

Intercalation of Ferrocene into $\text{Cd}_2\text{P}_2\text{S}_6(\text{CoCp}_2)_{0.8}$

G. T. LONG AND D. A. CLEARY

*Department of Chemistry, Washington State University,
Pullman, Washington 99164-4630*

Received November 22, 1989; in revised form March 15, 1990

We report the intercalation of ferrocene into $\text{Cd}_2\text{P}_2\text{S}_6(\text{CoCp}_2)_{0.8}$. The $\text{Cd}_2\text{P}_2\text{S}_6$ was first intercalated with cobaltocene, and then this intercalated material was reacted with ferrocene. Mass spectroscopy provides direct evidence for the presence of ferrocene in the $\text{Cd}_2\text{P}_2\text{S}_6$ host lattice. ESR measurements suggest that after the insertion of ferrocene into $\text{Cd}_2\text{P}_2\text{S}_6(\text{CoCp}_2)_{0.8}$, the concentration of neutral cobaltocene within $\text{Cd}_2\text{P}_2\text{S}_6$ is significantly reduced. X-ray diffraction and chemical analysis provide additional characterization. © 1990 Academic Press, Inc.

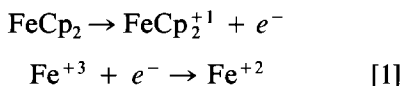
Introduction

The intercalation of metallocenes into the layered $M_2P_2X_6$ lattices, where M is a transition metal and X is sulfur or selenium, has been the subject of numerous investigations (1-11). Two mechanisms are invoked to describe the intercalation process: (i) charge transfer from the metallocene to the $M_2P_2X_6$ lattice or (ii) ion exchange, where for every $2 M^+Cp_2^+$ ions that enter the $M_2P_2X_6$ lattice, one M^{+2} ion leaves to maintain electrical neutrality. (Cp is the cyclopentadienyl anion, $C_5H_5^-$.) Our recent investigations of cobaltocene intercalation into $\text{Cd}_2\text{P}_2\text{S}_6$ have shown that while some charge transfer occurs from the cobaltocene to $\text{Cd}_2\text{P}_2\text{S}_6$, there remains a significant amount of neutral cobaltocene intercalated in the $\text{Cd}_2\text{P}_2\text{S}_6$ host lattice (1). The cobaltocene, therefore, adopts a mixed valence configuration upon intercalation into $\text{Cd}_2\text{P}_2\text{S}_6$. The evidence for this is the existence of a strong ESR signal from the intercalated neutral cobaltocenes.

(Oxidized cobaltocene is diamagnetic and therefore does not have an ESR spectrum.)

Given that both neutral and oxidized cobaltocene molecules were present in $\text{Cd}_2\text{P}_2\text{S}_6$, we sought to exchange the neutral cobaltocene molecules with neutral ferrocene molecules. There were several reasons for attempting this exchange reaction: (i) neutral ferrocene will not intercalate directly into large single crystals of $\text{Cd}_2\text{P}_2\text{S}_6$; (ii) to assess the strength of the bonding between the neutral cobaltocene and the host $\text{Cd}_2\text{P}_2\text{S}_6$; (iii) to provide an independent determination of the amount of neutral cobaltocene present in $\text{Cd}_2\text{P}_2\text{S}_6(\text{CoCp}_2)_{0.8}$.

Until very recently, the intercalation of ferrocene has been limited to strongly oxidizing lattices, such as FeOCl (12-17). Mössbauer spectroscopy has been used to show that the ferrocene is present as the ferricinium cation, FeCp_2^+ . In the host lattice, ferric ions are reduced to ferrous ions:



A recent report by Divigalpitiya, Frindt, and Morrison demonstrated a clever method for intercalating ferrocene into MoS_2 (18). The oxidation state of the ferrocene in this compound was not reported.

In the work reported here, crystals of $\text{Cd}_2\text{P}_2\text{S}_6$ were first intercalated with cobaltocene, and subsequently intercalated with ferrocene. Chemical analysis was used to show that the new material contained iron. Mass spectrometry was used to verify the presence of ferrocene. ESR and X-ray diffraction provided further characterization of the ferrocene-intercalated crystals.

Experimental

Synthesis. $\text{Cd}_2\text{P}_2\text{S}_6$ crystals were grown from the constituent elements via chemical vapor transport with iodine as previously reported (19, 20). The intercalated material was prepared by sealing off several crystals of $\text{Cd}_2\text{P}_2\text{S}_6$ in a toluene solution of cobaltocene (0.1 M). The sealed tube was placed in an oven ($180 \pm 5^\circ\text{C}$) for 3 days. The cobaltocene-intercalated crystals were rinsed with ethanol several times and allowed to air dry. After drying, the intercalation procedure was repeated using the cobaltocene-intercalated crystals and a solution of ferrocene in toluene (0.1 M). Again, the final product was rinsed several times with ethanol to remove surface-adsorbed metalocene.

Characterization. Mass spectroscopy was performed on a high resolution VG 7070 EHF mass spectrometer. The sample crystals were heated at the ionization source of the mass spectrometer. No ion current was detected before the sample was heated.

ESR spectra were recorded on a Varian E-9 spectrometer. The temperature of the sample (6–300 K) was controlled with an Air

Products Helitran using helium gas as the coolant.

X-ray diffraction data was collected on a Siemens automatic powder diffractometer. Only (001) reflections were collected. All spectra were recorded at room temperature.

Chemical analysis (for elements $Z > 8$) was done on an Camex electron microprobe. The elements cobalt, iron, cadmium, phosphorus, and sulfur were determined simultaneously for a single sample. Carbon and hydrogen cannot be analyzed because the X-ray emission from these elements is too weak. The weight percentage of the elements determined has a precision of $\pm 0.05\%$. A $20 \mu\text{m}$ beam diameter at 15 kV was used. Several analyses were run on the intercalated crystals.

Results

The mass spectrum of the ferrocene-intercalated material is shown in Fig. 1. The m/e peaks at 186 and 189 are the molecular ion peaks for ferrocene and cobaltocene, respectively (21, 22). This spectrum provides clear evidence for the intercalation of ferrocene into the $\text{Cd}_2\text{P}_2\text{S}_6$ crystal. The relative amplitudes of the two peaks, however, cannot be used to determine the relative

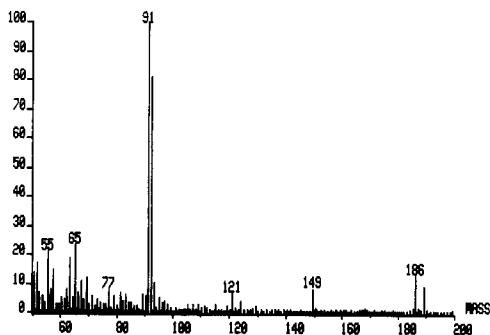
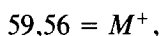
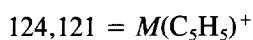
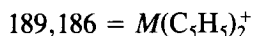


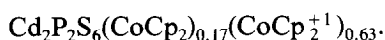
Fig. 1. Mass spectrum of the thermally deintercalated products from $\text{Cd}_{1.9}\text{P}_{2.0}\text{S}_{6.0}(\text{CoCp}_2^{+1})_{0.86}(\text{FeCp}_2)_{0.077}(\text{toluene})_{0.12}$. Temperature of the sample is $\approx 100^\circ\text{C}$.

amounts of cobaltocene and ferrocene intercalated into the $\text{Cd}_2\text{P}_2\text{S}_6$. In the cobaltocene-intercalated crystal, before the reaction with ferrocene, only the m/e peak at 189 is observed. The mass spectrum of ferrocene and cobaltocene has been reported, and the fragmentation peaks are assigned as follows:



where $M = \text{Co}$ or Fe . All of these peaks are present in the spectrum shown in Fig. 1. The sample temperature in Fig. 1 is $\approx 100^\circ\text{C}$. The m/e peaks at 91 and 92 are due to cointercalated toluene (23). It should be noted that the toluene:metallocene peak height ratio in Fig. 1 is not indicative of the relative amounts of toluene and metallocene present in the $\text{Cd}_2\text{P}_2\text{S}_6$ lattice. This ratio changes with temperature. At low temperatures, the toluene peak dominates and at high temperature, the ferrocene peak dominates. This is to be expected given that toluene has a higher vapor pressure than ferrocene at a given temperature.

$\text{Cd}_2\text{P}_2\text{S}_6(\text{CoCp}_2)_{0.80}$ has an intense ESR spectrum due to the presence of neutral cobaltocene, CoCp_2 (1, 2). Quantitative ESR measurements, along with chemical analysis, have established the stoichiometry of the cobaltocene-intercalated material to be



It should be noted, however, that the total amount of cobalt varies from crystal to crystal. A more meaningful way to express the stoichiometry would be



The ESR spectrum of the ferrocene-intercalated material shows a dramatic decrease in the ESR signal strength (at least 2 orders of magnitude) due to the cobaltocene. No

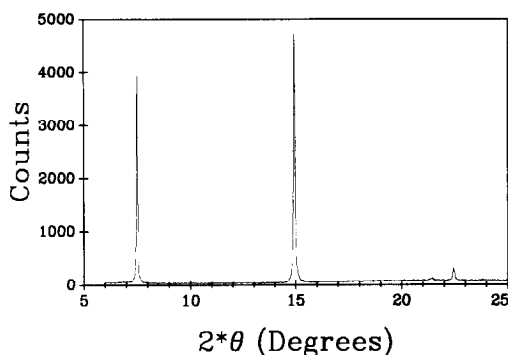


FIG. 2. The first three (001) X-ray diffraction lines from $\text{Cd}_{1.9}\text{P}_{2.0}\text{S}_{6.0}(\text{CoCp}_2^+)_{0.86}(\text{FeCp}_2)_{0.077}(\text{toluene})_{0.12}$. Sample is at room temperature.

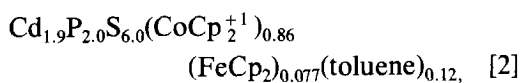
additional ESR resonances are observed from 6 to 300 K, specifically, no ferricinium (FeCp_2^+) ESR signal (24–26).

The first three (001) lines from the X-ray diffractogram are shown in Fig. 2. This spectrum was recorded at room temperature. The average value of d calculated from the three diffraction peaks is $11.73 \pm 0.03 \text{ \AA}$. This corresponds to an increase in the basal spacing of 5.21 \AA necessary to accommodate the cobaltocene and ferrocene molecules.

The results from the electron microbeam chemical analysis are as follows (average of four determinations):

Element	Percentage weight	Uncertainty
Cd	32.20	0.32
P	9.33	0.12
S	29.55	0.61
Co	7.79	0.31
Fe	0.66	0.08

As mentioned previously, carbon and hydrogen cannot be analyzed for using this technique. The percentage weight from above totals 79.53%. By assigning 2 (C_5H_5) units to each Co and Fe and the remaining unaccounted weight (1.72%) to toluene, we arrive at a stoichiometry of



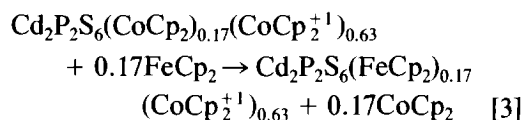
where now the percentage weight totals 100%. Note that the cobalt concentration in this crystal is higher than the average value of 0.8. (The intercalation reaction with ferrocene cannot add any cobalt to the sample.) All of the cobaltocene is assumed to be cationic because of the negligible ESR signal. The lack of any ESR signal also means that the ferrocene is neutral as opposed to cationic. It should be noted that the stoichiometry as written above is not charge balanced. This continues to be a problem in the metalocene intercalation of some $M_2P_2X_6$ lattices. The fate of the electrons being released by cobaltocene is unknown in this case.

Discussion

Bal *et al.* have reported the direct intercalation of ferrocene into $\text{Cd}_2\text{P}_2\text{S}_6$ (27, 28). It is unclear from their description whether the $\text{Cd}_2\text{P}_2\text{S}_6$ was in the form of a powder or single crystals. Our results indicate that ferrocene cannot be directly intercalated into single crystals of $\text{Cd}_2\text{P}_2\text{S}_6$. Attempts to do so have consisted of soaking single crystals ($1 \times 1 \times \sim 0.05$ mm) of $\text{Cd}_2\text{P}_2\text{S}_6$ in a 0.1 M solution of ferrocene in toluene at 185°C for up to 1 week. The $\text{Cd}_2\text{P}_2\text{S}_6$ crystals remain clear and colorless. The 001 X-ray diffraction lines match those of the pure $\text{Cd}_2\text{P}_2\text{S}_6$ with no additional lines. Cobaltocene, however, can be intercalated into $\text{Cd}_2\text{P}_2\text{S}_6$, and upon intercalation, it adopts a mixed valence configuration. Our evidence for this consists of the quantitative ESR analysis of the intercalated neutral cobaltocene (1). The ESR spectrum (at 6 K) of $\text{Cd}_2\text{P}_2\text{S}_6$ intercalated with cobaltocene consists of an eight-line spectrum consistent with that previously reported for cobaltocene (29). The double integration of the spectrum, however, only accounts for $\sim 20\%$ of the intercalated cobalt. The remainder is assumed to

be in the form of diamagnetic cobaltocenium. The room temperature infrared spectrum of the same material has absorption bands corresponding to cobaltocenium only. The presence of both neutral cobaltocene and cationic cobaltocenium within the van der Waals gap of the $\text{Cd}_2\text{P}_2\text{S}_6$ host lattice is intriguing and remains a subject of investigation. The goal of the present experiments, however, is to determine whether the *neutral* cobaltocene can be replaced with neutral ferrocene. Because both molecules have the same charge (0) and essentially the same dimensions, it should be straightforward to replace one with the other.

If exchange were as simple as shown in Eq. [3],

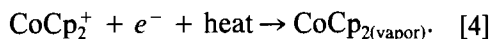


then the chemical analysis for iron in the exchanged material would indicate how much neutral cobaltocene was present in the initially intercalated material. The chemical analysis of the ferrocene-intercalated material shows much less iron than is indicated in Eq. [3]. From the proposed stoichiometry given in Eq. [2], it is clear that a complete exchange of neutral cobaltocene for neutral ferrocene has not occurred. Instead, it appears that the ferrocene has simply added to the cobaltocene intercalation compound with a negligible loss of cobalt species, and that, in the process, the neutral cobaltocene has converted to cobaltocenium. Thus we were unable to independently determine the amount of neutral cobaltocene in $\text{Cd}_2\text{P}_2\text{S}_6/\text{CoCp}_2$ using this technique of exchange.

The negligible loss of cobalt during the ferrocene intercalation suggests that the bonding between the cobaltocene (both neutral and cationic) and the $\text{Cd}_2\text{P}_2\text{S}_6$ host lattice is fairly strong. Essentially none of the cobaltocene left the lattice and went into solution despite the reaction temperature

(185°C) and the concentration gradient of cobaltocene. If the cobaltocene enters the lattice originally due only to the concentration difference (high in solution and zero in $\text{Cd}_2\text{P}_2\text{S}_6$), then one would expect a significant amount of cobaltocene to leave when the concentration of cobaltocene in solution is zero (as is the case for a ferrocene solution).

The mass spectrum shown in Fig. 1 has peaks at both 186 and 189 indicating that neutral cobaltocene is still present in the ferrocene-intercalated material. The concentration of neutral cobaltocene, if present, must be very low based on the lack of an ESR signal. Another possibility is that as the sample is heated, the cationic cobalticinium is reduced to neutral cobaltocene, and this neutral cobaltocene is thermally deintercalated:



Equation [4] is essentially the reverse of the intercalation reaction, except that the CoCp_2 is intercalated from a toluene solution instead of the gas phase. Work by Randzio and Boerio-Goates, using pyridine to intercalate $\text{Cd}_2\text{P}_2\text{S}_6$, has shown that the intercalation reaction is exothermic (30).

We are continuing to investigate the loss of the ESR signal due to neutral cobaltocene subsequent to ferrocene intercalation. One possibility is that the amount of neutral cobaltocene has not changed, but rather the relaxation time has decreased to the point where the linewidths are broadened beyond detection. Alternatively, if the cobaltocene has oxidized, then the challenge is to determine what has been reduced. The reduced species presumably is contained within the lattice because cadmium ions have not been discharged enough to compensate the positive charge of all the cobalticinium.

It is impossible to prove that the ferrocene in these materials is actually located in the van der Waals gap of the $\text{Cd}_2\text{P}_2\text{S}_6$ host lattice. A rough calculation using the size of a

typical sample crystal indicates that if the ferrocene were simply coating the surface of the crystal, then the weight percentage of iron would be $\approx 0.001\%$ as compared to the measured value of 0.66%. As already mentioned, the crystals are rinsed with ethanol in order to reduced this possibility. (Ferrocene is soluble in ethanol.)

Conclusion

Ferrocene has been intercalated into crystals of $\text{Cd}_2\text{P}_2\text{S}_6(\text{CoCp}_2)_{0.8}$ by first intercalating the $\text{Cd}_2\text{P}_2\text{S}_6$ with cobaltocene, and then further intercalating the lattice with ferrocene. Mass spectroscopic and chemical analysis data provide strong evidence for the existence of intercalated ferrocene within the $\text{Cd}_2\text{P}_2\text{S}_6$ host lattice. The strong ESR signal present after intercalation with cobaltocene is lost after intercalation with ferrocene. Apparently the ratio of neutral to oxidized cobaltocene decreases upon ferrocene intercalation. The intercalated ferrocene appears to be neutral based on the lack of a ferricinium ESR signal. The intercalated ferrocene does not replace neutral cobaltocene. One possibility is that the bonding between cobaltocene and $\text{Cd}_2\text{P}_2\text{S}_6$ is too strong to be disrupted by the presence of the ferrocene.

References

1. G. T. LONG AND D. A. CLEARY, *J. Phys. Chem.*, **94**, 3205 (1990).
2. R. BREC, *Solid State Ionics* **22**, 3 (1986).
3. D. A. CLEARY AND A. H. FRANCIS, *J. Phys. Chem.* **89**, 97 (1985).
4. C. SOURISSEAU, J. P. FORGERIT, AND Y. MATHEY, *J. Solid State Chem.* **49**, 134 (1983).
5. C. SOURISSEAU, J. P. FORGERIT, AND Y. MATHEY, *J. Phys. Chem. Solids* **44**, 119 (1983).
6. R. CLÉMENT, J.-P. AUDIERE, AND J.-P. RENARD, *Rev. Chim. Miner.* **19**, 560 (1982).
7. C. SOURISSEAU, Y. MATHEY, AND C. POINSIGNON, *Chem. Phys.* **71**, 257 (1982).
8. A. MICHALOWICZ AND R. CLÉMENT, *Inorg. Chem.* **21**, 3872 (1982).

9. R. CLÉMENT, J. J. GIRERD, AND I. MORGENSTERN-BADARAU, *Inorg. Chem.* **19**, 2852 (1980).
10. Y. MATHEY, R. CLÉMENT, C. SOURISSEAU, AND G. LUCAZEAU, *Inorg. Chem.* **19**, 2773 (1980).
11. J. P. AUDIERE, R. CLÉMENT, Y. MATHEY, AND C. MAZIERES, *Physica B* **99**, 133 (1980).
12. SCHÄFER-STAHL, H. *Mater. Res. Bull.* **17**, 1437 (1982).
13. G. VILLENEUVE, P. DORDOR, T. PALVADEAU, AND J. P. VENIEN, *Mater. Res. Bull.* **17**, 1407 (1982).
14. P. PALVADEAU, C. LAURENCE, J. ROUXEL, F. MÉNIL, AND L. FOURNÈS, *Mater. Res. Bull.* **16**, 1055 (1981).
15. T. R. HALBERT, D. C. JOHNSTON, L. E. MCCANDLISH, A. H. THOMPSON, J. C. SCANLON, AND J. A. DUMESIC, *Physica B* **99**, 128 (1980).
16. H. SCHÄFER-STAHL, *Mater. Res. Bull.* **15**, 1091 (1980).
17. H. STAHL, *Inorg. Nucl. Chem. Lett.* **16**, 271 (1980).
18. W. M. R. DIVIGALPITIYA, R. F. FRINDT, AND S. R. MORRISON, *Science* **246**, 369 (1989).
19. B. E. TAYLOR, J. STEGER, AND A. WOLD, *J. Solid State Chem.* **7**, 461 (1973).
20. R. NITSCHKE AND P. WILD, *Mater. Res. Bull.* **5**, 419 (1970).
21. L. FRIEDMAN, A. P. IRSA, AND G. WILKINSON, *J. Amer. Chem. Soc.* **77**, 3689 (1955).
22. G. M. BEGUN AND R. N. COMPTON, *J. Chem. Phys.* **58**(6), 2271 (1973).
23. D. J. PASTO AND C. R. JOHNSON, "Organic Structure Determination," p. 260, Prentice-Hall, Englewood Cliffs, NJ (1969).
24. R. PRINS AND F. J. REINDERS, *J. Amer. Chem. Soc.* **91**, 4929 (1969).
25. R. PRINS, *Mol. Phys.* **19**, 603 (1970).
26. A. HORSFIELD AND A. WASSERMANN, *J. Chem. Soc. Dalton Trans.*, 187 (1972).
27. B. BAL, S. GANGULI, AND M. BHATTACHARYA, *Hyperfine Interactions* **35**, 899 (1987).
28. B. BAL, S. GANGULI, AND M. BHATTACHARYA, *Physica B* **133**, 64 (1985).
29. J. H. AMMETER AND J. D. SWALEN, *J. Chem. Phys.* **57**, 678 (1972).
30. S. L. RANDZIO AND J. BOERIO-GOATES, *J. Phys. Chem.* **91**, 2201 (1987).