JOURNAL OF SOLID STATE CHEMISTRY **76**, 109–114 (1988)

Synthesis and Structures of Cs_3TaSe_4 and Cs_3NbSe_4

HOSEOP YUN, CLAYTON R. RANDALL, AND JAMES A. IBERS

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Received January 25, 1988

A study of the alkali metal tetraselenometalate system has afforded two new isostructural phases, Cs_3TaSe_4 and Cs_3NbSe_4. The structures of these phases have been determined by X-ray and neutron powder diffraction techniques. Cs_3TaSe_4 crystallizes in the orthorhombic system (D_{2h}^{16}-*Pnma*, $a = 10.277(1)$, $b = 11.918(1)$, $c = 10.238(1)$ Å) with four formula units in the cell. The structure contains discrete $TaSe_4^{3-}$ ions (Ta–Se, 2.369(4), 2.374(7), 2.397(6) Å) and Cs^+ cations. Out to 4 Å the Cs cations are surrounded by five or seven Se atoms.

Introduction

The tetrachalcogenometalates (MQ_4^{3-}, M = V, Nb, or Ta, Q = S or Se) have been prepared either in the solid state by direct combination of the constituent elements or for VS_4^{3-} by the reaction of H_2S with an aqueous solution of the corresponding oxometalate (*1*). When the oxometalates in question do not exist in solution, only the solid-state reactions have been effective. $[NH_4]_3[VS_4]$ has been prepared from the reaction of H_2S with NH_4VO_3 in aqueous NH_4OH solution (*2*). However, the synthesis of NbQ_4^{3-} and TaQ_4^{3-} (Q = S or Se) in solution has not been reported. The corresponding oxometalates do not exist even though the chalcogenometalates have been prepared from solid-state reactions (i.e., Tl_3MQ_4 (*3*), M = V, Nb, Ta; Q = S, Se and Cu_3MQ_4 (*4*), M = V, Nb, Ta; Q = S, Se, Te). Attempts to prepare MS_4^{3-} (M = Nb, Ta) from $M(OEt)_5$ and $(Me_3Si)_2S$ in acetonitrile solution did not lead to the desired products but to the polynuclear cage anions $M_6S_{17}^{4-}$ (*5*).

With the aim of preparing potentially soluble MQ_4^{3-} salts we have devised a route for the preparation of Cs_3NbSe_4 and Cs_3TaSe_4 by solid-state reactions. Here we report the synthesis of these new compounds as well as their structures as determined from neutron diffraction powder data.

Experimental Section

Synthesis. The approximate 8 g of material used in the neutron diffraction experiment was composed of nine separate samples prepared by an identical route. Ta powder (0.181 g (1.00 mmol); 99.98%, AESAR) and Se powder (0.316 g (4.00 mmol); 99.99%, ALFA) were placed in a fused silica tube that had been flame dried under vacuum. Inside a glove box under an Ar atmosphere, 0.399 g (3.00 mmol) of liquid Cs (99.5% AESAR) was added very slowly by pipet to the Ta/Se mixture. (Caution! This reaction is very exothermic.) The tube was then sealed under vaccum ($\sim 10^{-4}$ Torr). It was next heated in a furnace at 800°C for 8 days to afford Cs_3TaSe_4 as a

0022-4596/88 $3.00

yellow-green powder (about 95% yield). The color of the product implied the existence of the $TaSe_4^{3-}$ ion (*3*). A chemical analysis (Dornis und Kolbe, Mülheim, FRG) corresponded to the stoichiometry $Cs_{3.03}Ta_{1.00}Se_{4.06}$ and hence to Cs_3TaSe_4. X-ray powder diffraction patterns were recorded for each sample with Cu*Kα* radiation on an Enraf–Nonius Model FR552 Guinier camera. The patterns are consistent except for very weak extra peaks in two of the samples. From a comparison of line positions and relative intensities, the nine samples were judged to be essentially identical and thus were combined.

Cs_3NbSe_4 was prepared by an identical procedure and the red-brown color of the product implied the existence of the $NbSe_4^{3-}$ ion (*3*). The X-ray powder pattern of Cs_3NbSe_4 has similar peak positions but different relative intensities compared to the Cs_3TaSe_4 powder pattern.

Structural study. At the first stage of the structural investigation, the X-ray powder diffraction pattern was indexed on a tetragonal system with the program VISSER (*6*). Weighted least-squares analysis (*7*) of 30 reflections in the range $10° < 2\theta < 50°$ yielded unit cell parameters, $a = 10.262(3)$, $c = 11.892(7)$ Å. However, the X-ray powder pattern contains additional lines that are very close to the indexed lines. This implies the possibility of lower symmetry with similar cell constants. The possibly isostructural compound K_3VS_4 (*8*) crystallizes in space group *Pnma* of the orthorhombic system with $a = 9.143(4)$, $b = 10.59(1)$, $c = 9.107(4)$ Å. In K_3VS_4, a/b and c/b are 0.863 and 0.860, respectively. As a trial, we used these ratios to assign the cell parameters $a = 10.26$ Å and $c = 10.23$ Å in comparison to the longest axis $b = 11.892$ Å in Cs_3TaSe_4 and used as a starting point the positional parameters for K_3VS_4. The simulated X-ray diffraction pattern thus generated by the program LAZY PULVERIX (*9*) was in good agreement with the Guinier pattern.

Neutron diffraction data for Cs_3TaSe_4 powder were collected at room temperature on the general purpose powder diffractometer (GPPD) of the IPNS facility at Argonne National Laboratory (*10*). A general discussion of techniques involved in acquisition and analysis of data on this facility was given previously (*11*). Data were collected from the $2\theta = 148°$, 90°, and 60° detector banks, but only back scattering ($2\theta = 148°$) data were used in the profile refinement so as to achieve the highest possible resolution (*12*). Data reduction and least-squares refinement were carried out with the use of the programs of the IPNS Rietveld analysis package (*13*). In addition to the structural variables, a scale factor, five background parameters, and one of the peak broadening parameters (σ_1) were refined. After several cycles of successful refinement, the difference curve showed a significantly wavy background, probably from amorphous scattering of one or more impurity phases in the sample. Since the function used to calculate background in the IPNS Rietveld code is monotonic and slowly varying, it is incapable of handling such residual scattering. Richardson and Faber (*14*) developed a Fourier-filtering technique that facilitates the removal from the measured data of amorphous scattering contributions and yields information on such impurities. The residual scattering from Cs_3TaSe_4 that was not accounted for by the Rietveld refinement was Fourier transformed to generate a real-space correlation function similar to a radial distribution function. The identifiable interatomic spacings corresponded to 2.54 Å (Ta–Se?) and 3.81 Å (Cs–Se?). Thus the amorphous impurities could be binary tantalum and cesium selenides. From the inverse Fourier transformation of the correlation function with use of a value of $r_{\max} = 10.0$ Å, a Fourier-filtered fit of the residual amorphous scattering was calculated and then subtracted from the observed intensity data. These resulting data were used in the final least-squares refinement. This final re-

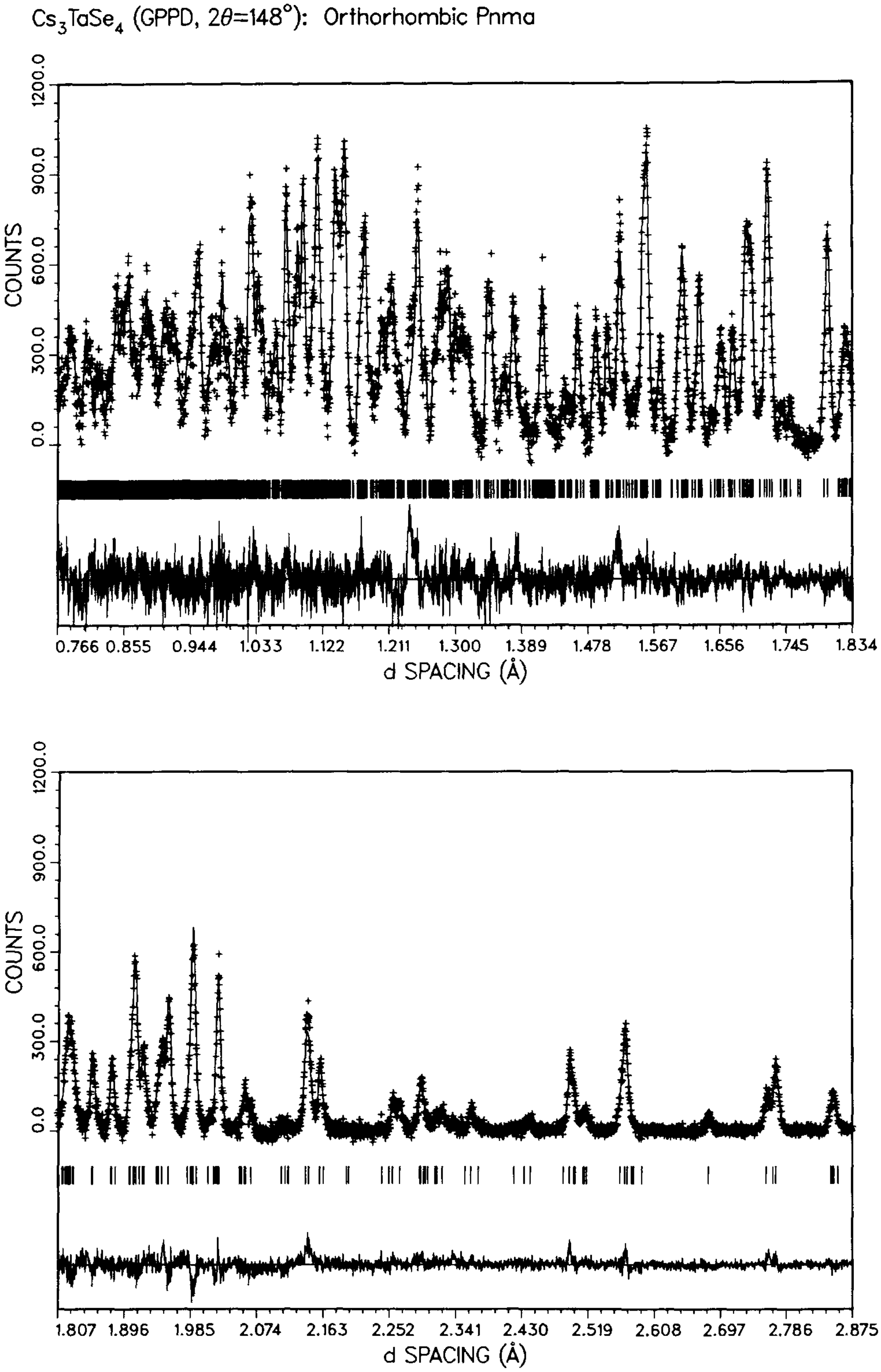

FIG. 1. Final Rietveld profile fit for Cs_3TaSe_4 after Fourier filtering. +, Data point; —, calculated profile; vertical lines below the profile indicate the positions of all allowed reflections. A difference plot appears at the bottom of each frame.

TABLE I

POSITIONAL PARAMETERS[a] FOR Cs_3TaSe_4

Atom	Wyckoff notation	Site symmetry	x	y	z	B_{eq} (Å^2)[b]
Cs(1)	4c	m	0.1487(7)	1/4	0.4063(7)	3.6(3)
Cs(2)	8d	1	0.0425(5)	0.9599(4)	0.2095(5)	2.0(1)
Ta	4c	m	0.2212(4)	1/4	0.9823(5)	0.9(1)
Se(1)	4c	m	0.0054(4)	1/4	0.0711(5)	1.3(1)
Se(2)	4c	m	0.2051(5)	1/4	0.7510(4)	2.0(3)
Se(3)	8d	1	0.3319(3)	0.0851(3)	0.0483(3)	2.5(1)

[a] Refined cell parameters are $a = 10.2772(2)$ Å, $b = 11.9181(3)$ Å, $c = 10.2380(2)$ Å, which we round to the nearest thousandth.

[b] $B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

finement included 4399 data points (representing 5-μsec-wide time channels) and 1492 independent reflections (0.7650 Å $< d <$ 2.8716 Å). The 52 parameters refined included a scale factor, cell parameters, atomic positional parameters, anisotropic thermal parameters, background parameters, and one of the peak broadening parameters (σ_1). The final agreement indices (*10*) are $R_p = 0.026$, $R_{wp} = 0.038$, and $R_B = 0.085$. The statistically expected value of R_E is 0.030. Figure 1 shows the final Rietveld profile fit for Cs_3TaSe_4. Atomic parameters and anisotropic thermal parameters are given in Table I and Table II, respectively.

Although the Fourier-filtering technique has reduced the contribution from amorphous scattering, there are still a few small peaks (e.g., $d = 2.337$ Å) that are not explained by the current cell. But such impurity peaks are of low intensity, and overall the agreement between the observed and calculated pattern of Cs_3TaSe_4 is very satisfactory.

The X-ray diffraction pattern of Cs_3NbSe_4 is in very good agreement with the pattern simulated from the Cs_3TaSe_4 structure with Nb at the Ta position. We thus conclude that Cs_3NbSe_4 is isostructural with Cs_3TaSe_4.

Discussion

The structure of Cs_3TaSe_4 consists of the packing of discrete Cs^+ and $TaSe_4^{3-}$ ions. A

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR Cs_3TaSe_4[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	0.0119(44)	0.1066(76)	0.0181(50)	0	0.0110(31)	0
Cs(2)	0.0242(31)	0.0260(30)	0.0260(34)	0.0064(27)	−0.0085(25)	0.0098(22)
Ta	0.0047(26)	0.0248(30)	0.0055(30)	0	−0.0042(20)	0
Se(1)	0.0064(24)	0.0212(29)	0.0217(29)	0	0.0085(22)	0
Se(2)	0.0163(27)	0.0417(38)	0.0183(30)	0	−0.0065(22)	0
Se(3)	0.0226(21)	0.0427(23)	0.0293(22)	0.0035(19)	0.0014(19)	0.0109(18)

[a] ORTEP II, Type 8.

view of the unit cell of the compound is given in Fig. 2. Distances and angles are given in Table III. The $TaSe_4^{3-}$ ion has crystallographically imposed *m* symmetry but shows approximate $\bar{4}3m$ molecular symmetry. Tetrahedrally coordinated Ta is not usual. The distances between Ta and Se atoms range from 2.369(4) to 2.397(6) Å. These distances are comparable with those in the solid-state compounds Tl_3TaSe_4 (*3*) and Cu_3TaSe_4 (*4*) (2.305–2.456 Å). However, as expected, they are shorter than in Ta_2NiSe_5 (*15*) (2.523(2) to 2.678(2) Å) where the Ta atom is octahedrally coordinated and where there is no discrete Ta entity. The average Ta–Se distance of 2.377 Å in Cs_3TaSe_4 is comparable to the average W–Se distance (2.317 Å) in $[NH_4]_2[WSe_4]$ (*16*) when account is taken of the differing covalent radii of Ta and W. The Se–Ta–Se angles in Cs_3TaSe_4 range from 108.3(2)° to 112.1(2)°, close to the tetrahedral value.

If one takes a cutoff of 4 Å then atom Cs(1) is coordinated to five Se atoms while atom Cs(2) is coordinated to seven. These $Cs(1)Se_5$ and $Cs(2)Se_7$ polyhedra are not easily described in terms of classic polyhedra. The Cs–Se distances vary from 3.576(8) to 3.841(6) Å and these distances are consistent with those observed in other cesium selenide structures (i.e., 3.545(7) to 3.930(8) Å in Cs_2Se_5 (*17*)). Although the $TaSe_4^{3-}$ anions have been found in Cu_3TaSe_4 and Tl_3TaSe_4 there appear to be interactions among the cations and selenium atoms in these materials. Thus, the distances of 2.41 Å for Cu···Se (*4*) and 3.22 Å for Tl···Se (*3*) are significantly shorter than the sums of the ionic radii (*18*), 2.58 Å for Cu–Se and 3.57 Å for Tl–Se. Attempts to solubilize the anion in Cu_3TaSe_4 have not been successful (*19*). In Cs_3TaSe_4, the average Cs–Se distance, 3.71 Å, is slightly longer than the sum of ionic radii (3.65 Å) (*18*).

TABLE III

Selected Distances (Å) and Angles (deg.) for Cs_3TaSe_4

Ta–2Se(3)	2.369(4)	Cs(2)–Se(2)	3.629(6)
Ta–Se(2)	2.374(7)	Cs(2)–Se(3)	3.714(6)
Ta–Se(1)	2.397(6)	Cs(2)–Se(3)	3.739(6)
Cs(1)–Se(2)	3.576(8)	Cs(2)–Se(1)	3.756(5)
Cs(1)–Se(1)	3.674(7)	Cs(2)–Se(1)	3.841(6)
Cs(1)–Se(1)	3.735(9)	Se(3)–Ta–Se(3)	112.12(23)
Cs(1)–2Se(3)	3.831(7)	2Se(3)–Ta–Se(2)	108.53(17)
Cs(2)–Se(2)	3.592(6)	2Se(3)–Ta–Se(1)	109.64(17)
Cs(2)–Se(3)	3.614(5)	Se(2)–Ta–Se(1)	108.28(24)

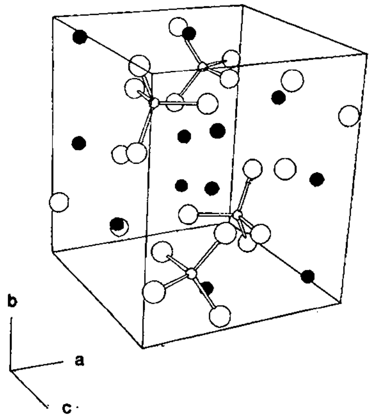

FIG. 2. View of the unit cell of Cs_3TaSe_4. Small open circles are Ta atoms, small filled circles are Cs atoms, and large open circles are Se atoms.

Prior to the present structural determination an attempt was made to prepare other $TaSe_4^{3-}$ salts by solution methods. A sample of Cs_3TaSe_4 was dissolved at room temperature in acetonitrile in the presence of 18-crown-6 ether and bis(triphenylphosphine)iminium chloride. This yielded not salts of $TaSe_4^{3-}$ but rather new salts of the unliganded Se_4^{2-} and Se_5^{2-} ions (*20*). Now that the presence of the $TaSe_4^{3-}$ ions in Cs_3TaSe_4 is established, further attempts at dissolution to yield new salts of this ion are underway.

Acknowledgments

This research was supported by the National Science Foundation Grant CHE 87-01007. The IPNS facility at Argonne National Laboratory is supported by the U.S. Department of Energy. We thank Drs. F. Rotella, J. Richardson, and R. Hitterman of Argonne National Laboratory for many helpful discussions. We are also indebted to Mr. Nathaniel Brese for initial indexing of the X-ray powder patterns.

References

1. A. Müller, E. Diemann, R. Jostes, and H. Bögge, *Angew. Chem. Int. Ed. Engl.* **20,** 934 (1981).
2. Y. Do, E. D. Simhon, and R. H. Holm, *Inorg. Chem.* **24,** 4635 (1985).
3. C. Crevecoeur, *Acta Crystallogr.* **17,** 757 (1964).
4. F. Hulliger, *Helv. Phys. Acta* **34,** 379 (1961).
5. J. Sola, Y. Do, J. M. Berg, and R. H. Holm, *Inorg. Chem.* **24,** 1706 (1985).
6. J. W. Visser, *J. Appl. Crystallogr.* **2,** 89 (1969).
7. J. Warczewski and P. M. de Wolff, *J. Appl. Crystallogr.* **7,** 585 (1974).
8. J. M. van den Berg and R. de Vries, *Proc. K. Ned. Akad. Wet., Ser. B* **67,** 178 (1964).
9. K. Yvon, W. Jeitschko, and E. Parthe, *J. Appl. Crystallogr.* **10,** 73 (1977).
10. J. Jorgensen and F. Rotella, *J. Appl. Crystallogr.* **15,** 27 (1982).
11. S. McEwen, J. Faber, Jr., and A. Turner, *Acta Metall.* **31,** 657 (1983).
12. E. Steichele and P. Arnold, *Phys. Lett. A* **44,** 165 (1973).
13. R. von Dreele, J. Jorgensen, and C. Windsor, *J. Appl. Crystallogr.* **15,** 27 (1982).
14. J. W. Richardson, Jr., and J. Faber, Jr., *in* "Advances in X-ray Analysis" (C. S. Barrett *et al.*, Eds.), Vol. 29, p. 143, Plenum, New York (1986).
15. S. A. Sunshine and J. A. Ibers, *Inorg. Chem.* **24,** 3611 (1985).
16. A. Müller, B. Krebs, and H. Beyer, *Z. Naturforsch. B* **23,** 1537 (1968).
17. U. Kretschmann and P. Böttcher, *Z. Naturforsch. B* **40,** 895 (1985).
18. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
19. C. N. Chau and J. A. Ibers, unpublished results.
20. N. E. Brese, C. R. Randall, and J. A. Ibers, *Inorg. Chem.* **27,** 940 (1988).