Chem. Mater. 1992, 4, 1344-1348

Fourier Transform Infrared Spectroscopic Studies of Charge-Transfer Intercalation Compounds

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Received June 24, 1992. Revised Manuscript Received September 18, 1992

Fourier transform infrared spectroscopy has been used to characterize the charge-transfer nature of cobaltocene, $Co(C_5H_5)_2$, intercalated into the layered host lattices $Cd_2P_2S_6$ and SnS_2. In the $Cd_2P_2S_6$ case, the infrared spectrum is consistent with the presence of both neutral cobaltocene and cationic cobaltocenium, $Co(C_5H_5)_2{}^{+1}$. Spectra taken after a reaction time of several hours as well as several weeks both lead to the same conclusion. Spatially resolved infrared spectra suggest that the intercalation reaction is a charge-transfer reaction followed by diffusion of neutral cobaltocene into the $Cd_2P_2S_6$ host. In the SnS_2 case, the infrared spectrum is consistent with the presence of only the cationic form of the cobaltocene with no evidence that neutral cobaltocene remains within the host. Electron spin resonance spectroscopy was used to further substantiate these conclusions.

Introduction

Layered chalcogenide lattices such as TaS_2 and $Cd_2P_2S_6$ have been used as host lattices for intercalation reactions with metallocenes.[1,2] The reactions have been characterized as charge-transfer reactions whereby the metallocene reduces the host lattice, and the metallocenium cation is intercalated into the van der Waals gap of the host to preserve charge neutrality:

$$x\mathrm{MCp}_2 + \mathrm{host} \rightarrow \mathrm{host}^{x-}\{\mathrm{MCp}_2{}^+\}_x \qquad (1)$$

One of the methods used to determine the oxidation state of metallocenes intercalated into such host lattices has been vibrational spectroscopy.[3-6] In all these cases, however, the metallocene was cationic, and hence the spectra showed only bands due to the cationic form of the metallocene.

The use of vibrational spectroscopy to ascertain the oxidation state of the metallocene is based, in part, on the extensive work of Fritz.[7] This work demonstrated that certain bands in the infrared spectrum of metallocenes were particularly sensitive to the oxidation state of the molecule. For example, the $\gamma_9(\mathrm{CH})\pi$ mode of cobaltocene occurs at 778 cm^{-1} in neutral cobaltocene and is shifted to 867 cm^{-1} in cobaltocenium.[8] Not all bands are useful for such a determination. The $\nu_{20}(\mathrm{CC})\nu$ mode shifts from 1412 cm^{-1} to only 1414 cm^{-1} on going from neutral to cationic cobaltocenium.

Our previous electron spin resonance study of $Cd_2P_2S_6$ intercalated with cobaltocene provided direct experimental evidence for the presence of neutral cobaltocene in the intercalated product.[9] A quantitative determination of the amount present indicated that about 20% of the intercalated cobaltocene was neutral. ESR is insensitive to the diamagnetic cobaltocenium, so it was presumed that the remaining 80% of the intercalated cobaltocene was cationic. In the present study, using infrared spectroscopy, both forms of the cobaltocene can be identified. Moreover, a series of spectra taken at different reaction time intervals supports the conclusion that the intercalation reaction is driven by a charge-transfer process from the guest to the host. The concentration profile of the neutral guest (at early reaction time) suggests that it is intercalated into the host only after the charge-transfer intercalation reaction has occurred. This observation has important implications concerning a model proposed by Parkinson et al. for the intercalation of cobaltocene into SnS_2.[10]

Experimental Section

Crystal Growth and Intercalation. $Cd_2P_2S_6$ single crystals were prepared from the constituent elements in a conventional high-temperature procedure. Stoichiometric amounts of cadmium (Johnson Mathey), amorphous red phosphorus (-100 mesh, Alfa), and sulfur (-60 mesh, Johnson Mathey) were ground together and transferred to a quartz reaction tube. The tube was evacuated and sealed under vacuum. The reaction tube was placed in a horizontal furnace (Marshall with ATS controller) and slowly heated to reaction temperature (≈1 h). External shunts were used to establish a temperature gradient across the reaction tube. The sample charge was at ≈630 °C, and the crystals grew at ≈600 °C. A good yield of large, colorless, transparent platelets was realized after about 2 weeks. After this time, the furnace was switched off and the sample was allowed to cool to room temperature.

SnS_2 crystals were prepared from tin and sulfur in a vertical zone refiner. Tin was in the form of -20 mesh granular powder and was supplied by Mallinckrodt. Stoichiometric amounts of tin and sulfur were added to a quartz reaction tube and sealed under vacuum. Total travel through the zone refiner was 40 cm/3 weeks. At the end of this time, a large single-crystal boule remained in the bottle of the reaction tube, and many large platelets were at the top of the reaction tube, having sublimed from the boule. The platelets were clear and orange.

$Cd_2P_2S_6$ crystals (cut into circular discs 2200-μm o.d., ≈50 μm thick) were intercalated with cobaltocene by soaking them in an acetonitrile solution of cobaltocene (0.050 M). The reactions were carried out in sealed glass tubes. All manipulations were performed in an inert atmosphere. The cobaltocene was supplied by Strem Chemicals and used as received. The acetonitrile was supplied by Aldrich (Sure-Seal anhydrous grade) and it was also used as received. Reaction temperatures of 90, 125, and 150 °C were investigated. Intercalation began within a few hours at 125 and 150 °C, but it did not occur at 90 °C even after several weeks. During the intercalation reaction, the crystals became progressively

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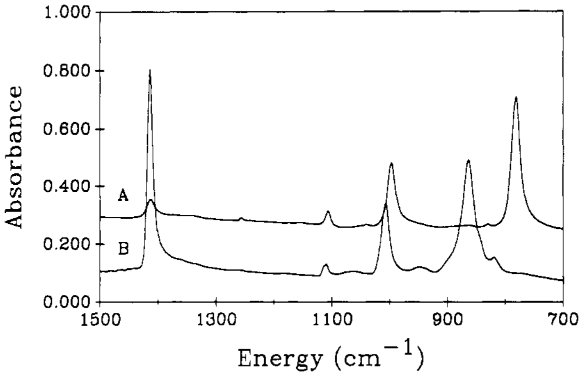

Figure 1. Infrared spectra of (A) cobaltocene and (B) cobaltocenium chloride. Samples were pressed in KBr pellets; 256 scans were collected. Resolution was 4 cm^{-1}.

opaque while remaining lustrous. At the conclusion of a given reaction, the sample tube was opened in air. The crystals were rinsed 4–5 times with 2-mL portions of fresh solvent and vacuum dried (0.01 Torr). IR spectra were recorded within 1 day of exposure to air. Samples were stored in a desiccator.

SnS_2 crystals (4 × 4 × 0.1 mm) were intercalated as described by Parkinson et al.[10] The crystals were soaked at room temperature in a solution of cobaltocene in ethylene glycol dimethyl ether (0.19 M). The reaction was carried out in an inert atmosphere. The total reaction time was 25 days, although the SnS_2 crystals immediately turned a lustrous blue-black upon exposure to the cobaltocene solution. At the completion of the reaction, the crystals were rinsed 4–5 times with 2-mL portions of fresh solvent. They were then dried under vacuum (<0.1 Torr). Infrared spectra were recorded within 1 h of exposure to air.

The cobaltocenium chloride crystals used in the infrared studies were prepared by a modified version of the procedure reported by Hartley and Ware.[11] A solution of 5 M HCl was added to solid cobaltocene. The mixture was gently heated on a hotplate for ≈15 min until all of the cobaltocene reacted. Hydrogen gas was evolved during this phase of the reaction. After all of the cobaltocene had reacted, the resulting solution was clear and yellow. This solution was filtered, and the filtrate was concentrated by returning it to the hot plate. Before the last free liquid evaporated, the sample was removed from the heat. The resulting green crystals were dried under vacuum (≈0.1 Torr) for ≈25 min.

Spectroscopy. Fourier transform infrared spectra were collected using a Perkin-Elmer 1700 FTIR spectrometer. Spectra were collected in one of two configurations. The first utilized a Spectra-Tech IR PLAN infrared microscope which was interfaced to the Perkin-Elmer spectrometer. In this configuration, spectra were collected from a circular sampling spot of 92-μm i.d. The microscope uses a liquid nitrogen cooled MCT detector which is insensitive below 700 cm^{-1}. The second method of collecting infrared spectra utilized a KBr beam condenser. Samples were mounted on a 500-μm-diameter aperture plate which was then inserted into the beam condenser. Using this method, a room-temperature TGS detector could be utilized which extended the low-energy region of the spectrum to 400 cm^{-1}. All spectra were collected at room temperature and in the transmission mode.

Electron spin resonance spectra were acquired on a Bruker ESP 300 E ESR spectrometer operating at X-band (9.4 GHz). Low temperatures (4.2–100 K) necessary for observing the cobaltocene spectra were achieved using an Air Products Heli-Tran and helium gas as a coolant.

Results and Discussion

As a first step in using infrared spectroscopy as a probe of oxidation state for intercalated cobaltocene, we verified the reported positions of the infrared bands for both cobaltocene and cobaltocenium chloride.[7,8] The spectra are shown in Figure 1. The samples were run as KBr pellets, with the cobaltocene pellet prepared in a drybox. The major difference is the strong band at 781 cm^{-1} in the neutral species (reported by Fritz at 778 cm^{-1}) which is absent in the cation. Conversely, the strong band in the cation at 864 cm^{-1} (reported by Fritz at 867 cm^{-1}) is absent in the neutral form. A sample containing a mixture of the neutral species and cation should display both of these bands.

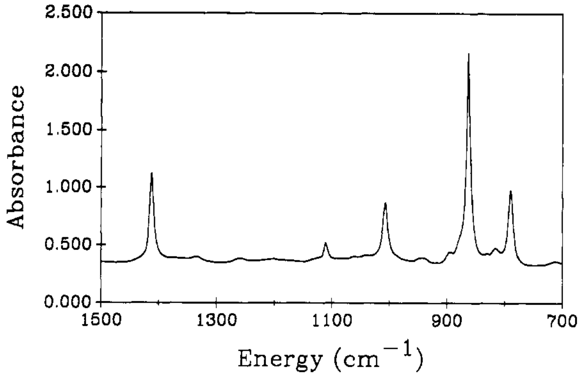

Figure 2. Infrared spectrum of $Cd_2P_2S_6$ intercalated with cobaltocene. The spectrum was collected using an infrared beam condenser (see text); 256 scans were collected. Resolution was 4 cm^{-1}.

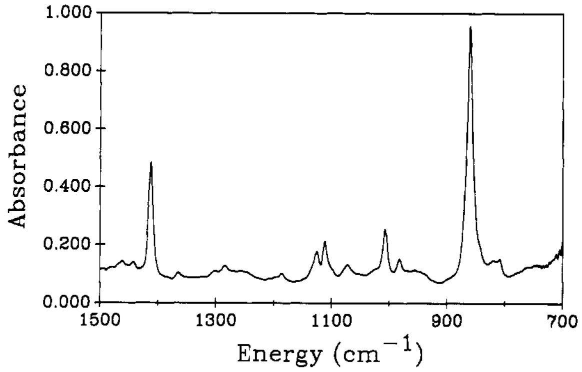

Figure 3. Infrared spectrum of SnS_2 intercalated with cobaltocene. The spectrum was collected using an infrared microscope (see text); 256 scans were collected. Resolution was 4 cm^{-1}.

The spectrum shown in Figure 2 is from just such a sample, $Cd_2P_2S_6$ intercalated with cobaltocene. This sample was intercalated at 125 °C for 15 days. The presence of both neutral and oxidized forms of the cobaltocene in the sample prepared at 125 °C is evident from the composite nature of the spectrum. All of the bands in the spectrum can be assigned to either the neutral species, the cation, or a trace of cointercalated solvent (acetonitrile). From thermogravimetric analysis, the amount of co-intercalated solvent is determined to be 2% by weight. The presence of the neutral species in this sample was previously demonstrated using electron spin resonance spectroscopy.[9] In the current samples as well, strong eight-line ESR spectra consistent with neutral cobaltocene are observed. ESR spectra are collected at 4.2 K because at room temperature the spectrum is not observed.

To further support the conclusion that infrared spectroscopy is a straightforward method for analysis of mixed-valence intercalation compounds, we selected a different host lattice which has also been reported to intercalate cobaltocene and result in both neutral and oxidized guests. SnS_2 intercalated with cobaltocene has been reported[10] to produce

$$(Sn^{4+}{}_{0.9}Sn^{2+}{}_{0.1})S_2\{[Co^{3+}Cp_2]^{+}{}_{0.2}[Co^{2+}Cp_2]^{0}{}_{0.1}\}$$

This is the only other reported example of mixed oxidation

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[11] Hartley, D.; Ware, M. J. *J. Chem. Soc. A* **1969**, 138.

Table I. Infrared Bands of Cobaltocene and Intercalated Cobaltocene

mode[a]	$CoCp_2^{0a}$	$CoCp_2^{0b}$	$CoCp_2^{+a}$	$CoCp_2^{+b}$	$Cd_2P_2S_6\{CoCp_2\}^b$	$SnS_2\{CoCp_2\}^b$
$\nu_8(CH)\nu$	*3041*	*3105, 3094, 3082*	*3106*	*3076sh, 3063*	3106, 3091	3092
$\nu_{20}(CC)\nu$	1412	1413	1414	1413	1412	1412
$\nu_{10}(CC)\nu$	1101	1106	1103	1109	1110	1111
$\nu_{18}(CH)\delta$	995	997	1008	1007	1007	1007
$\nu_{19}(CH)\pi$	828	831	820	820	816, 832	820
$\nu_9(CH)\pi$	778	781	867	864	789, 863	860

[a] References 7 and 8. [b] Present work.

states in a metallocene intercalation compound. The infrared spectrum of this material is shown in Figure 3. The spectrum is consistent with essentially all of the intercalated cobaltocene being present as cobaltocenium. The lack of an ESR spectrum from this material (4.2–300 K) also leads to the conclusion that no significant amount of neutral cobaltocene is present in this material. A summary of the observed infrared bands are presented in Table I.

One explanation for the discrepancy between our results on cobaltocene intercalated SnS_2 and those of Parkinson et al. may be that X-ray photoelectron (XPS) spectroscopy was used in the SnS_2 case to establish the presence of Co^{3+} and Co^{2+}. Our recent work on cobaltocene-intercalated $SnSe_2$ showed that the use of XPS in the characterization of intercalated materials can result in radiation damage to the material under investigation.[12] Specifically, the Co^{2+}/Co^{3+} ratio was found to increase with X-ray exposure time. Extrapolated to zero exposure time using a second-order kinetics fit resulted in a negligible concentration of Co^{2+}. A second possible explanation for the discrepancy is the use of phosphorus doping in the SnS_2 work. The pure SnS_2 was doped with phosphorus for XPES studies, but it is not clear if the intercalated material was also doped. However, it seems unlikely that a trace doping of phosphorus would dramatically alter the amount of intercalated neutral cobaltocene.

With the existence of two oxidation states of the intercalated cobaltocene, several points need to be addressed. One concerns what is being reduced when the cobaltocene becomes oxidized. The other concerns the time evolution of this mixture of oxidation states. For example, at early times in the reaction, the intercalated cobaltocene might be entirely cobaltocenium. As the reaction progresses, neutral cobaltocene would then diffuse into the lattice. Such a model was proposed by Parkinson et al. to account for the mixed oxidation states they observed in SnS_2.[10] To test this idea, we recorded the infrared spectrum of $Cd_2P_2S_6$ intercalated with cobaltocene after a series of reaction times. Using the ratio of integrated areas of the peak at 863 and 789 cm^{-1} as a measure of relative amount of cationic to neutral cobaltocene present in the lattice, it is apparent that this ratio is larger at short reaction times versus long reaction times. It is important to note that for the large crystals used in these experiments (2 × 2 × ≈0.05 mm), the short reaction times result in crystals that are not completely intercalated.

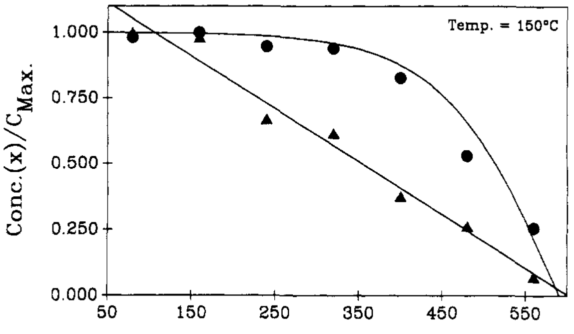

Figure 4. Concentration profile of cobaltocenium (●) and cobaltocene (▲). The sample was prepared at 150 °C. The spectrum was collected at room temperature.

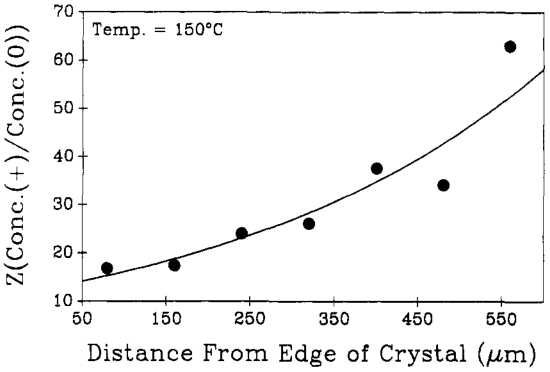

Figure 5. Ratio of cobaltocenium to cobaltocene as a function of distance into $Cd_2P_2S_6$ crystal. The solid line is a fit to Ae^{Bx} (see text).

This partial intercalation can be observed in two ways. First, infrared spectra of a 92-μm circular spot at the center of the sample are dominated by an interference pattern. This indicates that the material is nonabsorbing in this spectral range. When the sampling spot is moved to the edge of the sample, a spectrum like that shown in Figure 2 is obtained. The second indication that the crystal is only partially intercalated comes from optical microscopy. Pure, unintercalated $Cd_2P_2S_6$ is strongly birefringent, consistent with its crystal class (monoclinic).[13] Those samples which give an interference pattern at the center of the sample also display optical birefringence in the same area. The result is a sample where the center portion of the material is optically birefringent, and the surrounding border is not. Presumably, the lack of birefringence in the border is due to the disordered state of the intercalated phase and not to a high-symmetry phase such as cubic or hexagonal, which would also lack birefringence.[14]

Because of the large size of the single crystals of $Cd_2P_2S_6$ used in this study, the infrared microscope was capable of providing a spatially resolved concentration profile of both the cobaltocene and the cobaltocenium. The integrated areas of the peaks at 863 and 789 cm^{-1} versus distance from the edge of the crystal are shown in Figure 4. The areas of these peaks are proportional to the concentrations of the respective species, and for clarity, the concentrations have been normalized to the maximum value for each species: the cobaltocene concentration was divided by 1.67 and the cobaltocenium concentration was divided by 28.0. It is clear from this figure that the neutral cobaltocene and cationic cobaltocenium have dramatically

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different concentration profiles. The neutral concentration is almost linear, whereas the cation concentration is relatively constant near the edge of the crystal and then drops near the reaction front.

The ratio of cobaltocenium to cobaltocene for the same positions used in Figure 4 is shown in Figure 5. It is interesting to note that the ratios shown in Figure 5 vary with time and at long reaction times (several weeks), the ratio throughout the crystal was ≈3. It must be emphasized that these ratios represent only the integrated areas of the peak at 863 and 789 cm^{-1}. They are not the absolute concentration ratios because of small differences in path length and differences in molar absorptivities at these wavelengths for the cation and the neutral species. Nonetheless, it is clear that the concentration of the neutral species increases with time subsequent to the intercalation of the cation.

The solid line in Figure 5 is a fit of the data to $f(x) = Ae^{Bx}$. Such behavior is to be expected if the following assumptions are correct:[10,15] (1) The ratio of cation to neutral species is proportional to the energy difference between the Fermi level (E_f) of the host and the redox potential of the guest. (2) The Fermi level of the host rises as charge is transferred from the guest to the host. (3) The position of the host conduction band (E_c) varies only slightly with intercalation. (4) The position of the Fermi level relative to the conduction band as a function of charge density (n_d/N_c) is determined by the simple expression $E_F = E_c - kT \ln (N_c/n_d)$, which is appropriate for the saturation region of a doped semiconductor.

In these assumptions, n_d is the number of electrons transferred to the conduction band of the host, and N_c is the number of available states in the conduction band. The saturation region of a doped semiconductor is that region where changes in temperature do not alter the number of electrons in the conduction band, and hence it seems appropriate to view the present case as "saturated" despite the fact that not all of the guests are ionized. The result is that the bandgap of the material varies continuously from that of pure $Cd_2P_2S_6$ to that of fully intercalated $Cd_2P_2S_6$, $Cd_2P_2S_6\{cobaltocene\}_{0.8}$ This variation is consistent with the appearance of the samples under investigation. The center of the sample is clear and colorless, and the border is opaque with the intermediate region displaying concentric green, orange, and red rings.

In the case of SnS_2 intercalation, only the cationic form of cobaltocene is observed. Apparently the Fermi level of the intercalated SnS_2 never reaches the redox potential of cobaltocene in solution. Hence there is always a driving force for charge transfer from the cobaltocene to the conduction band of SnS_2. The intercalation of the cation is actually the end result of oxidation of the neutral species to the cation as part of the intercalation mechanism:

$$CoCp_2{}^0{}_{(solution)} \rightarrow CoCp_2{}^+{}_{(intercalted)} + e^-{}_{(?host)} \qquad (2)$$

where the fate of the electron donated by the neutral cobaltocene remains uncertain in the case of $Cd_2P_2S_6$ intercalation. The intercalation of neutral cobaltocene can be represented in a much simpler fashion:

$$CoCp_2{}^0{}_{(solution)} \rightarrow CoCp_2{}^0{}_{(intercalated)} \qquad (3)$$

where there is no need to account for charge transfer. The leading edge is a clearly recognizable green transparent region which separates the central, colorless, unintercalated portion of the crystal from the darker, red/orange, intercalated region. The green color of the leading edge is similar to the green color of cobaltocenium chloride crystals. In addition, the green region is the area where the ratio of cation to neutral species is largest for a partially intercalated crystal. At 150 °C after 2 h, the front travels at a steady 50 μm/h (the initial rate is slower). The data shown in Figures 4 and 5 were collected after a reaction time of 435 min where the front had advanced 566 μm. The distance to the center of the circular sample was 1100 μm.

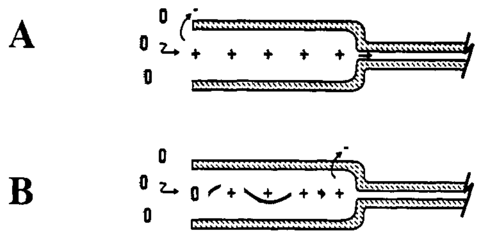

Figure 6. Two proposed models for the intercalation of cobaltocene into $Cd_2P_2S_6$: (A) charge transfer occurring at the edge of the $Cd_2P_2S_6$ host; (B) charge transfer occurring at the reaction front.

Considering the above arguments, at least two distinct mechanisms for the charge-transfer intercalation of cobaltocene into $Cd_2P_2S_6$ can be postulated. Both are shown diagrammatically in Figure 6. Figure 6A shows the oxidation of the cobaltocene occurring at the edge of the crystal. The $Cd_2P_2S_6$ accepts an electron into its conduction band, and the cobaltocenium enters the van der Waals gap. The cation at the reaction front, which is also the first cobaltocenium to have entered the van der Waals gap, proceeds further toward the center of the crystal. In Figure 6B, the neutral cobaltocene diffuses into the lattice until it reaches the reaction front where it undergoes oxidation. The resulting cobaltocenium remains in place. For the front to advance, additional neutral cobaltocene must diffuse through the immobilized cations to reach the front. In this second model, charge transfer occurs within the crystal, not at the crystal/solution interface as is the case in the first model. The first model requires that the conduction band of the intercalated material be a delocalized band. The second model does not require this. For example, individual $P_2S_6{}^{4-}$ units could be the reduced species in the lower model (see below). In either case, neutral cobaltocene is observed between the crystal edge and the center of the crystal due to diffusion into a partially intercalated space. It is difficult to unambiguously determine which, if either, of these models is a suitable description of the intercalation process. The constant velocity of the reaction front suggests that this velocity is independent of the concentration of intercalated neutral cobaltocene. This observation would tend to favor the model shown in Figure 6A. Conversely, the high concentration of cation relative to neutral species at the front lends support to the second model shown in Figure 6B.

As alluded to above, the nature of the reduced species in this system remains an open question. It has been suggested that in $Cd_2P_2S_6$, the reduced species is a phosphorus–phosphorus localized antibonding molecular orbital.[1] Support for this assumption was derived from infrared spectroscopy which demonstrated that the PS_3 deformation mode at 560 cm^{-1} was split upon intercalation with cobaltocene.[4,5] We observe just such a splitting in our investigation. Moreover, close inspection of the split PS, mode in the intercalated phase (Figure 7) reveals a peak at 560 cm^{-1}. This suggests that the split lines are due to reduced $P_2S_6{}^{-4}$ units, while the unreduced $P_2S_6{}^{-4}$ mode remains at 560 cm^{-1}. It should be noted, however, that this

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[15] Cox, P. A. *The Electronic Structure and Chemistry of Solids*; Oxford: New York, 1987; Chapter 7.

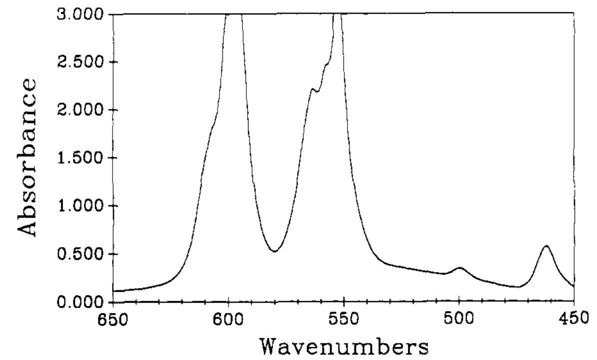

Figure 7. Infrared spectrum of $Cd_2P_2S_6$ fully intercalated with cobaltocene in the region of the PS_3 stretch.

splitting of th PS_3 mode has also been reported for cases where redox does not appear to be the operative mechanism.[5,16] Electronic structure calculations by Whangbo et al.[17] and Mercier et al.[18] on $M_2P_2X_6$ suggest that the acceptor levels in $M_2P_2X_6$ compounds are the divalent metal ions. For the present case, this would result in Cd^0 ($5s^24d^{10}$). Further investigations into the reduced component in this system are ongoing.

Conclusion

Infrared spectra of cobaltocene intercalation compounds of $Cd_2P_2S_6$ are consistent with earlier electron spin resonance studies which concluded that the intercalated cobaltocene is found in both the neutral and cationic state in this compound. Infrared studies on the only other lattice reported to produced mixed oxidation states when intercalated with cobaltocene, SnS_2, were consistent with only one oxidation state in this work. Additional electron spin resonance studies also support the conclusion that the cobaltocene intercalation compound of SnS_2 results in only intercalated cobaltocenium. These results can be interpreted as reflecting the absolute difference in the Fermi level of intercalated $Cd_2P_2S_6$ versus intercalated SnS_2. The time dependence of the infrared spectrum of $Cd_2P_2S_6$ intercalated with cobaltocene suggests that at early reaction times, the cationic form of the cobaltocene is dominant, but that as the reaction proceeds, a significant amount of the intercalated cobaltocene is in the neutral form. The results of this study are consistent with the electronic model proposed by Parkinson et al. to account for mixed valency in charge-transfer intercalation compounds.[10] The lack of neutral cobaltocene intercalated into SnS_2 suggests that in this intercalated material there remains a mismatch between the Fermi level and the redox potential of the cobaltocene in solution. In addition, on the basis of spatially resolved infrared spectra, we have proposed two distinct mechanisms to account for the intercalation and charge transfer processes occurring in the $Cd_2P_2S_6$–cobaltocene system. One involves charge transfer occurring at the edge of the crystal, while the other has charge transfer occurring within the bulk of the crystal.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation through Grant CHE-9007749 for the electron spin resonance spectrometer used in this work.

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Chemistry in Polar Intermetallic Compounds. The Interstitial Chemistry of Zr_5Sn_3

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Received July 7, 1992. Revised Manuscript Received August 31, 1992

The formation of stoichiometric Zr_5Sn_3Z derivatives through incorporation of Z within chains of confacial zirconium octahedra in the Zr_5Sn_3 (Mn_5Si_3-type) parent has been studied principally through reactive powder sintering in the range 1000–1350 °C and by X-ray diffraction means. Examples with Z = B, C, N, O, Al, Si, P, S, Cu, Zn, Ga, Ge, Sn, As, and Se have been quantitatively synthesized and characterized as powders. Complications are noted with arc-melting methods and for Z = Fe, Co, Ni where mixed Z–Sn interstitials occur. Single crystal diffraction for Z = C, O, and Ge and Rietveld powder refinement for Ga demonstrate how the host Zr_6 cavities contract or expand to accommodate Z. The $Zr_5Sn_3S_x$ system at 1050 °C is nonstoichiometric over the range $1 > x > \sim 0.5$. Volume trends as a function of Z follow the metallic/covalent radii of Z well.

Introduction

The chemistry of transition metal clusters has recently attracted much attention for its structural diversity and reactivity.[2] Traditionally, stable cluster compounds have been limited to those with discrete structural units in which well-defined electronic requirements are generally understood and satisfied. Metal-rich halides and chalcogenides are such examples.[3-5] Families of these com-

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[1] The Ames Laboratory-DOE is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of the Basic Energy Sciences, Materials Sciences Division.

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