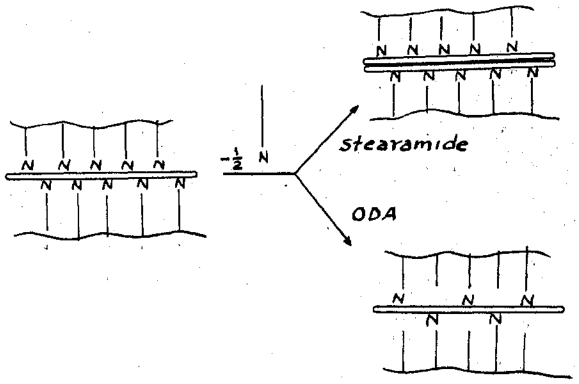

Figure 3. Two different courses followed by half evacuation of long chain guest complexes.

of partial deintercalation? In either 1/3 complex the density of the guest phase, and hence of the guest–guest interaction, is about the same. The essential difference between them is the presence of layer–layer bonding and all guest–host bonding on one surface for the amide, as compared with having the same number of guest–host bonds distributed on both sides of each sheet in the case of the amine (see Figure 3). The amine, being a stronger Lewis base, likely interacts more strongly with the layer, and this may be why regaining layer–layer bonding at the expense of losing opposing guest–host bonds does not occur.

A test of the assumption of the insignificance of guest–guest bonding differences between the 2/3 and 1/3 octadecylamine complexes of TaS_2 is the evaluation of the heat of melting of the two guest phases. This was accomplished using differential scanning calorimetry (DSC) on the two complexes at temperatures far below any observed weight loss. Both complexes undergo a reversible phase transition at about 10–15 °C above the normal fusion point of the free guest, in keeping with the previous observation[4] that intercalation modestly raises the melting transition temperature. *n*-Octadecylamine was first run to ascertain the accuracy of the method and yielded a value for its heat of fusion of 16.0 ± 1.5 kcal/mol. No literature comparison could be found, but an estimate using the group method was made by adding to the heat of fusion of octadecane (14.8 kcal/mol)[12] the difference in heats of fusion between methylamine and methane (1.24 kcal/mol).[12] In good agreement with the experiment, 16.0 kcal/mol is the resulting value.

The melting transition observed for the 1/3 octadecylamine–TaS_2 complex was very similar in shape, and occurred at about 7 °C higher (Figure 4). The heat of the transition amounted to 5.2 kcal/mol (of amine). Conceptually, this means that about one-third of the freedom of the liquid phase is realized in the transition. On cooling and reheating, the DSC curve is very closely repeated. As shown in the figure, the curve for the 2/3 complex was not as simple. The transition fell about 8 °C higher than the lower complex and exhibited additional structure. The measured enthalpy for all of the area amounts to 6.9 kcal/mol (of amine). However, reducing the area by ignoring the shoulder seen at 90 °C leads to the value 5.1 kcal/mol, in agreement with that of the 1/3 complex. On cooling and passing through the transition again, the area of the shoulder relative to the main transition increased. So with this reservation in mind, it can be concluded that the intermolecular bonding in the two complexes is very nearly equal.

A different perspective of this transition has been seen in the broad-line NMR (performed by B. G. Silbernagel). For both complexes, the proton signal at room temperature was about 6.5 G in breadth, as expected for crystalline packing. However, on raising the temperature to 75–80 °C, the lines are essentially completely narrowed, indicating liquid-like motion.

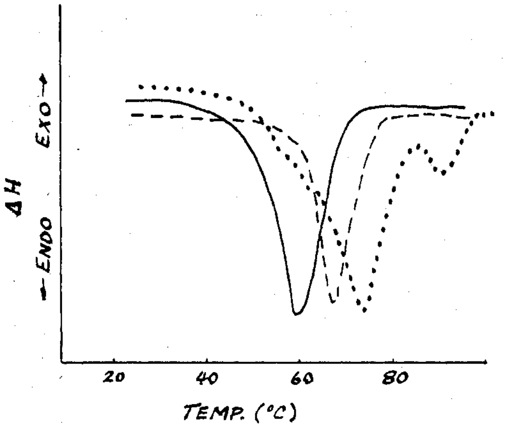

Figure 4. Differential scanning calorimetry results: solid line is *n*-octadecylamine, dashed line is the 1/3 TaS_2 complex, dotted line is the 2/3 complex. The scales are not the same. Data are in the text.

It has and will continue to be demonstrated that by studying the behavior of bulk lamellar intercalated phases as models for lipid structures or surface films, insights into the structure and dynamics can be relatively more easily gained, and the valuable function as a model is thus served.

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Registry No. $TaS_2(ODA)_{2/3}$, 54748-15-1; $TaS_2(ODA)_{1/3}$, 55907-37-4.

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Triplet–Singlet Emission of $Fe(CN)_5CO^{3-}$

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Excitation of a series of compounds containing Fe^{3+} with UV radiation gave in each case a broad structureless d–d luminescence band in the red[1] and near-infrared[2] regions. However, there are no known examples of emission from complexes of Fe^{2+}. It has been suggested that the absence of

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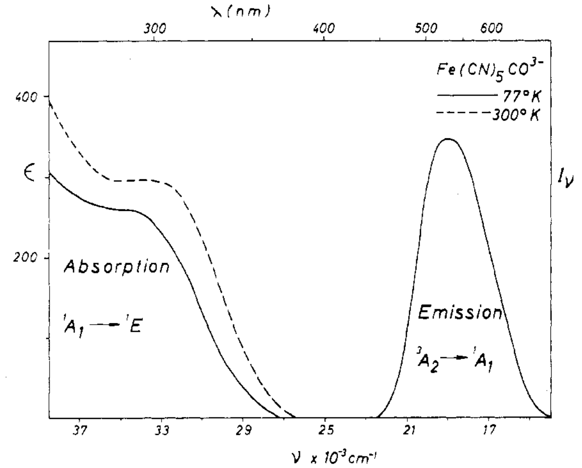

Figure 1. Absorption and emission spectra of $Fe(CN)_5CO^{3-}$. The emission intensity was measured directly from the sodium salt crystals.

detectable emission from $Fe(CN)_6{}^{4-}$ at low temperature reflects the fact that its lowest excited state lies in the IR region.[3] Experimental evidence on the photoelectron spectrum of $Li_4Fe(CN)_6$ suggests that a filled t_{2g} orbital configuration exists in the ground state.[4] Furthermore, the close similarity between the absorption spectra of $Co(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$ allows us to expect that the latter complex ion and monoderivatives of it should give rise to emissions in an accessible region of the spectrum as it has been found for other d^6 emitters.[5,6]

For the Fe^{2+} mentioned above we have searched for d–d emission from a suitable d^6 $Fe(CN)_5X$ complex so that the observed radiative decay can be related to the corresponding one for the parent compound. This correlating process is feasible for two reasons: (a) previous results[6] for cobalt(III) complexes indicate that the $^3T_{1g}$ (z component) is responsible for the observed emission of $M(CN)_6{}^{n-}$ since an e_g distortion (with compression along the z axis and expansion in the equatorial plane) is dominant in the nuclear configuration of the orbitally triply degenerate excited state, and (b) the $^3T_{1g}$ z component becomes $^3A_2$ for d^6 $M(CN)_5X^{n-}$ complexes keeping in this manner all the features governed by the CN^- ions (in equatorial positions) as in the $Fe(CN)_6{}^{4-}$ parent compound.[7] Moreover, the $^3T_{1g}$ (x,y components) transform as ^3E for the monoderivative complex. It is well-known that if the X ligand is stronger than CN^- (a necessary condition for this case), then ^3E will always be higher in energy than $^3A_2$ and the observed emission for $M(CN)_5X^{n-}$ keeps all the spectral features of the $^3T_{1g} \rightarrow {}^1A_{1g}$ decay for the parent compound. Finally, if the X ligand does not appreciably differ in mass and volume from the CN^- ion, then the $^3A_2$ emitting state will almost reach the same energy position as the $^3T_{1g}$ (z component) state of $Fe(CN)_6{}^{4-}$ in reference to the corresponding ground state.

Figure 1 shows the measured absorption and emission spectra of $Fe(CN)_5CO^{3-}$ where the $^1A_1 \rightarrow {}^1E$ transition at 33 500 cm^{-1} appears 2500 cm^{-1} to the blue of the corresponding $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption for the parent compound.[8] The $^3A_2 \rightarrow {}^1A_1$ emission centered at 18 900 cm^{-1} displays a half-bandwidth of ~4000 cm^{-1} and was obtained by direct excitation of the crystals (77 K) with UV light of λ 360 nm. The measured lifetime τ = 81 ms is in agreement with the spin-forbidden character of the transition. The detailed measurement procedure has been described elsewhere[6] and the compound was synthetized as the sodium salt by an already published method.[9]

It is very surprising that $Co(CN)_5X^{n-}$ complexes emit at a longer wavelength than $Fe(CN)_5CO^{3-}$ in spite of the fact that the absorption data for the corresponding parent compounds are very similar. This experimental observation can be related to the parent compounds according to our previous discussion and it suggests that the $^3T_{1g}$ emitting state for $Fe(CN)_6{}^{4-}$ should also be located near ~18 900 cm^{-1} in reference to the ground state. Thus, the lack of luminescence for the hexacyanoferrate(II) ion complex must be interpreted in terms of radiationless decays to the ground state and possible quenching processes due to photooxidation of the central metal ion.

In summary, we have found that the monocarbonyl derivative of $Fe(CN)_6{}^{4-}$ is a d^6 emitter well characterized within the limits of the ligand field theory. We also have to point out that attempts to induce triplet–singlet emission for $Fe(CN)_5X^{n-}$ for X lower than CO in the spectrochemical series have failed up to now. Further work along these lines is in progress.

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Registry No. $Fe(CN)_5CO^{3-}$, 17455-62-8.

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Reversible Formation of the Nickel(III) Complex Tribromo[*cis*-1,2-bis(diphenylphosphino)ethylene]nickel(III)

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A number of nickel(III) complexes have been reported,[2] but relatively few of these have been thoroughly characterized. The best established examples with heavy group 5B donor ligands are $[Ni(das)_2Cl_2]^+$ (das = *o*-phenylenebis(dimethylarsine)),[3,4] $[Ni(PMe_2Ph)_2Br_3]$,[5] and the recently reported $[Ni(mpp)_2Cl_2]^+$ (mpp = *o*-phenylenebis(dimethylphosphine)).[6] These complexes were obtained by oxidation of the nickel(II) analogues, a reaction which is often irreversible.[6] During a study of the coordination chemistry of group 8 metals in their higher oxidation states, we prepared tribromo[*cis*-1,2-bis(diphenylphospino)ethylene]nickel(III), $[Ni(VPP)Br_3]$, and observed that this complex reverts to the nickel(II) analogue over several weeks.

Experimental Section

Dibromo[*cis*-1,2-bis(diphenylphosphino)ethylene]nickel(II), $[Ni(VPP)Br_2]$, was prepared by the literature method.[7] Physical measurements were made as described previously.[8,9]

Tribromo[*cis*-1,2-bis(diphenylphosphino)ethylene]nickel(III). Method 1. Finely powdered $[Ni(VPP)Br_2]$ (1.75 g, 2.9 mmol) was suspended in benzene (15 mL), treated with a dilute solution (2% v/v) of bromine in benzene (10 mL), and allowed to stand for 1 h. The black product was filtered off, rinsed with benzene (5 mL), and dried in vacuo (1.87 g, ~90%). Anal. Calcd for $[Ni(VPP)Br_3 \cdot C_6H_6]$: C, 49.8; H, 3.6; Br, 31.2; Ni(III), 7.65. Found: C, 48.9; H, 3.7; Br,

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