

no Rh-Rh bond, while the Mo-Mo bond is over 0.4 Å longer than the Mn-Mn bond in I, the bending angle of a bridging allene is quite insensitive to its environment.¹⁵ Another structural parameter is more responsive to such effects. Thus, it has been observed that the central carbon of a coordinated allene lies closer to the metal than does the terminal carbon. The difference between these metal-carbon bond lengths is 0.08 (7σ) Å in the dimeric rhodium complex,¹⁴ 0.11 (4σ) Å in Cp₂Mo₂(CO)₄C₃H₄,⁶ and 0.20 (40σ) Å in I. The carbon-carbon bond length in I (1.394 Å) is 0.08 Å longer than in allene itself (1.312 Å).¹³

Mass Spectral Fragmentation. The 70-eV electron impact mass spectrum of Cp₂Mn₂(CO)₃(C₃H₄) indicates loss of a single CO ligand in overwhelming preference to loss of the allene fragment. The loss of allene or two carbonyls then become competitive paths. This contrasts with the mass spectral fragmentation of Cp₂Mn₂(CO)₄(μ₂-η¹-CCH₂),¹ in

(15) The allene bending angle in a η² nonbridging environment¹⁴ is 153°.

which loss of *even numbers* of carbonyl ligands occurs to the exclusion of loss of the vinylidene ligand; vinylidene loss is seen only after the fragment Cp₂Mn₂CCH₂⁺ has been achieved. This more facile loss of a four-electron donor allene compared to a two-electron donor vinylidene may at first appear paradoxical. In fact, it appears that this correlates with the lack of stability of the ejected fragment (i.e., vinylidene vs. allene), and therefore this could provide a spectroscopic probe for the mode of binding of isomeric hydrocarbon fragments (e.g., alkene vs. vinylidene).

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Supplementary Material Available: A listing of calculated and observed structure factors and anisotropic thermal parameters (24 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of MPSe₃(py)_{1/n} Complexes

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MPSe₃ (M = Mn, Fe) reacts with pyridine molecules to form intercalation complexes. In the MnPSe₃-pyridine (py) system, two complexes of MnPSe₃(py)_{1/3} and MnPSe₃(py)_{1/4} were obtained, and a FePSe₃(py)_{1/3} complex was prepared in the FePSe₃-pyridine system. From the results of one-dimensional electron density projections on the *c* axis, the arrangements of pyridine molecules between the MnPSe₃ layers were determined. The plane of the pyridine molecules is perpendicular to the MnPSe₃ layer for MnPSe₃(py)_{1/3} but parallel for MnPSe₃(py)_{1/4}. The electrical resistivity of the complexes was closely related to the arrangements of pyridine molecules in the interlayers.

Introduction

In recent years, it was found that the superconducting transition temperature of some transition-metal dichalcogenides (MX₂) was strongly influenced by the absorption of pyridine molecules between the successive MX₂ layers.¹⁻⁴ It has been said that metallic compounds with layer structures such as TaS₂ can form the charge-transfer-type complexes, but semiconductors such as MoS₂ are inert. Recently, however, it was found that the semiconductive FeOCl reacts with pyridine molecules to form intercalated compounds.⁵ This result indicates that some semiconductive inorganic layered compounds can react with pyridine molecules and the chemical-bond nature is quite different between MoS₂ and FeOCl. In order to conduct a further study on this problem, it is necessary to choose an appropriate semiconductive layered compound with strong covalent-bonding nature as a host material. The preparation and crystal structure of the host compounds MPSe₃ (M = Mn, Fe) have previously been reported by Klingen et al.^{6,7} and Taylor et al.⁸ The structure

of the compounds is related to that of the layered transition-metal dichalcogenides MX₂, as shown in Figure 1. MPSe₂ (M = Mn, Fe) compounds are insulators (ρ ≥ 10⁸ Ω cm) but intercalate some kinds of organic molecules with strong basicity. In the present investigation, we succeeded in forming intercalation compounds of MPSe₃-pyridine. The preparation and structure of the complexes are reported in this paper.

Experimental Section

Preparation of Host Compounds. For the preparation of MnPSe₃ and FePSe₃, Mn (99.99%), Fe (99.99%), P (99.99%), and Se (99.99%) powders were mixed in the desired ratio, sealed in evacuated silica tubes, and then heated at 650 °C for 1 week. After the reaction was completed, the reacted matter was cooled slowly to room temperature. Single crystals of MPSe₃ were grown by chemical vapor transport using iodine as a carrier gas. The chemical vapor transport reactions were carried out in a two-zone furnace with a temperature gradient (650-610 °C) for 1 week. The crystals obtained were hexagonal plates up to 0.1 × 3 × 3 mm³.

Preparation of Complexes. The reaction with pyridine was conducted in the closed system which was evacuated before the reaction.

In the case of the MnPSe₃-pyridine system, a complex (I) was obtained by heating MnPSe₃ at 30 °C for 4 days under the saturated vapor pressure of pyridine which was kept at room temperature. The complex (I) changed to another complex (II) by exposure to dry air for 1 day.

In contrast, FePSe₃ was less reactive with pyridine. The FePSe₃-pyridine complex was obtained by heating FePSe₃ in distilled

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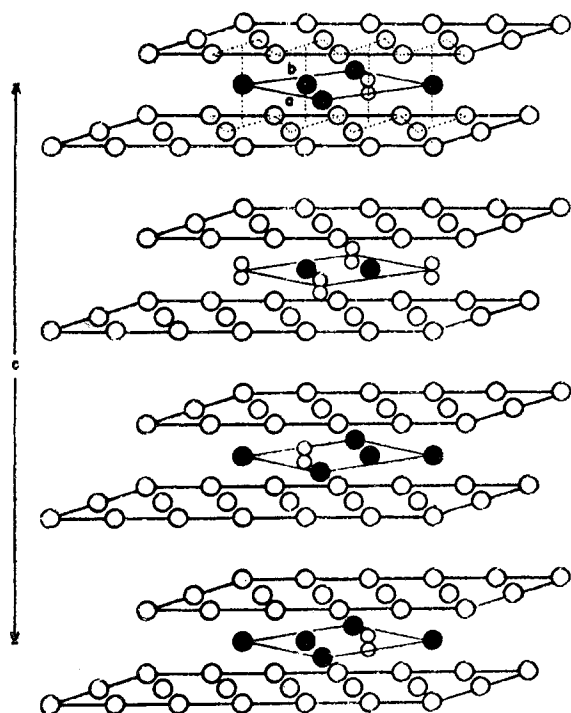


Figure 1. Crystal structure of FePSe_3 .⁸

pyridine at 60 °C for 4 days. The product was dried in dry air.

X-ray Analysis. Changes of the interlayer spacings due to intercalation were observed by X-ray powder diffractometry. The scanning speed was 0.25° 2 θ /min, and silicon was used as an internal standard. One-dimensional electron density projections on the *c* axis were examined by using six (00*l*) reflections for the $\text{MnPSe}_3(\text{py})_{1/3}$ and $\text{MnPSe}_3(\text{py})_{1/4}$ complexes.

DTA-TGA Measurement. For determination of the composition of the intercalated complexes and for examination of the thermal stability of the complexes, DTA-TGA was conducted from room temperature to 250 °C at a heating rate of 10 °C per min.

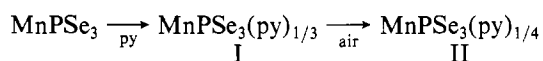
Magnetic Susceptibility Measurement. Magnetic properties were measured by using an automatic recording magnetic balance in the temperature range 77–300 K.

Electrical Resistivity Measurement. Since these complexes are not stable under vacuum, the measurements on the small flakes of the host materials and their pyridine complexes were carried out in the saturated vapor pressure of pyridine from room temperature to 225 K. The electrical resistivity along the *c* plane of the samples was measured by means of a two-probe dc method.

Results and Discussion

In the case of the MnPSe_3 -pyridine system, the complexes could not be obtained when the crystals larger than 1 mm were used as host materials. Only the edge of the crystals reacted with the pyridine molecules to form the complexes. Crystals less than 1 mm readily absorbed the pyridine molecules to form I.

As mentioned above, two complexes were obtained in the MnPSe_3 -pyridine system. The results of DTA-TGA measurements for these complexes are shown in Figure 2. After the thermal treatment the complexes reversed to the host compound whose composition was determined to be MnPSe_3 by chemical analysis. From the weight-loss data given in Figure 2, the compositions of the two complexes were determined to be $\text{MnPSe}_3(\text{py})_{1/3}$ for I and $\text{MnPSe}_3(\text{py})_{1/4}$ for II. Complex I, $\text{MnPSe}_3(\text{py})_{1/3}$, began to desorb the pyridine molecules at about 20 °C but could exist in air for 1 day.



Complex II, $\text{MnPSe}_3(\text{py})_{1/4}$, was more stable in air. All X-ray powder diffraction peaks of both complexes could be indexed

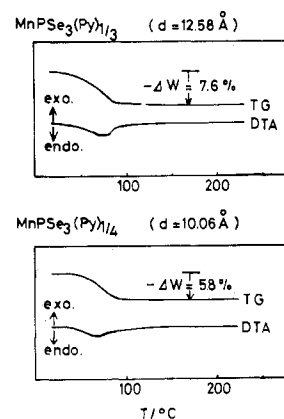


Figure 2. Differential thermal analysis and thermogravimetry of $\text{MnPSe}_3(\text{py})_{1/n}$.

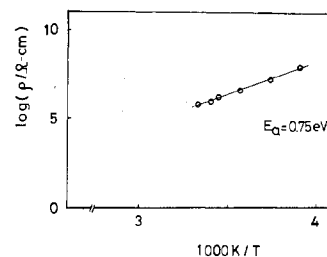


Figure 3. Temperature dependence of electrical resistivity of $\text{MnPSe}_3(\text{py})_{1/3}$.

Table I. Lattice Parameters of MnPSe_3 and $\text{MnPSe}_3(\text{py})_{1/n}$

	<i>a</i> /Å	<i>c</i> /Å	Δ <i>c</i> /Å
$\text{MnPSe}_3(\text{py})_{1/3}$	6.38	12.58	5.90
$\text{MnPSe}_3(\text{py})_{1/4}$	6.38	10.06	3.38
MnPSe_3	6.38	6.68 ^a	

^a *c*/3.

with the hexagonal symmetry of the host compound. Calculated lattice parameters were tabulated in Table I. As illustrated in this table, in both complexes, the *a* parameters had the same value for each of the host compounds, but the values of the *c* parameters were different. This result indicates that absorption of pyridine molecules induced little effect on atomic arrangements in the MnPSe_3 layer but had influence only on the interlayer separation.

The magnetic susceptibility data were collected for MnPSe_3 and its pyridine complexes. The magnetic moment for MnPSe_3 was calculated to be 6.1 μ_B , indicating the divalent state of the Mn ion. There was observed little difference in the moments between MnPSe_3 and the complexes.

The resistivity of the host compound and $\text{MnPSe}_3(\text{py})_{1/4}$ at room temperature was above $10^8 \Omega \text{ cm}$, but an electrical conductivity along the *c* axis of $\text{MnPSe}_3(\text{py})_{1/3}$ was larger by a factor of 10^3 – 10^4 than that of MnPSe_3 , as shown in Figure 3. The difference in electrical resistivity between the host material and $\text{MnPSe}_3(\text{py})_{1/3}$ is thought to arise from the different orientation of the lone-pair electron's orbital of pyridine molecules between the layers.

One-dimensional electron density projections on the *c* axis are shown in Figure 4. Although the peaks of Mn and Se appeared at the expected positions, the peaks of P were concealed by those of Se due to its low atomic number. In the case of $\text{MnPSe}_3(\text{py})_{1/4}$ there was observed only one peak between the layers. The expansion of interlayer distance of 3.38 Å was consistent with the van der Waals thickness of the pyridine molecular plane. These data revealed that $\text{MnPSe}_3(\text{py})_{1/4}$ was the complex in which the plane of the

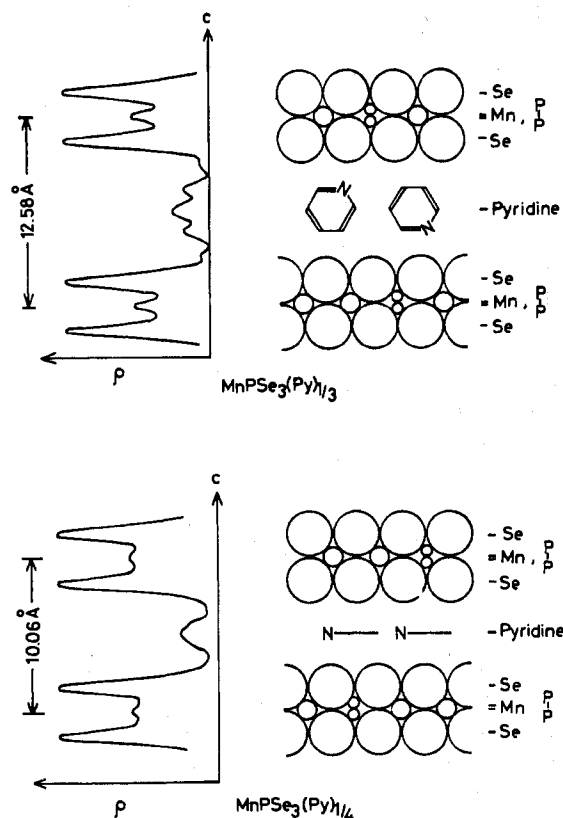


Figure 4. One-dimensional electron density projection on the *c* axis of MnPSe₃(py)_{1/3} and MnPSe₃(py)_{1/4}.

pyridine molecule was parallel to the MnPSe₃ layer as shown in Figure 4. In this configuration, pyridine molecules take a close packing in the interlayer region with the composition of MnPSe₃(py)_{1/4}. The intercalation of pyridine molecules over 1/4 has to result in expansion of the interlayer and change of orientation of the pyridine ring as followed.

In the case of MnPSe₃(py)_{1/3}, three peaks appeared between the layers. The expansion of the interlayer distance of 5.90 Å was consistent with the van der Waals diameter of the pyridine molecule. This result indicated that the plane of the pyridine molecule was perpendicular to the MnPSe₃ layer. From these results, two different models on the arrangement of pyridine molecules were deduced: (a) the twofold C/N symmetry axis parallel to the host layer and (b) the twofold axis making an angle to the layer. Recently, Schöllhorn et al.⁹ presented evidence that TaS₂(py)_{0.5} was not a simple intercalation compound of pyridine but contained (pyH)⁺ ions and bipyridine. They also explained the orientation of the

Table II. Lattice Parameters of FePSe₃ and FePSe₃(py)_{1/3}

	<i>a</i> /Å	<i>c</i> /Å	Δ <i>c</i> /Å
FePSe ₃ (py) _{1/3}	6.26	12.50	5.90
FePSe ₃	6.26	6.60 ^a	

^a *c*/3.

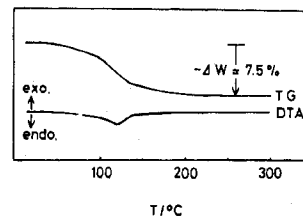


Figure 5. Differential thermal analysis and thermogravimetry of FePSe₃(py)_{1/3}.

pyridine ring determined by neutron diffraction (the twofold axis parallel to the layer) and the electrical property of the complex.

The electron density projected on the *c* axis of MnPSe₃(py)_{1/3} indicated a possibility that the twofold axis of the pyridine ring was parallel and also that the proved electric conductivity of MnPSe₃(py)_{1/3} might be explained by assuming ionic bonding between (pyH)⁺ ions and the negatively charged host layer. This ionic bonding made (pyH)⁺ ions more stable than pyridine molecules in the interlayer region of MnPSe₃, giving an assumption that pyridine molecules were desorbed prior to (pyH)⁺ ions during the conversion from MnPSe₃(py)_{1/3} to MnPSe₃(py)_{1/4}, and then the electrical conductivity of MnPSe₃(py)_{1/4} might be almost of the same order as MnPSe₃(py)_{1/3}, since the ionic bonding between (pyH)⁺ and (host layer)⁻ ions still remained in the former complex.

However, this assumption was not consistent with the observed electrical properties of MnPSe₃(py)_{1/4}. Therefore, it was expected that there were formed few (pyH)⁺ ions in the interlayer region of both complexes but that the plane of the pyridine molecule was perpendicular to the MnPSe₃ layer and the twofold axis made an angle to the layer such that the lone-pair electron faced the layer in MnPSe₃(py)_{1/3} as illustrated in Figure 4.

In the case of FePSe₃, only one complex was obtained and the lattice parameters were listed in Table II. The electrical resistivity of the complex was about 10⁶ Ω cm at room temperature, and it was smaller by a factor of 10² than that of the host compound, FePSe₃. From the result of the weight loss in the DTA-TGA measurements shown in Figure 5, the composition of the complex was determined to be FePSe₃(py)_{1/3}. The structure of the FePSe₃(py)_{1/3} complex was thought to be the same as that of the MnPSe₃(py)_{1/3} complex.

Registry No. MnPSe₃, 20642-10-8; FePSe₃, 21906-52-5; MnPSe₃(py)_{1/3}, 73017-50-2; MnPSe₃(py)_{1/4}, 73017-51-3; FePSe₃(py)_{1/3}, 73017-52-4.

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