

SPECTROSCOPIC AND ESR STUDIES OF $\text{Cd}_2\text{P}_2\text{S}_6$ INTERCALATED WITH PYRIDINE COMPLEXES OF FERRIC ION

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Abstract— $\text{Cd}_2\text{P}_2\text{S}_6$ crystallizes in a layered structure which is readily intercalated with a variety of Lewis bases. We have studied the intercalation reactions of this lattice with pyridine complexes of several transition metal ions and Ce^{4+} . In some instances (e.g. Mn^{2+}) the metal ion could be co-intercalated with pyridine with little or no effect on the distribution of reaction products formed within the van der Waals gap. However, certain transition metal ions had a dramatic effect on the product distribution obtained. Co-intercalation of Fe^{3+} , for example, results in the production of a highly colored polysulfide species within the van der Waals gap. The intercalated species were identified by mass spectroscopic analysis during thermal de-intercalation. The co-intercalated paramagnetic transition metal ions are useful as ESR spin-probes for the study of the structure and dynamics of the intercalate layer. Analysis of the ESR spectra indicate that co-intercalated Mn^{2+} can enter Cd^{2+} lattice vacancies at elevated temperatures.

Keywords: Intercalation, ESR, optical, pyridine.

1. INTRODUCTION

The transition metal phosphorus chalcogenides ($\text{M}_2\text{P}_2\text{X}_6$, M = transition metal, X = S or Se) crystallize in a layered structure with transition metal layers separated by two layers of chalcogenide atoms [1]. The transition metal atoms are coordinated to six chalcogenide atoms in a distorted octahedral arrangement. Van der Waals interactions between adjacent chalcogenide planes weakly bind the layers together. Because these are relatively weak interactions, it is possible to carry out a variety of solid state reactions in which molecules are intercalated between the adjacent chalcogen planes that form the van der Waals gap (VWG) [2]. Some of the reactions of the $\text{M}_2\text{P}_2\text{X}_6$ lattices are similar to the intercalation chemistry of the transition metal dichalcogenides (MX_2). These reactions have been described by Schöllhorn [3] as oxidation–reduction reactions, frequently involving electron transfer from the intercalate to the host lattice. These materials also exhibit a unique substitution–intercalation reaction in which cations are intercalated into the VWG and metal cations are displaced from the $\text{M}_2\text{P}_2\text{X}_6$ slabs [4].

In order to investigate the chemical structure, mechanism and kinetics of intercalation into $\text{M}_2\text{P}_2\text{X}_6$ lattices, we have employed ESR to follow the uptake of paramagnetic intercalant species [5]. ESR is useful for these purposes when either the reactant or the products are paramagnetic. Intercalation induced paramagnetism has been observed when narrow band-gap $\text{M}_2\text{P}_2\text{X}_6$ semiconductors (e.g. $\text{Ni}_2\text{P}_2\text{S}_6$) were intercalated with alkyl-amines [6]. Presumably, the paramagnetism is associated with electrons transferred from the highest filled orbital of the initially

diamagnetic intercalant to the conduction band of the host lattice.

$\text{Cd}_2\text{P}_2\text{S}_6$ is a wide band-gap diamagnetic lattice into which amines may be intercalated, but without the appearance of paramagnetism [5, 6]. In order to follow the progress of intercalation into large single crystals and to study the structure and intercalate dynamics within the VWG, we sought to introduce paramagnetic “spin probes” into the VWG. This was accomplished by complexing small amounts of various paramagnetic transition metal ions with pyridine. It was found that, in many cases, the transition metal complex could be co-intercalated with pyridine. A similar procedure was attempted by Inque and Negishi [7] to introduce Mn^{2+} into TiS_2 , however they failed to detect an ESR signal from intercalated manganese.

2. EXPERIMENTAL

$\text{Cd}_2\text{P}_2\text{S}_6$ was synthesized from the elements as described previously [8]. The observed {001} X-ray reflection yielded a basal plane separation of 6.55 Å, in agreement with published X-ray data [9], and the chemical analysis was consistent with the empirical formula: Cd (calc. = 46.92%, obs. = 45.89%), S (calc. = 40.15%, obs. = 41.83%) and P (calc. = 12.93%, obs. = 12.24%).

The $\text{Cd}_2\text{P}_2\text{S}_6$ crystals were transparent and colorless. Several large crystals of this material were sealed under vacuum with ca. 2 ml of a 0.02 M pyridine solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and the ampoule was allowed to stand at room temperature for 67 h. The ampoule was then opened and the product, consisting

of nearly opaque, dark blue lustrous crystals, was rinsed with ethanol and allowed to air dry. Single-crystal X-ray diffraction analysis determined the basal spacing of the product to be 12.30 Å. Several different crystals were analyzed for Cd, S, N, P and Fe. Elemental determinations from multiple analyses of a single crystal were reproducible to $\pm 0.2\%$. Analyses of different crystals agreed to within 0.4% by weight for any element. The average of these analyses for three crystals was: Cd(31.20%), S(32.76%), N(3.76%), P(11.26%) and Fe(0.24%). Assuming that all nitrogen present was due to pyridine, this analysis accounts for about 96% by weight of the sample. It is likely that the compound also contains some water. The resulting partial stoichiometry of the intercalation product is then $\text{Cd}_{0.76}\text{P}_{1.00}\text{S}_{2.81}(\text{C}_6\text{H}_5\text{N})_{0.79}\text{Fe}_{0.012}$. The compound is both sulfur and cadmium deficient in proportions such that the charge is balanced to within the experimental error of the chemical analyses. However, TGA gives the amount of volatile intercalate as 0.65, suggesting that some of the nitrogen indicated by the chemical analysis is present as the pyridinium ion.

$\text{Cd}_2\text{P}_2\text{S}_6$ was intercalated with small amounts of Ce^{4+} or Mn^{2+} by a procedure identical to that described above, but using 0.02 M pyridine solutions of Ce^{4+} [from $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$] or Mn^{2+} (from $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$). These compounds were characterized by TGA and X-ray diffraction only. The basal expansion of the Ce^{4+} intercalated lattice was 12.22 Å and the pyridine content was $x = 0.76$. The basal expansion of the Mn^{2+} intercalated lattice was 12.40 Å and the pyridine content was $x = 0.62$.

ESR spectra were recorded on a Bruker ER 200E-SRC X-band spectrometer with 100 kHz field modulation and a TM_{110} cavity. The sample temperature was controlled with a Varian model 4257 variable temperature accessory. Large single crystals (typically $4 \times 4 \times 0.02 \text{ mm}^3$) were mounted on a rotating sample support for measurements of the angular variation of the ESR spectrum.

Thermal gravimetric analysis (TGA) was done on a DuPont Instruments Model R90 Thermal Analyzer equipped with a Model 951 Thermogravimetric Analyzer. X-ray diffraction data was collected using both a Phillips automatic powder diffractometer and a Debye-Scherrer camera using CuK_α X-ray radiation.

The experimental details of the mass-spectrometric and spectroscopic analysis of the intercalated samples are presented below.

3. RESULTS AND DISCUSSION

Pyridine has been widely studied as an intercalate species in both MX_2 [10] and $\text{M}_2\text{P}_2\text{X}_6$ [5, 6, 11] lattices. Pyridine is also known to strongly complex many transition metal ions. Pyridine complexes of Mn^{2+} have been studied by McGarvey [12] whose ESR measurements suggested that, in each case, the transition metal ion is complexed by one or two

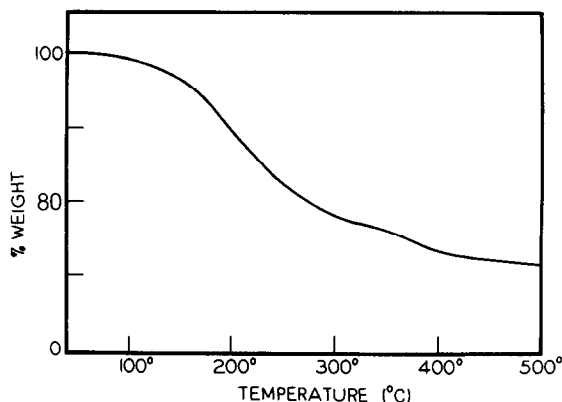


Fig. 1. Thermal gravimetric analysis of Fe^{3+} /pyridine intercalated $\text{Cd}_2\text{P}_2\text{S}_6$ single crystal.

pyridine molecules in dilute aqueous solutions of pyridine. When crystalline $\text{Cd}_2\text{P}_2\text{S}_6$ is treated with pyridine containing small amounts of the transition metal-pyridine complex, the transition metal ion is found to co-intercalate with the pyridine solvent. If the transition metal complex is viewed as a solvated ion, then the process is seen to be similar to the intercalation of solvated alkali metal ions into MX_2 lattices from aqueous solution, which has been studied extensively by Schöllhorn and co-workers [13].

The thermal gravimetric analysis of the Fe^{3+} /pyridine- $\text{Cd}_2\text{P}_2\text{S}_6$ reaction product, shown in Fig. 1, contains two weight loss regions. The first region corresponds to de-intercalation of pyridine. The species responsible for the second region was identified using mass spectrometry.

Mass spectroscopic analysis

Mass spectrometric analysis was accomplished by introducing single-crystal samples on a direct probe into the spectrometer inlet system and heating to 350°C at a rate of *ca.* 70°C/min. Figure 2 is a record of the total ion current as a function of time during the thermal de-intercalation of Fe^{3+} /pyridine intercalated $\text{Cd}_2\text{P}_2\text{S}_6$. A mass spectrum taken during the first de-intercalation peak identified the volatile material as predominantly pyridine. The thermal de-intercalation of pyridine is illustrated by the ion current at mass 79 vs time shown in Fig. 3(a). A spectrum taken during the second de-intercalation peak continued to show small amounts of residual pyridine, but also exhibited mass peaks due to 4,4'-bipyridine or 2,2'-bipyridine [mass 156, Fig. 3(b)]. Mass spectral analysis cannot easily distinguish between the fragmentation patterns of these two isomers. Chemical analyses by Schöllhorn on pyridine intercalated TaS_2 [14] suggest 4,4'-bipyridine is the isomer present. Schöllhorn also reported the presence of a small amount of 4,4'-bispyridine sulfide (MW = 188), which may be responsible for the ion of mass 111 ($\text{NC}_5\text{H}_4\text{SH}$).

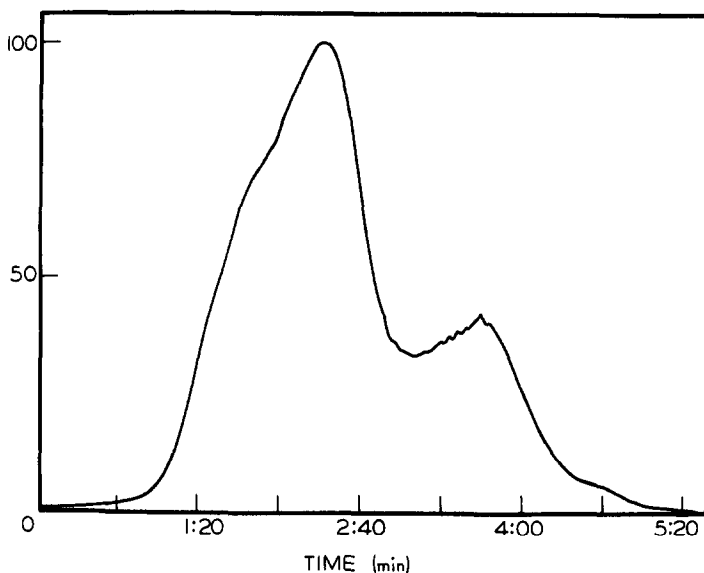


Fig. 2. Total ion current vs time during mass spectroscopic analysis of thermal de-intercalation products. Sample is heated from 25–350°C over a period of ca. 5 min.

Ions of the general formula P_xS_y were also observed [see Fig. 3(c), 3(d) and Table 1]. Although the same mass peaks are always observed, comparison of the mass spectra obtained from de-intercalation of different crystals indicates that the relative amount of each high-temperature de-intercalation product is dependent upon the crystal history.

The thermal de-intercalation behavior shown in Fig. 3 (for the Fe^{3+} /pyridine intercalated lattice) is very different from that exhibited during similar mass-resolved thermal de-intercalation of $Cd_2P_2S_6$ crystals intercalated with pyridine in the absence of iron or cerium. Notably, no bipyridine and only trace amounts of P_xS_y fragments were detected in the latter case.

Thus, only when Fe^{3+} or Ce^{4+} are added to the pyridine do significant amounts of P_xS_y fragments result upon thermal de-intercalation. The presence of these ions also results in loss of cadmium from the host lattice. Chemical analysis of the Fe^{3+} /pyridine intercalated $Cd_2P_2S_6$ lattice indicates that the reaction product is ca. 20% deficient in cadmium. The loss of lattice metal ions has been observed previously during the intercalation of wide band-gap materials where charge accumulation by the intercalated lattice must be compensated. Clement [15] demonstrated that the loss of Cd^{2+} compensates for charge acquired during the intercalation of the cobaltocenium cation. Poizat *et al.* [16] intercalated methyl viologen (MV^+) into $Cd_2P_2S_6$ and noted a loss of Cd^{2+} corresponding

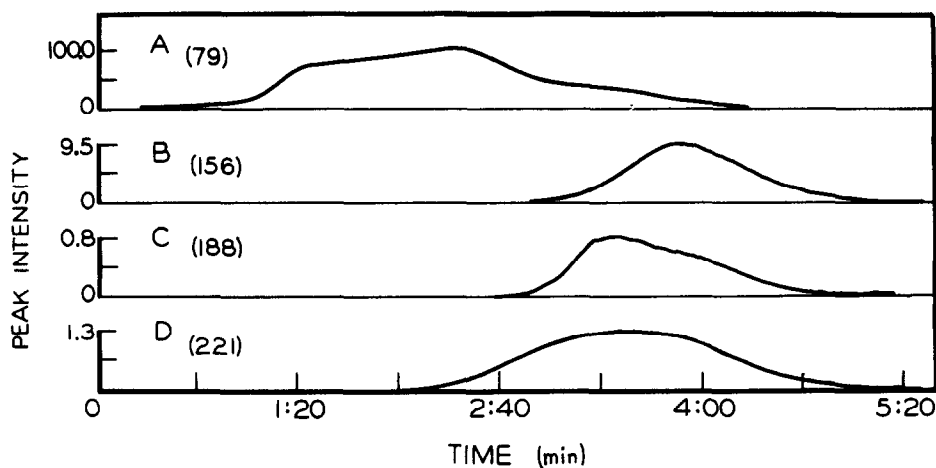


Fig. 3. Mass spectroscopic analysis of thermal de-intercalation products as the sample is heated from 25–350°C over a period of ca. 5 min. The (relative) peak intensities for masses 79, 156, 188 and 221 are given as ordinates. (a) Ion current at mass peak 79 vs time; (b) Mass peak 156 vs time; (c) Mass peak 188 vs time; (d) Mass peak 221 vs time.

Table 1.

Mass	Formula unit
348	P ₄ S ₇
316	P ₄ S ₆
284	P ₄ S ₅
253	P ₃ S ₅
221	P ₃ S ₄
188	P ₄ S ₂ & 4-4'-bispyridine sulfide
173	P ₂ SNC ₅ H ₅
156	4-4'-bipyridine
128	S ₄
111	NC ₅ H ₄ SH
94	P ₂ S
79	NC ₅ H ₅
78	NC ₅ H ₄

to the uptake of MV⁺. The intercalation–substitution mechanism has been discussed in detail for the M₂P₂X₆ materials by Brec *et al.* [4], and it has been shown that the high-spin, di-positive transition metal ions which are not stabilized by the crystal field (Cd, Zn and Mn) are relatively easily displaced from the lattice to compensate the charge of the intercalated ions.

There was no measurable loss of cadmium when Cd₂P₂S₆ was intercalated with pyridine in the absence of iron and, as noted above, the mass spectrum of the de-intercalation products then shows only trace amounts of P_xS_y fragments. This observation suggests that the loss of Cd²⁺ may create lattice defects which subsequently result in the liberation of P_xS_y fragments at elevated temperatures. The appearance of the S₄ ion is particularly noteworthy since it may indicate the presence of a precursor of the highly-colored polysulfide ions as discussed below.

ESR results

The ESR spectrum of Cd₂P₂S₆ intercalated with Mn²⁺/pyridine is shown in Fig. 4(a) and consists of the partially resolved hyperfine structure of the +1/2 ↔ -1/2 fine structure transition. The resolution of the hyperfine lines indicates that the Mn²⁺ is predominantly coordinated by water and not pyridine [12]. The spectrum is independent of the crystal angle with respect to the external field and is essentially temperature independent from room temperature to -150°C. The ESR spectrum is consistent

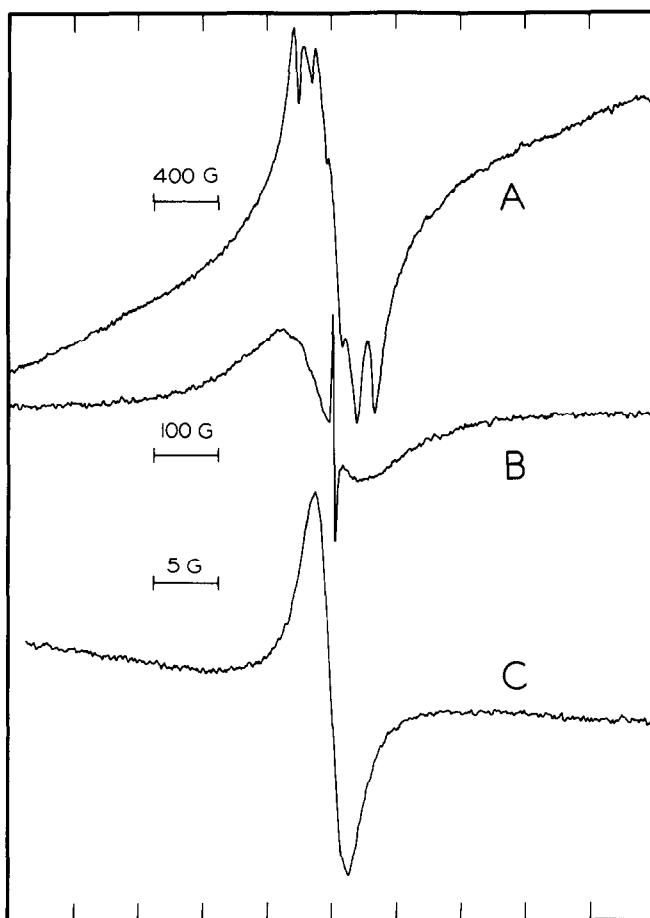


Fig. 4. (a) The ESR spectrum of Cd₂P₂S₆ intercalated with Mn²⁺/pyridine complex; (b) The ESR spectrum of Fe³⁺/pyridine solution in contact with Cd₂P₂S₆. The narrow line is due to intercalated Fe³⁺ superimposed on a very broad resonance due to Fe³⁺ in solution; (c) An expanded view of the intercalated Fe³⁺ resonance.

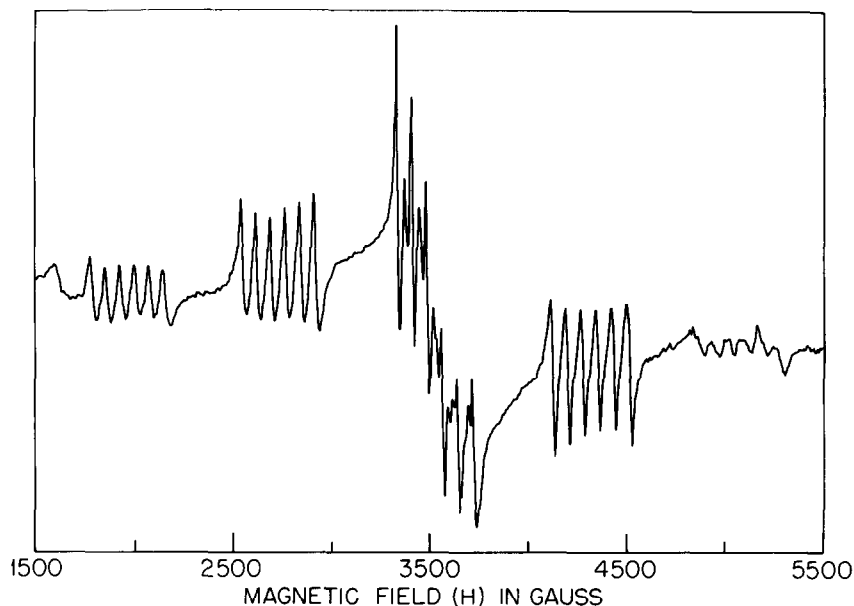


Fig. 5. The ESR spectrum of Mn^{2+} /pyridine intercalated $\text{Cd}_2\text{P}_2\text{S}_6$ after thermal de-intercalation to 700°C at $10^\circ\text{C}/\text{min}$.

with a random orientation of the manganese complex within the VWG. After briefly heating the sample to 700°C in a nitrogen atmosphere the ESR spectrum shown in Fig. 5 was obtained. This spectrum is identical to that reported previously for samples doped with Mn^{2+} during crystal growth [5] from the vapor. The detailed ESR analysis indicates that direct substitution of Mn^{2+} has occurred for Cd^{2+} in the metal plane. The integrated intensity of the ESR spectrum indicates that *ca.* 50% of the Mn^{2+} introduced into the VWG moves into Cd^{2+} vacancies upon thermal decomposition of the pyridine complex. Finally, the sharp-line ESR spectrum due to substitutional Mn^{2+} is indicative of a well ordered lattice.

The ESR spectrum of a $\text{Cd}_2\text{P}_2\text{S}_6$ crystal taken during intercalation with Fe^{3+} /pyridine solution is shown in Fig. 4(b) and (c) and consists of a single, sharp ($H = 5$ Gauss), isotropic line with $g = 2$ superimposed on the much broader resonance due to Fe^{3+} in pyridine solution. The sharper $g = 2$ resonance observed for intercalated Fe^{3+} is typical of a high-spin, d^5 iron in a weakly coordinating and disordered environment. The absence of additional Fe^{3+} ($S = 5/2$) fine-structure and the invariance of the ESR spectrum with respect to rotation of the crystal axes in the external field are both consistent with a disordered environment. The width of the line from the intercalated ion is much narrower than the ESR resonance of the starting solution. Thus, the resonances from solution and intercalated ion are easily distinguished and the progress of the intercalation reaction may be monitored. Our preliminary results from this experiment have shown that the intercalation process at room temperature begins within

30 s of contact between the reagent solution and a $\text{Cd}_2\text{P}_2\text{S}_6$ single crystal. The ESR signal amplitude approaches its limiting value within *ca.* 22 min. During this period, the lattice acquires a deep blue coloration.

Spectroscopic analysis

The deep blue coloration of $\text{Cd}_2\text{P}_2\text{S}_6$ when intercalated with pyridine complexes of either Fe^{3+} or Ce^{4+} is associated with the appearance of a single, broad absorption band with full width at half-maximum (FWHM) of 168 nm and peak intensity at 645 nm.

Intense coloration in transition metal compounds is often associated with mixed valence properties [17]. In fact, the mixed valence compounds of iron form by far the largest group presently known for any element and are frequently blue in color. Iron lazulite, a deep-blue iron phosphate, contains $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs in face-sharing octahedral coordination and the layered mica biotite, appears blue-black as a result of the substitution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs for $\text{Mg}^{2+}/\text{Al}^{3+}$ pairs. In $\text{Cd}_2\text{P}_2\text{S}_6$, mixed valence $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs could replace adjacent octahedrally coordinated cadmium ions, or could occupy sites in the VWG. However, since spectroscopically identical blue color centers are obtained from intercalation with a Ce^{4+} /pyridine complex, we do not believe the blue color centers are due to mixed valence pairs.

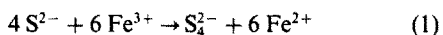
A variety of polysulfide ions are formed by oxidation of sulfur under a variety of conditions and are known to form intense blue color centers in many materials. Thus, the blue color centers in $\text{Cd}_2\text{P}_2\text{S}_6$ may result from the oxidation of sulfur by ferric or

ceric ions to form highly colored polynuclear sulfur cations [18] or anions [19]. Thompson [20] reported the blue coloration of intercalant solutions (ammonia, pyridine and aniline) when these amines react with TaS_2 . He concluded that the species responsible for the color is sulfur which was lost from the lattice and dissolved in the supernatant.

Sulfur can be quantitatively oxidized by As^{5+} , Sb^{5+} or SO_3 to the deep blue S_8^{2+} cation which exhibits a single, broad absorption maximum in mineral acid solutions at *ca.* 590 nm ($\epsilon = 2500$; FWHM = 230 nm). The spectrum is qualitatively similar to that of $\text{Cd}_2\text{P}_2\text{S}_6$ intercalated with either the Fe^{3+} /pyridine or the Ce^{4+} /pyridine complex. However, the S_8^{2+} ion has only been observed in strong mineral acid solution and there is no evidence that it is otherwise stable.

The hypersulfide anion S_2^- also forms blue color centers, e.g. in the mineral Lapis Lazuli, and is stable in neutral or basic aqueous solution. It is formed when sulfur is heated together with water and traces of a basic salt and its solution is characterized by a strong ($\epsilon = 2400\text{--}2500$) absorption band at 595 nm. In polar organic solvents [21] the absorption band is red-shifted relative to its position in protonating solvents by 20–30 nm. The absorption is associated with an $\pi^* \leftarrow n$ transition which is characteristically blue-shifted in protonating solvents due to selective stabilization of the non-bonding orbital. In the absence of solvent effects, this band will be maximally red-shifted (595 nm in water, 617 nm in DMF, 645 nm in $\text{Cd}_2\text{P}_2\text{S}_6$).

The S_2^- ion is formed by homolytic dissociation of the tetrasulfide anion ($\text{S}_4\text{S}_2^{2-}$) which may be produced by Fe^{3+} oxidation of lattice sulfur according to:

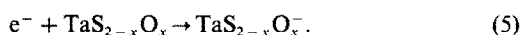
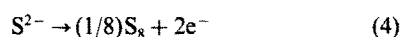


The presence of the S_4^{2-} anion is indicated in the mass spectrum analysis of the thermal de-intercalation products.

The concentration of S_2^- may be estimated from the measured absorbance at 645 nm of a sample of known thickness. Using the molar extinction coefficient of S_2^- in DMF [19], the crystal is estimated to contain about 0.6 mole% of the ion. This requires the amount of Fe^{2+} to be about 1.8 mole%. Chemical analysis indicates the presence of 1.2 mole% total iron. Finally, although the S_2^- ion is formally paramagnetic, it is unlikely that an ESR signal could be observed even at low temperatures due to rapid spin-relaxation processes [21].

The chemical and spectroscopic evidence suggests that the intercalation of pyridine complexes of strongly oxidizing metal ions (e.g. Fe^{3+} , Ce^{4+}) results in the oxidation of lattice sulfur and the formation of highly colored S_2^- anions. Previous investigations have demonstrated that, even in the absence of

strong oxidizing agents such as Fe^{3+} , lattice sulfur may be oxidized by either pyridine or trace amounts of water to produce elemental sulfur and an associated acceleration of the reaction. Schöllhorn [14] has proposed intercalation mechanisms to account for these observations. The presence of even small amounts of water can dramatically effect the rate of intercalation and the chemical structure of the intercalated species [13]. At room temperature, in the presence of water, the reaction proceeds according to the following mechanism:



In the presence of strong oxidizing agents, it is postulated here that small concentrations of S_2^- can be produced in the VWG by oxidation of either S_8 or S^{2-} .

SUMMARY AND CONCLUSION

Ce^{4+} , Fe^{3+} and Mn^{2+} have been intercalated into the VWG of the layered $\text{Cd}_2\text{P}_2\text{S}_6$ lattice by complexing with pyridine. The complexed transition metal ions may prove useful for studies of the kinetics and mechanism of intercalation, as well as for investigation of the structure and dynamics within the intercalate phase.

The presence of complexed iron and cerium during the pyridine intercalation of $\text{Cd}_2\text{P}_2\text{S}_6$ has a dramatic effect on the final product distribution. In particular, blue color centers are formed within the VWG. The chemical species responsible for the blue color centers has been tentatively identified as the hypersulfide anion S_2^- . It is suggested that the S_2^- ion is produced from oxidation of lattice sulfur by the action of the strong metal ion oxidizing agents.

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