At higher temperatures, the photosolvation and the other deactivation reactions become so fast that the luminescence and the absorption of the triplet are no longer observable.

Registry No. $[(n\text{-}C_4H_9)_4N]_3Co(CN)_6$, 20792-39-6; $[(n\text{-}C_4H_9)_4N]Co(CN)_5H_2O$, 106800-13-9.

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Stability of d^3 Diimine Complexes: Molybdenum(III) vs. Chromium(III)

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The number of well-characterized complexes of Cr(III) has increased enormously since the early days of coordination chemistry, when they already played an important part in the development of new theories.[1] On the other hand, coordination compounds of Mo(III) have not been studied in great detail, except some complexes, especially the aquo ions[2] and species like $Mo(edta)^-$.[3] This striking difference between elements of the same transition-metal group has been generally attributed[4] to an instability of Mo(III) and W(III) compared to that of higher oxidation states. It was often assumed that Mo(III) and W(III) would be as inert as Cr(III) owing to their d^3 configuration.[5]

In view of the capability of the chelate ligand 2,2′-bipyridine (bpy) to act as a relatively strong π acceptor and thus stabilize low oxidation states as e.g. in $Ru(bpy)_3^{2+}$, we attempted to study the properties of $Mo(bpy)_3^{3+}$.

This complex has been reported to exist in the compounds $Mo(bpy)_3X_3$ ($X = I^-, Br^-, Cl^-$),[6,7] but more recent results raise doubts about the existence of these compounds.[8]

Among the few tris-bidentate mononuclear Mo(III) complexes described in the literature, the work of Ghosh and Prasad[9] is noteworthy. These authors prepared tris complexes of several bidentate ligands, including ethylenediamine (en) and 2-(2-pyridyl)benzimidazole, from $(NH_4)_2MoCl_5(H_2O)$. We report here the synthesis of $Mo(bpy)_3(PF_6)_3$ from the same starting material. ^2H NMR of complexes containing deuteriated ligands[10,11] is used to study the species in solution.

Experimental Section

General Considerations. Chemicals were purchased from Fluka or Aldrich. Methanol was distilled over Mg. bpy was recrystallized from hexane. $(NH_4)_2MoCl_5(H_2O)$ was prepared by the procedure of F. A. Cotton.[12] All manipulations were carried out under N_2 with use of Schlenk apparatus.

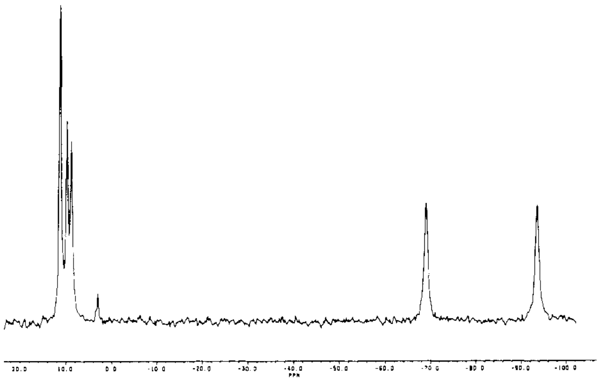

Figure 1. ^2H NMR spectrum of "$Mo(bpy\text{-}6,6'\text{-}d_2)_3^{3+}$" in acetone.

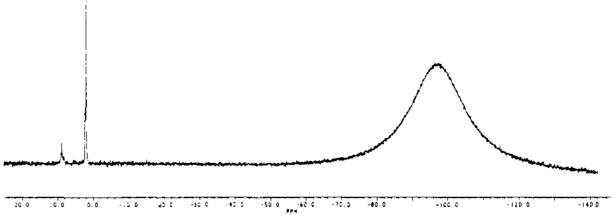

Figure 2. ^2H NMR spectrum of $Cr(bpy\text{-}6,6'\text{-}d_2)_3^{3+}$ in acetone.

Table I. Electrochemical Data for Molybdenum Complexes with 2,2′-Bipyridine

	half-wave potentials vs. SCE, V[a]				
	IV/III	III/II	II/I	I/0	ref
$Mo(bpy)_3^{3+}$	1.00[b]	−0.58	−1.05		this work
$Mo(bpy)_3$		−0.01[b]	−0.42	−1.13	17
$Mo(bpy)_2Cl_2^+$	0.92[b]	−0.63[c]	−1.08[c]		17

[a] All values obtained at a rotating platinum electrode unless noted otherwise. [b] Irreversible anodic process. [c] Values obtained at a dropping mercury electrode.

Measurements. Cyclic voltammetry: Metrohm Polarecord, Model E 506; VA scanner, Model E 612; X-Y printer, Model MP 704 4A; platinum-disk electrode, platinum auxiliary electrode, $Ag/AgNO_3$ reference electrode; supporting electrolyte tetra-*n*-butylammonium perchlorate. ^2H NMR: Bruker AM 360 spectrometer; sealed tubes. Magnetic susceptibility: Bruker BMNS 50/50 1S/BE10, Faraday method; room temperature on powdered samples; calibration with $HgCo(NCS)_4$.

Synthesis. $Mo(bpy)_3(PF_6)_3$ was obtained by mixing 2 mmol of $(NH_4)_2MoCl_5(H_2O)$ with 3 equiv of bpy in 100 mL of dry methanol for 5 h at room temperature. After filtration of the reaction mixture the complex was precipitated by adding an excess of NH_4PF_6 in methanol. The solid was recrystallized from acetone/ether; 540 mg of a violet microcrystalline product was collected. Anal. Calcd for $C_{30}H_{24}F_{18}MoN_6P_3$: C, 36.01; H, 2.41; N, 8.41. Found: C, 37.75; H, 2.71; N, 9.00. $\mu_{eff} = 3.54\ \mu_B$.

Bpy-*6,6′*-d_2 was obtained by treating 6,6′-Li_2-bpy[13] in ether at −90 °C with an excess of CH_3OD. After hydrolysis and isolation of the solid, the crude product was purified by chromatography (alumina, ether/hexane 1:1).

$Cr(bpy)_3(PF_6)_3$[14] and $Cr(bpy)_2(DMF)_2(PF_6)_3$[15] were prepared by published methods.

Results

An examination of the ^2H NMR spectrum of $Mo(bpy\text{-}6,6'\text{-}d_2)_3(PF_6)_3$ in acetone (Figure 1) shows two resonances of equal intensity at −94 and −69 ppm, corresponding to deuterons of bpy-*6,6′*-d_2 bound to a paramagnetic Mo(III), thus indicating the existence of two sets of equivalent deuterons. In the diamagnetic region the spectrum exhibits one resonance at 8 ppm corresponding

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to the deuterons of free bpy and two more signals at 7.7 and 10.1 ppm assigned to a diamagnetic complex.

The ^{2}H NMR spectrum of Cr(bpy-*6,6′-d*$_2$)$_3$(PF$_6$)$_3$ in acetone (Figure 2) yields only one signal at −97 ppm, indicating equivalence of all six deuterons of the three bpy ligands and implying the expected D_3 symmetry of the complex.

In DMF the cyclic voltammogram of the dissolved Mo(bpy)$_3$(PF$_6$)$_3$ exhibits two reversible reduction waves at −0.58 and −1.05 V and one irreversible oxidation wave at 1.00 V (Table I).

The spin-only magnetic moment expected for an octahedral d^3 complex is $\mu_{\text{eff}} = 3.87\ \mu_B$.[16] After one recrystallization Mo(bpy)$_3$(PF$_6$)$_3$ has a magnetic moment of 3.54 μ_B. Two more recrystallizations yield a product that has a correct C,H,N analysis but a strongly diminished magnetic moment (0.1 μ_B).

Discussion

There is no doubt that for the solid state all analytical data (IR, elemental analysis) agree with a formulation of Mo(bpy)$_3$(PF$_6$)$_3$ as a salt of the octahedral complex Mo(bpy)$_3^{3+}$. The spectroscopic data of Mo(bpy)$_3$(PF$_6$)$_3$ and Mo(bpy-*6,6′-d*$_2$)$_3$(PF$_6$)$_3$ in acetone, in DMF, or in MeOH are inconsistent with the assumption of an octahedral D_3 tris-chelate complex.

The solution behavior, i.e. reduction of the D_3 symmetry as observed by ^{2}H NMR, could be due to the following reasons: (a) oxidation, (b) coordination number greater than 6, (c) polymerization, and (d) loss of one bpy.

The resonances at −69 and −94 ppm for the deuterons bound to a paramagnetic species are typical for three unpaired electrons, therefore excluding reason a.

A coordination number greater than 6 would not explain the signal of the deuterons bound to free bpy. A polymerization with one or two bridging bpy's will give more than two resonances of equal intensities in the paramagnetic region.

The substitution of one bpy by the solvent results in a bis-chelate complex: Mo$^{\text{III}}$(bpy)$_2$(solvent)$_2^{3+}$. In the case where the two solvent molecules are in cis positions, the six deuterons bound to the paramagnetic species produce two resonances of equal intensity. The deuterons belonging to the liberated bpy show one signal at 8 ppm.

The ^{2}H NMR spectrum is entirely in agreement with this interpretation. This result shows that in solution the Mo(bpy)$_3^{3+}$ is thermodynamically unstable and dissociates rapidly into Mo(bpy)$_2$(solvent)$_2^{3+}$ and bpy.

The resonances at 7.7 and 10.1 ppm and the decreased magnetic moments of products, which were recrystallized several times, could be due to the formation of polymers, stabilized by Mo–Mo bonds. Attempts to prepare salts of Mo(bpy)$_2$((CH$_3$)$_2$CO)$_2^{3+}$ failed, due to the formation of polymeric products that cannot easily be characterized. The signals in the ^{2}H NMR spectra at −69 and −94 ppm disappear after several days completely even if oxygen is strictly excluded. Several signals in the "diamagnetic" region indicate the presence of more than one species.

It would be interesting to compare the ^{2}H NMR spectrum of Mo(bpy-*6,6′-d*$_2$)$_2$(solvent)$_2^{3+}$ with the ^{2}H NMR spectrum of Cr(bpy-*6,6′-d*$_2$)$_2$(solvent)$_2^{3+}$, but unfortunately no resonance was observed for the latter complex between +20 and −200 ppm.

The hypothesis of rapid dissociation of one bpy ligand deduced from ^{2}H NMR data is corroborated by the redox behavior (Table I). The cyclic voltammogram of "Mo(bpy)$_3^{3+}$" in DMF solution is very similar to that of Mo(bpy)$_2$Cl$_2^+$ but different from the second and third oxidation waves of Mo(bpy)$_3$. The third oxidation wave of neutral Mo(bpy)$_3$, on the other hand, is irreversible, indicating the instability of Mo(bpy)$_3^{3+}$.

Conclusion

The difficulties in preparing Mo(bpy)$_3^{3+}$, mentioned in the literature[8,18,19] and reiterated in our laboratory, can now be explained as follows:

Contrary to the widespread belief that 4d^3 second-row transition elements form complexes more inert than first-row 3d^3 elements, Mo(III) seems to be much more substitutionally labile than Cr(III), at least with bpy ligands. Moreover, Mo(bpy)$_3^{3+}$ is thermodynamically unstable toward dissociation of one bpy ligand in most common solvents. Formation of the tris complex in the solid state is due to the insolubility of Mo(bpy)$_3$(PF$_6$)$_3$. Two alternative pathways for the rapid dissociation reaction can be envisaged: (a) accessibility of an associative pathway for the substitution reaction and (b) catalytic amounts of complexes having higher oxidation states of Mo initiating the substitution of a bpy ligand.

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On the Electronic Structure of MPS$_3$ Phases

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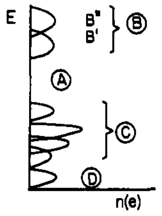
Because of their topochemical,[1,2] electrochemical,[3] optical,[4–6] and magnetic[4,7–9] properties, two-dimensional materials of the MPS$_3$ family (Figure 1) have been the subject of intense investigation during the past decade. As a result, there is now a wealth of experimental data concerning these remarkable systems. Nevertheless, the rationalization of some of these data has led to a series of very puzzling questions. This was in part due to the absence of detailed band structures for these materials.

Recently Whangbo, Brec, Ouvrard, and Rouxel[10] reported an extended Hückel tight-binding analysis of the electronic structure of FePS$_3$. They were able to show that the acceptor levels under alkali-metal intercalation are the partially filled 3d orbitals. Later, Brec, Whangbo, et al.[11] interpreted some unusual Mössbauer phenomena in Li$_x$FePS$_3$ using similar computations. Since revised structural data on many of these phases have recently appeared,[12] we felt it useful to look again at their electronic structure. Therefore, we have carried out extended Hückel tight-binding calculations on a series of MPS$_3$ systems (M = Mn, Fe, Co, Ni, Cd) using parameters and exponents given in the Appendix.

The computed densities of states for all these phases have a number of common features schematically shown in **1**. A sizable gap (A) separates the predominantly metal region (C) from what would be the lowest empty levels region for d^{10} cases (B). B contains two contributions, the lowest one (B′) being predominantly made of the s and p levels of the metal. The P–P (and



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