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Formation of Model Compounds of Biological Molybdenum(IV)

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Sir:

Because of a long-term interest in the chemistry of biological molybdenum,[1] the recent report of Selbin and coworkers[2] concerning the formation of a series of molybdenum(IV)–flavin compounds came to our attention. In their paper the Selbin group concluded that the isolated compounds are in the form of molybdenum(IV)–flavin complexes with the molybdenum in an anion group and the flavin as a protonated cation, $(HFl^+)(Mo^{IV}OCl_3^-)$. This conclusion is based on elemental analyses, differential thermal analyses, thermogravimetric analyses, infrared spectra, uv–visible spectra, NMR spectra, and ESR measurements.

The proposition that a complex is formed between $Mo^{IV}OCl_3^-$ and HFl^+ is in conflict with the results of Hemmerich and coworkers.[3] The latter group did not observe any interaction between flavin molecules and metal ions in acidic media. The Hemmerich group also observed that molybdenum(V) interacts with flavin molecules in acetonitrile to give a charge-transfer complex of a molybdenum(VI)–flavin anion radical with an absorption maximum at 406 nm. When zinc(II) ion is combined with flavin in acetone, the resulting combination gives absorption maxima at 475 and 380 nm.[4]

The second proposition of the Selbin paper is that the species $Mo^{IV}OCl_3^-$ is produced by hydrolysis (which, for the synthetic conditions, requires that the chloroform solvent contain 0.06 *M* H_2O)

$$Mo^{IV}Cl_4 + H_2O \rightarrow Mo^{IV}OCl_3^- + HCl + H^+ \tag{1}$$

and is stable in the presence of protonated flavin. The infrared, uv–visible, and ESR data of the paper do not support this conclusion. Haight[5] has shown that Mo(V) ions dimerize to $Mo^V_2O_3Cl_8^{4-}$ in 1–5 *F* HCl to give a diamagnetic species with absorption maxima at 710, 450, and 310 nm. This species, as $(Et_4N^+)_4(Mo^V_2O_3Cl_8^{4-})$, has been studied by infrared analysis (in KBr)[6] and exhibits a strong band due to Mo=O at 983 cm^{-1} (as well as weaker bands at 958, 735, and 516 cm^{-1}). This frequency is identical with that for the purported $(HFl^+)(Mo^{IV}OCl_3^-)$ complexes. Mitchell[7] has studied the $Mo^V_2O_3Cl_4(bipy)_2$ complex by infrared and uv–visible spectroscopy and observed a strong Mo=O infrared band at 966 cm^{-1} and λ_{max} at 704, 513, and 413 nm. Similarly, for $Mo^V_2O_3(NCS)_8^{4-}$ there is a Mo=O band[8] at 950 cm^{-1} and λ_{max} at 813 and 529 nm, and for $Mo^V_2O_3(oxine)_4$ there is a Mo=O band at 940 cm^{-1} and λ_{max} at 540 and 400 nm. All of these oxo-bridged Mo(V) complexes $(Mo^V_2O_3L_nX_m)$ are dark red or dark purple, as are the compounds in the Selbin paper (λ_{max} at 509–525 nm). In contrast, previously reported[9-11] $Mo^{IV}O(oxine)_2$ and $Mo^{IV}OX_2L_2$ compounds are light pink, lilac, light green, or light blue, with an infrared band at 930–950 cm^{-1}. The molybdenum(IV)–oxine complex exhibits weak uv–visible absorption bands at 689, 585, and 524 nm. The reported absence of infrared bands due to Mo–O–Mo in the Selbin compounds may result because they are obscured by flavin bands or are too weak to observe.

On the basis of electrochemical data in aprotic solvents,[1] reaction 1 almost certainly would be followed by an oxidation of the Mo(IV) species by either air or protons (under acidic conditions)

$$4Mo^{IV}OCl_3^- + O_2 + 4H^+ \rightarrow 4Mo^VOCl_3 + 2H_2O \tag{2a}$$

$$Mo^{IV}OCl_3^- + H^+ \rightarrow Mo^VOCl_3 + {}^1/_2H_2 \tag{2b}$$

and then a dimerization reaction, analogous to that of Haight,[5] to give a dark red or dark purple diamagnetic species

$$2Mo^VOCl_3 + H_2O \rightarrow Mo^V_2O_3Cl_6^{2-} + 2H^+ \tag{3}$$

Hence, the probable overall reaction is either

$$4Mo^{IV}Cl_4 + O_2 + 4H_2O \rightarrow 2Mo^V_2O_3Cl_6^{2-} + 4HCl + 4H^+ \tag{4a}$$

or

$$2Mo^{IV}Cl_4 + 3H_2O \rightarrow Mo^V_2O_3Cl_6^{2-} + H_2 + 2HCl + 2H^+ \tag{4b}$$

In turn, the excess protons would protonate the flavin molecules

$$Fl + H^+ \rightarrow HFl^+ \tag{5}$$

and lead to the formation of an ionic salt or adduct

$$2HFl^+ + Mo^V_2O_3Cl_6^{2-} \rightarrow (HFl^+)_2(Mo^V_2O_3Cl_6^{2-}) \tag{6}$$

Previous work[12] has established that the major uv–visible absorption bands for protonated flavins (HFl^+) occur at λ_{max} 390, 262, and 200 nm, while the neutral flavin species (Fl) has bands at λ_{max} 450, 350–370, 270, and 218–230 nm. The data in the Selbin article for the neutral flavin models have bands at λ_{max} 440, 330–350, and 265–270 nm. For their isolated molybdenum–flavin compounds the absorption bands were observed at λ_{max} 375–417 and 303–310 nm; in contrast, the tetraacetate derivative of riboflavin in combination with $MoCl_4$ gave a product with λ_{max} at 450 and 350 nm (which are analogous to the bands for neutral flavins[12]).

The change in the frequencies for the flavin infrared bands with the addition of $MoCl_4$ that is observed by the Selbin group can be rationalized equally well as being the result of protonation of N(5) in HFl^+, rather than N(1). This would cause the C=O(2) frequency to increase and the C=O(4) frequency to decrease and would give the observed N—H band. The NMR data of Table III in the Selbin paper also are indicative of N(5) protonation.

The conclusion that the actual isolated species really are salts or adducts with the formula $[(HFl^+)_2(Mo^V_2O_3Cl_6^{2}\ )]$ is supported by the elemental analysis data of Table I in the Selbin paper. Recalculation of the elemental content on the basis of this formula gives values that overall are in closer agreement with the experimental values, especially in the case of molybdenum, chlorine, and nitrogen.

To test the proposition that $Mo^{IV}Cl_4$ is oxidized to Mo(V) and dimerized under the conditions of the Selbin studies, we added Mo^VOCl_3 to acetonitrile and recorded the uv–visible spectrum for the solution; λ_{max} are observed at 700, 463, and 363 nm. In a second experiment $Mo^{IV}Cl_4$ was added to acetonitrile to give a solution with λ_{max} at 700, 500, and 402 nm.[13] These data are analogous to those for $Mo^V_2O_3Cl_n$ complexes[5] and indicate that $Mo^{IV}Cl_4$ is hydrolyzed by residual water, oxidized by the resultant protons and/or oxygen, and dimerized to an oxo-bridged Mo(V) species. Addition of 8-quinolinol (2:1 mole ratio) and water[14] to the preceding $\mathrm{Mo^{V}OCl_3}$ and $\mathrm{Mo^{IV}Cl_4}$ solutions resulted in absorption spectra with λ_{max} at 527, 376, and 310 nm for the $\mathrm{Mo^{V}OCl_3}$ system and λ_{max} at 535, 375, and 310 nm for the $\mathrm{Mo^{IV}Cl_4}$ system. These data are similar to those for monooxo-bridged dimeric Mo(V) complexes[7,8] and support the conclusion that the same dimeric molybdenum(V)–8-quinolinol salt or adduct is formed whether one starts with $\mathrm{Mo^{IV}Cl_4}$ or $\mathrm{Mo^{V}OCl_3}$ (see eq 4 and 6 for the flavin analogy of the probable formation process).

In summary, the dark purple color of the isolated compounds is characteristic of diamagnetic monooxo-bridged dimeric molybdenum(V) ($\mathrm{Mo^{V}{}_2O_3X_{4-8}}$), as is the Mo=O infrared band at 983 $\mathrm{cm^{-1}}$ and the visible band at a λ_{max} 509–525 nm. The uv, infrared, and NMR data also are indicative of the $\mathrm{HFl^+}$ species. The elemental analysis data in the Selbin paper support the conclusion that the isolated compounds have the general formula $\mathrm{(HFl^+)_2(Mo^{V}{}_2O_3Cl_6{}^{2-})}$. Their data do not support the proposition that a coordination complex is formed between $\mathrm{Mo^{IV}OCl_3{}^-}$ and $\mathrm{HFl^+}$, nor do they support the conclusion that the isolated compounds contain Mo(IV).

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(14) Prior to the addition of water both solutions were dark green with absorption maxima at 625 and 400–450 nm, which is indicative of monomeric Mo(V) with the likely formula $\mathrm{Mo^{V}OCl_3(8\text{-}quinolinol)^-}$.

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Raman Spectroscopic Identification of Metal–Metal Stretching Frequencies

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Sir:

Raman spectroscopy has proven to be very useful in the detection of metal–metal stretching frequencies for a variety of metal complexes.[1,2] Frequently, metal–metal stretching modes are found to exhibit high intensity; however their assignment on the basis of Raman intensity alone can be ambiguous. It is the purpose of this correspondence to illustrate some of the pitfalls in data collection and interpretation for metal–metal bonded systems and to correct some erroneous assignments.

The high intensity of $\nu_{\mathrm{M-M}}$ arises in many cases from the fact that the sample is irradiated within or near an electronic transition involving the metal framework. This may lead to enhanced Raman scattering via resonance or preresonance mechanisms. An unwanted aspect of the electronic absorption is sample decomposition which occurs with many heat-sensitive colored materials. As first shown by Kiefer and Bernstein, this problem can be significantly alleviated by sample spinning[3] or by related methods of energy dispersion.[4] One of the simplest versions of this technique involves the rotation of a pressed solid sample. This type of apparatus is widely available from Raman instrument manufacturers and works well in many cases; however, the combined influence of the intense laser beam and exposure to the atmosphere can lead to unexpected results. For example, this spinner would seem adequate for $\mathrm{Fe_2(CO)_9}$ which is reasonably stable in air and is photochemically fairly stable. Recently this technique was used on the determination of the Fe–Fe stretch of $\mathrm{Fe_2(CO)_9}$ and $\mathrm{Fe_3(CO)_{12}}$,[2] but as described below the reported spectra are those of decomposition products.

Raman spectra were obtained for polycrystalline samples under an inert atmosphere in disposable sealed 12-mm Pyrex tubes. Details of the sample spinner and back-scattering illumination are available in the literature.[5] For $\mathrm{Fe_2(CO)_9}$, Raman bands of weak to medium intensity were observed at 78, 101, 122, 390, and ca. 453 $\mathrm{cm^{-1}}$, but as shown in Figure 1, the spectrum is devoid of the reported intense 225-$\mathrm{cm^{-1}}$ Fe–Fe stretch. It is certain that the failure to observe this band does not arise from lack of sensitivity because other low-frequency modes as well as the CO stretching frequencies were observed. Samples of $\mathrm{Fe_2(CO)_9}$ used in these experiments were identical with those employed in a detailed investigation of the CO stretch region and are of high purity as judged by carbon analyses and by the lack of infrared and Raman bands of probable impurities.[6] Thus, it is likely that the Raman spectrum reported earlier for $\mathrm{Fe_2(CO)_9}$ arises instead from a decomposition product. Similarly, the reported metal–metal stretch for $\mathrm{Fe_3(CO)_{12}}$ is reproduced only under conditions in which the sample is decomposed or laser damaged. Based on these results we suggest that Raman data on colored organometallics should be collected using inert-atmosphere conditions in conjunction with sample spinning, and spurious features should be sought by obtaining a spectrum for the laser-damaged material.

The erroneous assignments which are discussed above resulted in part from the high intensity of the observed bands and the currently accepted idea that M–M stretch modes may be assigned solely on the basis of high intensity. In this particular case the correlation of high intensity with M–M stretching modes was misleading, owing to the presence of decomposition products having intense low-frequency modes. Ambiguities also may arise in the assignment of M–M stretching modes when other intense vibrations appear in the low-frequency region. Metal carbonyls are especially troublesome since C–M–C deformation modes often appear in the same region of the spectrum as M–M stretches.

A comparison of spectra for $\mathrm{Re_2(CO)_8Br_2}$, $\mathrm{Re_2(CO)_8Cl_2}$, and $\mathrm{Re_2(CO)_{10}}$ provides a striking example of this problem. As shown in Figure 2, the solid-state Raman spectra are quite similar for all three compounds. In the case of $\mathrm{Re_2(CO)_{10}}$ the strong band around 125 $\mathrm{cm^{-1}}$ has been assigned to the Re–Re stretch,[7] and this assignment is supported by solution intensity analysis,[8a] which shows α(Re–Re) to be in the range expected for single metal–metal bonds. This assignment appears reasonable by all the currently available criteria for the detection of M–M stretching modes. As with much spectral work on complex molecules, there is the possibility of an alternate assignment,[8c,9] but most workers agree with the original assignment.[8]

It is, however, illogical to assign the ca. 125-$\mathrm{cm^{-1}}$ feature of $\mathrm{Re_2(CO)_8Br_2}$ and $\mathrm{Re_2(CO_8)Cl_2}$ as an M–M stretch, because these compounds do not contain metal–metal bonds. Both