Inorg. Chem. 1995, 34, 5705−5706

Synthesis and Structural Characterization of a New Rare-Earth Selenodiphosphate(IV): $KLaP_2Se_6$

John H. Chen and Peter K. Dorhout*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received August 9, 1995

There has been new interest in using the thio(seleno)pnictide anion as a building block in the preparation of new metal−phosphate-like materials (see for example refs 1−6). Indeed, explorations of the rich chemistry of the MPS_3 layered solids has produced some unique selenophosphates such as $CuCrP_2Se_6$.[7] Very recent advances in the preparation of chalcopnictide materials include the early-transition metal chemistry of Tremel ($K_4Ti_2P_6S_{25}$, KVP_2S_7, $K_3V_2P_3S_{12}$, $K_3Ti_2P_5S_{18}$, $K_2VP_2S_7$[8]), the supercritical fluid chemistry of Kolis (KCu_2AsS_3, KCu_4AsS_4,[9] Tl_3AgSbS_4, Rb_2AgSbS_4, $Cs_3Ag_2Sb_3S_8$, $Cs_2Ag_3Sb_3S_7$, and $Cs_2Ag_3Sb_8S_{14}$, built from anions such as $(Sb_{12}Se_{20})$,[10] $(P_2Se_8^{2-})$,[11] (PSe_4-PSe_2)[12]), Brockner's synthesis and vibrational analyses ($Pb_2P_2Se_6$,[13] $PrPS_4$,[14] $K_2Mn(Fe)P_2S_6$,[15,16] $CuHgPS_4$,[17] $TlSnPS_4$,[18] $Hg_2P_2Se_6$,[19] $Tl_4P_2Se_6$,[20] and $Eu_2P_2S_6$, the first rare-earth thiodiphosphate(IV)[21]), and the molten thiophosphate chemistry of Kanatzidis (KMP_2Se_6 (Sb, Bi),[22] $Cs_8M_4(P_2Se_6)_5$ (Sb, Bi),[23] $ABiP_2S_7$ (K, Rb),[24] $A_2MP_2Se_6$ (Mn, Fe), $A_2M_2P_2Se_6$ (Cu, Ag),[25] and, most recently, $A_4Pb(PSe_4)_2$ and $K_4Eu(PSe_4)_2$[26]). We have also prepared a new copper selenophosphate, $K_3Cu_3P_3Se_9$,[27] as a result of our studies of the trigonal family of thermoelectric materials, MBi_2Q_3, MBi_2Q_4, $M_2Bi_2Q_5$, and MBi_4Q_7 (M = tetrelide, Q = Se, Te).[28,29] We present in this communication the synthesis and structural characterization of the first quaternary lanthanoid selenodiphosphate(IV), $KLaP_2Se_6$.

There has been very limited chemistry explored in the area of lanthanoid and actinoid chalcophosphates, studies that have shown them to be useful luminescent materials.[30] Lanthanoid chalcogenide and lanthanoid halide chemistries are well-known, the solids belonging to the Fe_2As and BiI_3 structure types, respectively.[28] The PbFCl structure type of GdPS, a phosphide, is related to the LnS_2 orthorhombic type, and the $M^{II}PS_3$ structure type is related to the layered BiI_3 type. Given these structural relationships, we believed that lanthanoid chalcophosphates with structures of this type or other types could form. Evaluating the known lanthanoid chalcophosphates, we found $LnPS_4$,[14,30] $LnPS$,[31] $ScPS_4$,[32] $Eu_2P_2S_6$,[21] $TlEuPS_4$,[33] and $K_4Eu(PSe_4)_2$.[26] Indeed, until recently,[22−24] there had only been two reports of M^{III} ternary or quaternary selenodiphosphates(IV): $In_2[P_3Se_9]$[34] and a family of $M^IM^{III}(P_2Se_6)$ compounds related to $FePS_3$.[7] Our new ternary M^IM^{III} selenodiphosphate(IV), $KLaP_2Se_6$, assembles in a unique structure type and is, to our knowledge, the first rare-earth selenodiphosphate(IV).

Yellow plates of $KLaP_2Se_6$ were prepared by the molten alkali-metal polychalcogenide technique.[35−38] A single-crystal X-ray structure was determined.[39,40] The structure resembles that of the $KBiP_2Se_6$ prepared earlier,[22] but the larger coordina-

---

[1] Zagler, R. Darstellung und Strukturchemie von Chalkogenido-Polyanionen und Chalkogenidoindaten, -germanaten, -stannaten, arsenaten, -antimonaten bzw. -telluraten mit kompexierten und nicht komplexierten Kationen. Dr.-Ing. Thesis, Technischen Hochschule Darmstadt, 1988.

[2] Hönle, W.; Wibbelmann, C.; Brockner, W. *Z. Naturforsch.* **1984**, *39B*, 1088−1091.

[3] Toffoli, P.; Khodadad, P.; Rodier, N. *Acta Crystallogr., Sect. B.* **1977**, *33*, 1492−1494.

[4] Elder, S. H.; Van der Lee, A.; Brec, R. *J. Solid State Chem.* **1995**, *116*, 107−112.

[5] McCarthy, T. J.; Ngeyi, S. P.; Liao, J. H.; Degroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331−340.

[6] Pfitzner, A. *Z. Anorg. Allg. Chem.* **1995**, *621*, 685−688.

[7] Pfeiff, R.; Kniep, R. *J. Alloys Compd.* **1992**, *186*, 111−133.

[8] Tremel, W. Manuscript in preparation.

[9] Jerome, J. E.; Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1994**, *33*, 1733−1734.

[10] Martin, T. M.; Wood, P. T.; Kolis, J. W. *Inorg. Chem.* **1994**, *33*, 1587−1588.

[11] Zhao, J.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* **1992**, 265−266.

[12] O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1486−1488.

[13] Becker, R.; Brockner, W.; Schäfer, H. *Z. Naturforsch.* **1984**, *39A*, 357−361.

[14] Wibbelmann, C.; Brockner, W.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch.* **1984**, *39A*, 190−194.

[15] Menzel, F.; Brockner, W.; Carrillo-Cabrera, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1081−1086.

[16] Carrillo-Cabrera, W.; Sassmannshausen, J.; von Schnering, H. G.; Menzel, F.; Brockner, W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 489−494.

[17] Menzel, F.; Brockner, W.; Carrillo-Cabrera, W. *Heteroat. Chem.* **1993**, *4*, 393−398.

[18] Becker, R.; Brockner, W.; Eisenmann, B. *Z. Naturforsch.* **1987**, *42A*, 1309−1312.

[19] Brockner, W.; Paetzmann, U. *Z. Naturforsch.* **1987**, *42A*, 517−518.

[20] Brockner, W.; Ohse, L.; Paetzmann, U.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch.* **1985**, *40A*, 1248−1252.

[21] Brockner, W.; Becker, R. *Z. Naturforsch.* **1987**, *42A*, 511−512.

[22] McCarthy, T. J.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1994**, 1089−1090.

[23] McCarthy, T. J.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1994**, *6*, 1072−1079.

[24] McCarthy, T. J.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 1061−1063.

[25] McCarthy, T. J.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 1257−1267.

[26] Chondroudis, K.; McCarthy, T. J.; Kanatzidis, M. G. *Inorg. Chem.*, in press.

[27] Dorhout, P. K.; Malo, T. M. *Z. Anorg. Allg. Chem.*, submitted.

[28] Hulliger, F. *Structural Chemistry of Layer-Type Phases*; Reidel: Dordrecht, 1976; p 377.

[29] Spiridonov, E. M.; Ersova, N. A.; Tananaeva, O. I. *Geol. Rudn. Mestorozhd., Petrogr. Mineral.* **1989**, 98−102.

[30] Volodina, A. N.; Kuvshinova, T. B.; Maksimova, S. I.; Murav'ev, E. N.; Niyazov, S. A.; Orlovskii, V. P.; Palkina, K. K.; Chibiskova, N. T. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1978**, *32*, 1684−1685.

[31] Hulliger, F.; Schmelczer, R.; Schwarzenbach, D. *J. Solid State Chem.* **1977**, *21*, 371−374.

[32] Lee, S.; Hilt, R. J. *J. Alloys Compd.* **1992**, *189*, 269−271.

[33] Carrillo-Cabrera, W.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 557−561.

[34] Katty, A.; Soled, S.; Wold, A. *Mater. Res. Bull.* **1977**, *12*, 663−666.

[35] Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202−6204.

[36] Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767−3769.

[37] Crystals of $KLaP_2Se_6$ were prepared from the reaction of 13.9 mg (0.1 mmol) of La (99.999%, Ames Laboratory), 12.4 mg (0.400 mmol) of P (99.999%, Johnson Matthey), and 79.0 mg (1.0 mmol) of Se (99.999%, Johnson Matthey) with 39.4 mg (0.100 mmol) of K_2Se_4 (prepared from stoichiometric amounts of K and Se in liquid ammonia; see ref 38). The reactants were heated in a fused silica ampule, sealed under vacuum, to 700 °C for 120 h and cooled to ambient temperature at 5 °C/h. Yield: 80% based on La (from X-ray powder diffraction). Semiquantitative EDS confirmed the elemental composition. The isostructural praseodymium compound was also prepared: $KPrP_2Se_6$; $a = 12.302(3)$ Å, $b = 7.735(1)$ Å, $c = 11.860(2)$ Å, $\beta = 109.28(2)°$. Yttrium forms a different, orthorhombic phase: KYP_2Se_6; $a = 6.739(1)$ Å, $b = 7.428(1)$ Å, $c = 21.608(4)$ Å.

[38] Liao, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1992**, *31*, 431−439.

0020-1669/95/1334-5705$09.00/0

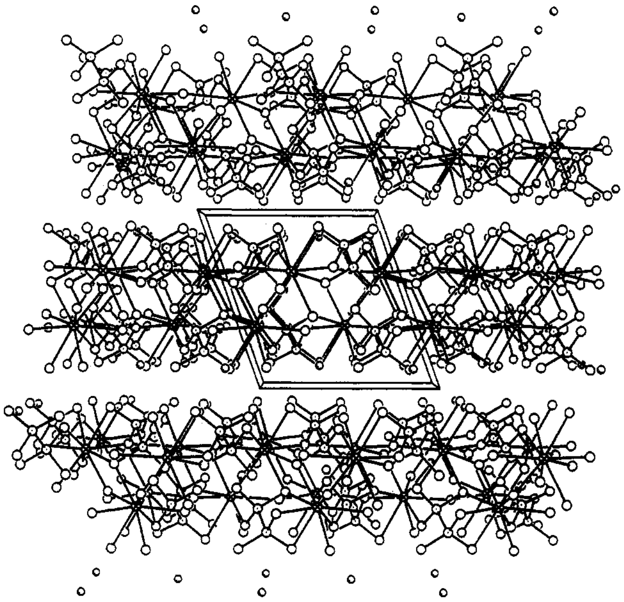

Figure 1. Solid state crystal structure of $KLaP_2Se_6$ viewed along *b* showing the layered morphology of the structure. Open circles are Se, stippled atoms are P, crossed atoms are La, and shaded atoms are K.

tion sphere of lanthanum creates a more intricate, selenodiphosphate linkage. A view of the layers running along the *bc*-family of crystal planes is shown in Figure 1. The potassium cations lie within 8-coordinate, distorted square antiprisms of selenium ions and are not found in the center of the interlayer void, but rather they are nestled in holes that penetrate the layers, with ionic K−Se interlayer distances (average = 3.443 Å). These holes are slightly elliptical with a diameter of 5.12 Å.

The lanthanum atoms are linked within the layers through an intricate selenide network. Each lanthanum atom lies within a distorted, bicapped pentagonal bipyramid of nine selenium atoms. Each selenium atom in the net belongs to a selenodiphosphate unit. The bonding of the diphosphate unit in this structure is truly unique. Figure 2 shows the diphosphate(IV) unit in which one diphosphate acts as a cap to one of the triangular faces of each of two $LaSe_9$ units (Se3, Se4, and Se5; Se1, Se4, and Se6). Se1 and Se5 are then poised to interact with the interlayer potassium cations and form a bridge to the next layer, as does Se2, which only forms one other bond to another $LaSe_9$ unit. The last two selenium atoms (Se3, Se6) of the diphosphate form a μ_2-bridge to a fourth $LaSe_9$ unit. The type of selenodiphosphate bonding in this structure is unlike any other we have found.[7,8,11,13,15,16,18−23,25,27,28,34]

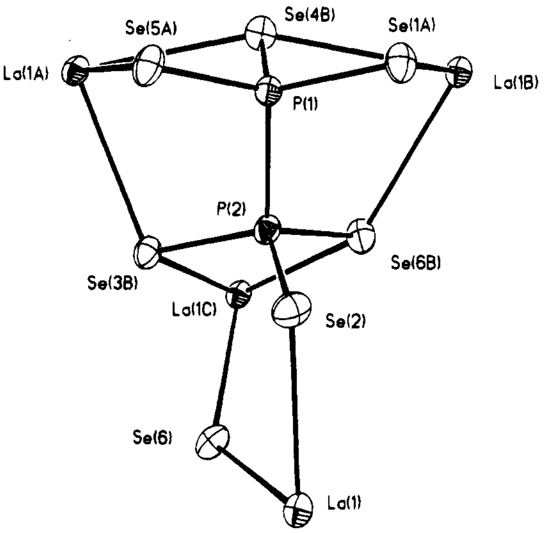

Figure 2. Environment around the diphosphate(IV) unit (50% probability ellipsoids shown). Selected bond distances (Å) and angles (deg): P1−Se1a, 2.183(3); P1−Se5a, 2.158(3); P1−Se4b, 2.179(3); P2−Se2; 2.173(3); P2−Se3b, 2.199(3); P2−Se6b, 2.205(3); P1−P2, 2.231(4); La1b−Se1a, 3.1070(12); La1−Se2, 3.1344(12); La1c−Se3b, 3.2225(12); La1a−Se3b, 3.2366(11); La1b−Se4b, 3.3777(12); La1a−Se4b, 3.1381(11); La1a−Se5a, 3.3625(12); La1c−Se6b, 3.1506(12); La1b−Se6b, 3.1898(12); La1a−Se4b−La1b, 157.81(4); La1b−Se6b−La1c, 131.81(4); Se1a−La1b−Se4b, 65.64(3); Se4b−La1b−Se6b, 63.92(3); Se1a−La1b−Se6b, 79.41(3).

We have shown that the ubiquitous alkali-metal polyselenide melt is useful in preparing new lanthanoid materials. The diffuse reflectance spectrum of $KLaP_2Se_6$ shows a broad absorption near 435 nm, indicative of a moderately wide, indirect band gap semiconductor material. We are currently investigating other new lanthanoid chalcopnictides prepared by this synthetic method[41] that may be useful phosphor agents or thermoelectric materials.

Acknowledgment. P.K.D. gratefully acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp. Cottrell Scholar Fellowship for financial support. We also thank S. M. Miller for help during crystallographic data collection and C. M. Zelenski for EDS spectra.

Supporting Information Available: Listings of solution and refinement data, atomic positions, bond distances and angles, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

IC9510340

---

(39) Crystal structure analysis of $KLaP_2Se_6$: monoclinic, $P2_1/c$; a = 12.4247(12) Å, b = 7.8047(5) Å, c = 11.9279(9) Å, β = 109.612(8)°, V = 1089.6(2) Å^3, Z = 4, ρ_{calcd} = 4.352 g/cm^3; $F(000)$ = 1240; 2544 reflections collected on a Siemens P4 diffractometer at 23 °C using Mo Kα radiation (θ−2θ scans (6.28−50° 2θ range), μ = 24.571 mm^{-1}, semiempirical absorption correction using ψ scans); 1906 unique reflections (R_{int} = 0.0737, $I \geq 2\sigma I$) used to refine 92 parameters, by the refinement program SHELXL-93,[40] against $|F^2|$ to R1 = 0.0477, wR2 = 0.1157, and GOF = 1.069.

(40) Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation.

(41) Several other new phases are currently being analyzed: $KLaSb_2Se_6$, $Pna2_1$, a = 16.949(2) Å, b = 16.617(2) Å, c = 4.233(1) Å; $K_2Pr_2Sb_2Se_9$, $Pbam$, a = 11.554(3) Å, b = 17.636(5) Å, c = 4.3104(9) Å.