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Charge-Transfer Spectra and Photochemistry of the Hexakis(isothiocyanato)ferrate(III) Ion at Cryogenic Temperatures in Diluent Crystals

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Iron(III) ions readily enter the host lattices of the general formula $R_3Ln(NCS)_6$, where Ln is a lanthanide ion and R is a large organic cation. For Ln = Nd, Sm, and Gd and R = tetra-*n*-butylammonium, the iron-doped crystals are strongly dichroic at room temperature. When they are cooled and then irradiated with white UV-visible light, new spectroscopic features appear, which are largely reversible on warming and recooling the crystals. A brief explanation of the origins of these phenomena is offered.

Introduction

Several authors have noted that when hexakis(isothiocyanato)metalate(III) complexes are prepared, the products are often pink due to contamination of the commercial metal salts by iron(III).^{1,2} As a consequence of some preparative work for an NMR project,³ large, well-formed crystals of $[Bu_4N]_3Gd(NCS)_6$ (Bu_4N = tetra-*n*-butylammonium) appeared from the mother liquor of the standard preparation¹ and were strongly dichroic when examined in polarized light. The color is readily identified as due to the electronically allowed ligand to iron(III) charge-transfer band.

As part of our general interest in low-temperature spectra in single crystals, we decided to examine the absorption features at low temperature (10 K) using polarized light. In the scanning of the near-IR region of the spectrum of a Cary 14 spectrophotometer, the crystal is exposed to large doses of white light. Upon returning to the visible region, we noted that the visible spectra at low temperature had changed dramatically as a result of the irradiation. The original bands were noticeably reduced, especially in one polarization, and in addition, several new spectroscopic features appeared, one of these being highly polarized as well.

In view of the highly interesting results obtained with gadolinium, we decided to extend our spectroscopic investigations of the $Fe(NCS)_6^{3-}$ ion to host lattices containing other trivalent lanthanide ions and also other organic counterions. We here present these results together with some tentative suggestions concerning the origins of this strange and interesting photochemical phenomenon.

The mode of binding between iron and thiocyanate ions in complexes is reasonably well understood through IR,⁴ Raman,⁵ and X-ray studies,⁶ and $Fe(NCS)_6^{3-}$ species have been prepared with a variety of organic counterions.⁷ There are some unusual reports of pressure-induced isomerizations from the stable N-bonded form to S-bonded forms,⁸ but we feel that it is safe to conclude that the iron is N-bonded in the compounds reported here. Other pseudohalides, e.g., NCS^- and NNN^- , also give hexakis N-bonded complexes with iron(III), which have been characterized by IR and other techniques.^{9,10} These complexes also possess low-energy charge-transfer bands.

The UV-visible reflectance spectrum of $Fe(NCS)_6^{3-}$ with several counterions has received attention in the past.^{11,12} Very weak features have been seen in the spectrum of $[(CH_3)_4N]_3Fe(NCS)_6$ at 10 640 and 17 500 cm^{-1} , which are attributed to the spin-forbidden ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ and ${}^4T_{2g}(G)$ transitions, respectively, within the d manifold.¹¹ An intense band at 21 400 cm^{-1} , however, dominates the spectrum of this compound.¹¹ This band was found by Schmidtke at 20 600 cm^{-1} in the same lattice and was assigned to the $t_{1u} \rightarrow t_{2g}$ (ligand

to metal) charge-transfer transition.¹² Allowed bands of higher energy at 31 200 and 40 100 cm^{-1} have been assigned to the $t_{1u} \rightarrow e_g$ and $t_{2u} \rightarrow t_{2g}$ ligand to metal charge-transfer processes, respectively.¹² The spectra of iron(II) thiocyanato complexes have been investigated also.¹¹ In these compounds charge-transfer processes occur at much higher energies than in the corresponding iron(III) systems.

Of some importance to our study is the structure of the host lattices, particularly at the trivalent metal center. The X-ray structure of $[(C_6H_5)_4P]_3In(NCS)_6$ has been determined.¹³ It shows that the complex anion is a regular octahedron within experimental error. The X-ray structure of $[Bu_4N]_3Tc(NCS)_6$ also reveals a complex anion with only minor (less than 5°) angular deviations from octahedral symmetry.¹⁴ This lattice is apparently not isomorphic with $[Bu_4N]_3Er(NCS)_6$,² the difference may be due to the differing ionic radii of the trivalent cations ($Tc-N = 2.04 \text{ \AA}$, $Er-N = 2.34 \text{ \AA}$). As is frequently observed in other cases, the MNC angles deviate somewhat from 180°. While structural data are not available for $[Bu_4N]_3Ln(NCS)_6$ (Ln = lanthanide ion) for Ln other than Er, preliminary results indicate that variation of lanthanide ion size has a significant overall effect.¹⁵ These investigations will be the subject of future reports.

Experimental Section

Crystal Preparation. $[Bu_4N]_3Ln(NCS)_6$ and $[BuPPH_3]_3Ln(NCS)_6$ ($BuPPH_3$ = *n*-butyltriphenylphosphonium) were prepared as previously described.^{1,3} Crystals of the latter suitable for spectroscopy were grown from acetonitrile-ethyl acetate mixtures. Approximately 0.1% iron(III) was introduced by adding 1 mg of $[Bu_4N]_3Fe(NCS)_6/g$ of lanthanide complex. Lanthanide analyses were performed by EDTA back-titration with zinc sulfate at 80 °C using Eriochrome Black T as indicator. Results were excellent in all cases.

Growth of $(Bu_4N)_3Ln(NCS)_6$ Crystals. Ln = Nd. Two grams of the crude complex was dissolved with gentle heating in 15 mL of 2-propanol containing 5% (v/v) acetone; iron(III) was added as above.

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After the solution stood for 2 days in a covered container, strongly dichroic diamond-like crystals deposited.

Ln = Sm, Gd. These were prepared as above except that 2-propanol containing 10% (v/v) acetone was used. Highly dichroic crystals usually appeared within a few hours.

Ln = Y, Yb. Crystals were best grown from acetone by slow evaporation. Large crystals also formed from dichloromethane solution. Loss of optical quality was, however, rapid due to efflorescence of entrained solvent.

Spectroscopic Measurements. Polarized crystal spectra were taken at room temperature and about 10 K with use of Cary 14 spectrophotometer and a Displex cryogenic refrigerator. Two calcite polarizers were used to polarize the radiation. Spectra were recorded with the electric vector of the light parallel to the orthogonal extinction axes of the crystal. Intense light sources for irradiation were provided by the Cary 14 IR source and by a UV dark light source.

Results and Discussion

Growth Habit and Observed Dichroism. All iron-doped crystals of $\text{R}_3\text{Ln}(\text{NCS})_6$ exhibit some dichroism on visual examination in polarized light. For crystals of $[\text{Bu}_4\text{N}]_3\text{Ln}(\text{NCS})_6$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Gd}$), it is possible to prepare crystals of differing dichroism by varying the growth conditions. Low supersaturation and very slow cooling during crystal deposition (2 days) produce crystals that are markedly less dichroic than those produced under conditions of high supersaturation and more rapid crystal growth (1–2 h). When $\text{Ln} = \text{Y}$, it is possible to produce very dichroic crystals from 2 g of complex in 15 mL of 10% acetone (v/v) in 2-propanol, but on standing in the mother liquor the crystals initially produced dissolve and are replaced over the course of several days by the crystals of less dichroic habit. When $\text{Ln} = \text{Yb}$, only one phase showing reduced dichroism could be detected, irrespective of growth conditions. We cannot exclude the possibility that in some cases, notably when $\text{Ln} = \text{Y}$, more than one lattice type can exist for a given compound.

The high dichroism of the $[\text{Bu}_4\text{N}]_3\text{Ln}(\text{NCS})_6$ crystals persists indefinitely, provided the crystals are thoroughly dried and prolonged exposure to atmospheric moisture or residual mother liquor is not allowed to take place. If the crystals are left in the mother liquor for periods of several months, their dichroism disappears even though there is no apparent change in external crystal appearance. Strongly dichroic crystals are unchanged on heating in vacuo at a temperature of 110 °C for periods of up to 6 h.

The orientation of the extinction axes relative to the crystal edges varies with metal ion in the tetrabutylammonium crystals; for $\text{Ln} = \text{Sm}$ and Gd , the extinction axes are parallel and perpendicular to a crystal edge while, for $\text{Ln} = \text{Y}, \text{Yb}$, and Nd , this is not the case.

Spectra before Irradiation. The frequencies of all the observed iron(III) absorption bands at 10 K are listed in Table I. As expected, the band maxima do not shift greatly on cooling, nor are there major integrated intensity changes. This is consistent with the electronic selection rules. The principal band at about 20 000 cm^{-1} appears at somewhat different energies in the two orthogonal polarizations in all cases. We have labeled the *a* polarization as that in which this band appears at higher energy. When viewed in polarized light, the more dichroic crystals appear yellow in *a* and red in the orthogonal polarization, *b*. The splitting of this band is greatest in the very dichroic gadolinium complex, and this will be used as the principal example of the effects we observe. The 10 K spectra of this complex are shown in Figure 1. While the main band in polarization *a* is symmetrical, in polarization *b* a distinct shoulder appears on the high-energy side. Thus, two transitions are seen *b*; this effect is *not* due to mixing of polarizations, as will be seen shortly. The spectra of the Nd and Sm salts are quite similar to those of the Gd complex. The spectra of the tetrabutylammonium salts of Y and Yb are similar to each other; we were unable to find in either the

Table I. Spectra of Iron Centers in $\text{R}_3\text{Ln}(\text{NCS})_6$ Host Lattices at 10 K^a

Ln (<i>t</i>) ^b	before irradiatn		after irradiatn	
	pol <i>a</i>	pol <i>b</i>	pol <i>a</i>	pol <i>b</i>
	R = Bu ₄ N			
Y (30)	21 210	20 700	16 200 w	16 200 w
			20 710	20 670
	26 180 w	25 990 w	24 270 sh ^c	24 180 sh ^c
		28 570	28 570	
		33 840 ^c	34 080 ^c	
Nd (91)	35 150	35 240	35 110	35 270
			sh ^d	15 810 sh
	21 320	20 410	20 700	20 580
			24 870	
	26 110 w	26 110 w		
			30 140 sh	30 590 sh
			31 000 sh	
Sm (94)	21 240	19 550	15 610	15 810
		21 510 sh	20 940	19 380
			24 670 sh, w	21 050 sh
			24 790	
		28 670	28 780	
Gd (64)	21 450	19 610	17 020	16 060
		21 740 sh	21 140	19 370
				21 430 sh
			24 690	
			28 990 sh ^e	
Yb (25)	31 750 sh, w	31 750 sh, w		31 400 sh
	21 420	20 750	21 380	20 700
	R = BuPPh ₃			
Yb (45)		17 860 sh		17 860 sh
	20 330	20 090	20 240	20 040
Tb (17)	21 620	20 320	21 620	20 200
	32 790	33 020	32 820	33 200

^a Data in cm^{-1} ; w = weak, sh = shoulder. ^b Maximum time in min of irradiation with Cary 14 IR source. ^c These features, weak or barely visible after 30 min of irradiation, became quite strong with additional exposure to UV radiation for 43 min. ^d Spectral features due to Fe are obscured by f-f transitions. ^e This disappeared after 64 min of irradiation but was present in spectra recorded after shorter irradiation periods.

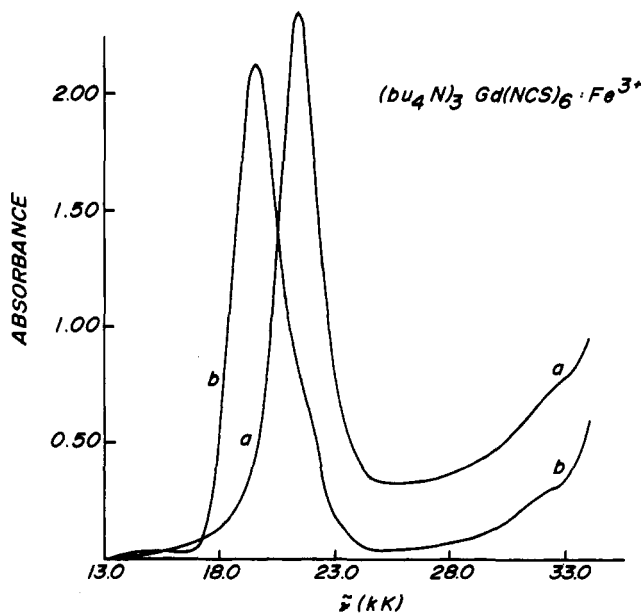


Figure 1. Polarized single crystal electronic spectra of the $t_{1u} \rightarrow t_{2g}$ charge-transfer transition in iron(III) centers in the $[\text{Bu}_4\text{N}]_3\text{Gd}(\text{NCS})_6$ host lattice at 10 K. 1 kK = 1000 cm^{-1} .

distinct high-energy shoulder seen in the *b* spectra of the other three crystals.

Origin of the Band Splitting. Deviations from octahedral symmetry in charge-transfer spectra are evident in the tet-

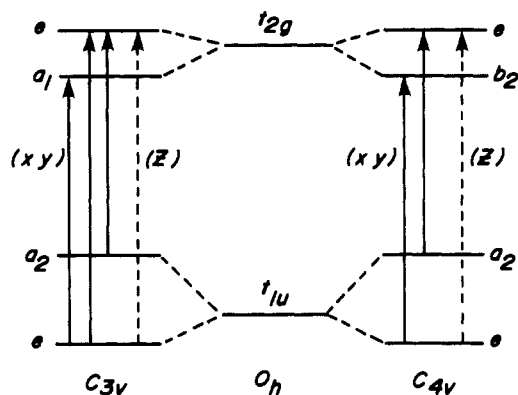


Figure 2. Energy-level diagram for $t_{1u}(\text{ligand}) \rightarrow t_{2g}(\text{metal})$ charge-transfer transition in trigonal, octahedral, and tetragonal symmetries.

ragonal $\text{FeCl}_5\text{H}_2\text{O}^{2-}$ ion, where strongly polarized bands and large band splittings ($2000\text{--}3000\text{ cm}^{-1}$) are observed.¹⁶ In the case of our thiocyanate complexes, the symmetry of the iron center is not quite so well-defined for two reasons. First, although it is highly likely that iron is present as the hexakis(thiocyanato) ion, the possibility that it is there as some other species cannot be entirely excluded. Very small amounts of $\text{trans-}[\text{Fe}(\text{H}_2\text{O})_4(\text{NCS})_2]^+$ could, for example, substitute for the large organic cation and still yield intensely colored dichroic crystals. Second, while X-ray crystallography can establish with high precision the site symmetries for the lanthanide ions in the host lattices, this technique cannot guarantee the site symmetry of a guest $\text{Fe}(\text{NCS})_6^{3+}$ ion; deviations will be expected as the difference in ionic radii between iron and the host metal cation increases. For small lanthanide ions, the iron center will more likely resemble the host center. Thus, $[\text{Bu}_4\text{N}]_3\text{Yb}(\text{NCS})_6$ (and probably the Y analogue) undoubtedly resembles closely the erbium analogue of known structure. The somewhat smaller band splitting observed in the Yb host lattice is thus in keeping with a smaller deviation from cubic symmetry expected for the iron center.

We have examined the spectra of $\text{Cr}(\text{NCS})_6^{3-}$ ions in the $[\text{Bu}_4\text{N}]_3\text{Yb}(\text{NCS})_6$ host lattice. The ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ band, which is usually the most sensitive to the effects of low-symmetry fields, is split by less than 200 cm^{-1} at 10 K. This is to be contrasted with the 670-cm^{-1} band splitting in the iron(III) spectra. Charge-transfer spectra may accordingly be a more sensitive probe of low-symmetry fields than the bands of the d-d spectrum.

In analyzing the spectra of the Nd, Sm, and Gd analogues, we postulate the existence of the hexakis(isothiocyanato)-ferrate(III) chromophore and maintain the level assignments of Schmidtke.¹² If we assume that the splitting of the t_{1u} orbitals is considerably greater than that of the t_{2g} orbitals, as expected from the above discussion, then the observed spectra can be rationalized on the basis of either a trigonal or tetragonal distortion of the octahedral chromophore (Figure 2). In either case the selection rules predict a single high-energy band in one polarization, z , which would be our a . The other polarization, xy , should have one (C_{4v}) or two (C_{3v}) bands at nearly the same energy as the z band; this would be the ill-defined shoulder in b . In addition b should show a single band at lower energy ($a_2 \rightarrow e$). Site symmetries lower than axial may indeed be the case, but major deviations from axiality would be expected to give rise to a larger number of bands than we have observed.

Schmidtke¹² has assigned a transition at $31\,200\text{ cm}^{-1}$ in $[\text{NMe}_4]_3\text{Fe}(\text{NCS})_6$ (Me = methyl) to the $t_{1u} \rightarrow e_g$ transition.

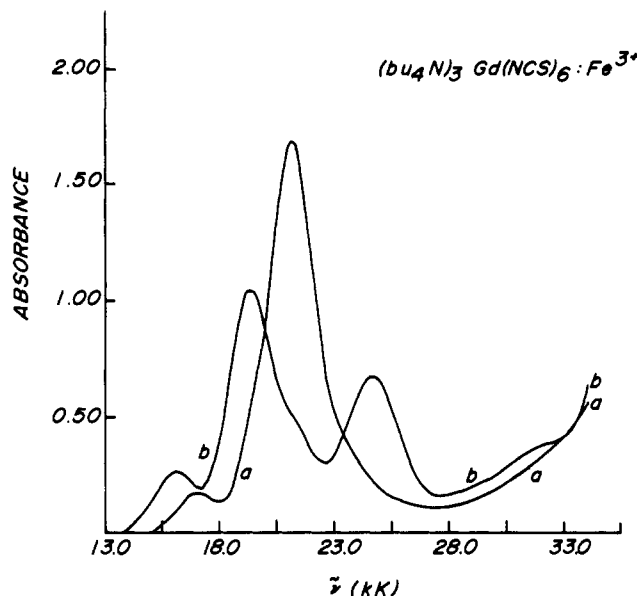


Figure 3. Effect of intense white light on a single crystal of $[\text{Bu}_4\text{N}]_3\text{Gd}(\text{NCS})_6:\text{Fe}^{3+}$ at 10 K. The spectra were obtained after 64-min irradiation with the Cary 14 IR source. $1\text{ kK} = 1000\text{ cm}^{-1}$.

It is likely that some of the bands we observe around $31\,000\text{ cm}^{-1}$ on the steeply rising background can also be assigned to this transition. More detailed experiments would, however, be needed to clarify this matter.

Changes in Spectra on Irradiation. Exposure to intense white light provided by the IR source of the Cary 14 spectrophotometer causes dramatic changes in the iron spectra in certain $[\text{Bu}_4\text{N}]_3\text{Ln}(\text{NCS})_6$ lattices. An impressive example of the irradiation effect is shown in Figure 3, and the band maxima observed in irradiated samples are collected in Table I.

In general, there is a rapid onset of the effect, the decrease in size of the principal band being most noticeable at the beginning of the irradiation. Thus, for example, 1-min irradiation of the Gd complex causes a 30% decrease in size of the principal band, with further band shrinkage being caused by longer irradiation. In some other cases, as for example the two Yb complexes, there is a small but noticeable decrease (about 5–10%) with 1-min irradiation and then very little change on further irradiation.

We may generalize the effects observed as follows: with continued irradiation the main bands decrease markedly in intensity in both polarizations, but especially in b , and the band maxima for the most part shift to lower energies by several hundred wavenumbers. New, strongly polarized bands appear at $16\,000\text{--}17\,000\text{ cm}^{-1}$ and at about $24\,000\text{ cm}^{-1}$. The latter band is unique to polarization b . Iron in the Yb lattice does not, however, appear to generate new bands on irradiation. Iron in the Y lattice, on the other hand, produces a band at about $16\,000\text{ cm}^{-1}$, but no band at about $24\,000\text{ cm}^{-1}$. A shoulder at the latter position in the Y lattice was produced only after changing the irradiation source from white light to ultraviolet and continuing the irradiation. Exposure to white light caused changes in the region above $25\,000\text{ cm}^{-1}$ also. The rising absorption base line extending into the UV region appears to increase in intensity on irradiation in all cases. As can be seen in Table I, other new features appear in most of the lattices, the exact energy depending significantly on the lattice.

The effects noted above persist indefinitely, provided the system is maintained at 10 K, but disappear on warming to room temperature. The systems are quasi-reversible, in that on recooling and reirradiation essentially the same phenomena can be produced again, but at a somewhat reduced rate. In strong contrast to the above behavior, the iron bands in

[BuPPh₃)₃Ln(NCS)₆ lattices develop no new features on irradiation. The only observable effect is a slight initial drop in the intensity of the main band on commencing irradiation, followed by no further change.

Analysis of the Phenomena. The photolysis of iron thiocyanate complexes in solution is well-known. Detailed studies have been undertaken¹⁷ that indicate the production and consequent decay of thiocyanogen radicals (NCS) and the formation of ferrous iron. It is unlikely that a similar mechanism exists in crystals at cryogenic temperatures for the following reason. New bands appear at frequencies quite similar to those in the normal iron(III) complex, while if an iron(II) complex were the product of the photolysis, bands at considerably higher energies would be expected.¹¹

It appears most probable that what occurs on irradiation is the dissociation of an NCS⁻ group, leaving the Fe(NCS)₅²⁻ chromophore. This new iron(III) complex is expected to have a spectrum like the old, since the two differ by only one ligand. The bands that appear at 17 020 cm⁻¹ in *a* and 16 060 cm⁻¹ in *b* in the Gd spectrum lie about 4000 cm⁻¹ below the principal bands of the nonirradiated complex and may be assigned to analogous transitions in the new complex. If the new band in *b* possesses a shoulder similar to that observed in the original spectrum, it would lie under the band due to the original complex.

The new band at 24 690 cm⁻¹ in *b* is completely polarized. Since it lies 8600 cm⁻¹ above the other new band, it is not likely to be a split component arising from the same ligand level; splittings of such large magnitude are not expected. If it were from the next lowest ligand level (probably t_{2u}), it is not clear

why an analogous band was not observed in the spectrum of the initial complex. It probably represents a transition within some other species, the most likely one being the isolated NCS⁻ group. A band found between 27 800 and 29 400 cm⁻¹ in the spectra of aqueous thiocyanates has been assigned to a π → π* transition on the NCS⁻ ion, specifically ¹Σ⁺ → ³Σ⁺.¹⁸ Under spin-orbit coupling this becomes Σ⁺ → Π + Σ⁻. Only the transition to the former states is allowed and then only in the *xy* polarization. This is consistent with our observations, since our *a* and *b* spectra seem best interpreted as *z* and *xy*, respectively. McDonald et al.¹⁸ also note that their data are best interpreted if the equilibrium geometry of the ³Σ⁺ excited state is assumed to be bent.

An alternate explanation would have the photolysis give rise to angular rearrangements without dissociation, such that one or more FeNC angles change upon irradiation. The strong polarization of the spectra indicates that such changes must take place only in certain directions in the lattices containing Nd, Sm, or Gd. The appearance of unpolarized bands on irradiation in the yttrium lattice under severe conditions seems to correlate with the fact that there are fundamental differences in structure between the host lattices formed by the larger early lanthanide ions and the smaller trivalent yttrium cation. These issues will, we hope, be clarified in forthcoming papers.

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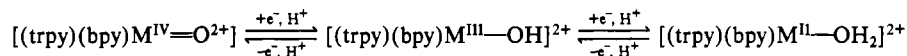
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Redox and Spectral Properties of Monooxo Polypyridyl Complexes of Ruthenium and Osmium in Aqueous Media

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The complexes [(trpy)(bpy)M—OH₂]²⁺ (M = Ru, Os; trpy = 2,2',2''-terpyridine; bpy = 2,2'-bipyridine) have been prepared and their redox properties in aqueous solution investigated by using electrochemical techniques. Evidence for two one-electron redox processes has been obtained for M(IV/III) and M(III/II) couples and for an irreversible Os(IV/V) oxidation. In certain pH ranges the couples are proton dependent because of loss of both protons and electrons upon oxidation; e.g., at pH 7 the couples are



*E*_{1/2} vs. pH studies over a broad pH range (0–13) can be interpreted in terms of simple acid–base chemistry on the basis of the Nernst equation. The *E*_{1/2} vs. pH data are revealing in terms of the relative stabilities of the various oxidation states and of the use of pH variations to control redox potentials for these known redox catalysts. Comparisons between data for the equivalent Os and Ru complexes also give insight into shifts in p*K*_a values in pH domains of oxidation-state stability and into the probable role of the M–O interaction in oxo and hydroxo complexes in determining the redox properties of these systems.

Introduction

A number of mechanistic studies and catalytic redox applications involving the couples [(trpy)(bpy)Ru=O]²⁺/[(trpy)(bpy)Ru—OH₂]²⁺ or [(bpy)₂(py)Ru=O]²⁺/[(bpy)₂(py)Ru—OH₂]²⁺ (trpy = 2,2',2''-terpyridine; bpy = 2,2'-bipyridine; py = pyridine) and a variety of organic and inorganic substrates have recently appeared.¹ In order to characterize

the redox characteristics of monooxo complexes in further detail, we report here the results of a series of studies that were

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