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Compound Formation and Local Structure in Ternary Metal–Phosphorus–Selenium Systems

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The formation of ternary compounds is investigated in a variety of M–P–Se systems (M = Cd, Sn, Zn, Ca, Cu, In), using X-ray powder diffraction and ^{31}P, ^{77}Se, ^{113}Cd, ^{119}Sn MAS NMR. Compound formation in these systems is dominated by the P–Se anions, $[P_2Se_6]^{4-}$ and $[PSe_4]^{3-}$. These two types of local structures can be identified on the basis of ^{31}P chemical shift ranges and distinguished with the help of the Dipolar Recovery at the Magic Angle (DRAMA) technique. A new compound was found and characterized as $Ca_2P_2Se_6$, orthorhombic, a = 5.73(1) Å, b = 9.86(1) Å, c = 15.78(1) Å, with $[P_2Se_6]^{4-}$ units. © 1994 Academic Press, Inc.

INTRODUCTION

Crystalline and amorphous inorganic chalcogenides (Ch = S, Se) constitute an interesting class of chemical systems due to their potential application as semiconductors, solid electrolytes (1–4), photoconductors, and low-frequency waveguide materials (5, 6). From a structural viewpoint, the vast range of possible chemical substitutions and the incomplete occupancy of certain cation sites in crystalline systems are of interest, giving rise to order–disorder phenomena, phase transitions, high cation mobility, and the ability to conduct intercalation chemistry (7). In addition, the structural features of glassy chalcogenide systems have attracted interest because of their unusual and unexpected short-range order behavior and the possible occurrence of intermediate-range order phenomena (8).

The structural chemistry of ternary metal–phosphorus–sulfur systems has been found to be particularly rich and diverse (9, 10). For instance, ionically conducting glasses are formed in Li–P–S (11) and Ag–P–S (12) systems over well-defined compositional ranges. In addition, numerous crystalline phases are known in these systems. The phase diagram of the Ag–P–S system contains no less than eight different known ternary phases (12, 13), with stoichiometries Ag_7PS_6, Ag_3PS_4, $Ag_7P_3S_{11}$, $Ag_4P_2S_6$ (two polymorphs), $Ag_4P_2S_7$ (two polymorphs), and $Ag_2P_2S_6$. Figure 1 summarizes the structural features of these and other ternary M–P–S compounds as known from single-crystal X-ray diffraction. Recently we have shown that ^{31}P solid state NMR is a powerful tool for identifying and differentiating such environments and for gaining detailed structural insights into amorphous systems (11, 12).

In contrast to the situation in ternary M–P–S systems, very little is known to date about analogous systems with selenium. The P–Se system forms glasses over a wide compositional region, from 0 to 52 and 62 to 80 mole% P. Between these two ranges, the glass formation is apparently inhibited by the formation of the crystalline compound P_4Se_3. Currently known crystalline phases are P_4Se_3 (three allotropic forms (14)), P_4Se_4 (15), P_4Se_5 (16), and P_2Se_5 (17). Figure 2 shows the molecular geometries which to date have been either verified by single-crystal X-ray diffraction or inferred by NMR spectroscopy. In addition, the glasses in the binary P–Se system have been characterized extensively by a range of ^{31}P dipolar (18) and MAS (19) NMR techniques, neutron diffraction (20), and Raman spectroscopy (21).

Ternary M–P–Se systems have been mostly explored as semiconducting two-dimensional phases with stoichiometry $M_2P_2Se_6$. These phases can intercalate various metal ions or molecules in their van der Waals gaps in aqueous or alcoholic media (22, 23) and are thus promising cathode materials in secondary batteries. Their structures contain $[P_2Se_6]^{-4}$ anions, having a phosphorus–phosphorus bond. Compounds based on this structural unit have been identified with monovalent (Li, Ag (24, 25)), divalent (Cd, Sn, Hg, Pb, Fe, V, etc. (26–28)), and trivalent (In (29)) cations.

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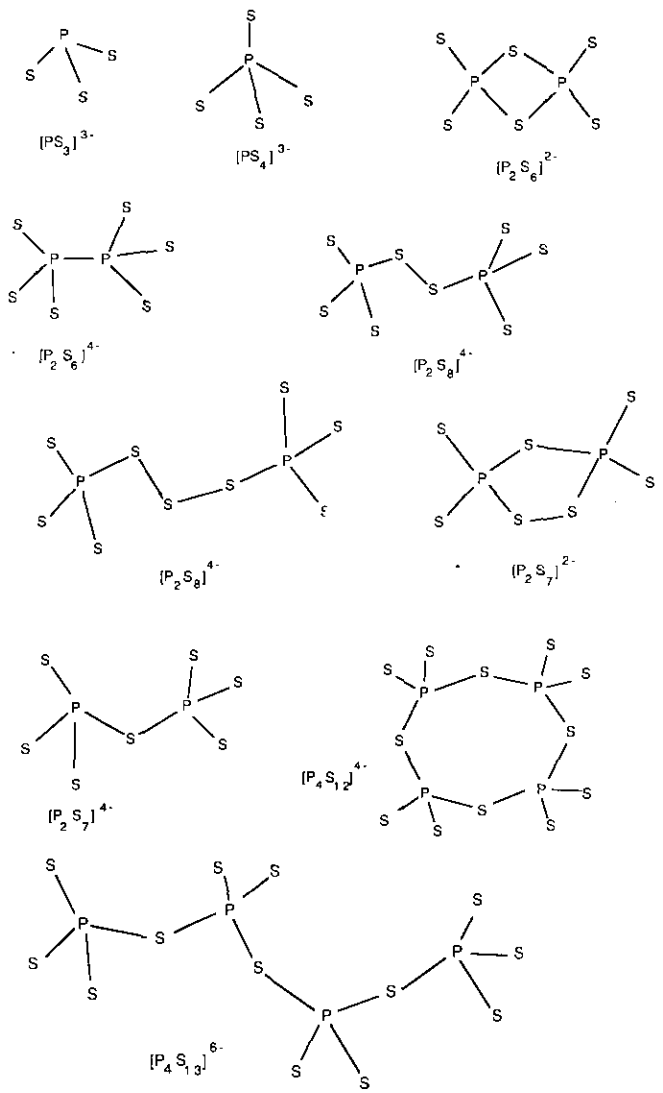

FIG. 1. Structural geometries of P–S anions in ternary *M*–P–S compounds.

Only a few metal–phosphorus–selenides with other stoichiometries have been reported. The structures of Tl_3Se_4 (30) and Cu_3PSe_4 (31) have been determined by single-crystal X-ray diffraction, revealing the presence of isolated $[PSe_4]^{3-}$ tetrahedra. Furthermore, Cu_7PSe_6 (32) and Ag_7PSe_6 (33) have been reported as representatives of the argyrodite family (34). The structures of these compounds are based on $[PSe_4]^{3-}$ groups in addition to isolated Se^{2-} anions. Other ternary compounds include TlPSe, $TlPSe_2$ (35), NbPSe (36), and PdPSe (37). Finally, the $[P_2Se_8]^{2-}$ anion, with two diselenide groups bridging the two P atoms, was isolated as its $[Pph_4]^+$ salt (38).

Recently, a detailed account of compound formation in the Li–P–Se system has established the existence of two new compounds with stoichiometries Li_7PSe_6 and $Li_4P_2Se_6$ (24). In the present study we report results of a systematic search for compound formation in ternary *M*–P–Se systems with higher-valent (Ca, Cd, Zn, Sn, In) cations. The structural features of these systems are discussed on the basis of solid state NMR data and compared to those present in the better known analogous sulfide systems.

EXPERIMENTAL

Powdered P (99.999%, Aldrich Chemical Co.), Se (99.999%, Aldrich Chemical Co.), and the metal (copper (powder, 99.999%, Aldrich Chemical Co.), reduced cadmium (powder, 325 mesh, 99.5%, Aldrich Chemical Co.), tin (granular, 30 mesh, Aldrich Chemical Co.), zinc (powder, 100 mesh, 99.999%, Aldrich Chemical Co.), lead (powder, 99.999%, Aldrich Chemical Co.), indium (granules, 99.999%, Aldrich Chemical Co.)) were mixed in stoichiometric proportions, sealed into evacuated silica glass ampoules (10^{-3} Torr), and heated during 60 to 84 hr at 700 to 750°C. Stoichiometric mixtures of Ca (granular, 6 mesh, 99%, Aldrich Chemical Co.), P, and Se were heated

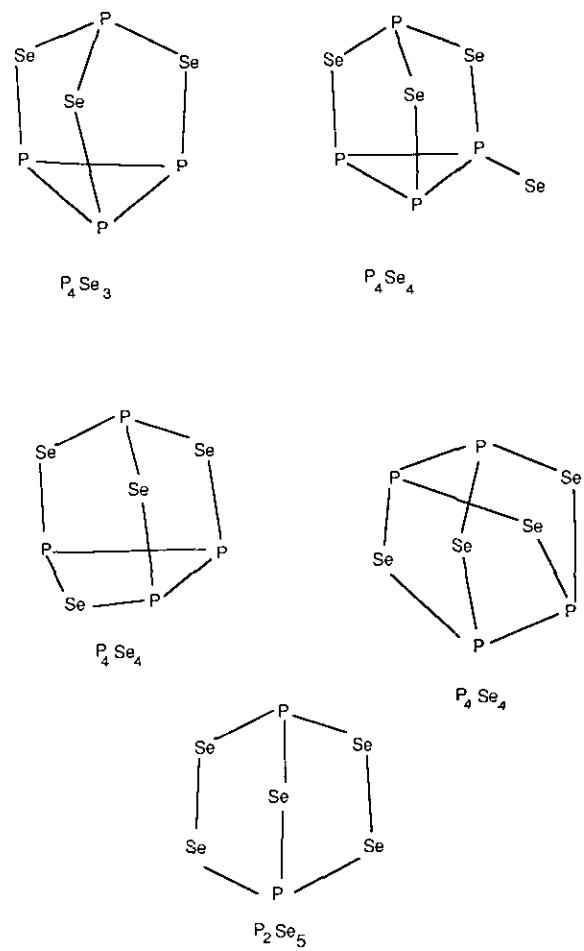

FIG. 2. Molecular structures of crystalline P–Se compounds.

at 850°C, during 24 hr, and then crushed and heated again during periods from 24 to 48 hr at 1100°C. $Hg_2P_2Se_6$ was prepared from mercury (redistilled, Fisher Scientific Co.), phosphorus, and selenium heated during 60 hr at 350°C and 48 hr at 400°C. The reaction was not complete, but the presence of $Hg_2P_2Se_6$ as a major component was confirmed by X-ray powder diffraction (27). $Cd_2P_2S_6$ was synthesized from a stoichiometric mixture of Cd, P, and S (powder, 99.999%, Aldrich Chemical Co.), heated at 400°C for 6 hr and at 750°C for 60 hr. $Cd_7P_2S_{12}$ was prepared from Cd, P_2S_5 (powder, 99%, Aldrich Chemical Co.) and S, treated at 400 and 680°C, to avoid decomposition to $Cd_2P_2S_6$ (39). In all cases, the temperature was decreased at an average cooling rate of 10°C/hr. All the substances were handled in a stainless steel glove box under argon atmosphere.

All samples were examined by X-ray powder diffraction, using a Scintag diffractometer with a Cu$K\alpha$ source. Multinuclear MAS–NMR studies were carried out on a General Electric GN-300 wide-bore system, equipped with a magic-angle spinning probe from Doty Scientific and an Explorer fast digitizer. Samples were spun within silicon nitride spinners of 7-mm o.d. at speeds between 3 and 8 kHz. ^{31}P MAS–NMR spectra were recorded at 121.65 MHz, using a 90° pulse length of 6 μsec and a relaxation delay of 600 sec. In addition to simple single-pulse experiments, multiple-quantum filtered ^{31}P MAS–NMR spectra were obtained using the DRAMA (Dipolar Recovery at Magic Angle) pulse sequence, recently introduced by Tycko and co-workers (40). The spectral editing sequence uses a rotor-synchronized train of ($90°-\tau_1-90°-\tau_2-180°-\tau_2-90°-\tau_1-90°-\tau_1$) pulses, to reintroduce the dipole–dipole interactions that are usually eliminated by magic-angle spinning. The application of the pulse sequence to the present systems focuses on the distinction between $[PSe_4]^{3-}$ and $[P_2Se_6]^{4-}$ groups. Due to the presence of the P–P bond in the latter, such compounds have substantially stronger ^{31}P–^{31}P dipole–dipole couplings, compared to compounds with isolated $[PSe_4]^{3-}$ units. Thus, under appropriate conditions, it should be possible to detect them selectively, while the signal due to isolated $[PSe_4]^{3-}$ groups is removed by phase cycling. Figure 3 verifies this prediction with the known reference compounds $Cd_2P_2S_6$ (41) and $Cd_2P_2Se_6$ (27, 28) (P–P bond) versus $Cd_7P_2S_{12}$ (34) and Cu_3PSe_4 (31) (isolated P atoms), respectively. Typical acquisition parameters for the DRAMA sequence were 90° pulse length of 6 μs; τ_1 = 72 μsec; τ_2 = 36 μsec; recycle delay, 600 sec; spinning speed, 6.3 kHz. ^{77}Se MAS–NMR spectra were obtained at 57.27 MHz with a 90° pulse length of 8 μsec and a 30-min relaxation delay. For ^{113}Cd, a spectral frequency of 66.71 MHz, a 90° pulse length of 6 μsec, and a relaxation delay of 900 sec were used. For ^{119}Sn, the spectral frequency was 112.0122 MHz, and 90° pulses of 6 μsec length and a relaxation delay of 1 hr were used. Chemical shifts are externally referenced to 85% H_3PO_4 (^{31}P), solid cubic CdSe (^{77}Se), $Cd(CH_3)_2$ (^{113}Cd), and Sn $(CH_3)_4$ (^{119}Sn), respectively.

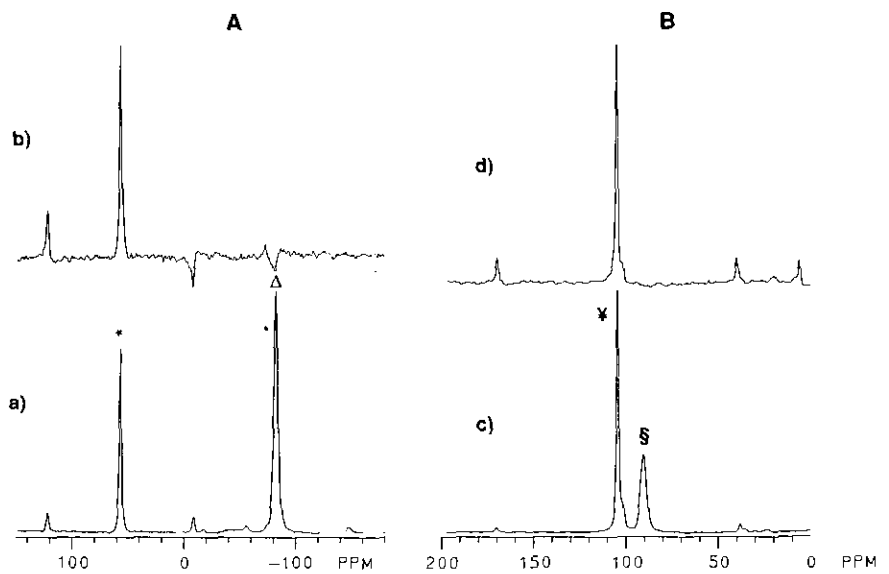

FIG. 3. ^{31}P MAS–NMR spectra for mixtures of reference compounds illustrating the spectral editing effect of the DRAMA pulse sequence. (A) $Cd_2P_2Se_6$ and Cu_3PSe_4. (a) Single-pulse experiment, four acquisitions, and 600-sec delay time. * indicates the resonance for $Cd_2P_2Se_6$ at 55.3 ppm, and Δ indicates the resonance at −84.5 ppm for Cu_3PSe_4. (b) DRAMA experiment; 160 acquisitions; spinning speed, 8 kHz. (B) $Cd_2P_2S_6$ and $Cd_7P_2S_{12}$. (c) Single-pulse experiment, eight acquisitions, and 300-sec delay time. ¥ indicates the resonance for $Cd_2P_2S_6$ at 103.9 ppm, and § indicates the resonance at 90.0 ppm for $Cd_7P_2S_{12}$. (d) DRAMA experiment; 160 acquisitions; spinning speed, 8 kHz.

RESULTS AND DISCUSSION

Table 1 summarizes all of the compositions investigated and the reaction products identified by X-ray diffraction or solid state NMR. Table 2 summarizes the NMR chemical shift parameters of the ternary M–P–Se compounds studied. The results can be summarized as follows.

Cd–P–Se

The only ternary compound in this system is $Cd_2P_2Se_6$ (27, 28). All other compositions studied resulted in mixtures of $Cd_2P_2Se_6$, CdSe, and P–Se glasses, as shown by X-ray diffraction and ^{31}P MAS–NMR spectra. $Cd_2P_2Se_6$ gives rise to a single sharp peak near 55 ppm, whereas the amorphous fraction of the sample yields broad resonances around 120–140 ppm, the known chemical shift range of binary phosphorus–selenium glasses (18, 19). In addition, several samples show resonances near −2 to −5 ppm and near −20 to −23 ppm which are attributable to Cd–P–O phase impurities, presumably formed by reaction with the quartz ampoules or with oxygen impurities in the starting materials.

Cu–P–Se

Investigation of the Cu–P–Se system over a range of compositions (Table 1) reveals that the two known compounds, Cu_3PSe_4 (31) and Cu_7PSe_6 (32), are the sole crystalline phases. All other compositions reveal the ^{31}P MAS–NMR spectra due to these phases and broad resonances attributed to P–Se glasses.

Zn–P–Se

For all four compositions prepared in the Zn–P–Se system, crystalline ZnSe and P–Se glass were observed as the sole products. There are no indications of any ternary compound formation in this system, and even the selenium analog to $Zn_2P_2S_6$ (28, 42) does not exist.

Sn–P–Se

Investigation of the Sn–P–Se system reveals the known phase $Sn_2P_2Se_6$ (27, 28, 43) as the only ternary compound. Both $Sn_2P_2Se_6$ and $Pb_2P_2Se_6$ are isomorphous and form structures that are based on $[P_2Se_6]^{4-}$ groups. However, in contrast to the other $M_2P_2Se_6$ compounds, these materials are not layered but form three-dimensional frameworks (43). The metal cations are situated in distorted trigonal prisms with three additional Se atoms, at the vertical prism faces, yielding a coordination number of nine. Compositions with other stoichiometries show resonances attributable to P–Se glass and/or X-ray diffraction lines belonging to SnSe.

Ca–P–Se

While none of the samples studied yielded phase-pure compounds, they show clear evidence of a new ternary compound besides CaSe and P–Se glass. Based on the compositional dependence of X-ray powder patterns and solid state NMR spectra, we conclude that this new compound has the stoichiometry $Ca_2P_2Se_6$. The X-ray powder diffraction pattern (Table 3) is indexed in the orthorhom-

TABLE 1
Compositions Investigated in the *M*–P–Se Systems

Cd–P–Se	Cu–P–Se	Zn–P–Se	Sn–P–Se	Ca–P–Se	In–P–Se
$Cd_2P_2Se_6$[c]	Cu_3PSe_4[a]	$Zn_2P_2Se_6$[f,h]	$Sn_2P_2Se_6$[c]	$Ca_2P_2Se_6$[c,f]	$In_4(P_2Se_6)_3$[d]
$Cd_3P_2Se_8$[c,f,i]	Cu_7PSe_6[b]	$Zn_4P_2Se_6$[f,h]	$Sn_3P_2Se_8$[f,h]	$Ca_7P_2Se_{12}$[f,h]	$InPSe_4$[d,f,j]
CdP_2Se_6[c,h]	$Cu_5P_2Se_6$[b,h]	ZnP_2Se_6[f,h]	$Sn_7P_2Se_{12}$[f,h]	$Ca_5P_2Se_{10}$[f,h]	$In_4P_6Se_{12}$[d,f,g,h]
$Cd_4P_2Se_9$[c,f]	$Cu_2P_2Se_5$[a,h]	ZnP_2Se_8[f,h]	SnP_2Se_6[f,h]	$Ca_4P_2Se_9$[f,h]	In_3PSe_3[e]
$Cd_5P_2Se_{10}$[c,f,i]	$Cu_4P_2Se_6$[a]		$Sn_5P_2Se_{10}$[f,h]	$Ca_3P_2Se_8$[f,h]	$In_2P_3Se_5$[f,g,h]
$Cd_7P_4Se_{12}$[c,f,h,i]	$CuPSe_2$[a,h]				In_3PSe_4[e,f,j,k]
$Cd_4P_2Se_6$[c,i]	$Cu_4P_2Se_7$[a]				
$Cd_7P_2Se_6$[c,f,i]	$CuPSe_3$[a,h]				
$Cd_5P_2Se_6$[c,h,i]	Cu_3PSe_3[a,h]				
Cd_5PSe_6[c,f,h,i]	Cu_5PSe_3[a,h]				
Cd_7PSe_6[c,f,i]	$Cu_7P_2Se_{12}$[a,f]				
$Cd_7P_2Se_{12}$[c,f,i]	$Cu_7P_{10}Se_6$[a,h]				
Cd_2PSe_6[c,f,h,i]					
Cd_3PSe_6[c,f,h,i]					
Cd_5PSe_3[c,f,h]					
Cd_7PSe_3[c,f,h,i]					
Cd_4PSe_3[c,f,i]					

Note. Compounds identified: [a]M_3PSe_4, [b]M_7PSe_6, [c]$M_2P_2Se_6$, [d]$M_4[P_2Se_6]_3$, [e]In_3PSe_3, [f]MSe or M_2Se_3, [g]P_4Se_3, [h]P–Se glass, [i]Cd–P–O impurities, [j]Se, [k]P_4.

TABLE 2
Compound Formation in *M*–P–Se Systems and Chemical Shifts (ppm) for ^{31}P MAS NMR of Ternary Phases Identified

M–P–Se	Ternary compound	CS	$\partial(^{31}P)$ [ppm]	Anionic species	Ref.
Zn–P–Se	None	—	—	—	—
Cu–P–Se	Cu_3PSe_4	o	−84.5	$[PSe_4]^{3-}$	28
	Cu_7PSe_6	c	−30.3	$[PSe_4]^{3-}$; Se^{2-}	29
Li–P–Se	Li_7PSe_6	c	−80.2; −82.8	$[PSe_4]^{3-}$; Se^{2-}	21
	$Li_4P_2Se_6$	o	55.1; 46.5	$[P_2Se_6]^{4-}$	21
Ag–P–Se	Ag_7PSe_6	c	−51.5	$[PSe_4]^{3-}$; Se^{2-}	30
	$Ag_4P_2Se_6$	o	77.5; 91.0	$[P_2Se_6]^{4-}$	22
Cd–P–Se	$Cd_2P_2Se_6$	r (h)	55.3	$[P_2Se_6]^{4-}$	25
Hg–P–Se	$Hg_2P_2Se_6$	m	63.7	$[P_2Se_6]^{4-}$	24
Pb–P–Se	$Pb_2P_2Se_6$	m	29.1	$[P_2Se_6]^{4-}$	40
Sn–P–Se	$Sn_2P_2Se_6$	m	28.7	$[P_2Se_6]^{4-}$	40
Ca–P–Se	$Ca_2P_2Se_6$	o	44.7	$[P_2Se_6]^{4-}$	
In–P–Se	$In_4(P_2Se_6)_3$	o	52.7	$[P_2Se_6]^{4-}$	26
	In_3PSe_3	c	−187	P^{3-}; Se^{2-}	43

Note. $Cd_2P_2Se_6$, $\partial(^{113}Cd)$ = −184.1 ppm; $Sn_2P_2Se_6$, $\partial(^{119}Sn)$ = −608.0 ppm. CS, crystal system; m, monoclinic; o, orthorhombic; r, rhombohedral; c, cubic.

bic system, $a = 5.73(1)$ Å, $b = 9.86(1)$ Å, $c = 15.78(1)$ Å, $V = 891$ Å^3, $d_{(calc)} = 4.59$ g cm^{-3}, $Z = 4$. It is not isomorphous to either $Mg_2P_2Se_6$ or $MgCaP_2Se_6$, which are rhombohedral (27). Comparison of the ^{31}P chemical shift with the data shown in Table 2 for known compounds is consistent with presence of $[P_2Se_6]^{4-}$ units. Additional support for P–P bonding is provided by the DRAMA experiment, as demonstrated in Fig. 4 for a mixture containing $Ca_2P_2Se_6$ and the model compound $Sn_2P_2Se_6$. The MAS–NMR spectra show further that both P atoms are crystallographically equivalent.

TABLE 3
Observed and Calculated Distances (Å) between Crystallographic Planes (*hkl*) and Relative Intensities of X-Ray Diffraction Lines, in $Ca_2P_2Se_6$ ($a = 5.73(1)$, $b = 9.86(1)$, $c = 15.78(1)$ Å)

d(obs) (Å)	*hkl*	*d*(calc) (Å)	*I*(rel)
4.04	0 0 4	3.94	34
3.296	0 3 0	3.288	39
3.136	0 0 5	3.155	30
3.106	1 1 4	3.085	44
2.748	2 1 0	2.750	93
2.695	2 0 2	2.692	30
2.679	1 3 2	2.682	24
2.362	2 2 2	2.363	14
2.352	0 4 2	2.354	100
1.959	0 5 1	1.958	13
1.811	1 5 2	1.815	18
1.682	1 5 4	1.686	20
1.664	0 4 7	1.664	43
1.645	0 6 0	1.644	21

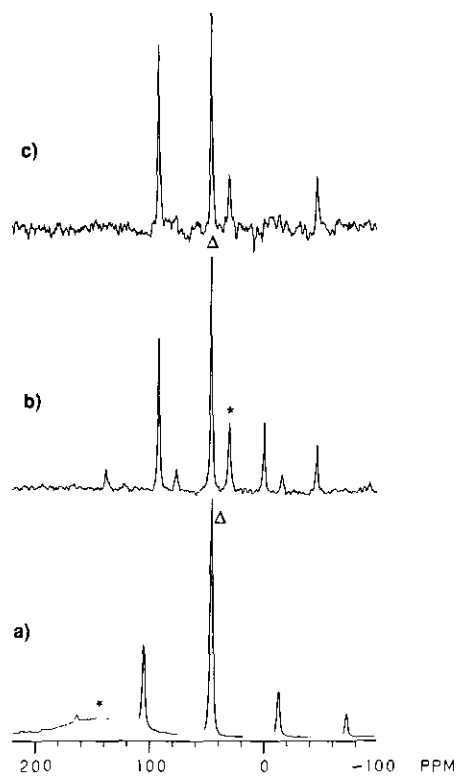

FIG. 4. ^{31}P NMR characterization of $Ca_2P_2Se_6$. (a) Single-pulse MAS NMR for a sample with stoichiometry $Ca_5P_2Se_{10}$ showing one sharp resonance at 44.7 ppm (Δ) and a broader one (*) due to P–Se glass. Unmarked peaks are spinning sidebands. (b) Single-pulse experiment of a mixture of $Ca_2P_2Se_6$ and $Sn_2P_2Se_6$ with four acquisitions. Δ indicates the resonance for $Ca_2P_2Se_6$ and * for $Sn_2P_2Se_6$ (28.7 ppm). (c) DRAMA spectrum, 128 acquisitions and 5.5 kHz spinning speed. Note that the signal due to $Ca_2P_2Se_6$ is observed under conditions where the signal due to the $Sn_2P_2Se_6$ standard is observable as well.

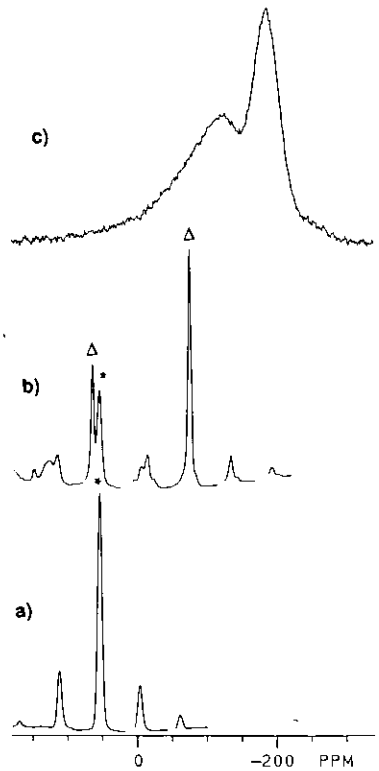

FIG. 5. Representative ^{31}P MAS–NMR spectra for compounds in the In–P–Se system. (a) $In_4(P_2Se_6)_3$. * indicates the main band. Unmarked peaks are spinning sidebands. (b) A sample with composition $In_4P_6Se_{12}$. The spectrum reveals $In_4(P_2Se_6)_3$ (whose resonance at 53.0 ppm is indicated by *) and P_4Se_3 (resonances at 62.9 and −76.2 ppm, indicated by Δ). (c) In_3PSe_3, revealing one resonance at −187 ppm and one shoulder at −135 ppm.

In–P–Se

Investigation of the In–P–Se systems reveals $In_4(P_2Se_6)_3$ and In_3PSe_3 as the sole compounds. The X-ray powder diffraction pattern of $In_4(P_2Se_6)_3$, with $[P_2Se_6]^{4-}$ anions, can be indexed by both closely related unit cells, hexagonal (44) and orthorhombic (29), previously proposed for this material. The observed peaks agree with those proposed by Brusilovets and Fedoruk (45), which are included among the ones observed by Diehl and Carpentier (29). The material is structured in layers, and the preferential orientation of a number of crystalline plates can lead to a distorted intensity pattern. In_3PSe_3 (46) possesses a cubic sphalerite-type structure and is to be viewed as a mixed indium phosphide selenide rather than a selenophosphate. The ^{31}P MAS–NMR spectrum shows severe broadening effects due to ^{115}In–^{31}P scalar coupling and dipolar effects previously reported in the ^{31}P spectrum of InP (47). Figure 5 shows representative ^{31}P MAS–NMR spectra illustrating excellent chemical shift discrimination between $[P_2Se_6]^{4-}$ and P^{3-} sites.

CONCLUSIONS

The systematic search of the various *M*–P–Se systems reported here indicates much less structural variety compared to the situation in analogous ternary sulfide systems. The only P–Se anions observed in high-temperature inorganic reactions are $[PSe_4]^{3-}$ and $[P_2Se_6]^{4-}$. In addition, the Se^{2-} anion is present in the argyrodite family representatives (M_7PSe_6) and in In_3PSe_3, which also is the only one to contain P^{3-} anions. Overall, distinct ^{31}P chemical shift ranges are observed for all of these species (Table 2), and the chemical shift discrimination is much more clear cut than in the analogous sulfide systems (see Fig. 1 and Refs. (11, 12)). The results of the present study show also proof that the DRAMA experiment, a multiple-quantum filtering technique associated with MAS, is an extremely useful spectral editing technique and a valuable source of structural information in the study of these inorganic systems.

ACKNOWLEDGMENTS

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