the compounds A_2BUO_5 do not exist, but are oxidized to A_2BUO_6 during synthesis.

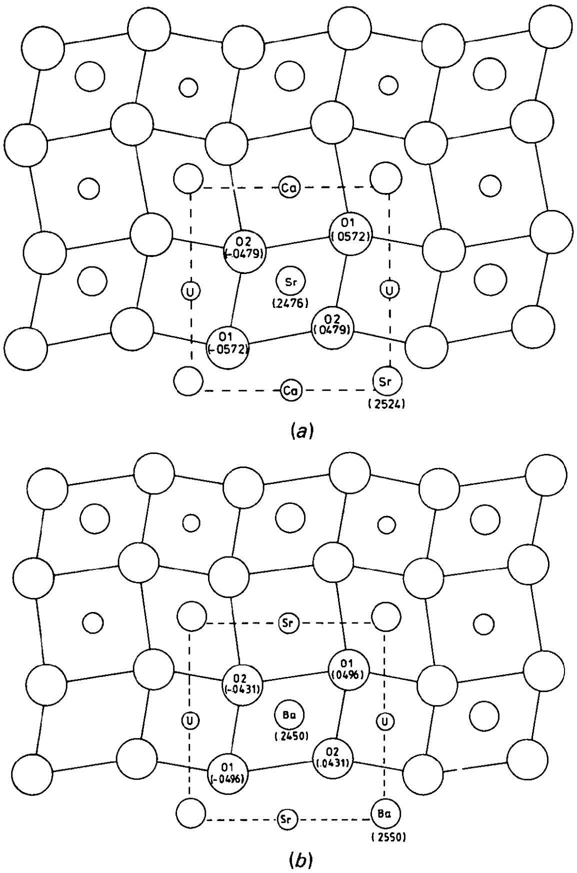

Fig. 2. The structure of (*a*) Sr_2CaUO_6 and (*b*) Ba_2SrUO_6 projected along the *c* axis. Fractional coordinates along the *c* axis are given.

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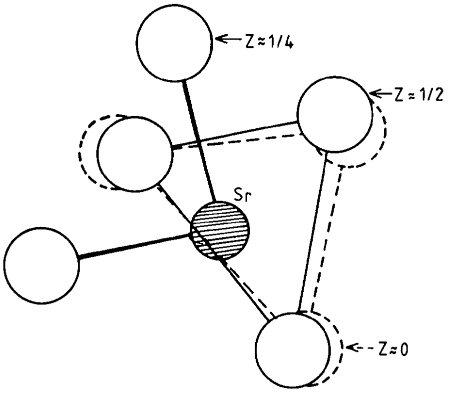

Fig. 3. The coordination of Sr in Sr_2CaUO_6 projected along the *c* axis. Fractional coordinates are indicated.

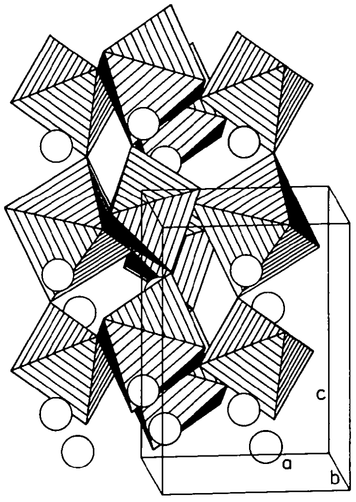

Fig. 4. An impression of the structure of Sr_2CaUO_6.

Table 3. *Rotation angles* (°) *for the* BO_6 *and the* UO_6 *octahedra* (*w is the rotation angle around a fourfold axis and j is the rotation angle around the twofold axis*)

Sr_2CaUO_6		Ba_2SrUO_6	
w(Ca)	10·1 (1)	*w*(Sr)	8·2 (1)
w(U)	11·4 (1)	*w*(U)	9·7 (1)
j(Ca)	11·0 (1)	*j*(Sr)	12·2 (1)
j(U)	12·7 (1)	*j*(U)	14·5 (1)

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Structure of the Binuclear Rhodium(II) Complex Dichloro-di-μ-formato-bis(1,10-phenanthroline)dirhodium(II)

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Abstract. $[Rh_2Cl_2(C_{12}H_8N_2)_2(CHO_2)_2]$, $M_r = 727\cdot2$, orthorhombic, $Pbca$, $a = 24\cdot278\ (10)$, $b = 15\cdot127\ (7)$, $c = 13\cdot398\ (7)$ Å, $V = 4920\ (5)$ Å^3, $Z = 8$, $D_m = 1\cdot96\ (1)$, $D_x = 1\cdot963$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot57$ mm^{-1}, $F(000) = 2864$, $T = 293$ K, final $R = 0\cdot030$ for 3244 reflections. The coordination sphere of each Rh atom is octahedral, consisting of two O atoms from different formato groups [Rh—O 2·063 (3)–2·069 (4) Å], two N atoms of a chelating 1,10-phenanthroline ligand [Rh—N 1·999 (4)–2·010 (4) Å], one Cl atom [Rh—Cl 2·496 (2), 2·504 (1) Å] and one Rh atom [Rh—Rh 2·576 (1) Å]. The Rh atoms are bridged by two formato groups.

Introduction. Rhodium(II) compounds are relatively rare. A number of dimeric and polymeric Rh^{II} carboxylates which contain Rh—Rh bonds have, however, been reported. These are mainly dirhodium(II) tetrakis(μ-carboxylates), but a few compounds with only two or three carboxylato bridges are also known (Boyar & Robinson, 1983). Thus, $Rh_2(\mu\text{-}CH_3COO)_2(dmg)_2(PPh_3)_2.H_2O$ (dmg = dimethylglyoximato) containing two carboxylato bridges and $[Rh_2(dpnp)(\mu\text{-}CH_3COO)_3].PF_6$ [dpnp = 2,7-di(2-pyridyl)-1,8-naphthyridine] with three carboxylato bridges and one naphthyridine bridge have been prepared and their crystal structures determined (Halpern, Kimura, Molin-Case & Wong, 1971; Tikkanen, Binamirs-Soriaga, Kaska & Ford, 1983).

The present paper describes the structure of $Rh_2Cl_2(HCOO)_2(phen)_2$ (phen = 1,10-phenanthroline). Such complexes, as noted in our previous paper (Pasternak, Lancman & Pruchnik, 1985) are precursors of very active ketone hydrogenation catalysts.

Experimental. The compound was prepared by the method described by Pasternak & Pruchnik (1976), dimensions 0·35 × 0·35 × 0·40 mm; density measured in a mixture of CCl_4 and $C_2H_4Br_2$; orthorhombic from Weissenberg photographs, $Pbca$; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, Mo $K\alpha$ radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections $20° \leq 2\theta \leq 30°$ measured on diffractometer; 4336 independent reflections measured; variable θ–2θ scan, scan rate 2·0–29·3° min^{-1} (depending on intensity), $2\theta \leq 50°$; index range h 0 to 28, k 0 to 17, l 0 to 15; two standards measured every 50 reflections, variation in their intensities was ±2·5%; corrected for Lorentz and polarization, not for absorption; 3244 with $I \geq 3\cdot0\sigma(I)$ used for structure determination; calculation performed with Syntex (1976) *XTL/XTLE*; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); structure determined by heavy-atom method, full-matrix least-squares refinement (on F); $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F)$; the positions of all H atoms were calculated, non-H atoms refined with anisotropic thermal parameters; H atoms with fixed coordinates ($B = 5\cdot00$ Å^2); $(\Delta/\sigma)_{max} = 0\cdot01$, $(\Delta\rho)_{max} = 0\cdot3$ e Å^{-3}; $(\Delta\rho)_{min} = 0\cdot3$ e Å^{-3}; $R = 0\cdot030$, $wR = 0\cdot031$, $S = 2\cdot048$; 343 variables, no correction

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