

**Discussion.** The structure determined deviates distinctly from the stoichiometry and the model given by Carim, de Jong & de Leeuw (1988) and Peng *et al.* (1989). It was found that the Y sites were substituted by almost equal parts of Ca and La. The Cu(1) position shows a mixed occupancy by Cu and Al. The aluminium content is much higher than previously seen for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ -type single crystals. The two positions O(1a) and O(1b) are caused by different Cu—O and Al—O bond distances [Cu(1)—O(1b) = 1.88 (2) Å and Al—O(1a) = 1.63 (2) Å]. The occupation of these two O sites corresponds to the Cu to Al ratio. We observe a strikingly short distance between the Ba and the O(1a) site [Ba—O(1a) = 2.34 (1) Å] indicating a partial substitution of Ba by La. A mixing of these two elements on one site cannot be detected by X-ray analysis. X-ray photoelectron spectroscopy investigations are in progress.

No indication was found of either a superstructure (Carim, de Jonge & de Leeuw, 1988) or of orthorhombic symmetry in the case of the present investigations. From  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  it is known that Al doping causes a change in symmetry from orthorhombic to tetragonal. The compound investigated contains a considerable amount of Al. Investigations

into whether the tetragonal symmetry is caused by the Al content or is an intrinsic feature of the  $(\text{La,Ca})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  system are in progress.

We are grateful to D. Thiery for his help with a numerical absorption correction and to Professor Dr Dr h.c. H.G. von Schnering and Dr E. Schönher for supporting our experimental work.

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*Acta Cryst.* (1990). **C46**, 2003–2005

## Structure Refinement of Pyrite-Type Ruthenium Disulfide, $\text{RuS}_2$ , and Ruthenium Diselenide, $\text{RuSe}_2$

BY H. D. LUTZ, B. MÜLLER, TH. SCHMIDT AND TH. STINGL

*Universität Siegen, Anorganische Chemie I, D-5900 Siegen, Federal Republic of Germany*

(Received 12 December 1989; accepted 2 February 1990)

**Abstract.**  $\text{RuS}_2$ :  $M_r = 165.20$ , cubic,  $P\bar{a}3$ ,  $a = 5.6106$  (3) Å,  $V = 176.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 6.21$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 104.32$  cm<sup>-1</sup>,  $F(000) = 304$ ,  $T = 293$  K,  $R = 0.021$  for 573 reflections.  $\text{RuSe}_2$ :  $M_r = 258.99$ , cubic,  $P\bar{a}3$ ,  $a = 5.9336$  (4) Å,  $V = 208.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 8.23$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 414.10$  cm<sup>-1</sup>,  $F(000) = 448$ ,  $T = 293$  K,  $R = 0.021$  for 537 reflections. The intermolecular distances of the  $\text{S}_2$  and  $\text{Se}_2$  dumbbells are much smaller than the sums of the corresponding van der Waals radii. The intra-ionic Se—Se bond length of  $\text{RuSe}_2$  [2.4532 (2) Å] resembles the sum of the covalent radii for tetrahedral coordination; the corresponding S—S

distance [2.1707 (8) Å,  $\text{RuS}_2$ ] is smaller than that based on the covalent radii, but larger than both normal S—S single bonds and the S—S distances in ionic disulfides.

**Introduction.** Hitherto structure determinations of the pyrite-type ruthenium chalcogenides  $\text{RuS}_2$  and  $\text{RuSe}_2$  have been performed by X-ray powder methods (Sutarno, Knop & Reid, 1967; Stassen & Heyding, 1968). Because we need structural data of high quality for lattice dynamical calculations (Müller, 1990) we redetermined the crystal structures of these compounds on the basis of single-crystal X-ray measurements.

**Experimental.** Single crystals of RuS<sub>2</sub> were grown from a tellurium flux (Ezzaouia, Heindl & Loriers, 1984), those of RuSe<sub>2</sub> by the chemical vapour transport technique using ICl<sub>3</sub> as transporting agent (Bichsel, Levy & Berger, 1984). Approximately spherical crystals 0.30 mm (RuS<sub>2</sub>) and 0.16 mm (RuSe<sub>2</sub>) in diameter were transferred to an Enraf-Nonius CAD-4 diffractometer. Graphite-monochromatized Mo K $\alpha$  radiation was used. The intensity data of 1703 (1737) reflections [ $2\theta \leq 140^\circ$ ,  $\omega-2\theta$  scan, range of  $hkl$   $0 \leq h \leq 14$ ,  $0 \leq k \leq 14$ ,  $0 \leq l \leq 8$ ] were corrected for Lorentz and polarization effects with *NRCVAX* (Gabe, Lee & Le Page, 1985) and Enraf-Nonius *SDP* (B. A. Frenz & Associates, Inc., 1982), respectively. Of the 573 (656) unique reflections,  $R_{\text{int}} = 0.014$  (0.022), 0 (119) with  $I \leq 3\sigma_I$  ( $\sigma_I$  from counting statistics) were considered unobserved. Absorption corrections were applied assuming spherical crystal shapes [ $\mu R = 1.56$  (3.31)] by using the absorption correction factors of Weber (1969) and from *International Tables for X-ray Crystallography* (1972). The minimum and maximum transmission values are 12.0 and 21.2% (2.1 and 9.8%). As standard reflections in order to control intensity variations 600, 060, 006 (026, 080, 246, 553) were chosen. The variations in intensity throughout the data collection were less than 1%. The structures were refined by full-matrix least-squares refinements of the positional and anisotropic thermal parameters, the extinction coefficient, and the scale factor ( $N_p = 7$ ) using scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1974) including the terms for anomalous dispersion. The initial parameters for the atomic positions were taken from Sutarno, Knop & Reid (1967) and Stassen & Heyding (1968), respectively. The final refinements based on the  $F$  magnitudes of 573 (537) observations with  $I \geq 3\sigma_I$  resulted in  $R = 0.021$  (0.021), ( $w = 1$ ),  $wR = 0.022$  (0.023) ( $w = 1/\sigma_I$ ),  $S = 4.838$  (0.958). The secondary-extinction parameter of RuS<sub>2</sub> converged to  $4.8(1) \times 10^{-1}$ . A primary extinction parameter for RuSe<sub>2</sub> was refined to  $2.10(3) \times 10^{-6}$ . The ratios of the maximum least-squares shift to e.s.d. in the final cycle were  $< 0.001$ , and the max. and min. heights in the final difference Fourier syntheses were  $-1.45$  and  $1.09$  ( $-2.90$  and  $4.25$ )  $e \text{ \AA}^{-3}$ . The final atomic coordinates and thermal parameters are given in Table 1.\*

The cell parameters were obtained by least-squares methods from Guinier powder patterns of the ground single crystals (Huber FR 600 system,

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53017 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and anisotropic displacement parameters ( $\times 10^{-2} \text{ \AA}^2$ ) with e.s.d.'s in parentheses*

		$x$	$u_{11}$	$u_{12}$
RuS <sub>2</sub>				
Ru	4(a) ( $\bar{3}$ )	0	0.225 (4)	-0.0127 (17)
S	8(c) (3)	0.38831 (4) [0.3885 (7)]	0.305 (6)	0.023 (5)
RuSe <sub>2</sub>				
Ru	4(a) ( $\bar{3}$ )	0	0.301 (2)	-0.004 (3)
Se	8(c) (3)	0.38065 (3) [0.381 (3)]	0.364 (2)	0.016 (3)

Data from Sutarno, Knop & Reid (1967) and Strassen & Heyding (1968), respectively, in square brackets.

Table 2. *Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for RuX<sub>2</sub> (X = S, Se) with e.s.d.'s in parentheses*

	S	Se	
Ru—X	2.3520 (3)	2.4707 (2)	6 $\times$
	3.5445 (3)	3.8090 (3)	6 $\times$
	3.7736 (5)	3.9121 (1)	2 $\times$
Ru—Ru	3.9673 (2)	4.1957 (3)	12 $\times$
X—X	2.1707 (8)	2.4532 (2)	1 $\times$
	3.2060 (3)	3.3475 (2)	6 $\times$
	3.4423 (4)	3.6348 (3)	6 $\times$
X—Ru—X	85.93 (1)	85.29 (1)	6 $\times$
	94.07 (1)	94.71 (1)	6 $\times$
Ru—X—X	103.13 (1)	101.38 (1)	3 $\times$
Ru—X—Ru	115.00 (1)	116.29 (1)	3 $\times$
X—X—X	64.94 (1)	65.76 (1)	6 $\times$

Cr K $\alpha_1$  radiation, 8 reflections,  $\alpha$ -quartz as internal standard,  $a = 4.9136$ ,  $c = 5.4054 \text{ \AA}$ ).

**Discussion.** The crystal structures of the pyrite type ruthenium chalcogenides RuS<sub>2</sub> and RuSe<sub>2</sub> were confirmed. The standard deviations of the atomic coordinates and bond lengths (Tables 1 and 2) are by one order of magnitude smaller than those of the literature data. Whereas the intermolecular X...X distances (X = S, Se) of both compounds are much smaller than the sums of the van der Waals radii (Bondi, 1964), *i.e.* 3.2060 and 3.3475  $\text{\AA}$  instead of 3.60 and 3.80  $\text{\AA}$ , the intra-ionic Se—Se bond length of RuSe<sub>2</sub>, *viz.* 2.4532  $\text{\AA}$ , is in good agreement with 2.450  $\text{\AA}$  calculated from the covalent radii derived for tetrahedral coordination (Van Vechten & Phillips, 1970). The same applies to pyrite type RuTe<sub>2</sub> (Lutz, Jung & Wäschenbach, 1987). The intra-ionic S—S distance of RuS<sub>2</sub> (2.1707  $\text{\AA}$ ), however, is significantly shortened compared to the sum of the covalent radii (2.25  $\text{\AA}$ ), but elongated with respect to both normal S—S single bonds [2.06  $\text{\AA}$ , Flamm (1986)] and ionic disulfides [2.11  $\text{\AA}$ , Böttcher (1979)]. The varying S—S distances observed for pyrite type sulfides are associated with the different strengths of the intra-ionic S—S bonds in these compounds (Elliot, 1960).

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*Acta Cryst.* (1990). **C46**, 2005–2007

## Crystal Chemistry of *cyclo*-Hexaphosphates. XII. Structure of Ammonium Calcium *cyclo*-Hexaphosphate Hexahydrate

BY M. T. AVERBUCH-POUCHOT

*Laboratoire de cristallographie, associé à l'Université J. Fourier, CNRS, 166X, 38042 Grenoble CEDEX, France*

(Received 8 December 1989; accepted 26 February 1990)

**Abstract.**  $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ ,  $M_r = 698\cdot 154$ , orthorhombic,  $P2_12_12$ ,  $a = 12\cdot 821$ ,  $b = 12\cdot 537$  (6),  $c = 7\cdot 029$  (2) Å,  $V = 1130$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2\cdot 052$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0\cdot 7107$  Å,  $\mu = 1\cdot 021$  mm<sup>-1</sup>,  $F(000) = 712$ ,  $T = 294$  K, final  $R = 0\cdot 035$  for 1667 reflections. This compound is the first reported example of a  $\text{P}_6\text{O}_{18}$  ring anion with twofold internal symmetry. The  $\text{P}_6\text{O}_{18}$  ring anions and one of the ammonium groups alternate along the twofold axis, parallel to the  $c$  direction. The second ammonium group, also located on a binary axis, and the Ca atoms interconnect these rows.

**Introduction.** This work is part of a systematic investigation of monovalent–divalent cation *cyclo*-hexaphosphates. Several structure types have already been described for such compounds:  $\text{Mn}_2\text{Li}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$  (Averbuch-Pouchot, 1989),  $\text{Cd}_2\text{Na}_2\text{P}_6\text{O}_{18}\cdot 14\text{H}_2\text{O}$  (Averbuch-Pouchot, 1990),  $\text{Ca}_2\text{Li}_2\text{P}_6\text{O}_{18}\cdot 8\text{H}_2\text{O}$  (Averbuch-Pouchot & Durif, 1990*a*),  $\text{Cu}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 8\text{H}_2\text{O}$  (Averbuch-Pouchot & Durif, 1990*b*).  $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ , described in the present work, is the fifth structure type observed so far in this area of *cyclo*-hexaphosphate chemistry.

**Experimental.** Single crystals of the title compound were prepared by adding solid gypsum to an aqueous

solution of ammonium *cyclo*-hexaphosphate at room temperature. After some days, large orthorhombic prisms of  $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$  appear in the solution.

Crystal size:  $0\cdot 26 \times 0\cdot 16 \times 0\cdot 19$  mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 17 reflections ( $11\cdot 0 < \theta < 13\cdot 0^\circ$ ) for refining unit-cell dimensions.  $\omega$  scan, scan width:  $1\cdot 10^\circ$ , scan speed:  $0\cdot 02^\circ \text{ s}^{-1}$ , total background measuring time: 6 s. 3223 reflections collected ( $3 < \theta < 30^\circ$ ),  $\pm h$ ,  $k$ ,  $l$ ,  $h_{\text{max}} = 18$ ,  $k_{\text{max}} = 17$ ,  $l_{\text{max}} = 9$ . Two orientation and intensity-control reflections ( $\bar{6}40$  and  $640$ ) measured every 2 h without any significant variation. 1667 reflections after averaging Friedel pairs ( $R_{\text{int}} = 0\cdot 022$ ). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain & Woolfson, 1977). H atoms located by difference Fourier synthesis. Anisotropic full-matrix refinement (on  $F$ ), isotropic for H atoms. Unit weights. Final refinement using 1667 reflections (no rejection). Final  $R = 0\cdot 035$  ( $wR = 0\cdot 041$ ),  $S = 1\cdot 278$ ,  $\Delta/\sigma_{\text{max}} = 0\cdot 04$ . Maximum peak height in the final difference Fourier map  $0\cdot 280 \text{ e } \text{Å}^{-3}$ . No secondary-extinction correction. Scattering factors for neutral atoms and  $f'$ ,  $f''$  from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf–