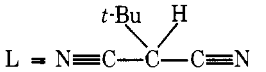
Communications to the Editor

Binuclear Mixed Valence Rutheniumammine Complexes with *tert*-Butylmalononitrile as Bridging Ligand

Sir:

In pursuing our interest in the properties of mixed valence molecules, the binuclear pentaammine ruthenium complexes with *tert*-butylmalononitrile



$$L = N{\equiv}C{-}\overset{t\text{-Bu}\;\;H}{C}{-}C{\equiv}N$$

as the bridging ligand have been synthesized and studied as well as the mononuclear forms. Other complexes of the malononitrile series have been prepared and studied, but that dealt with in this communication features the important effects with the least complications from side reactions.

The binuclear complex was prepared by adding a stoichiometric amount of *tert*-butylmalononitrile[1] to a deaerated solution of $[(NH_3)_5RuOH_2]^{3+}$. The resulting mixture was reduced for 2 h using zinc-mercury amalgam under continuous argon flow. The ion $[((NH_3)_5Ru)_2L]^{4+}$ was precipitated by adding NH_4PF_6. The salt was collected by filtration, washed with ethanol and ether, and was vacuum dried. The corresponding mononuclear complex was prepared similarly but using a 30-fold excess of ligand, instead of a stoichiometric amount, and a 60:40 ethanol/0.1 M CF_3SO_3H mixture as the solvent. Anal. Calcd for $[((NH_3)_5Ru)_2L](PF_6)_4$: C, 7.82; H, 3.75; N, 15.64; Ru, 18.81. Found: C, 8.23; H, 3.66; N, 15.33; Ru, 18.91. Calcd for $[(NH_3)_5RuL](PF_6)_2$: C, 14.05; H, 4.21; N, 16.29; Ru, 16.89. Found: C, 14.05; H, 4.21; N, 16.29; Ru, 16.92.

The $[((NH_3)_5Ru)_2L]^{4+}$ ion to be denoted $[2, L, 2]^{4+}$, shows a band in the uv-visible at 255 nm ($\log \epsilon = 4.49$) interpreted as $\pi^* \leftarrow \pi d$, with a broad shoulder at 350 nm while the corresponding charge transfer band for the mononuclear complex is at 249 nm ($\log \epsilon = 4.28$). The deprotonated fully oxidized mononuclear and binuclear ions, to be denoted $[3, L^-]^{2+}$ and $[3, L^-, 3]^{5+}$, have charge transfer bands at 790 nm ($\log \epsilon = 4.18$) and 786 nm ($\log \epsilon = 4.45$), respectively, these now being interpreted as $L \rightarrow M$.

Room temperature (21.0 °C) magnetic susceptibility measurements for the $[3,L^-,3](PF_6)_5$ complex gave a value of 0.98 μ_B as the corrected magnetic moment per mole of binuclear complex.[2] Similar values are found when the bridging ligand is malononitrile.

The pK_a value for the mononuclear ion, obtained by spectrophotometric titration, is 3.85 ± 0.05 while pK_a as obtained by potentiometric measurements for the binuclear mixed valence complex is 2.4 ± 0.3.[3] The pK_a value for the free ligand is 13.10 ± 0.02.[5] Thus, since the lower limit estimated for the pK_a of the $[2,L,2]^{4+}$ ion is >15, there is a decrease of at least 12.5 orders of magnitude in K_a for the ligand by one-electron oxidation of the complex. It should be noted as well that the mixed valence ion, $[2, L, 3]^{5+}$, is more acidic by 1.4 pK_a units than is the corresponding mononuclear ion.

In contrast to other systems of the bispentaammineruthenium series,[6-10] in this case the distribution between the mixed valence form on the one hand and the [2, 2] + [3, 3] on the other is sensitive to acidity, and in fact, for the present system, owing to the strong proton affinity of the $[2, L^-, 2]^{3+}$ form, the mixed valence species becomes unstable with respect to disproportionation below pH ~5. Of special interest is the value of the conproportionation constant for the deprotonated forms

$$[2, L^-, 2]^{3+} + [3, L^-, 3]^{5+} = 2\,[2, L^-, 3]^{4+} \qquad (1)$$

Since E_f for the $[3, L^-, 3] + e = [2, L^-, 3]$ is known (0.37 V) as well as E_f for $H^+ + [2, L^-, 3] + e = [2, L, 2]$ for a range of pH, usng the lower limit of pK_a for [2, L, 2], a lower limit for the equilibrium constant of reaction 1 can be calculated; the value is 10^{10}.

The mixed valence binuclear complex, $[2, L^-, 3]^{4+}$ can easily be generated by oxidizing the $[2, L, 2]^{4+}$ ion in aqueous solution. It has a band in the near-ir at 1170 nm (in D_2O, pH 5.0), with an extinction coefficient of 1.6×10^4 M^{-1} cm^{-1}. The uv-visible-near-ir spectra for the $[2, L, 2]^{4+}$, $[3, L^-, 3]^{5+}$ complexes is shown in Figure 1; the near-ir band for the $[2, L^-, 3]^{4+}$ is shown in Figure 2.

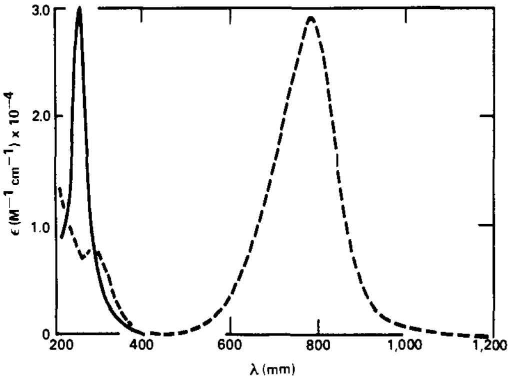


Figure 1. Spectra of $[2, L, 2]^{4+}$ (solid line) and $[3, L^-, 3]^{5+}$ in 0.1 M hydrochloric acid.

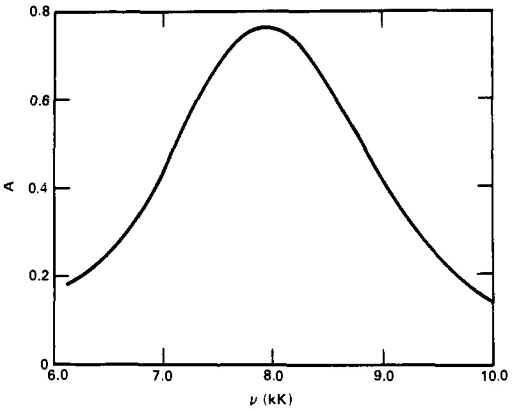


Figure 2. The near-infrared band for the $[2, L^-, 3]^{4+}$ species in DMF.

The solvent dependency of the near-ir band for the mixed valence compound was investigated by oxidizing the [2, 2] complex in the solvent of choice. The values for the band maxima and the corresponding value for the $(1/n^2 - 1/D)$ term, where n is the refractive index of the solvent and D its static dielectric constant, are: 1170 nm, 0.576 (D_2O); 1160 nm, 0.526 (CH_3CN); 1260 nm, 0.473 (DMF); 1260, 0.458 (dimethylacetamide); 1275 nm, 0.437 (Me_2SO); and 1170 nm, 0.394 (acetone). The band width at half height is 2.12 kK. The value calculated using the high temperature limit of Hush's[11] model is 4.44 kK.

Our choice of bridging group in the malonodinitrile series was influenced by the stability for the mixed valence complex. While the half-lives for the decomposition of the $[3, L^-, 3]^{5+}$ and $[2, L, 2]^{4+}$ ions are several hours and days, respectively, the mixed valence complexes of several related malononitrile derivatives decompose rapidly in aqueous solutions. Among the reactions contributing to the instability of the mixed valence ion are: -CN hydrolysis in the protonated mixed valence ion, disproportionation, and, apparently isomerization and internal reduction for some of the bridging ligands used. Some of these reactions are avoided by using the *tert*-butyl derivative. The mixed valence complex derived from it also decomposes rather rapidly—on the time scale of minutes at 25 °C in water but much less rapidly in nonaqueous solvents.

Whereas in the Ru(II)-Ru(III) species heretofore studied, the coupling between the metal centers involves mainly $\pi d-\pi^*$ delocalization, in the present system the principal mechanism is almost certainly delocalization from a π level on the ligand (π electrons becoming available on deprotonation) to vacancies in the πd orbitals on the metal ion. The enormous increase in the acidity of the ligand on one-electron oxidation of the [2, L, 2] form speaks directly to this point as does the fact that the coupling becomes strong only on deprotonation (π^* levels will become less stable on deprotonation thus decreasing $\pi d-\pi^*$ delocalization). The very large value of ϵ for the IT transition, the largest so far recorded for the bisruthenium series, also supports the conclusion about the coupling mechanism. In the μ-cyanogen bis(pentaammineruthenium) case,[9] where coupling is so strong that the system is valence delocalized, the value of ϵ is only $4.1 \times 10^2\ M^{-1}\ cm^{-1}$. In this ion, the yz and zx orbitals, where z is the metal ligand axis, are stabilized by back-donation. As a result, the electron hole in the 5+ ion is expected to develop in an xy orbital, and the low extinction coefficient is ascribable to weak overlap between xy orbitals on separate ions. In consequence, the energy required to make the metal centers equivalent is probably gained largely from the delocalization of the yz and zx electrons, while that from delocalization of the electron hole may make a relatively small contribution. In the present system, where $p\pi$ delocalization from ligand into metal ions is postulated, the electron hole lies in an orbital along the axis of the molecule, and a higher transition probability is expected. Finally, the strong interaction between the Ru(III) ions in the fully oxidized state, as shown by the low value of the magnetic moment, also is in line with the coupling mechanism suggested.

It is of interest to note that an intervalence transition is observed also for the mixed valence species with dialkylated malononitrile as the bridging group. In this case, however, the extinction coefficient is smaller (ϵ 180 $M^{-1}\ cm^{-1}$) and the band is at higher energy (925 nm in Me_2SO). Moreover, it is more nearly of normal width (5.86 kK, compared to a calculated value of 4.99 kK).

The large value of the conproportionation constant for reaction 1, the large value of ϵ for the intervalence band and the narrowness of the near-ir band[12] indicate substantial valence delocalization for the species $[3, L^-, 2]$. The fact that the energy of the near-ir band does depend on the solvent is not at variance with this conclusion. The molecule is not linear, and if, as is likely, on excitation there is a change in the distribution of electron density between bridging ligand and metal ions, the dipole moment will change and as a result the energy of the transition is expected to depend on solvent properties. The solvent dependency, it should be noted, does not follow the function $(1/n^2 - 1/D)$ as is the case for linear, trapped valence systems. The decision as to whether the two CN frequencies are averaged for the mixed valence species under present consideration, as they are in the μ-cyanogen case, will have to wait on the outcome of experiments which will be very difficult to perform. The criterion based on averaging or nonaveraging of valence trapping vibrational modes seems the most appropriate of any to apply in deciding when it is useful to regard a species as being valence trapped or valence averaged.

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References and Notes

(1) Prepared by Friedel–Craft alkylation of malononitrile following the procedure of P. Boldt et al., *Justus Liebigs Ann. Chem.*, **718**, 101 (1968).

(2) The value obtained for the corrected magnetic moment at 21.0 °C for the $[(NH_3)_5RuCl]Cl_2$ under the same conditions was 2.13 μ_B. A study of the temperature dependence for the magnetic interaction for this complex will be made in the future.

(3) At pH 5.0, the conproportionation constant, K_c, equals 1.0 and at higher pH values, it increases. In this pH range, two stages in the oxidation of the [2, 2] can be seen. Below pH 5, $K_c < 1.0$ and the oxidation of [2, 2] proceeds with no significant accumulation of [2, 3] in an equilibrium measurement, but in cyclic voltammetry, the oxidation wave for the 2,2 form is discernible. This is invariant with pH over a wide range, including low pH where the reduction wave in relation to oxidation wave approaches reversible behavior. The value of E_f for:

$$[2, L, 3]^{5+} + e^- = [2, L, 2]^{4+}$$

so determined, 0.50 V, is identical (±0.01 V) with that for the acetonitrile complex, and to that for both the mononuclear and binuclear forms of the succinonitrile complex. The value of E_f in question together with the results of potentiometric titration define pK_a for the 2,3 complex.

(4) Heinz Krentzien, Ph.D. Thesis, Stanford University, 1976.

(5) F. Hibbert and F. A. Long, *J. Am. Chem. Soc.*, **93**, 2836 (1971).

(6) C. Creutz, Ph.D. Thesis, Stanford University, Stanford, Calif., July 1970; C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **91**, 3988 (1969); **95**, 1086 (1973).

(7) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7827 (1974).

(8) R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Am. Chem. Soc.*, **96**, 7829 (1974).

(9) G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, **97**, 5310 (1975).

(10) G. M. Tom, Ph.D. Thesis, Stanford University, Stanford, Calif., July 1975.

(11) N. B. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1971).

(12) J. K. Beattie, N. S. Hush, and P. R. Taylor, *Inorg. Chem.*, **4**, 993 (1975).

Heinz Krentzien, Henry Taube*
Department of Chemistry, Stanford University
Stanford, California 94305

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Biosynthesis of *Cephalotaxus* Alkaloids. 2. Biosynthesis of the Acyl Portion of Deoxyharringtonine[1]

Sir:

There is currently great interest in the alkaloids produced by conifers of the genus *Cephalotaxus.*[2] This interest is due in large measure to the potent antitumor activity exhibited by several alkaloids which occur in *C. harringtonia.*[3] The active alkaloids are esters of cephalotaxine (**1**) and include deoxyharringtonine (**2**), harringtonine (**3**), isoharringtonine (**4**), and homoharringtonine (**5**).[4] We wish to report experiments which clarify the mode of biosynthesis of the acyl portion of deoxyharringtonine.

In deoxyharringtonine, cephalotaxine is linked to 3-carboxy-3-hydroxy-6-methylheptanoic acid (**6**). The resemblance of this compound to 3-carboxy-3-hydroxy-4-methylpentanoic acid which is an intermediate in the biosynthesis of L-leucine (**7**) from L-valine[5] suggests that the biosynthesis of **6** may proceed in a manner analogous to the mode of formation of the pentanoic acid derivative. If this hypothesis is correct, then the biosynthesis of **6** should involve the steps outlined in Scheme I.[5] Evidence in support of the biosynthetic pathway shown in this scheme was obtained from the experiments discussed below.

The hypothesis predicts that 3-hydroxy-3-carboxy-5-methylhexanoic acid (**8**) should be an intermediate in the biosynthesis of **6** and that carbon atoms 3–8 of **8** should be