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Phenanthroline–Polyoxometalate Hybrid Compounds and the Observation of Intramolecular Charge Transfer

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A phenanthroline ligand has been covalently modified at the 2 and 9 positions by an aminophenylhexamolybdate substituent. The ^{1}H NMR spectrum indicated a strong electron-withdrawing effect of the hexamolybdate ($Mo_6O_{19}{}^{2-}$) moiety on the phenanthroline ligand. UV–vis and cyclic voltammetry showed extended conjugation of the hybrid phenanthroline–polyoxometalate compound and the possibility of easy oxidation of the extended phenanathroline ligand. Further EPR experiments provided strong evidence for an intramolecular charge-transfer process with the formation of a phenanthroline cation radical and a reduced hexamolybdate.

Polyoxometalates are anionic clusters of discrete structure commonly based on molybdenum or tungsten oxides. One set of important applications of polyoxometalates are based on their potential as electron acceptors. In catalysis, this leads to the definition of polyoxometalates as oxidants via electron transfer,[1] and in materials research, this leads to the possibility of the formation of charge-transfer or electron donor−acceptor materials with interesting electronic and magnetic properties.[2] A topic of recent interest in catalysis research, associated with the electron-acceptor properties of polyoxometalates, has been to modify the electronic properties of a metal center via metal−polyoxometalate and metal complex−polyoxometalate interactions. Thus, a platinum(IV)−oxo species has been stabilized by $[PW_9O_{34}]^{9-}$,[3] and the formation of a platinum(II)−bipyrimidine−$H_5PV_2Mo_{10}O_{40}$ hybrid compound has been utilized for the catalytic, aerobic oxidation of methane.[4] In the past, we have also noted that covalent attachment of a $[SiW_{11}O_{39}]^{8-}$ moiety to a metallosalen leads to the stabilization of a higher-valent metallosalen species.[5] In the present report, we wish to demonstrate that covalent attachment of a hexamolybdate, $[Mo_6O_{19}]^{2-}$, species to a phenanthroline ligand via a phenyl spacer leads to the significant modification of the electronic properties of the phenanthroline ligand through intramolecular charge transfer.

Organic−polyoxometalate hybrid materials are often prepared by assembly approaches through use of electrostatic interactions (organic cation, polyoxometalate anion), which are often unpredictable and have limited reaction control.[6] An alternate, but less common, approach is the formation of hybrids via covalent bonding such as insertion of organometallic compounds into lacunary polyoxometalate species or linkage of the organic and inorganic components;[7] in this case, we have used an imido linkage. The synthetic route used to prepare the phenanthroline−polyoxometalate hybrid compound is summarized in Figure 1.[8]

First, 4-lithium-*N*,*N*-bis(trimethyl-silyl)aniline was synthesized according to a procedure described by Pratt et al.[9] The 4-lithium-*N*,*N*-bis(trimethyl-silyl)aniline was then reacted directly with 1,10-phenanthroline to form the 2,9-disubstituted 1,10-phenanthroline in good yields using a procedure previously described for the reaction of 1,10-phenanthroline with phenyllithium.[10] The trimethylsilyl protecting groups were removed by hydrolysis under acidic

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(1) (a) Kozhevnikov, I. V. *Catalysis by Polyoxometalates*; Wiley: Chichester, England, 2002. (b) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407−455. (c) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113−252. (d) Neumann, R. *Prog. Inorg. Chem.* **1998**, *47*, 317−370. (e) Khenkin, A. M.; Weiner, L.; Wang, Y.; Neumann, R. *J. Am. Chem. Soc.* **2001**, *123*, 8531−8542.

(2) (a) Coronado, E.; Gómez-García, C. J. *Chem. Rev.* **1998**, *98*, 273−296. (b) Yamase, T. *Chem. Rev.* **1998**, *98*, 307−326.

(3) Anderson, T. M.; Neiwert, W. A.; Kirk, M. L.; Piccoli, P. M. B.; Schultz, A. J.; Koetzle, T. F.; Musaev, D. G.; Morokuma, K.; Cao, R.; Hill, C. L. *Science* **2004**, *306*, 2074−2077.

(4) Bar-Nahum, I.; Khenkin, A. M.; Neumann, R. *J. Am. Chem. Soc.* **2004,** *126*, 10236−10237.

(5) Bar-Nahum, I.; Cohen, H.; Neumann, R. *Inorg. Chem.* **2003**, *42*, 3677−3684.

(6) (a) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77−112. (b) Villanneau, R.; Delmont, R.; Proust, A.; Gouzerh, P. *Chem. Eur. J.* **2000**, *6*, 1184−1192. (c) Sanchez, C.; de A. A. Soler-Illia, G. J.; Ribot, F.; Lalot, T.; Mayer, C. J.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061−3083. (d) Proust, A.; Thouvenout, R.; Chaussade, M.; Robert, F.; Gouzerh, P. *Inorg. Chim. Acta* **1994**, *224*, 81−95.

(7) Peng, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 930−935 and references therein.

(8) The phenyl spacer is required because we were not successful in forming the hexamolybdate−phenanothroline imido linkage directly using 2,9-diaminophenanthroline as substrate.

(9) Pratt, J. R.; Massey, W. D.; Pinkerton, F. H.; Thames, S. F. *J. Org. Chem.* **1975**, *40*, 1090−1094.

(10) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Tetrahedron Lett.* **1982**, *23*, 5291−5294.

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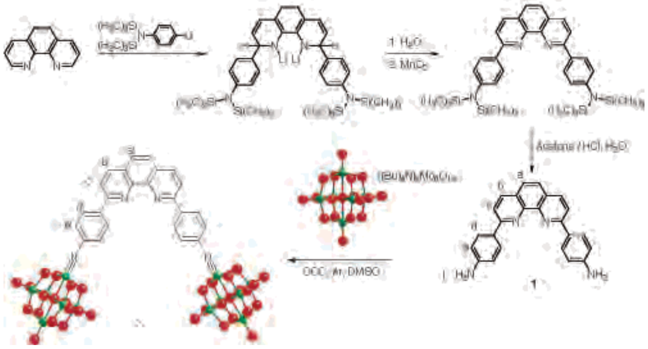

Figure 1. Synthetic scheme for the preparation of the phenanthroline−polyoxometalate hybrid compound.

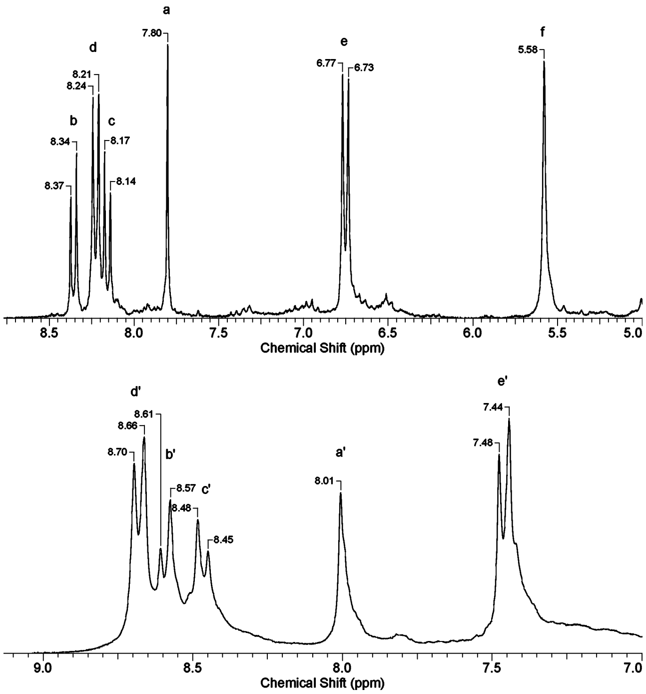

Figure 2. ^{1}H NMR spectra of **1** (top) and **2** (bottom) (see Figure 1 for the position labels).

conditions to obtain the desired bis-2,9-di(4-aminophenyl)-1,10-phenanthroline, **1**, which was purified by flash chromatography. The covalent attachment of the hexamolybdate polyoxometalate, $[Mo_6O_{19}]^{2-}$ to bis-2,9-di(4-aminophenyl)-1,10-phenanthroline was unsuccessful using a direct coupling procedure in the presence of triethylamine,[11] or by activation with dibromotriphenylphosphorane to form the phosphinimine−phenanthroline intermediate.[12] However, good results were obtained using dicyclohexylcarbodiimide (DCC) as a coupling reagent.[13] The hybrid compound, **2**, obtained was soluble in polar, aprotic solvents such as DMSO, DMF, and benzonitrile.

The ^{1}H NMR spectra (aromatic region) of compounds **1** and **2** are shown in Figure 2. Both spectra show clearly resolved signals that can be unambiguously assigned. Noticeably, the aromatic proton signals were broadened after the attachment of the hexamolybdate; however, this is *not* due to the larger angular momentum in hybrid molecule (see below). All protons in **2** exhibited downfield chemical shifts compared with the chemical shifts of **1**; this is consistent with electron-withdrawing properties of the hexamolybdate moiety. The protons ortho to the amine group showed the largest shift, from 6.76 to 7.46 ppm. Even distal protons (a′ versus a) are shifted by 0.2 ppm.

The electronic properties of the hybrid compounds were also studied by UV−vis spectroscopy in DMF (see Figure S1). In the phenanthroline−polyoxometalate hybrid compound (**2**), the molybdenum−oxygen charge-transfer absorption peak of $Mo_6O_{19}{}^{2-}$ ($\lambda_{max} = 326$ nm, $\epsilon = 8900$ cm^{-1} M^{-1}) was significantly shifted to the red, coupled with an increase of an order of magnitude in the optical density ($\lambda_{max} = 384$ nm, $\epsilon = 76500$ cm^{-1} M^{-1}). The bathochromic shift observed implies that the formation of the Mo−N π bonds lead to increased delocalization of the aromatic π electrons. This strong electronic interaction between the polyoxometalate cluster and the organic moiety has already been observed and has been noted to be dependent on the conjugated system.[14] Thus, the electronic interaction between hexamolybdate and a small aromatic derivative, for example, the hexamolybdate imido derivative of 2,6-dimethylaniline leads to a shift to the red of only 25 nm.[13]

The electrochemical properties of the phenanthroline−polyoxometalate hybrid compound were also evaluated by cyclic voltammetry[15] (CV) and compared to the various components of the hybrid compound (see Figure S2). Thus, the CV of the parent polyoxometalate showed a reversible reduction at −840 mV that was shifted by ~300 mV to −1140 mV upon attached of 2,6-dimethylaniline similar to what was reported in the literature.[13] The increase in the potential has been associated with the strong electron-donating properties of the 2,6-dimethylaniline substituent to the polyoxometalate. Notably, the CV of bis-2,9-di(4-aminophenyl)-1,10-phenanthroline alone showed apparently irreversible oxidation (+180 and +550 mV) and reduction (−1480 mV) waves. Finally, the CV of the hybrid compound showed a more complex picture. First, an irreversible reduction wave was observed at −1230 mV that may be associated to the more difficult reduction of the polyoxometalate due to the electron-donating properties of the 2,9-di(4-aminophenyl)-1,10-phenanthroline toward the polyoxometalate. This is a similar, but larger, effect compared to what has been shown with 2,6-dimethylaniline as substitutent and is consistent with the UV−vis data. Importantly, one

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(11) Clegg, W.; Errington, R. J.; Fraser, K. A.; Holmes, S. A.; Schäfer, A. *J. Chem. Soc., Chem. Commun.* **1995**, 455−456.

(12) Du, Y.; Rheingold, A. L.; Maatta, E. A. *J. Am. Chem. Soc.* **1992**, *114*, 345−346.

(13) Wei, Y.; Xu, B.; Barnes, C. L.; Peng, Z. *J. Am. Chem. Soc.* **2001**, *123*, 4083−4084.

(14) (a) Strong, J. B.; Yap, G. P. A.; Ostrander, R.; Liable-Sands, L. M.; Rheingold, A. L.; Thouvenot, R.; Gouzerh, P.; Maatta, E. *J. Am. Chem. Soc.* **2000**, *122*, 639−649. (b) Xu, B.; Wei, Y.; Barnes, C. L.; Peng, Z. *Angew. Chem., Int. Ed.* **2001**, *40*, 2290−2292. (c) Lu, M.; Wei, Y.; Xu, B.; Cheung, C.; Peng, Z.; Powell, D. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1566−1568.

(15) Glassy carbon working electrode, an Ag/$AgNO_3$ reference electrode, and a Pt auxiliary electrode. Measurements were carried out on 1−10 mM solutions in DMF with 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte. Scan rates were 100 mV/s at $I/V = 5-50$ μA/V. Under these conditions, the $[Cp_2Fe]/[Cp_2Fe]^+$ couple was observed at $E_{1/2} = 50$ mV.

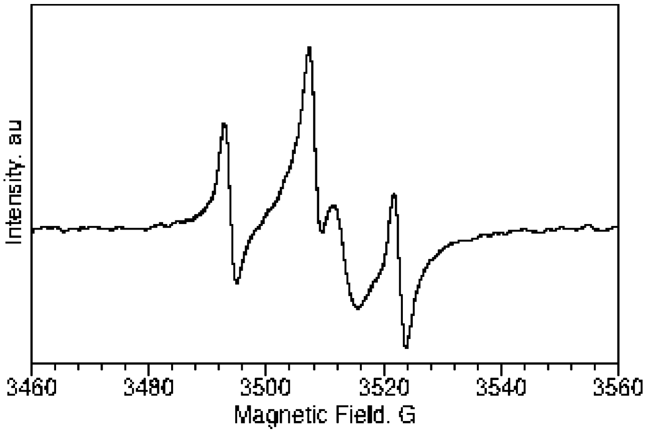


Figure 3. CW EPR (first derivative) spectrum of **2** at ambient temperature.

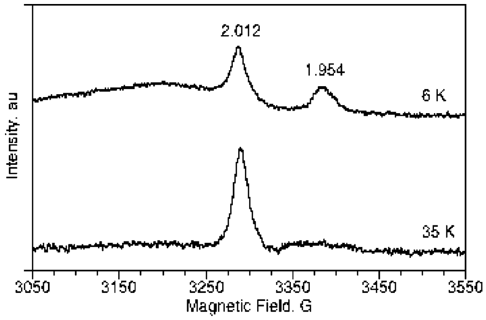


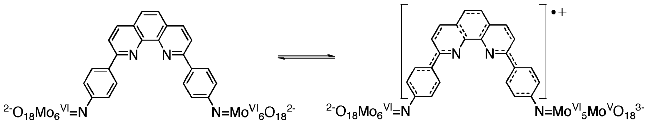
Figure 4. Field sweep echo detected EPR absorption spectrum of **2** at 6 and 35 K (the broad peak in the background at 6 K is due to an impurity in the cavity in the low-field side).

also observes a new reversible wave at −510 mV. We interpret this as being due to the relatively facile oxidation of the 2,9-di(4-aminophenyl)-1,10-phenanthroline moiety due to the very strong electron-withdrawing effect of the polyoxometalate on the phenanthroline moiety (see below).

Although the peak-broadening in the ^{1}H NMR spectrum of **2** could have been attributed to the large increase in molecular weight, we suspected that formation of a paramagnetic species could also be at the root of this broadened spectrum, noting also the possibility of facile oxidation of the substituted phenanthroline moiety indicated by the cyclic voltammetry measurement. To verify this hypothesis, we measured the EPR spectrum of **2** at ambient temperature, Figure 3 and at 6 K, Figure 4. At low temperature, two features may be observed in the EPR spectrum, both without any hyperfine splitting. At $g = 2.012$, there is a peak that can be associated with a localized unpaired electron (cation radical)[16] in the 2,9-diphenylphenanathroline ligand, and at $g = 1.954$, there is a peak that can be associated with a localized electron (Mo(V)) in the hexamolybdate moiety.[17] As the temperature is raised, the peak at $g = 1.954$ is broadened (25 K) and then is no longer observable (>∼35 K), while the peak at $g = 2.012$ slightly increases in intensity. At room temperature, hyperfine splitting associated with the organic cation radical may be discerned. Here there also appear to be two features: one major feature associated with coupling of the unpaired electron with ^{14}N ($A_N = 14.5$ G) and another minor, apparently noncoupled feature. One cannot rule out that the latter minor feature may be due to the presence of a small impurity, although comparative reference spectra of the parent polyoxometalate, the 2,6-dimethylanilino-substituted hexamolybdate, and the bis-2,9-di(4-aminophenyl)-1,10-phenanthroline were all EPR silent.

From the EPR experiments, it seems clear that, upon attaching an acceptor polyoxometalate to a phenanthroline ligand, an intramolecular charge transfer takes place. Since the 2,6-dimethylanilinohexamolybdate species, 2,6-diMePhN═Mo$_6$O$_{18}$, was EPR silent both at low and room temperatures, one may conclude that the charge transfer is a result of the extended aromatic 2,9-diphenylphenanthroline moiety. It should be also noted that the compound was stable and showed the same phenomena over a long time period (2 years). A further important point is that the integration of the EPR peaks indicated that only a fraction (5−10%) of **2** was paramagnetic on the EPR time scale. Plausibly, there is an equilibrium between a species with no charge transfer and a charge-transfer complex, Scheme 1. This equilibrium may be viewed as a type of valence tautomerism.

Scheme 1. Charge Transfer Complex Equilibrium



In conclusion, we have shown that a phenanthroline ligand can be modified by a polyoxometalate appendage through a covalent imido linker. A strong electronic effect was observed upon attachment of the hexamolybdate, leading to an intramolecular charge separation and description of **2** as a charge-transfer complex. The combination of the novel electronic state of the phenanthroline ligand and the considerable steric bulk of the polyoxometalate appendage will be used to prepare catalysts with unique electronic and topological character.

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Supporting Information Available: Detailed procedures for the preparation of **1** and **2**, a description of the experimental procedures used, and figures showing the UV−vis and CV measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) One should note that, although phenanthroline may be considered an electron-poor species and a poor candidate for oxidation, in fact its gas-phase ionization potential (IP) is ∼8.3 eV (less than that of toluene and diphenylmethane) http://webbook.nist.gov/chemistry/. The presence of two aminophenyl groups should significantly reduce this IP. Note that the IP of 4-aminobiphenyl is 7.5 eV versus benzene 9.25 eV.

(17) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3194−3202.