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The Structure of the New Quaternary Layered Material $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$

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The new quaternary layered compound $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ has been prepared and structurally characterized. This compound crystallizes in the monoclinic system (C^3_{2h}–$C2/m$, a = 13.089(18), b = 3.425(3), c = 24.436(25) Å, and β = 104.9(1)°) with two formula units in the cell. The structure contains Ta atoms in both trigonal prismatic and octahedral sites, Co atoms in a square-pyramidal environment, and Pt atoms with both square-pyramidal and square-planar coordination. This compound is related to the $Co_2Ta_4PdSe_{12}$ structural type where an additional $TaSe_2$ unit has been added to the chains of metal atoms.

Introduction

The dominant feature of the structures of the early transition-metal dichalcogenides (MQ_2, M = Group IV, V, or VI; Q = S, Se) is the two-dimensional layer that stacks to produce the three-dimensional structure. This low dimensionality can be preserved when a ternary element is added to the binary system (*1–4*). Thus, the ternary compounds Ta_2PdQ_6 (*1*), Ta_2NiQ_5 (*3*), $Nb_2Pd_{0.71}Se_5$ (*2*), and $Nb_3Pd_{0.72}Se_7$ (*4*) all have layered structures that can be thought of as arising from the addition of a second type of metal atom (Pd or Ni) within the slabs of the TaQ_2 or NbQ_2 structure. The structural similarities between $Nb_2Pd_{0.71}Se_5$ and $Nb_3Pd_{0.72}Se_7$ (*4*) suggest that the number of Pd atoms inserted into the $NbSe_2$ framework can be varied without substantial change in the structural chemistry of the ternary phase. Here we describe a similar chemistry in the quaternary system Co–Pt–Ta–Se. The new compound $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ has been isolated and structurally characterized. We compare it with $Co_2Ta_4PdSe_{12}$ (*2*) and relate it to the Nb–Pd–Se system mentioned above.

Experimental

The compound $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ was prepared by combining Co powder (ALFA, 99.8%), Ta powder (AESAR, 99.98%), Pt powder (Johnson-Matthey, 99.98%), and Se powder (ATOMERGIC, 99.999%), in a 2 : 4 : 1 : 12 ratio in a quartz tube that was then evacuated (~10^{-5} Torr) and sealed. In a furnace the tube was heated at 700 K for 72 hr and then at 1175 K for 144 hr before it was radiatively cooled. Small, black, flat needles formed throughout the tube. Qualitative chemical analysis with the microprobe of a Hitachi S-570 scanning electron microscope confirmed the presence of all four elements in the crystals.

Analysis of Weissenberg photographs of several crystals revealed the presence of

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two types of visually indistinguishable crystals both belonging to the monoclinic system. One compound has a unit cell (a = 13.011(5), b = 3.412(2), c = 19.046(5) Å, and β = 109.40(3)°) similar to that of $Co_2Ta_4PdSe_{12}$ (*2*) and is thus assumed to be the Pt analogue of this phase. The second type of crystal has cell dimensions different from those of other known compounds and was studied further by single-crystal X-ray techniques. The Weissenberg photographs exhibit the systematic absence hkl, $h + k = 2n + 1$ indicative of the space groups C_2^3–$C2$, C_s^3–Cm, and C_{2h}^3–$C2/m$.

Intensity data were collected with an ω step-scan technique (77 steps of 0.03° in ω) on a Picker FACS-1 diffractometer. Such a large scan range was needed because of crystal mosaicity. Six standard reflections, measured every 100 reflections, showed no significant variation in intensity throughout the data collection. The crystal and data collection parameters are given in Table I.

TABLE I

CRYSTAL DATA AND INTENSITY COLLECTION FOR $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$

Molecular weight	2730.08
Space group	C_{2h}^3–$C2/m$
a (Å)	13.089(18)
b (Å)	3.425(3)
c (Å)	24.436(25)
β (deg)	104.9(1)
V (Å^3)	1058.6
Z	2
T of data collection (K)[a]	120
Density (calc.) (g cm^{-3})	6.09
Crystal volume (mm^3)	2.70 × 10^{-5}
Crystal shape	Flattened needle bound by {001}, {$\bar{2}$01}, {010}
Radiation	Graphite monochromated MoK_α ($\lambda(K_{\alpha_1})$ = 0.7093 Å)
Linear absorption coefficient (cm^{-1})	518
Transmission factors[b]	0.282–0.691
Detector aperture (mm)	Horizontal—4.3 Vertical—4.6 32 cm from crystal
Takeoff angle (deg)	2.5
Scan type	77 steps of 0.03° in ω, 1 sec at each step
λ^{-1} sin θ, limits (Å^{-1})	0.0246–0.5958, $2° \leq 2\theta$ (MoK_{α_1}) $\leq 50°$
Background counts[c]	10 sec at each end of scan
Data collected	$\pm h \pm k \pm l$
p factor	0.04
No. of unique data including $F_o^2 < 0$	1099
No. of unique data with $F_o^2 > 3\sigma(F_o^2)$	501
No. of variables	78
$R(F^2)$	0.090
$R_w(F^2)$	0.105
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.035
Error in observation of unit weight, e^2	0.88

[a] The low-temperature system is based on a design by J. C. Huffman, Ph.D. thesis, Indiana University, 1974.

[b] The analytical method was used for the absorption correction (J. de Meulenaer and H. Tompa, *Acta Crystallogr.* **19**, 1014 (1965)).

[c] The diffractometer was operated under the Vanderbilt disk oriented system (P. G. Lenhert, *J. Appl. Crystallogr.* **8**, 568 (1975)).

All calculations were performed on a Harris 1000 computer with programs standard in this laboratory (*5*). The absorption-corrected intensities were averaged in point groups $2/m$, 2, and m (*6*); the corresponding agreement indices were 0.15, 0.13, and 0.13, respectively. Since the data were collected from a very mosaic crystal and because the absorption correction is sensitive to small imperfections in the crystal, we consider these agreement indices to be equal. Hence we chose to describe the structure in the centrosymmetric space group $C2/m$. The Pt atom, two Ta atoms, and six Se atoms were located by direct methods. The positions of the remaining atoms were determined from ensuing electron density maps. Refinement of the isotropic temperature factors resulted in a large negative value for the Co atom. A subsequent electron density map indicated that approximately 43 e/Å^3 were located at the Co site. As Pt is the only other metal atom in the structure that is likely to possess square-pyramidal coordination, a model including disorder of Co and Pt over this site was adopted. Initially the site was set to be 68% Co and 32% Pt(2) so as to agree with the electron density map. In ensuing refinement cycles the occupancies were then varied with the constraint that the sum of the occupancies be equal to unity. The final cycle of refinement performed on F_o^2 with anisotropic thermal parameters for each atom and a variable occupancy for the Co/Pt site resulted in the

TABLE II

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$

Atom	Wyckoff notation	Site symmetry	x	y	z	B_{eq} (Å^2)
Ta(1)	4*i*	*m*	0.48472(17)	0	−0.110996(74)	0.74(5)
Ta(2)	4*i*	*m*	0.03347(16)	0	0.235332(72)	0.53(5)
Ta(3)	4*i*	*m*	0.16043(16)	0	0.431587(71)	0.45(4)
Pt(1)	2*a*	2/*m*	0	0	0	0.72(7)
Pt(2)[a]	4*i*	*m*	0.05296	$\frac{1}{2}$	0.33803	0.5
Co	4*i*	*m*	0.05296(32)	$\frac{1}{2}$	0.33803(14)	0.5(1)
Se(1)	4*i*	*m*	0.15860(40)	$\frac{1}{2}$	0.20665(17)	0.7(1)
Se(2)	4*i*	*m*	0.89679(38)	$\frac{1}{2}$	0.18116(16)	0.7(1)
Se(3)	4*i*	*m*	0.14327(40)	0	0.08572(18)	0.7(1)
Se(4)	4*i*	*m*	0.18209(39)	0	0.33157(17)	0.7(1)
Se(5)	4*i*	*m*	0.87340(39)	0	0.05857(17)	0.7(1)
Se(6)	4*i*	*m*	0.07599(39)	0	0.69406(17)	0.8(1)
Se(7)	4*i*	*m*	0.18607(36)	0	0.54383(17)	0.7(1)
Se(8)	4*i*	*m*	0.48147(36)	0	0.56885(18)	0.6(1)

[a] The positional and thermal parameters of Co and Pt(2) were constrained to be equal. The sum of the multiplicities for Co and Pt(2) was fixed to be 1.0. From the final cycle of least-squares refinement the composition is $[Co_{1.49(2)}Pt_{0.51(2)}]Ta_6PtSe_{16}$.

residuals 0.090 and 0.105 for R and R_w, respectively. The final composition based on this refinement is $[Co_{1.49(2)}Pt_{0.51(2)}]Ta_6PtSe_{16}$. An analysis of F_o^2 as a function of F_o^2, $\lambda^{-1} \sin \theta$, and setting angles revealed no unusual trends. The final difference electron density map contains no feature greater than 5% the height of a Pt atom. The final positional and equivalent isotropic thermal parameters are given in Table II. Anisotropic thermal parameters and structure amplitudes are provided in Tables S-I and S-II, respectively.[1]

Discussion

A view of the structure of $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ along the [010] direction with the labeling scheme is given in Fig. 1. This structure is a new laminar type with the layers extending parallel to $(20\bar{1})$. A drawing of an individual slab as viewed orthogonal to $(20\bar{1})$ is provided in Fig. 2a. Metrical data

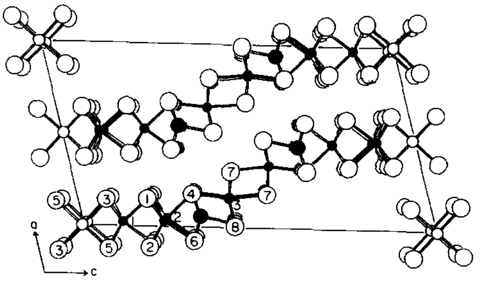

FIG. 1. A view of the structure of $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ viewed along [010]. Here and in Fig. 2, small solid circles are Ta atoms, small open circles are Pt atoms, large black circles are Co/Pt(2) atoms, and large open circles are Se atoms.

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[1] See NAPS document No. 04464 for 6 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

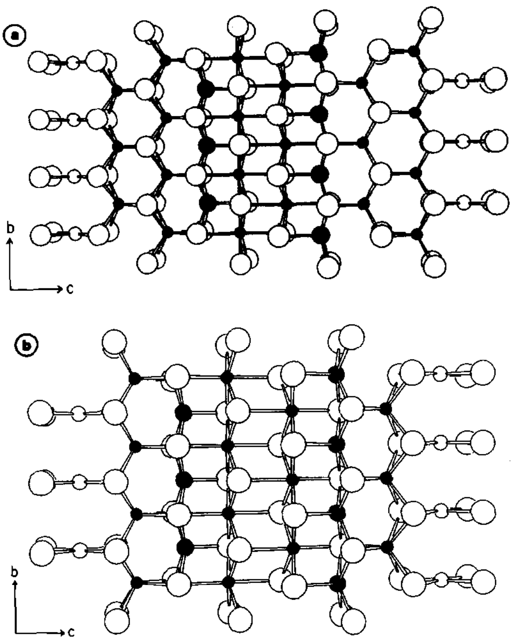

FIG. 2. (a) Drawing of an individual layer of $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ as viewed orthogonal to $(20\bar{1})$. (b) An individual layer of $Co_2Ta_4PdSe_{12}$ as viewed orthogonal to $(20\bar{1})$. Small solid circles are Ta atoms, small open circles are Pt atoms, large black circles are Co atoms, and large open circles are Se atoms.

for the structure are summarized in Table III.

The structure of $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ is similar to that of $Co_2Ta_4PdSe_{12}$ (*2*), shown in Fig. 2b, with two important differences. First, an extra Ta atom with trigonal-prismatic coordination has been added to the chain of metal atoms. Second, the square-pyramidal site that is occupied exclusively by Co atoms in $Co_2Ta_4PdSe_{12}$ contains both Co and Pt atoms (75% Co, 25% Pt) in $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$.

The bond distances and bond angles found in $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ are in good agreement with those found in related structures (*2*, *7*, *8*). The environment around the Ta(2) atom is very similar to that found around the Ta atom with trigonal prismatic coordination in $Co_2Ta_4PdSe_{12}$. In both structures the distances between the Ta atom and the Se atoms of the base of the Co square-pyramid are highly asymmetric. A similar asymmetry is found in the octahedral coordination of atom Ta(3), as the distance to one apical atom is considerably longer than that to the second apex (Ta(3)–Se(7) = 2.676(5), Ta(3)–Se(4) = 2.532(5) Å). Similar behavior is seen in $Co_2Ta_4PdSe_{12}$. The bond distances around atom Ta(1) are more uniform; it is more nearly centered in the trigonal prism of Se atoms. The geometry about the Co/Pt atom in the square-pyramid of Se atoms is closer to that found in $Co_2Ta_4PdSe_{12}$ than in other structures containing Pt atoms in square-pyramidal coordination (*7*, *8*). Most notably, the distance from the Co/Pt atom to the apical Se atom (Se(8)) is not significantly longer than the other *M*–Se distances in the square-pyramid. In both Ta_2PtSe_7 and $Ta_2Pt_3Se_8$ the distance from the Pt atom to the apical Se atom is the longest Pt–Se distance in the square pyramid.

The ability to add metal atoms to a ter-

TABLE III

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$

Co/Pt(2)–2Se(6)	2.391(5)	Pt(1)–2Se(5)	2.452(5)
Co/Pt(2)–1Se(8)	2.431(6)	Pt(1)–2Pt(1)	3.425(3)
Co/Pt(2)–2Se(4)	2.439(5)		
Co/Pt(2)–2Ta(3)	2.913(4)	Se(8)–Co/Pt(2)–Se(6)	91.3(2)
Co/Pt(2)–2Ta(2)	2.995(4)	Se(8)–Co/Pt(2)–Se(4)	111.0(2)
Co/Pt(2)–2Co/Pt(2)	3.425(3)	Se(6)–Co/Pt(2)–Se(6)	91.5(2)
Ta(1)–2Se(3)	2.579(5)	Se(3)–Ta(1)–Se(3)	83.2(2)
Ta(1)–1Se(2)	2.590(6)	Se(3)–Ta(1)–Se(5)	81.5(2)
Ta(1)–1Se(1)	2.595(6)	Se(3)–Ta(1)–Se(1)	81.5(2)
Ta(1)–2Se(5)	2.608(4)	Se(2)–Ta(1)–Se(5)	81.6(1)
Ta(1)–2Pt(1)	3.170(3)	Se(2)–Ta(1)–Se(1)	79.7(2)
Ta(1)–2Ta(1)	3.425(3)	Se(1)–Ta(2)–Se(1)	82.9(2)
Ta(2)–1Se(6)	2.509(6)	Se(1)–Ta(2)–Se(2)	80.0(2)
Ta(2)–2Se(2)	2.583(4)	Se(1)–Ta(2)–Se(4)	82.4(2)
Ta(2)–2Se(1)	2.588(5)	Se(6)–Ta(2)–Se(2)	84.8(2)
Ta(2)–1Se(4)	2.634(6)	Se(6)–Ta(2)–Se(4)	78.9(2)
Ta(2)–2Ta(2)	3.425(3)	Se(8)–Ta(3)–Se(8)	85.4(2)
Ta(3)–2Se(8)	2.524(4)	Se(8)–Ta(3)–Se(7)	94.5(1)
Ta(3)–1Se(4)	2.532(5)	Se(8)–Ta(3)–Se(4)	105.1(1)
Ta(3)–2Se(7)	2.591(4)	Se(7)–Ta(3)–Se(7)	82.8(2)
Ta(3)–1Se(7)	2.676(5)	Se(7)–Ta(3)–Se(4)	87.2(1)
Ta(3)–2Ta(3)	3.425(3)	Se(7)–Ta(3)–Se(4)	166.8(2)
Pt(1)–2Se(3)	2.427(5)	Se(3)–Pt(1)–Se(5)	89.1(2)

nary chalcogenide has been demonstrated previously (*4*). To go from $Nb_2Pd_{0.71}Se_5$ to $Nb_3Pd_{0.72}Se_7$, a chain of Nb-centered trigonal prisms that share quadrilateral faces is added to the structure in much the same way as $Co_2Ta_4PdSe_{12}$ is converted into $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$. The possibility of adding additional chains to the $Nb_3Pd_{0.72}Se_7$ structure was also addressed (*4*). Yet, synthesis of a mixture of $Co_2Ta_4PtSe_{12}$ and $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ as well as the disordering of Co and Pt atoms in this latter structure suggest that the synthesis of a single phase in systems that are so similar in composition (e.g., $Co_2Ta_4PtSe_{12}$ and $Co_2Ta_6PtSe_{16}$ or $Nb_3Pd_{0.72}Se_7$ and $Nb_4Pd_{0.72}Se_9$) is unlikely. The substitution of Pt in the square-pyramidal Co site suggests that further substitutional chemistry may be possible.

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