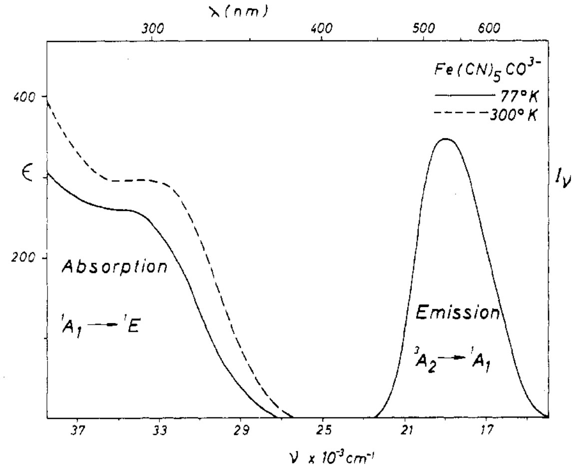

Figure 1. Absorption and emission spectra of $Fe(CN)_5CO^{3-}$. The emission intensity was measured directly from the sodium salt crystals.

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 $^3T_{1g} \to {}^1A_{1g}$ 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 $^1A_1 \to {}^1E$ transition at 33 500 cm^{-1} appears 2500 cm^{-1} to the blue of the corresponding $^1A_{1g} \to {}^1T_{1g}$ absorption for the parent compound.[8] The $^3A_2 \to {}^1A_1$ 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 $\tau = 81$ 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, 31.1; Ni(III), 7.65 (iodometric determination).

Method 2. A solution of [Ni(VPP)Br$_2$] (2.0 g, 3.3 mmol) in the minimum amount of chloroform was treated with bromine in chloroform (20 mL, ~5% v/v). On standing for a few hours, black crystals separated; these were filtered off, rinsed with diethyl ether (5 mL), and dried in vacuo (1.9 g, 64%). Anal. Calcd for [Ni(VPP)Br$_3$]: C, 44.9; H, 3.2; Br, 34.55. Found: C, 44.8; H, 3.1; Br, 34.5.

Results and Discussion

Treatment of the orange diamagnetic [Ni(VPP)Br$_2$] with bromine in chloroform or benzene yields the brown–black [Ni(VPP)Br$_3$], obtained as a monosolvate from the latter solvent. The complex is unstable in solution but behaves as a nonelectrolyte in freshly prepared 10^{-3} M 1,2-dichloroethane or nitromethane. The magnetic susceptibility ($\mu_{\text{eff}} = 1.98\ \mu_B$) is consistent with the presence of low-spin d^7 nickel(III).[2] The far-IR spectrum contains three absorbtions attributable to ν(Ni–Br) at 276, 265, and 220 cm^{-1} [10] and is consistent with a five-coordinate complex. The electronic spectrum in dichloromethane exhibits absorptions at 0.81 (ϵ 22), 1.43 (ϵ 138), 2.10 (ϵ 2820), 2.69 (ϵ 2190), and 3.41 (ϵ 13 200) μm^{-1}, and the solid reflectance spectrum is essentially similar, exhibiting bands at 0.83, 1.35, 2.10, and 2.50 μm^{-1}. The spectrum is again consistent with a five-coordinate monomer but does not distinguish between a trigonal-bipyramidal (C_{2v}) or a square-pyramidal (C_s) structure since four spin-allowed transitions are expected for either structure.

The EPR spectrum of powdered [Ni(VPP)Br$_3$] at −150 °C consists of a single broad absorbtion ($g = 2.06$). In dichloromethane solution at room temperature the spectrum shows a quartet ($g = 2.16$, $A_{\text{iso}} = \sim 65$ G) due to coupling to a single bromine atom (^{79}Br, ^{81}Br, $I = {}^3/_2$), upon which further fine structure in the form of a 1:2:1 triplet is evident, consistent with two equivalent phosphorus atoms (^{31}P, $I = {}^1/_2 A_{\text{iso}} = \sim 9$ G). These data are consistent with a C_{2v} structure (I) in which the unpaired electron shows resolvable coupling only to the P$_2$Br donors in the equatorial plane. The alternative square-pyramidal (C_s) structure would be expected to show coupling to two equivalent bromines and two phosphorus atoms in the basal plane.

A sample of [Ni(VPP)Br$_3$] evolved bromine on strong heating (>300 °C), and [Ni(VPP)Br$_2$], identified by analysis and its electronic spectrum[7] remained. The solid also decomposed slowly in an open vessel at room temperature. The decomposition could be monitored by observing the decrease in μ_{eff} from 1.98 to ~0.2 μ_B (corresponding to the measured susceptibility of [Ni(VPP)Br$_2$] and probably attributable to temperature-independent paramagnetism). The rate of decomposition varied with the state of subdivision of the sample, being fastest for very thin films of the solid and slowest for the bulk solid; the average time to revert completely to [Ni(VPP)Br$_2$] is about 2 months. A sample kept in a sealed tube showed very little decomposition in this time. This suggests that [Ni(VPP)Br$_3$] slowly evolves bromine, the reaction proceeding to completion only when the bromine can escape, but if the bromine is not removed, decomposition is minimal. Certainly, powdered [Ni(VPP)Br$_2$] rapidly turns to black [Ni(VPP)Br$_3$] when exposed to bromine vapor. A careful examination (analysis and IR and electronic spectra) of the "[Ni(VPP)Br$_2$]" produced by this decomposition showed it to be identical with a genuine sample.[7] Neither the phosphorus nor the unsaturated backbone of the ligand are attacked by the evolved bromine under these conditions.[11]

The stability of nickel(III) complexes of this type is very sensitive to changes in the ligand. The tetrahedral [Ni(tVPP)Br$_2$]$_n$[12] (tVPP = *trans*-1,2-bis(diphenylphosphino)ethylene) is not oxidized by bromine, while for [Ni(VPP)$_2$Br]BPh$_4$ [7] or [Ni(VAA)Br$_2$][13] (VAA = *cis*-1,2-bis(diphenylarsino)ethylene) oxidation to nickel(III) does occur, but the products are unstable, decomposing in a few hours.

Registry No. Ni(VPP)Br$_3$, 64771-39-7; Ni(VPP)Br$_2$, 23467-50-7.

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Bis(dimethylamido)tetrakis(*N*,*N*-dimethylcarbamato)dimolybdenum

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We report our preparation and characterization of the title compound, Mo$_2$(NMe$_2$)$_2$(O$_2$CNMe$_2$)$_4$, I, formed in the reaction between Mo$_2$(NMe$_2$)$_6$ and carbon dioxide.

Alkane solutions of Mo$_2$(NMe$_2$)$_6$[1] react rapidly with CO$_2$ (>6 equiv) at room temperature to give I as a pale yellow microcrystalline precipitate. When I is dissolved in benzene or toluene and reacted with a further excess of CO$_2$, the solution turns gray; we have been unable to isolate any pure compound from these solutions. When the reaction I + CO$_2$ (>2 equiv) is carried out in an NMR tube and followed by ^{1}H NMR spectroscopy, all proton resonances disappear with time.

These observations show a marked difference in the reactivity of Mo$_2$(NMe$_2$)$_6$ compared with W$_2$(NMe$_2$)$_6$.[2] The latter compound reacts[3] with CO$_2$ (≥6 equiv) to give W$_2$(O$_2$CNMe$_2$)$_6$ which has been structurally characterized.[4,5]

I is a pale yellow, air-sensitive, diamagnetic compound; it is appreciably soluble in toluene and benzene but only very sparingly soluble in alkane solvents. It is this fact which accounts for its ready isolation from the reaction between alkane solutions of Mo$_2$(NMe$_2$)$_6$ and CO$_2$. Attempts to recrystallize I were thwarted because I slowly decomposed in solution. The stability of I in this regard is comparable to that of W(NMe$_2$)$_3$(O$_2$CNMe$_2$)$_3$.[3,6]

In the mass spectrometer I shows a strong molecular ion Mo$_2$(NMe$_2$)$_2$(O$_2$CNMe$_2$)$_4^+$ (m/e 632) together with many other Mo$_2$-containing ions. The most intense ion (base peak) occurred at m/e 544. A comparison of the mass spectra obtained from protio Mo$_2$(NMe$_2$)$_2$L$_4$ and the labeled compounds Mo$_2$(NMe$_2$)$_2$L$_{4-x}$L$'_x$, where L = O$_2$CN(CH$_3$)$_2$, L$'$ = O$_2$CN(CD$_3$)$_2$, and x = 1–4, indicates that the base peak corresponds to Mo$_2$(O$_2$CNMe$_2$)$_4^+$.

The IR spectrum showed a strong broad band at 1578 cm^{-1}, typical of ν(NCO$_2$) in a bidentate carbamate ligand.[3] Full IR data are recorded in the Experimental Section.

Proposed Structure of Mo$_2$(NMe$_2$)$_2$(O$_2$CNMe$_2$)$_4$

We believe that Mo$_2$(NMe$_2$)$_2$(O$_2$CNMe$_2$)$_4$ adopts a structure akin to that found[4,5] for W$_2$Me$_2$(O$_2$CNEt$_2$)$_4$ and that the central Mo$_2$N$_2$(O$_2$C)$_4$ moiety may be represented by

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