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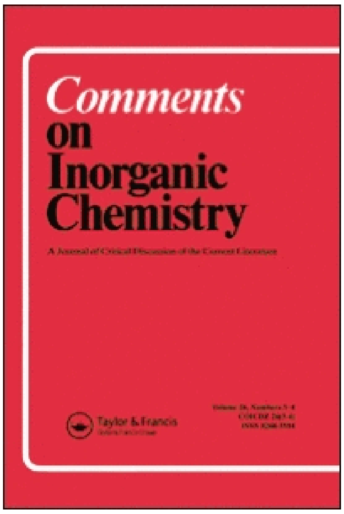

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Electroprotic Phenomena and Metal Oxidation States

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Electroprotic Phenomena and Metal Oxidation States

INTRODUCTION

A ubiquitous reaction in transition metal chemistry is electron transfer[1,2] deriving from the variable valence capability of the metal center. When the coordinated ligand has one or more potentially labile protons, electron transfer at the metal (M) *may* proceed with symbiotic proton transfer at the ligand (L), Fig. 1. Such a coupled transfer will be called[3] an electroprotic reaction. An important extension of Fig. 1 can be the transfer of externally added redox equivalents to the ligand via the metal thereby effecting a metal-catalyzed electroprotic transformation of the ligand. The scope of electroprotic phenomena is obviously wide and spans many reactions in chemistry and biology. This Comment has the limited objective of recounting some of our personal experiences in this fascinating field which we gained in the course of our dealing with the synthetic chemistry and redox activity of multiple oxidation states of copper, nickel, ruthenium, and molybdenum.

All formal potentials (E^0) reported in this article were measured by cyclic voltammetry or by related techniques at 298 K with reference to saturated calomel electrode. The protic ligand is represented either by its chemical formula or simply as L or L′. Other ligands are abbreviated as specified in the text.

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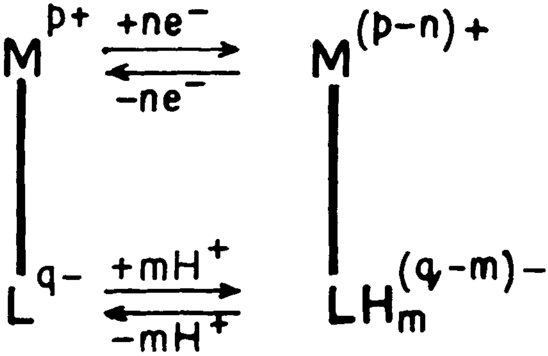


FIGURE 1 The electroprotic reaction.

CONCERTED TRANSFER AND ELECTROPROTIC EQUILIBRIA: RUTHENIUM HYDROXAMATES

The coupled electron-transfer and proton-transfer processes of Fig. 1 can, under suitable circumstances, be expressed in a facile electroprotic equilibrium in solution, Eq. (1). Here transfer of electrons and protons

$$[\mathrm{ML}]^{(p-q)+} + ne^- + mH^+ \rightleftharpoons [\mathrm{M(H_mL)}]^{(p+m-q-n)+} \tag{1}$$

$$E^0 = \bar{E}_p + 0.059(m/n)\mathrm{pH} \tag{2}$$

occur in a "concerted" manner. Protic solvents are usually required since fast movement of protons is implicit in electroprotic equilibria. The formal potential of couple (1) is given by Eq. (2) where $\bar{E}_p$ is the average of cyclic voltammetric cathodic and anodic peak potentials.

The recently isolated[3,4] hydroxamates of bis[2,2'-bipyridine]ruthenium(II), $\mathrm{Ru(bpy)_2^{2+}}$, and bis[2-phenylazo)pyridine]-ruthenium(II), $\mathrm{Ru(pap)_2^{2+}}$, are well-suited for illustration. We shall consider here the specific chelates shown in Fig. 2. In a 60:40 water–dioxane mixture these act as weak acids due to dissociation of the N–H proton. The stronger[5-7] π-acceptor character of pap compared to bpy, makes $[\mathrm{Ru(HL)(pap)_2}]^+$ (p$K = 7.15 \pm 0.05$) a stronger acid

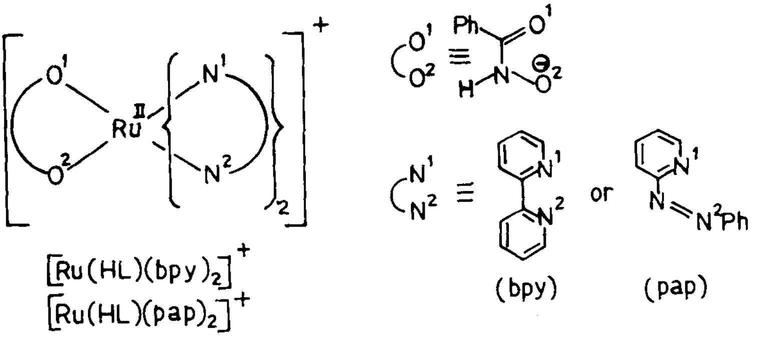


FIGURE 2 Ruthenium hydroxamates.

than $[Ru(HL)(bpy)_2]^+$ (pK = 9.00 ± 0.05). Below pH 6 the electroprotic processes (3) and (4)

$$[Ru^{III}(L)(pap)_2]^+ + e^- + H^+ \rightleftharpoons [Ru^{II}(HL)(pap)_2]^+,\ E^0 = 0.88\ V, \tag{3}$$

$$[Ru^{III}(L)(bpy)_2]^+ + e^- + H^+ \rightleftharpoons [Ru^{II}(HL)(bpy)_2]^+,\ E^0 = 0.48\ V, \tag{4}$$

operate. The pK's of the protonated species corresponding to the ruthenium(III) complexes in Eq. (3) and (4) are estimated to be <2.

The oxidation in Eq. (4) can be quantitatively achieved by chemical means, Eq. (5). Simultaneously one proton is liberated. The

$$[Ru(HL)(bpy)_2]^+ + Ce^{4+} \rightarrow [Ru(L)(bpy)_2]^+ + H^+ + Ce^{3+} \tag{5}$$

$[Ru(L)(bpy)_2]^+$ complex has been isolated as perchlorate salt and its electroprotic behavior is correctly represented by Eq. (4).

HOMOGENEOUS OXIDATION OF WATER TO DIOXYGEN: CATALYSIS BY OXORUTHENIUM(IV) SPECIES

The formal potential of couple (3) is relatively high. This is a general characteristic of pap complexes of ruthenium and arises from strong

Ru-pap π bonding. We therefore explored the possibility of finding an electroprotic couple based on Ru-pap chemistry that could drive the water oxidation reaction, Eq. (6). Such a couple was indeed found and is shown[8] in Eq. (7). The cyclic voltammetric peak-to-peak separation for

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{6}$$

$$\begin{aligned}&[Ru^{IV}O(pap)_2(py)]^{2+} + 2e^- + 2H^+ \\ &\qquad \rightleftharpoons [Ru^{II}(OH_2)(pap)_2(py)]^{2+},\ E^0 = 1.20\ V,\end{aligned} \tag{7}$$

couple (7) is 30 ± 5 mV and $\bar{E}_p$ shifts by 60 mV per unit change of pH in the pH range 1–4. The two electrons move more or less in a single step. The conversion of the aquo to the oxo complex can be conveniently achieved chemically using Ce^{4+} in 1 M aqueous $HClO_4$. In solution the brown oxo complex is spontaneously reconverted to the pink aquo complex liberating O_2, Eq. (8). When excess Ce^{4+} is present, the catalytic

$$[RuO(pap)_2(py)]^{2+} + H_2O \rightarrow [Ru(OH_2)(pap)_2(py)]^{2+} + \frac{1}{2}O_2 \tag{8}$$

cycle of Fig. 3 becomes operative.

While the intimate mechanism of reaction (8) is unknown, the high potential of couple (7) and its single step two-electron character are believed to be crucial for the facile interfacing of this couple and the

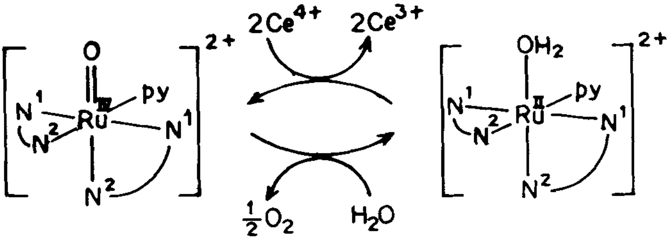


FIGURE 3 Catalyzed oxidation of water (N^1 and N^2 are of pap ligand, see Fig. 2; py = pyridine).

water oxidation reaction (6). The oxidation of the bpy analog of the aquo complex of Eq. (7) to the corresponding oxo complex occurs in two one-electron steps and this analog fails[9] to mediate the catalytic oxidation of water to dioxygen by Ce^{4+}. The oxo-bridged ruthenium(III) dimer $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$, however, mediates[10] this oxidation presumably via the intermediacy of the corresponding $Ru^{V}{=}O$ species.

TWO-ELECTRON AND ONE-ELECTRON TRANSFERS: OXIMATES OF BIVALENT, TRIVALENT AND TETRAVALENT NICKEL

Implicit in Fig. 1 is the possibility that metal oxidation states could be modulated by the level of ligand protonation. Where a protonated ligand is found to strongly sequester a metal in a certain oxidation state, the deprotonated ligand might sustain a higher level of oxidation. This is a very useful rule of thumb and is worthy of consideration whenever one is looking for high oxidation states. In the previous section we saw this rule in action, e.g., $Ru^{II}OH_2$ versus $Ru^{IV}O$. In the next section further examples occur: $Cu_2^{II}Cu^{I}OH$, $Cu_3^{II}OH$, $Cu_3^{II}O$, and $Cu^{III}Cu_2^{II}O$.

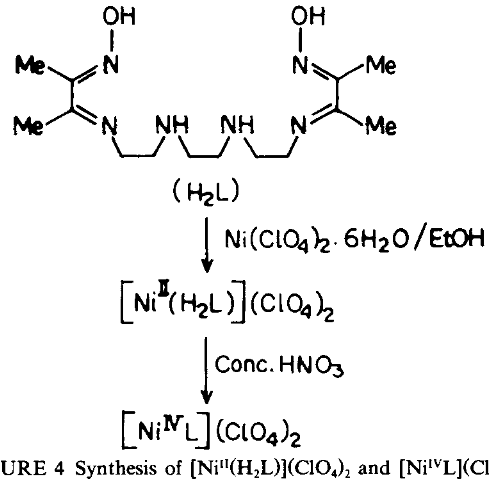
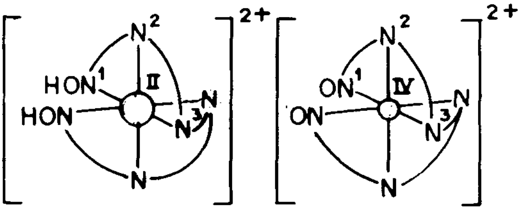


FIGURE 4 Synthesis of $[Ni^{II}(H_2L)](ClO_4)_2$ and $[Ni^{IV}L](ClO_4)_2$.



$Ni-N^1$	2.119[3]	1.953[8]
$Ni-N^2$	2.005[4]	1.871 [3]
$Ni-N^3$	2.098[3]	1.995 [4]

FIGURE 5 Structures of $[Ni^{II}(H_2L)]^{2+}$ and $[Ni^{IV}L]^{2+}$.

In this section we consider electroprotic reactions connecting the oxidation states +2, +3, and +4 in nickel complexes of some oxime ligands. That the deprotonated oxime function ($>C=N—O^-$) binds higher oxidation states of nickel has been known for a long time[11] and recent work[12-18] continues to augment this truth.

In the synthesis[13] of the nickel(IV) complex that is of central interest to us, a hexadentate ligand[19] was utilized (Fig. 4) to ensure sufficient stability by multiple chelate ring formation. This complex, $[NiL](ClO_4)_2$, has turned out to be a *model nickel(IV) complex*—easy to synthesize and isolate, yet reactive enough to undergo facile electroprotic transformations that can be tracked and understood quantitatively. The cation is stable enough to be optically resolved.[20] The structures of $[NiL](ClO_4)_2$ and its nickel(II) precursor $[Ni(H_2L)](ClO_4)_2$ are both accurately known.[21] The difference in metal oxidation levels is clearly reflected in the Ni–N distances (Fig. 5).

In buffered aqueous media, cyclic voltammetry of $[NiL]^{2+}$ reveals[14] the presence of electroprotic equilibria—electron transfer and proton transfer occurring respectively at the metal and oxime-oxygen. Below pH 5 the $2e^- - 2H^+$ process (9) operates. The proton dissociation

$$\text{pH} < 5 : [Ni^{IV}L]^{2+} + 2e^- + 2H^+ \rightleftharpoons [Ni^{II}(H_2L)]^{2+},\ E^0 = 0.71\ \text{V} \quad (9)$$

constants of $[Ni(H_2L)]^{2+}$ are: pK_1, 5.90: pK_2, 7.80. Above pH 5 the reduced species therefore appears as $[Ni(HL)]^+$ and/or [NiL]. A remarkable effect of this is the breakdown of couple (9) into two separate 1e^- couples (10) and (11), or (10) and (12). In a narrow pH range around pH 5 the nickel(III)/nickel(II) couple is of type:

$$\text{pH, 5–10}: [\text{Ni}^{\text{IV}}\text{L}]^{2+} + e^- \rightleftharpoons [\text{Ni}^{\text{III}}\text{L}]^+, E^0 = 0.42\ \text{V} \qquad (10)$$

$$\text{pH, 6–8}: [\text{Ni}^{\text{III}}\text{L}]^+ + e^- + H^+ \rightleftharpoons [\text{Ni}^{\text{II}}(\text{HL})]^+, E^0 = 0.64\ \text{V} \qquad (11)$$

$$\text{pH, 8.5–10}: [\text{Ni}^{\text{III}}\text{L}]^+ + e^- \rightleftharpoons [\text{Ni}^{\text{II}}\text{L}], E^0 = 0.15\text{V} \qquad (12)$$

$$[\text{Ni}^{\text{III}}\text{L}]^+ + e^- + 2H^+ \rightleftharpoons [\text{Ni}^{\text{II}}(\text{H}_2\text{L})]^{2+}, E^0 = 1.00\ \text{V} \qquad (13)$$

Using the E^0 values of couples (10) and (13) and the pK value[22] (4.05) of the protonated nickel(III) complex $[\text{Ni(HL)}]^{2+}$ we can compute the E^0 values of the *unobservable* but thermodynamically significant couples (14) and (15). This computation is based on the principle of additivity[23] of free energy changes due to electron transfer and proton transfer, Eq. (16) and (17). The subscript on E^0 refers to the couple concerned

$$[\text{Ni}^{\text{IV}}\text{L}]^{2+} + e^- + H^+ \rightleftharpoons [\text{Ni}^{\text{III}}(\text{HL})]^{2+}, E^0 = 0.66\text{V} \qquad (14)$$

$$[\text{Ni}^{\text{III}}(\text{HL})]^{2+} + e^- + H^+ \rightleftharpoons [\text{Ni}^{\text{II}}(\text{H}_2\text{L})]^{2+}, E^0 = 0.76\ \text{V} \qquad (15)$$

$$(E^0)_{14} = (E^0)_{10} + 0.059\ \text{p}K \qquad (16)$$

$$(E^0)_{15} = (E^0)_{13} - 0.059\ \text{p}K \qquad (17)$$

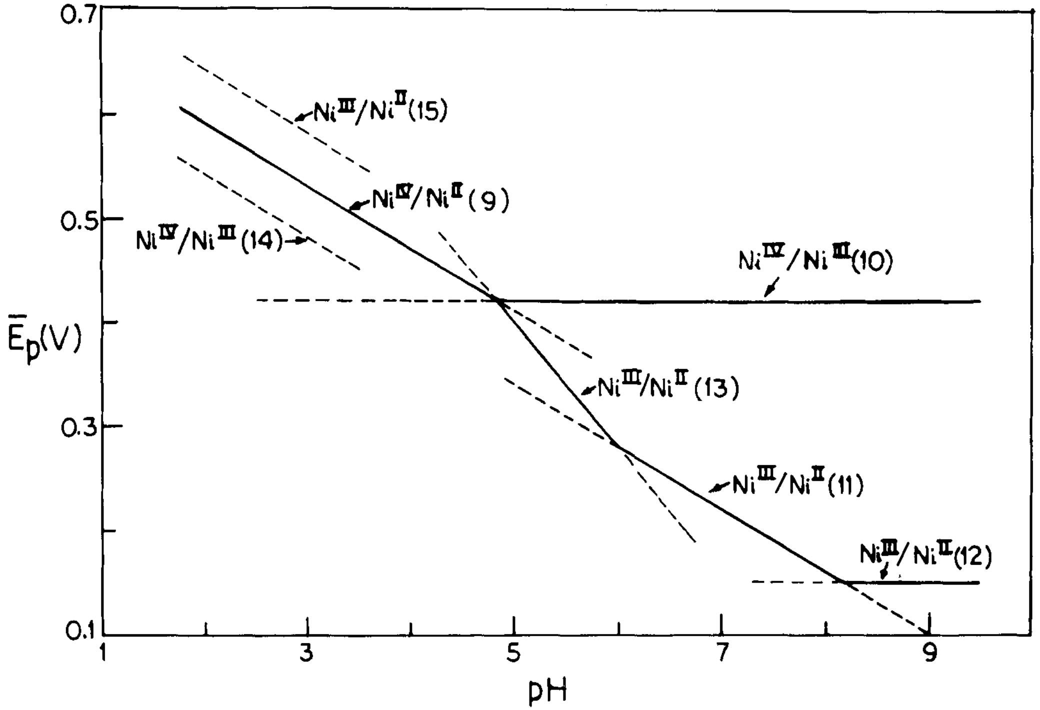


FIGURE 6 Plot of $\overline{E}_p$ vs. pH (the solid line represents the observed behavior; the numbers in parentheses are serial numbers of couples as in the text).

and pK = 4.05. For a given value of n, larger m means higher E^0. The pH profile of the various couples in terms of $\bar{E}_p$ [Eq. (2)] are in Fig. 6.

We can now trace the events that lead to the observed pattern. On progressive decrease of pH, [NiL] is protonated twice before $[NiL]^+$ protonates even once: $[NiL]^{2+}$ does not protonate at all (pK < 1). Thus the nickel(III)/nickel(II) potential is raised so much at low pH that it tends to go above the nickel(IV)/nickel(III) potential. Under this condition nickel(II) is directly oxidised to nickel(IV), Eq. (9).

The transfer of more than one electron at the same potential is a matter of considerable interest. In a mononuclear complex this could be achieved *electrochemically* by electroprotic control as shown above. Known instances of this among coordination complexes are relatively few. The reactions of Eq. (7) and (9) are therefore of special interest. The crucial evidence[24] in both cases in the ~30 mV cyclic voltammetric peak-to-peak separation along with current height data.[8,14]

Mechanistic studies of the electroprotic transformation of $[NiL]^{2+}$ by one-electron and two-electron *chemical* reductants have received considerable recent attention.[22,25,26] The cation acts as an outer-sphere oxidant with large self-exchange rates ($> 10^3$ $M^{-1}s^{-1}$). The most important result is that the observed reduction of $[NiL]^{2+}$ is biphasic going via two one-electron steps even at low pH. The expectation that $[NiL]^{2+}$ might act as a complementary $2e^-$ oxidant towards chemical reducing agents, at least towards those that are potential $2e^-$ reductants such as ascorbic acid and catechol, remains unfulfilled. The time constants and transfer configurations being different, chemistry can be different from electrochemistry.

Generation of a solution of the nickel(III) cation $[NiL]^+$ in aqueous media[14,22] at alkaline pH or in nonaqueous media[17] presents few problems. In aqueous acids (pH $\leq$ 4) the protonated complex $[Ni(HL)]^{2+}$ is subject to spontaneous disproportionation, Eq. (18). This reaction

$$2[Ni(HL)]^{2+} \rightarrow [NiL]^{2+} + [Ni(H_2L)]^{2+} \qquad (18)$$

is an algebraic sum of couples (14) and (15) and we can write

$$0.059 \log K = (E^0)_{15} - (E^0)_{14} \qquad (19)$$

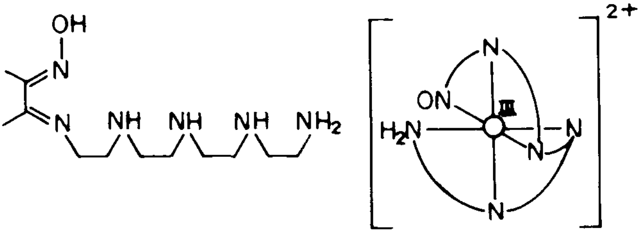


FIGURE 7 Ligand HL′ and complex $[Ni^{III}L']^{2+}$.

where K, the disproportionation constant is ~50. The equilibrium concentration of $[Ni(HL)]^{2+}$ will be approximately 10%. Even freshly synthesized "pure" samples of $[NiL](ClO_4)_2$ contain[13,14] a very small but measurable concentration of an EPR active nickel(III) species, presumably $[Ni(HL)]^{2+}$. On exposing crystals of $[NiL](ClO_4)_2$ to a moist atmosphere the concentration of this ion increases.[27]

Interestingly, the mono-oxime ligand HL′ shown in Fig. 7 affords a stable nickel(III) complex $[NiL'](ClO_4)_2$ which displays[15] the electroprotic reaction (20) in aqueous solution. Here no evidence for

$$\text{pH, 5-7: } [Ni^{III}L']^{2+} + e^- + H^+ \rightleftharpoons [Ni^{II}(HL')^{2+},\ E^0 = 0.68\ \text{V} \qquad (20)$$

the formation of nickel(IV) exists. It seems that for each unit increase in the oxidation state of nickel (above +2) at least one oxime proton must be transferred. Thus H_2L can afford both nickel(III) and nickel(IV) species while HL′ furnishes only the former.

THE PROTON-VALVE AND STRUCTURAL FACTORS IN TRINUCLEAR BIVALENT AND MIXED-VALENCE COPPER

We now turn to a situation where the proton transfer component of Fig. 1 is not observable. Here it appears as though the static proton controls the flow of electrons in a valve-like fashion. The relevant chemical species[28-30] are trinuclear copper(II) complexes of isonitrosoketones (Hink): $[Cu_3O(ink)_3]^+$ and $[Cu_3(OH)(ink)_3]^{2+}$, Fig. 8. Similar complexes are also afforded[30,31] by pyridine-2-aldoximes but these will not be explicitly considered here. The triangular structure in Fig.

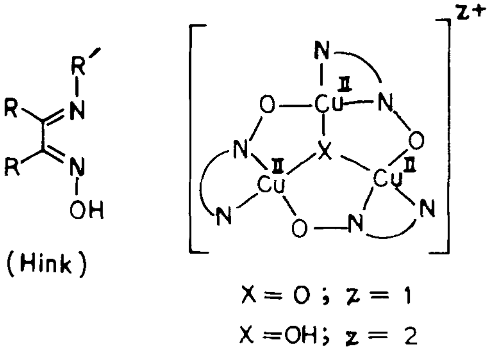


FIGURE 8 Ligand Hink and its trinuclear copper(II) complexes.

7 is proven in a few cases by x-ray crystallography.[31,32] The complexes are strongly antiferromagnetic and usually contain only one unpaired electron ($S = 1/2$) per Cu_3X unit (X = O or OH). In MeCN, Cu_3O is quantitatively converted[30] to Cu_3OH by stoichiometric amounts of $HClO_4$: the reverse transformation can be brought about by NEt_3. The oximato function in the present complexes, unlike that in the previous section, bridges two metal ions and is therefore not available for proton transfer.

The reversible couple (21) is generally observable[29,30] in

$$[\mathrm{Cu^{III}Cu_2^{II}O(ink)_3}]^{2+} + e^- \rightleftharpoons [\mathrm{Cu_3^{II}O(ink)_3}]^+ \qquad (21)$$

solvents such as MeCN and MeOH. The mixed-valence oxidized complex has been isolated[33] in pure form as a perchlorate in one case (R = Ph, R = n-C_3H_7, Fig. 7). This unique compound is diamagnetic, valence-delocalized and displays two intense intervalence ab-

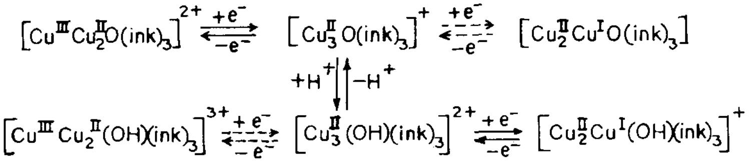


FIGURE 9 Transformations of trinuclear copper species; dotted arrows represent unobserved processes.

sorption bands (700–900 nm). The Cu_3OH complexes do not show any oxidative response of type (21) below 1.0 V. On the other hand these are reversibly reducible,[29,30] Eq. (22), with $E^0 \sim -0.35$ V. The corresponding reduction

$$[\mathrm{Cu_3^{II}(OH)(ink)_3}]^{2+} + e^- \rightleftharpoons [\mathrm{Cu_2^{II}Cu^{I}(OH)(ink)_3}]^+ \qquad (22)$$

of $[\mathrm{Cu_3O(ink)_3}]^+$ is not seen above -1.0 V.

These observations are conveniently summarized in Fig. 9. In effect the proton in $[\mathrm{Cu_3^{II}(OH)(ink)_3}]^{2+}$ acts like a valve, allowing an extra electron to come in (Eq. (22)), but blocking the removal of any of the original electrons. No evidence for electroprotic equilibria could be found in these systems even when a protic solvent such as aqueous methanol was used (pure water cannot be used because of solubility problems). The electroprotic response appears to lie at an inaccessibly high potential. While the weak acidity of Cu_3OH could be responsible for this [see Eq. (16)] the following structural factor may be important.

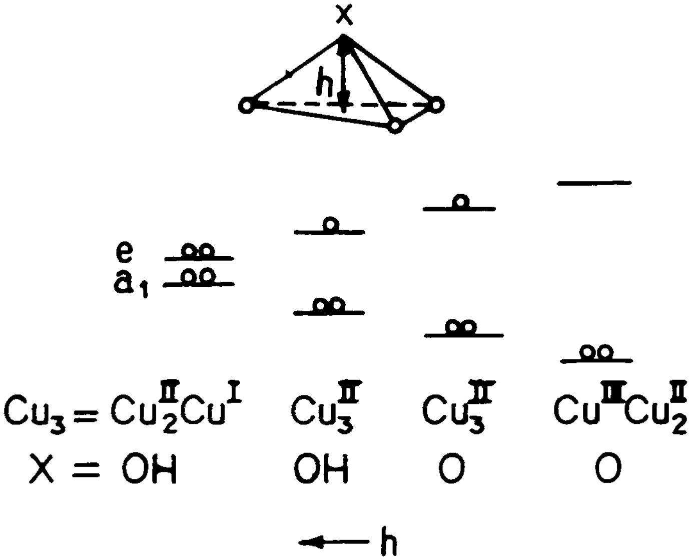


FIGURE 10 Qualitative energy levels in trinuclear copper species.

In Cu_3OH and Cu_3O the central oxygen atom (Fig. 7) lies above the Cu_3 plane by ~0.7 Å and ~0.3 Å respectively[31,32]. We assume[33] that the corresponding displacements (parameter h in Fig. 7) in $Cu^{II}_2Cu^{I}OH$ and $Cu^{III}Cu^{II}_2O$ are, respectively, >0.7 Å and <0.3 Å. In effect the oxygen-mediated intermetal interaction increases as:

$$Cu^{II}_2Cu^{I}OH < Cu^{II}_3OH < Cu^{II}_3O < Cu^{III}Cu^{II}_2O.$$

The least stable $3d$ orbital on each copper is $d_{x^2-y^2}$ (singly occupied).[28] In C_{3v} symmetry the three $d_{x^2-y^2}$ orbitals of the Cu_3 unit combine to furnish molecular orbitals of e and a_1 symmetry. A qualitative energy level diagram, constructed by setting e higher than a_1 in energy and incorporating the order of intermetal interaction as stipulated above is in Fig. 10. The $S = 1/2$ nature of Cu_3O and Cu_3OH and the diamagnetic character of $Cu^{III}Cu^{II}_2O$ fall in place. The observation of single one-electron redox processes in each of the two parent complexes is understandable since the redox level e is well separated from a_1 and is singly occupied. The relative energies of the e level of Cu_3OH and Cu_3O suggest that the oxidation of the former should occur at a higher potential than that of latter. This shift will be further augmented by the charge of the proton. In practice no oxidation is observed for Cu_3OH. By the same logic, reduction of Cu_3OH should be easy and that of Cu_3O difficult. We thus have a molecular basis for the proton valve action.

ANOTHER EXAMPLE: MOLYBDENUM(VI) HYDROXAMATES

A strange proton-valve operates in aqueous solutions of octahedral hydroxamates[34] of dioxomolybdenum(VI), $MoO_2(LH)_2$ where LH is the same hydroxamate as in Fig. 2. The structure[35] of this complex, which acts

$$[MoO_2(LH)_2] \rightleftharpoons [MoO_2(LH)(L)]^- + H^+, \; pK_1 = 3.45 \qquad (23)$$

$$[MoO_2(LH)(L)]^- \rightleftharpoons [MoO_2(L)_2]^{2-} + H^+, \; pK_2 = 5.89 \qquad (24)$$

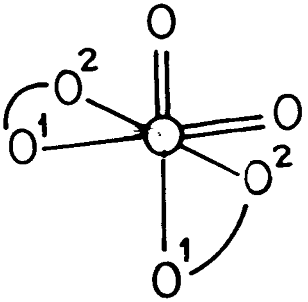


FIGURE 11 Structure of $MoO_2(LH)_2$; the hydroxamate ligand is as in Fig. 2.

as a dibasic acid, Eq. (23) and (24), is shown in Fig. 11.

In cyclic voltammetry,[34] the complex shows a cathodic reduction peak at −0.40 V corresponding to $Mo^{VI} + e^- \rightarrow Mo^V$. The anodic response is absent due to instability of the Mo^V species in water. While the reductive peak-potential remains virtually pH-invariant, the peak-height decreases progressively as the pH increases from ~2 to ~6. Thereafter the peak is no longer discernible. These changes are fully reversible and the full height of the reduction peak is re-established on acidification.

Three species are present in solution, Eq. (23) and (24). The reductive peak-height varies linearly with the equilibrium concentration of $MoO_2(LH)_2$ with zero intercept. We thus have the result that *only* the fully protonated complex is reducible near −0.4 V, Eq. (25):

$$[Mo^{VI}O_2(LH)_2] + e^- \rightarrow [Mo^VO_2(LH)_2]^-. \qquad (25)$$

Surprisingly, there is no observable influence of the protic equilibria (23) and (24) on the electron transfer potential, as though proton movement is very slow compared to electron movement.

CONCLUDING REMARKS

We have tried to view in a particular manner the formation and reactivity of transition metal oxidation states complexed by ligands having one or more labile protons. The role of such protons in the control of metal-centered electron transfer and in the stabilization of metal oxidation states—particularly uncommon states—is emphasized. This is a view of the metal from the side of the proton—a view that is unifying and revealing.

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