# Ruthenium(II) and Iron(II) Complexes of 4,4-Dithiodipyridine. Synthesis, Characterization, and Reactivity Studies

**Icaro de Sousa Moreira† and Douglas Wagner Franco*,‡**

Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, Fortaleza-CE, Brazil, and Instituto de Física e Química de São Carlos-USP, Cx. Postal 369, 13560–970, São Carlos-SP, Brazil

*Received August 4, 1992®*

The compounds $[Ru(NH_3)_5DTDP](PF_6)_2$, $K_3[Ru(CN)_5DTDP]\cdot 3H_2O$, $Na_3[Fe(CN)_5DTDP]\cdot 4H_2O$, $[\{Ru(NH_3)_5\}_2DTDP](PF_6)_4$, and $Na_6[\{Fe(CN)_5\}_2DTDP]\cdot 6H_2O$ (DTDP = 4,4′-dithiodipyridine) have been synthesized and characterized by infrared, electronic, and nuclear magnetic resonance spectroscopies, microanalyses, and cyclic voltammetry. The extent of back-bonding M(II)→DTDP in the complexes was determined to be $[Ru(NH_3)_5DTDP]^{2+} > [Ru(CN)_5DTDP]^{3-} > [Fe(CN)_5DTDP]^{3-}$, based on p$K_a$, electrochemical, and spectroscopic data. The p$K_a$ for the acids $[Ru(NH_3)_5DTDPH]^{3+}$, $[Ru(CN)_5DTDPH]^{2-}$, and $[Fe(CN)_5DTDPH]^{2-}$ are 5.25, 4.70, and 4.40 (25.0 ± 0.2 °C, $\mu$ = 0.10 M ($NaCF_3COO$)), respectively. The rates of aquation of the DTDP ligand from the complexes $[Fe(CN)_5DTDP]^{3-}$, $[Ru(CN)_5DTDP]^{3-}$, and $[Ru(NH_3)_5DTDP]^{2+}$ were determined to be $1.1 \times 10^{-3}$, $1.2 \times 10^{-4}$, and $4.5 \times 10^{-5}$ s$^{-1}$, respectively. Electrochemical and near-infrared data for the binuclear complexes $[\{Ru(NH_3)_5\}_2DTDP](PF_6)_4$, $Na_6[\{Fe(CN)_5\}_2DTDP]$, and their respective mixed-valence derivatives indicate intense electron delocalization between the two ruthenium centers.

## Introduction

Despite the importance of the disulfide bridge on redox reactions in biological systems, the electron-transfer mechanism through the –S–S– bridge is far from being well understood.[1]

We undertook this work to gain a better understanding of the effectiveness of electron transfer through the –S–S– bridge. Simple and easy implementable models were chosen using 4,4′-dithiodipyridine as the bridging ligand and $[Ru(NH_3)_5(H_2O)]^{3+/2+}$, $[Ru(CN)_5(H_2O)]^{3-/2-}$, and $[Fe(CN)_5(H_2O)]^{3-/2-}$ as the metal complexes.

Crystallographic studies[2] indicate that in aromatic disulfides strong $\pi$ interactions exist between pyridine ring filled $p_\pi$ and sulfur vacant $d_\pi$ orbitals as well as between sulfur filled $p_\pi$ and pyridine ring $p_\pi$* orbitals in the DTDP molecule.

The interactions of Ru(II) and Fe(II) with pyridine ligands are well-known.[3–5] The low-spin $d^6$ configuration of these complexes provides filled orbitals of proper symmetry to interact with relatively low-energy, unoccupied $\pi^*$ orbitals on the pyridine ligands. These M(II)–py (or M(III)–py) bonds are thermodynamically very stable and kinetically inert.

The back-bonding, M(II) → py, is an important component of the ruthenium–pyridine interaction in this oxidation state. Conversely, the $\sigma$ bond component is the most important when the metal oxidation state is III.

This paper describes the synthesis, characterization, and reactivity of the monomeric species, M(II)–DTDP and the binuclear complexes $[\{Ru(NH_3)_5\}_2DTDP](PF_6)_4$ and $Na_6[\{Fe(CN)_5\}_2DTDP]\cdot 6H_2O$.

## Experimental Section

Double-distilled water was used throughout. Potassium hexacyanoruthenate(II) (Alfa), sodium nitroprusside (Aldrich), ruthenium trichloride (Aldrich), and 4,4′-dithiodipyridine (DTDP) (Aldrich) were used as recieved. Other chemicals were reagent grade.

Reagent grade ethanol, acetone, and ethyl ether were purified as described in the literature.[6]

The complexes $[Ru(NH_3)_5(H_2O)](PF_6)_2$ and $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ were synthesized and characterized according to literature procedures.[7,8] The $[Ru(CN)_5H_2O]^{3-}$ complex was generated[9] "in situ" from the reaction of $Ru(CN)_6^{4-}$ with $Br_2$, during the synthesis of the $[Ru(CN)_5DTDP]^{3-}$ complex.

All preparations and measurements were carried out under argon, using standard techniques for manipulation of air sensitive compounds.[10]

**Synthesis of New Complexes. $Na_3[Fe(CN)_5DTDP]\cdot 4H_2O$.** A 300-mg sample of DTDP was dissolved in 10 mL of a 70% ethanol/water mixture, at 50 °C. The resulting solution was cooled to room temperature and filtered to eliminate any residue. In a separate flask, 220 mg of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was dissolved in 10 mL of a 50% ethanol/water mixture. An orange color developed upon mixing the DTDP and the Fe(II) solutions. After 1 h the orange solution was filtered, and the filtrate was added to a flask containing 100 mL of NaI solution (30% of NaI in 100 mL of ethanol). An orange solid formed and was collected by filtration, washed with absolute ethanol and ethyl ether, and stored under vacuum, in the absence of light. Anal. Calcd: C, 18.42; H, 2.76; N, 25.77. Found: C, 18.30; H, 2.73; N, 26.01. Yields were better than 60%.

**$K_3[Ru(CN)_5DTDP]\cdot 3H_2O$.** A 50-mg sample of $K_4[Ru(CN)_6]\cdot 3H_2O$ was dissolved in 5 mL of a 50% ethanol/water mixture. Then 10 mL of a $Br_2$ solution in water (0.10 mM $Br_2$; 1 mM KBr) were added dropwise with stirring. After 10 min, 5 mL of the DTDP solution, prepared as described above, were added. The resulting solution developed an intense yellow color and was cooled down in an ice bath. After 45 minutes of reaction and upon the slow addition of cold acetone, a yellow precipitate was obtained and collected by filtration, washed with ethanol and ethyl ether, dried, and stored under vacuum, in the absence of light. Anal. Calcd: C, 28.31; H, 2.26; N, 16.79. Found: C, 28.92; H, 2.25; N, 16.80. Yields were better than 65%.

**$[Ru(NH_3)_5DTDP](PF_6)_2$.** A 150-mg sample of DTDP was dissolved in 10 mL of acetone at 50 °C, under a stream of argon, followed by the addition of 100 mg of $[Ru(NH_3)_5H_2O](PF_6)_2$. The solution developed an orange color. After 1 h, the solution was cooled in a ice bath and cold ether (peroxide free) was added dropwise with stirring. A dark yellow

† Universidade Federal do Ceará.

‡ Instituto de Física e Química de São Carlos-USP.

® Abstract published in *Advance ACS Abstracts*, March 1, 1994.

(1) Morgan, R.; Tasch, C.; Gushard, R.; McAdom, J.; Warme, P. *Int. J. Peptide Protein Res.* **1978**, *11*, 209.

(2) Lee, J. D.; Bryant, M. W. R. *Acta Crystallogr.* **1969**, *B25*, 825, 2497.

(3) Ford, P. C.; Rudd, F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1969**, *90*, 1187.

(4) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039.

(5) Hoddenbagh, J. M. A.; Macartney, D. H. *Inorg. Chem.* **1986**, *25*, 2099.

(6) Perrin, D. D.; Almarego, W. L. F.; Perrin, D. R. *Purification of Laboratories Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

(7) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(8) Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1965.

(9) Legros, J. C. *R. Hebd Seances Acad. Sci.* **1959**, *248*, 1339.

(10) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants*; Chapman and Hall Ltd.: London, 1962.

0020-1669/94/1333-1607$04.50/0 

solid precipitated. The material was collected by filtration, washed with a solution of 20% acetone in ethyl ether and then with ether, dried, and stored under vacuum, in the absence of light. Anal. Calcd: C, 17.24; H, 3.31; N, 14.02. Found: C, 16.92; H, 3.51; N, 13.92. Yields were generally better than 60%.

**[{Ru(NH$_3$)$_5$}$_2$DTDP](PF$_6$)$_4$.** Solid [Ru(NH$_3$)$_5$DTDP](PF$_6$)$_2$ (142 mg) was added to 10 mL of acetone containing dissolved [Ru(NH$_3$)$_5$(H$_2$O)](PF$_6$)$_2$ (101 mg). After 2 h under stirring, the initial pale yellow solution turned red-brownish. The complex was precipitated by adding 0.5 g of NH$_4$PF$_6$ followed by 60 mL of diethyl ether. The precipitate was filtered off and washed with a 7:3 diethyl ether–acetone mixture, dried, and stored under vacuum in the absence of light. Anal. Calcd: C, 10.24; N, 14.33; H, 3.21. Found: C, 10.18; N, 13.98; H, 3.24. Yields were better than 70%.

**Na$_6${Fe(CN)$_5$}$_2$DTDP]·6H$_2$O.** A 50-mg sample of Na$_3$[Fe(CN)$_5$NH$_3$]·3H$_2$O dissolved in 5 mL of water was added to 5 mL of aqueous Na$_3$[Fe(CN)$_5$DTDP]·4H$_2$O (90 mg). After 1 h, 0.3 g of solid NaI was added into the reaction flask. A yellow solid was obtained upon the slow addition of cold absolute ethanol (50 mL). The solid was filtered, washed with absolute ethanol and ethyl ether, dried, and stored under vacuum in the absence of light. Yields were better than 60%. Anal. Calcd: C, 28.64; N, 20.05; H, 2.39. Found: C, 27.94; N, 18.83; H, 2.31.

The voltammetric and electronic spectra of these DTDP complexes, when stored under vacuum, show that they are stable for more than 2 weeks.

The corresponding [Ru(NH$_3$)$_5$DTDP]$^{3+}$ and [Fe(CN)$_5$DTDP]$^{2-}$ ions were generated in solution by the electrochemical oxidation of the respective Ru(II) and Fe(II) complexes. During the electrolysis of the solution containing the [Ru(CN)$_5$DTDP]$^{3-}$ ion, the platinum anode was covered by a brownish solid while the solution became colorless. The electrode could not be cleaned by electrochemical reduction, by reversing the electrode polarity.

**Kinetic Measurements.** The aquation of the DTDP complexes was studied in the presence of a large excess of dimethyl sulfoxide (DMSO) as auxiliary ligand at 25 ± 0.2 °C, as follows:

$$[MA_5DTDP]^n + H_2O \underset{k_{DTDP}}{\overset{k_{-DTDP}\ \text{slow}}{\rightleftarrows}} [MA_5(H_2O)]^n + DTDP$$

$$[MA_5(H_2O)]^n + DMSO \xrightarrow{\text{fast}} [MA_5DMSO]^n + H_2O$$

$n$ = 3– when M = Ru and A = CN$^-$; $n$ = 2+ when M = Ru and A = NH$_3$.

An aliquot of the solution of the desired complex was added to a solution containing DMSO, the supporting electrolyte, and the previously adjusted hydrogen ion concentration (both solutions were previously deaerated and thermostated at 25 ± 0.2 °C). The disappearance of the complexes [ML$_5$DTDP]$^n$ was monitored spectrophotometrically at the $\lambda_{max}$ of the MLCT bands of the respective DTDP derivatives.

In order to avoid contributions of the back-reaction, $k_{DTDP}$, the concentration of the [ML$_5$DTDP]$^n$ complexes was kept smaller than 1.0 × 10$^{-4}$ M.

Specific rate constants were calculated from the plots of $\log(A_\infty - A_t)$ *versus* time. These plots were linear for more than 3 half-lives.

**Determination of p$K_a$.** The pKa for the reactions

$$[M(CN)_5DTDPH]^{2-} + H_2O \rightleftarrows [M(CN)_5DTDP]^{3-} + H_3O^+$$

where M = Ru(II) and Fe(II), and

$$[Ru(NH_3)_5DTDPH]^{3+} + H_2O \rightleftarrows [Ru(NH_3)_5DTDP]^{2+} + H_3O^+$$

were measured spectrophotometrically.[11]

For the pentacyano complexes, the absorbance was measured at the $\lambda_{max}$ of the intraligand bands (IT), as a function of pH values.

The higher p$K_a$ of DTDP, as compared to pyrazine pz[12] and 2,6-dimethylpyrazine (dmpz)[13] pentacyano complexes, allows one to work under experimental conditions such that protonation of the cyanide ligands is not as critical as in the pz-containing systems.

For the pentaammine system, the absorbance was measured at the maxima of both the intraligand band (IT) and the charge transfer (MLCT) bands.

The p$K_a$ values for the system [Ru(NH$_3$)$_5$DTDP]$^{3+,2+}$ were also determined by cyclic voltammetry following standard procedures.[14]

The excited state p$K_a$ and p$K_a$* values were calculated using the expression

$$pK_a^* = pK_a + \frac{2.86(\nu_1 - \nu_2)}{2.3RT}$$

where p$K_a$ refers to the ground state and $\nu_1$ and $\nu_2$ are the MLCT band frequencies of the complex in the deprotonated and protonated forms, respectively.

**Apparatus.** The electronic spectra were recorded on a HP 8452A diode array spectrophotometer. The electrochemical measurements were performed using a PARC System Model 173 potentiostat/galvanostat, a Model 175 universal programmer and a RE 0074X-Y recorder and a Model 264A polarographic analyzer. For cyclic voltammetry a glassy carbon electrode was used as the working electrode vs SCE as reference, with a platinum wire as a auxiliary electrode. For electrolysis experiments, a platinum net (area of 13.6 cm$^2$) was used as the working electrode.

The IR and $^1$H NMR spectra were recorded on Nicolet 55XC and Bruker AC-200 spectrometers, respectively. The NMR spectra were performed with D$_2$O solutions, using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard. The NMR assignments have been checked by decoupling experiments.

The near-infrared spectra were recorded on a Cary 17D spectrophotometer, in D$_2$O, at 25 °C.

The [II,III] species have been generated in the D$_2$O solutions by oxidation of the corresponding [II,II] complexes with Br$_2$.

## Results

The spectral characteristics and the band assignments for the electronic spectra of the [Ru(NH$_3$)$_5$DDTP]$^{2+}$, [Ru(CN)$_5$DDTP]$^{3-}$, and [Fe(CN)$_5$DDTP]$^{3-}$ complexes are summarized in Table 1. The ligand field bands were not observed and are probably overlapped by the more intense charge transfer bands. These spectra exhibit a metal-to-ligand charge transfer band, in addition to the bands of the ligand.

The high intensity absorption bands below 300 nm are similar in energy and intensity to those observed for the free ligand[15] and therefore have been assigned to ligand internal transitions.

The MLCT bands have been attributed to electronic transitions from the B$_2$ level (d$_\pi$) of the metal to the B$_2$ level ($\pi$*) of the coordinated aromatic ring.[3]

The LMCT band for the solutions containing the [Ru(NH$_3$)$_5$DTDP]$^{3+}$ complex ion could be observed at 314 nm despite some overlapping with IT bands. The LMCT band for [Fe(CN)$_5$DTDP]$^{2-}$ could not be assigned due to the strong absorption of the ligand below 300 nm.

The electronic spectra of solutions containing the [Ru(NH$_3$)$_5$DTDP]$^{2+}$, [Ru(CN)$_5$DTDP]$^{3-}$, and [Fe(CN)$_5$DTDP]$^{3-}$ ions are sensitive to changes in pH. In the pH range 7.0–3.0, the MLCT bands exhibit bathochromic shifts due to the protonation at the uncoordinated pyridinic DTDP nitrogen atom. The spectral characteristics of solutions containing the protonated complexes are shown in Table 1.

At hydrogen ion concentrations higher than 10$^{-3}$ M, the [Ru(CN)$_5$DTDPH]$^{3-}$ and [Fe(CN)$_5$DTDPH]$^{2-}$ complexes undergo a second protonation, at the cyanide groups. When the complexes are fully protonated, the LMCT bands exhibit an hypsochromic shift, (see Table 1).

The formal potentials for the Ru(III)/Ru(II) couples on the title complexes are shown on Table 1. On the basis of cyclic voltammetric data, the Ru(III)/Ru(II) couples are reversible

(11) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill Co.: New York, 1969.
(12) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 1117.
(13) Toma, H. E.; Staddler, E. *Inorg. Chem.* **1985**, *24*, 3085.
(14) Meites, L. *Polarographic Techniques*; 2nd ed.; Interscience: New York, 1965; Chapter 5.
(15) Grassetti, D. R.; Murray, J. F. *Arch. Biochem. Biophys.* **1987**, *119*, 41.

**Table 1.** Formal Potential and Spectral Data for Ruthenium(II) and Iron(II) Complexes

| species | $E°'_{M(III)/M(II)}$,[a] | $\lambda^{MLCT}$,[b] nm | ε, $M^{-1} cm^{-1}$ | $f$[c] | $\lambda^{IT}$,[d] nm | ε, $M^{-1} cm^{-1}$ |
|---|---|---|---|---|---|---|
| | | | | | 256 | $1.5 \times 10^4$ |
| $[Ru(NH_3)_5DTDP]^{2+}$ | 0.095 | 458 | $1.3 \times 10^4$ | 0.286 | 286 (sh) | $1.0 \times 10^4$ |
| $[Ru(NH_3)_5 4,4'\text{-bpy}]^{2+}$ | | 475[i] | | | | |
| $[Ru(NH_3)_5py]^{2+}$ | 0.058[f] | 407[e] | | | | |
| $[Ru(NH_3)_5DTDPH]^{3+}$ | | 474 | $1.4 \times 10^4$ | | 292 | $1.2 \times 10^4$ |
| | | | | | 260 (sh) | $1.1 \times 10^4$ |
| $[Fe(CN)_5DTDP]^{3-}$ | 0.255 | 412 | $5.0 \times 10^3$ | 0.150 | 286 (sh) | $1.0 \times 10^4$ |
| | | | | | 252 | $1.5 \times 10^4$ |
| $[Fe(CN)_5 4,4'\text{-bpy}]^{3-}$ | | 432[i] | | | | |
| $[Fe(CN)_5py]^{3-}$ | 0.288[g] | 362[e] | | | | |
| $[Fe(CN)_5DTDPH]^{2-}$ | | 436 | $5.0 \times 10^3$ | | 294 | $1.3 \times 10^4$ |
| | | | | | 264 (sh) | $1.0 \times 10^4$ |
| $[HCN(CN)_4FeDTDPH]^{-}$ | | 400 | $\sim 10^3$ | | 294 | $\sim 10^4$ |
| | | | | | 264 (sh) | $\sim 10^4$ |
| $[Ru(CN)_5DTDP]^{3-}$ | 0.710 | 348 | $6.0 \times 10^3$ | 0.222 | 286 (sh) | $8.0 \times 10^3$ |
| | | | | | 256 | $1.4 \times 10^4$ |
| $[Ru(CN)_5 4,4'\text{-bpy}]^{3-}$ | | 365[e] | | | | |
| $[Ru(CN)_5py]^{3-}$ | 0.710[h] | 316[e] | | | | |
| $[Ru(CN)_5DTDPH]^{2-}$ | | 360 | $4.0 \times 10^3$ | | 294 | $1.2 \times 10^4$ |
| | | | | | 262 (sh) | $9.5 \times 10^3$ |

[a] Versus SCE, 25 °C, $\mu$ = 0.10 M ($NaCF_3COO$); $C_{H^+} = 1.0 \times 10^{-6}$ M. [b] MLCT = metal-to-ligand charge transfer band. [c] Oscillator strength, calculated as described in ref 21. [d] IT = intraligand band; sh = shoulder. [e] Reference 17. [f] Reference 25. [g] Reference 24. [h] Reference 23. [i] Reference 19.

**Table 2.** $pK_a$, $pK_a^*$, and $\Delta pK_a^*$ Data for DTDP Complexes and the Free Ligand

| species | $pK_a$[a] | $pK_a^*$[a] | $\Delta pK_a^*$[d] |
|---|---|---|---|
| $[Fe(CN)_5DTDP]^{2-}$ | 4.40 | 7.19 | 2.79 |
| $[Ru(CN)_5DTDPH]^{2-}$ | 4.70 | 6.70 | 2.00 |
| $[Ru(NH_3)_5DTDPH]^{3+}$ | 5.25[a,b] | 6.78 | 1.53 |
| $[Ru(NH_3)_5DTDPH]^{4+}$ | 3.20 | | |
| $DTDPH^+$ | 4.80[c] | | |

[a] Uncertainties of ±0.10 $pK_a$ units. [b] Obtained independently through spectrophotometric and voltammetric measurements. [c] Reference 37. [d] $\Delta pK_a^* = pK_a^* - pK_a$.

for all the complexes studied. The Fe(III)/Fe(II) couple becomes irreversible as the concentration of the protonated form in solution increases.

The changes in $\Delta E_{1/2}$ as a function of the hydrogen ion concentration are smaller for the Ru(III)/Ru(II) couple in $[Ru(CN)_5DTDP]^{3-/2-}$ than in the $[Ru(NH_3)_5DTDP]^{3+/2+}$ system.

The cyclic voltammograms of solutions containing the $[Ru(NH_3)_5DTDP]^{2+}$ ions show reversibility over a wide range of hydrogen ion concentrations. Voltammetric experiments allow the evaluation of the $pK_a$ for the acids $[Ru(NH_3)_5DTDPH]^{3+}$ and $[Ru(NH_3)_5DTDPH]^{4+}$. The $pK_a$ value for the Ru(II) species, calculated from the cyclic voltammetry data, is in very good agreement with the one calculated from spectrophotometric experiments (see Table 2).

The infrared spectra of the DTDP complexes are the superposition of the ligand bands and the bands of the corresponding aquo complex. The $\nu(CN_{ax})$, bands appear at 2093 (sh) and 2100 (sh) $cm^{-1}$ and the $\nu(CN_{eq})$ bands appear at 2051 (s) and 2057 (s) $cm^{-1}$, for the Fe(II) and Ru(II) complexes, respectively. The infrared spectra of $[Ru(NH_3)_5DTDP](PF_6)_2$, $\{[Ru(NH_3)_5]_2DTDP\}(PF_6)_4$, $Na_3[Fe(CN)_5DTDP]\cdot 4H_2O$, and $Na_6[\{Fe(CN)_5\}_2DTDP]\cdot 6H_2O$ are very similar, exhibiting some group frequencies displacements within the limits of the experimental error (±5 $cm^{-1}$).

The proton NMR spectrum of the 4,4′-ditiodipyridine ligand consists of two multiplets in an $A_2X_2$ system.[16]

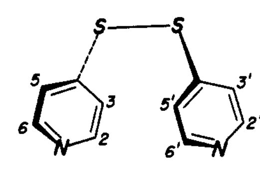
The chemical shifts of 8.44 and 7.42 ppm were assigned to the 2,6- and 3,5-protons of the two DTDP pyridine rings, respectively. The $DTDPH_2^{2+}$ $^1H$ NMR spectrum exhibits two multiplets centered at 8.54 and 7.91 ppm assigned to the 2,6-protons ($H_2$, $H_6$ and $H_{2'}$, $H_{6'}$) and 3,5-protons ($H_3$, $H_5$ and $H_{3'}$, $H_{5'}$), respectively. The observed Δδ on $DTDPH_2^{2+}$, with respect to the DTDP molecule, is −0.10 for the 2,6-protons and −0.49 for the 3,5-protons.

(16) Forchioni, A.; Pappalardo, G. *Spectrochim. Acta* **1975**, *31A*, 1367.

**Table 3.** Rate and Equilibrium Constants for Ligand Substitution in $[MA_5L]^n$ Complexes

| $[MA_5L]$ | $k_{-1}$, $s^{-1}$ | $K$, $M^{-1}$ |
|---|---|---|
| $[Fe(CN)_5py]^{3-}$ | $1.1 \times 10^{-3}$ [a] | $3.3 \times 10^5$ [a] |
| $[Fe(CN)_5DTDP]^{3-}$ | $1.1 \times 10^{-3}$ | |
| $[Ru(CN)_5py]^{3-}$ | $3.34 \times 10^{-5}$ [b] | $1.6 \times 10^5$ [b] |
| $[Ru(CN)_5DTDP]^{3-}$ | $1.2 \times 10^{-4}$ | |
| $[Ru(NH_3)_5py]^{2+}$ | $4.6 \times 10^{-5}$ [c] | $2.7 \times 10^7$ [c] |
| $[Ru(NH_3)_5DTDP]^{2+}$ | $4.5 \times 10^{-5}$ | |

[a] Reference 25. [b] Reference 24. [c] Reference 26.




When coordinated to the $Ru(NH_3)_5^{2+}$, $Ru(CN)_5^{3-}$, and $Fe(CN)_5^{3-}$ moieties, the DTDP moieties present four multiplets in their spectra as shown in Figure 1. These aspects will be discussed in the next section.

The aquation of the DTDP complexes was studied as described in the experimental section, and the results for $k_{-DTDP}$ are shown in Table 3. The results for $k_{obs}$ obtained for each complex with DMSO concentrations higher than 0.50M were very reproducible (±9%). Under these conditions, the aquation reaction becomes independent of the auxiliary ligand (DMSO) concentration.

## Discussion

The MLCT bands of the DTDP complexes were attributed to $nd_\pi \rightarrow p_\pi^*$ transitions. The $4d_\pi$ orbitals of the Ru(II) are closer in energy to the $p_{\pi^*}$ orbitals of the pyridine ring in the pentaammine complex than in the pentacyano species.[17] As inferred from the DTDP complexes' electronic spectra, the substitution of all the $NH_3$ ligands by $CN^-$ groups in the coordination sphere of Ru(II) stabilizes the $4d_\pi$ orbitals of the metal by about 20 kcal $mol^{-1}$. As a result of better mixing between the metal $4d_\pi$ orbitals with the $p_{\pi^*}$ (DTDP) orbitals, an oscillator strength of 0.286 is observed for the MLCT in the $[Ru(NH_3)_5DTDP]^{2+}$ species compared to 0.222 for the $[Ru(CN)_5DTDP]^{3-}$ complex. Again, if we compare the energy of the MLCT bands in the $[Fe(CN)_5DTDP]^{3-}$ and

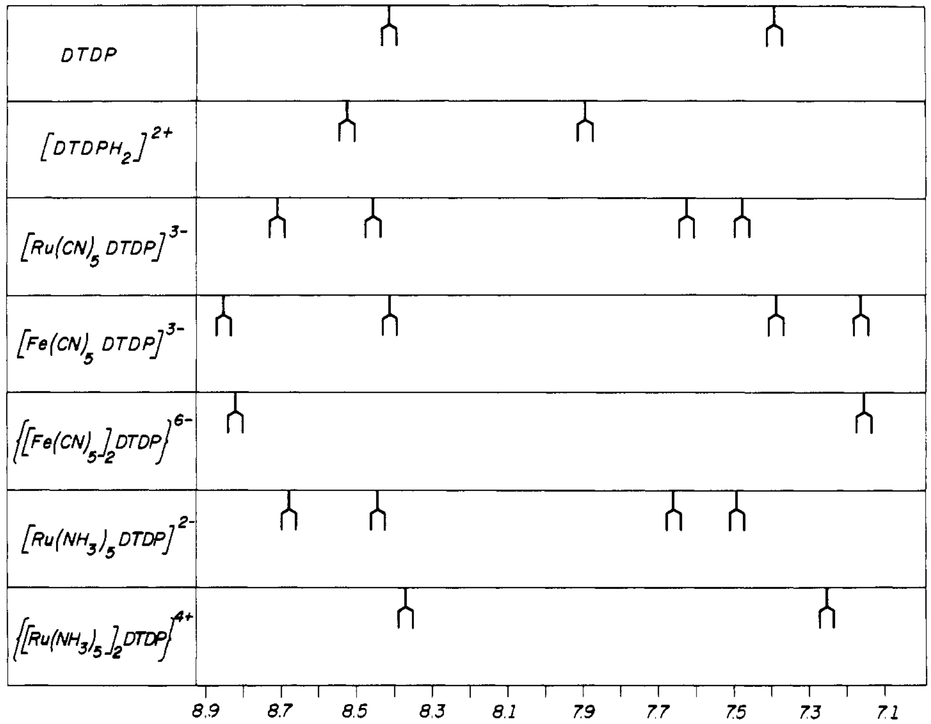



**Figure 1.** Simplified diagram for the $^1$H nuclear magnetic resonance spectra of ruthenium and iron complexes.

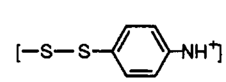
$[Ru(CN)_5DTDP]^{3-}$ complexes, a stabilization of 13 kcal mol$^{-1}$ is observed favoring the 3d$_\pi$ orbitals relative to the 4d$_\pi$ orbitals. An increase of about 50% is observed in the oscillator strength for the Ru(II) complex in comparison with the Fe(II) analogue, (see Table 1).

As can be observed in Table 1, the MLCT absorptions for the $[Ru(NH_3)_5DTDP]^{2+}$ and $[Ru(CN)_5DTDP]^{3-}$ species occur at lower energy than those of the corresponding py complexes, (7.8, 8.2, and 9.6 kcal mol$^{-1}$, respectively), but at higher energy than the 4,4′-bipyridine analogues (2.2, 3.8, and 3.3 kcal mol$^{-1}$, respectively). As pointed out by Johnson and Shepherd,[17] little mixing is expected to occur between the metal and ligand orbitals in the $[Fe(CN)_5L]^{3-}$ series. Therefore, the difference between the MLCT energies for the $[Fe(CN)_5L]^{3-}$ series can be considered a reasonable estimative of the energy differences between the L $\pi^*$ orbitals. On the basis of this simplified model,[17] the Table 1 data indicate that the $\pi^*$ orbital in the DTDP ligand is about 9 ± 1 cal mol$^{-1}$ more stable than the corresponding $\pi^*$ orbital in the py ligand but about 3 ± 1 kcal mol$^{-1}$ less stable than the $\pi^*$ orbital in the 4,4′-bipy ligand.

The MLCT absorption for the binuclear $\{[Ru(NH_3)_5]_2DTDP\}^{4+}$ species was assigned at 466 nm ($\epsilon$ = 1.9 × 10$^4$ M$^{-1}$ cm$^{-1}$), slightly red-shifted (≅1 kcal) with respect to the corresponding transition for the complex ion $[Ru(NH_3)_5DTDP]^{2+}$. For the $[\{Fe(CN)_5\}_2DTDP]^{6-}$ species the MLCT band occurs at the same energy observed for the mononuclear species: 412 nm ($\epsilon$ = 9.3 × 10$^3$ M$^{-1}$ cm$^{-1}$).

Through Gaussian deconvolution of the electronic spectra in the 300-220-nm region, a group of three bands could be identified for all the complexes under study. They have been attributed to ligand absorptions and are located in the following ranges: 280–286 nm ($\epsilon$ = (1.0–0.80) × 10$^4$ M$^{-1}$ cm$^{-1}$); 256–252 nm ($\epsilon$ = (1.5–1.3) × 10$^4$ M$^{-1}$ cm$^{-1}$) 227–223 nm ($\epsilon$ = (1.5–1.0) × 10$^4$ M$^{-1}$ cm$^{-1}$).

On protonation of the DTDP complexes, the MLCT bands are shifted to lower energy with respect to those observed in the corresponding deprotonated species (see Table 1). The observed bathochromic shifts, upon protonation of the DTDP ligand, can easily be understood as the stabilization of the p$_{\pi^*}$ orbital by the effect of the presence of the electron withdrawing group




bound to the pyridine ring, coordinated to the metal center. On the basis of these bathochromic shifts, the stabilization of the p$_{\pi^*}$ orbitals could be estimated as being 2.1 kcal mol$^{-1}$ for the pentaammine complex and 2.7 and 3.8 kcal mol$^{-1}$ for the Ru(II) and Fe(II) pentacyano species, respectively.

Although the observed p$_{\pi^*}$ stabilization energies are small they are significant since they reflect the effect of a proton on the pyridine ring, separated from the $[ML_5py]^{2+}$ moiety by a disulfide bridge.

Zang and Shepperd[18] recently pointed out the advantages of using 4,4′-bipH$^+$ complexes instead of the corresponding pzH$^+$ species for the analysis of the Ru(II) d$_\pi$ back-donation, based on p$K_a$, p$K_a$*, and Δp$K_a$* data. In the 4,4′-bipyH$^+$ complexes the protonated nitrogen is more isolated from the ruthenium center and therefore less exposed to the metal and ligand environment electrostatic effects than in the pzH$^+$ species.

Since the ligand DTDP resembles more 4,4′-bipy than pz, it could be expected that the trends observed on p$K_a$, p$K_a$* and Δp$K_a$* on the DTDP complexes will follow the same trend observed for 4,4′-bipy systems.

Our experimental data did not confirm this prediction for the DTDPH$^+$ systems.

In the DTDP pentaammine complexes the effect is similar to those observed for the pyrazine system.[3,12,13] Due to the predominance of the back-bonding Ru(II) → DTDPH$^+$, over the electron density polarization by the Ru(II) center, $[Ru(NH_3)_5DTDPH]^{+3}$ is a weaker acid than DTDPH$^+$ by 0.45 p$K_a$ units. Although this difference is much smaller than that observed for the pyrazine system,[3] it becomes relevant when compared with similar data for related bipyridine systems.[19] In these cases the negative Δp$K_a$ data have been interpreted assuming[23] that the

(17) Johnson, C. R.; Shephard, R. E. *Inorg. Chem.* **1983**, *22*, 2439.

(18) Zhang, S.; Shepherd, R. W. *Transition Met. Chem. (Weinheim, Ger.)* **1992**, *17*, 199.

(19) Lavalle, D. K.; Fleisher, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583.

major effect of complexation over these ligands is the polarization of the electron density by the Ru(II) ion.

In the $[Ru(NH_3)_5DTDP]^{2+}$ species, an increase in basicity on the nitrogen atom of the uncoordinated pyridine ring is observed as a consequence of the efficiency of the S–S bridge to conduct a flow of electron density. Conversely, in the absence of the back-bonding and since the polarization effects of the Ru(III) are greater than that of Ru(II), the acid $[Ru(NH_3)_5DTDPH]^{+4}$ exhibits a p$K_a$ value which is 1.40 units smaller than that of the free $DTDPH^+$ ion.

The p$K_a$ values for the acids $[Ru(CN)_5DTDPH]^{2-}$ and $DTDPH^+$ are about the same within the limits of the experimental error. Similar results have been described in the literature[12,13] regarding the $[Ru(CN)_5dmpzH]^{2-}$ and $[Ru(CN)_5pzH]^{2-}$ systems and the corresponding free ligands. The back-bonding effects of the sixth ligand in the ruthenium(II) pentacyano complexes due to the presence of good $\pi$-acids— the cyanides— are smaller than the ones observed for $[Ru(NH_3)_5DTDP]^{2+}$.

However, the same cannot be argued for the polarization effects of the metal center, in the cyanometalated species. Despite the difference in formal charge between $DTDPH^+$ and $[Ru(CN)_5$-$DTDPH]^{2-}$, the p$K_a$ values differ by only 0.10 unit. The $[Fe(CN)_5DTDPH]^{2-}$ acid is 0.40 p$K_a$ unit stronger than the corresponding free acid $DTDPH^+$, exhibiting the same behavior as found for the $[Fe(CN)_5dmpzH]^{2-}$ and $[Fe(CN)_5pzH]^{2-}$ acids.[11,12] For the three iron pentacyano complexes discussed above, the $\sigma$ polarization effects on the Fe(II) $\leftarrow$ L bond must dominate over the back-bonding of Fe(II) $\rightarrow$ $DTDPH^+$.

The $\Delta pK_a^*$, the difference between the pKa values of the ground and excited state, is an indicator of the mixing of the metal and the ligand orbitals.[3,20–22] The higher the $\Delta pK_a^*$ value, the smaller will be the degree of mixing of the metal and ligand orbitals in the ground state and therefore the back-bonding M $\rightarrow$ L will also be smaller. On the basis of this argument and considering the data in Table 2, the extent of the back-bonding M $\rightarrow$ DTDP should decrease in the following sequence: $[Ru(NH_3)_5]^{+2}$ > $[Ru(CN)_4]^{3-}$ > $[Fe(CN)_5]^{3-}$. This sequence is in agreement with the oscillator strength values calculated for the MLCT bands of the DTDP derivatives; see Table 1.

The different environment of the ligands will also affect the stabilization of the M(II) $d_\pi$ orbitals and therefore the $E^{\circ\prime}_{M(III)/(II)}$ potentials. The cyanides being strong $\pi$-acids stabilize the $d_\pi$ metal orbitals of the $[Fe(CN)_5DTDP]^{3-}$ and $[Ru(CN)_5DTDP]^{3-}$ complexes through $d_\pi \rightarrow p_\pi^*(CN^-)$ back-bonding interactions. The $NH_3$ ligands in the $[Ru(NH_3)_5DTDP]^{2+}$ complex are considered as $\pi$-innocent ligands and do not play a role in the metal center stabilization by back-bonding.

The $[Ru(CN)_5L]^{2-/3-}$ (L = py, pz,[23–25] DTDP) potentials not only are the highest in the monomer series but also show very little dependence on the nature of the sixth ligand. Actually, the $E_{1/2}$ = 0.72 ± 0.010 V value observed for the couple $[Ru(CN)_6]^{4-/3-}$, under the same experimental conditions as the title complexes, is very close to the ones found for the couples $[Ru(CN)_5L]^{2-/3-}$ (L = py, pz, DTDP), indicating that the sixth ligand competes in disadvantage with the cyanides in the electrochemical stabilization of the Ru(II) center.

The more positive the $E_{1/2}$ values for the couples M(III)/M(II) in the $[MA_5L]^n$ complexes (M = Fe, Ru), the stronger will be the stabilization of the metal(II) centers by the $d_\pi$–$p_\pi^*$ back-bonding between M(II) and L.[23–29] On the basis of $E_{1/2}$ data (Table 1) and the energy of the MLCT for these complexes, the ligand DTDP behaves as stronger $\pi$-acid than py.

Despite the different dimensions of py and DTDP, the rate of aquation of DTDP ($k_{-DTDP}$) and pyridine ($k_{-py}$) from $[Fe(CN)_5L]^{3-}$ and $[Ru(NH_3)_5L]^{2+}$ are equivalent (Table 3).[5,12,13,17,26–30] On the $[Ru(CN)_5L]^{3-}$ species, DTDP aquates only 3.6 times faster than py.

Substitution reactions for the $[MA_5L]^n$ systems[5,12,13,17,26–29] show that the stability of the complex formed, $[MA_5L]^n$, is not dictated by the rate of the complex formation but is extremely sensitive to the rate of L aquation ($k_{-L}$). Thus the affinities of the $[MA_5]^n$ moieties for py and DTDP are expected to be similar.

The high affinity of the $[MA_5]^n$ fragments for DTDP and the slow aquation of the DTDP ligand from $[MA_5DTDP]^n$ species (see Table 3) show that these complexes are good candidates for building blocks in the synthesis of binuclear and trinuclear complexes.

The affinity of the $[MA_5]^n$ moiety for the DTDP ligand increases in the following order: $[Fe(CN)_5]^{3-} < [Ru(CN)_5]^{3-} < [Ru(NH_3)_5]^{2+}$ (Table 3).

The proton NMR spectra of all DTDP monomer complexes consist of four multiplets. The features of these spectra are consistent with the coordination of DTDP to the metal centers in the ratio 1:1 via the nitrogen atom of one of the pyridine rings.

Two of the multiplets originate from 2,6- and 3,5-protons of the pyridine ring near the metal centers and the other two originate from 2,6- and 3,5-protons of the remote pyridine ring.

The analysis of the proton chemical shifts of the (4,4'-dithiodipyridine)pentaammineruthenium(II) monomer shows multiplets at 8.45 and 7.50 ppm, which are in the same region as found for the 2,6- and 3,5-protons of the free DTDP molecule (8.44 and 7.42 ppm, respectively). These have been assigned to the $H_2'$, $H_6'$ and $H_3'$, $H_5'$ protons of the remote pyridine ring, respectively.

The multiplets at 8.68 and 7.67 ppm were assigned to the $H_2$, $H_6$ and $H_3$, $H_5$ centers, respectively. These attributions were made on the basis of the similarity in the chemical shift change observed in pyridine, 4,4'-bipyridine, and 1,2-bis(4-pyridyl)-ethylene molecules upon complexation.[19]

It is not clear for us the reason for the downfield shift of both 2,6- (–0.24) and 3,5-protons (–0.25) observed for $[Ru(NH_3)_5$-$DTDP]^{2+}$ with respect to the free DTDP molecule.

Contrary to the back-bonding Ru(II) $\rightarrow$ py arguments, the chemical shift suggests a decrease in the $\pi$-electron density in the pyridine ring. This apparent conflict can be understood if the metal center effects are considered. The Ru(II) ion anisotropic effect in the distortion of the H 1s orbital spatial distribution could lead to proton deshielding.[19,30] Therefore, the observed proton chemical shift might reflect the predominance of the Ru(II) anisotropy effect over the Ru(II) $\rightarrow$ py back-bonding.

The NMR spectra of the binuclear $\{[Ru(NH_3)_5]_2DTDP]^{4+}$ and $[\{Fe(CN)_5\}_2DTDP]^{6-}$ species resemble the one of the free ligand. The multiplet at 8.37 and 7.26 ppm for ruthenium complex, (8.84 and 7.17 ppm for iron species), have been attributed to the 2,6- and 3,5-protons respectively.

In the interpretation of the $[Ru(CN)_5DTDP]^{3-}$ and $[Fe$-$(CN)_5DTDP]^{3-}$ spectra, the anisotropy of the cyanide ligands must also be taken into account. The anisotropy of the cyanides due to the perpendicular induced field at the C≡N bonds could deshield the 2,6-protons of the coordinated pyridine ring. This phenomenum is more effective for the 2,6-protons due to the unfavorable distance between the cyanide ligands and the 3,5-protons of the coordinated pyridine ring.

(20) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Chem.* **1967**, *12*, 131.
(21) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984.
(22) Gray, H. B.; Beach, N. A. *J. Am. Chem. Soc.* **1963**, *85*, 2922.
(23) Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1985**, *24*, 2398.
(24) Toma, H. E.; Creutz, C. *Inorg. Chem.* **1977**, *16*, 545.
(25) Hrepic, M. V.; Malin, J. M. *Inorg. Chem.* **1979**, *18*, 409.
(26) Hoddenbagh, J. M. A.; Macartney, D. H. *Inorg. Chem.* **1986**, *25*, 2099.
(27) (a) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039. (b) *Inorg. Chem.* **1973**, *12*, 2080.
(28) Taube, H. *Comments Inorg. Chem.* **1981**, 17 and references therein.
(29) Macartney, D. H. *Rev. Inorg. Chem.* **1988**, *9*, 101.
(30) Miller, R. G.; Stauffer, R. D.; Fahey, D. R.; Parnell, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 1511.

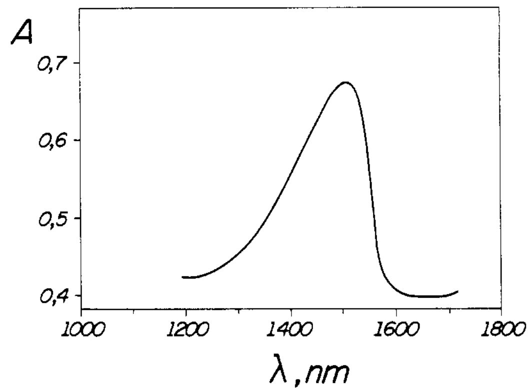



**Figure 2.** Near-infrared spectra for the mixed valence species [$Ru^{II}$,$Ru^{III}$] in $D_2O$.

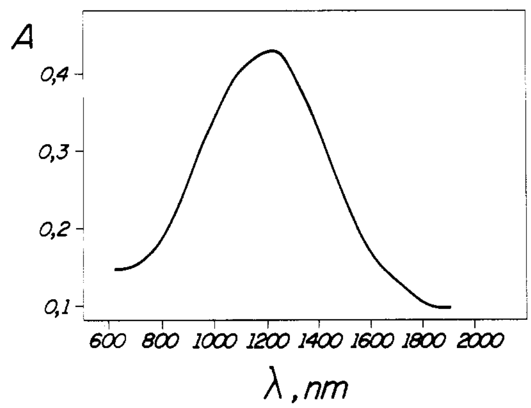



**Figure 3.** Near-infrared spectra for the mixed-valence species [$Fe^{II}$,$Fe^{III}$] in $D_2O$.

On the basis of the preceeding arguments the peaks centered at 8.86 and 8.72 ppm in the spectra of $Fe(CN)_5DTDP^{3-}$ and $Ru(CN)_5DTDP^{3-}$, respectively, were assigned to $H_2$ and $H_6$ absorptions of the DTDP coordinated pyridine ring.

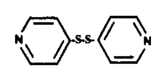
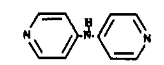
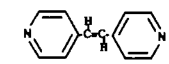
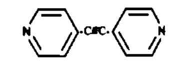
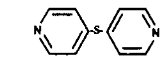
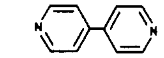
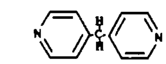
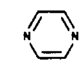
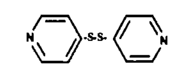
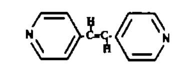
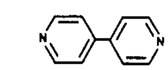
The downfield shift of the 2,6-protons chemical shift of $[Ru(CN)_5DTDP]^{3-}$ ($\Delta\delta$ = –0.28), is smaller than that observed for $[Fe(CN)_5DTDP]^{3-}$ ($\Delta\delta$ = –0.42), possibly suggesting that the $d_\pi \rightarrow p_y$ back-bonding ability of Ru(II) is greater than that of the Fe(II) center.

The multiplets at 8.42 and 8.46 ppm in the $[Fe(CN)_5DTDP]^{3-}$ and $[Ru(CN)_5DTDP]^{3-}$ spectra, respectively, are very close to the observed chemical shifts for 2,6-protons in the DTDP free molecule and therefore have been assigned to the absorption of $H_2'$ and $H_6'$ of the DTDP uncoordinated pyridine ring.

The different nature of shifts in the chemical shift of 3,5-protons of the $[Fe(CN)_5DTDP]^{3-}$ and $[Ru(CN)_5DTDP]^{3-}$ spectra deserve some comments. For the Fe(II) complex the peaks centered at 7.41 ppm are very close to the 3,5-proton absorption of the free DTDP molecule and therefore have been attributed to $H_3'$, $H_5'$. The absorption at 7.18 ppm was assigned to $H_3$, $H_5$, and since the cyanide anisotropy is not expected to have noticeable influence over the meta protons, the observed chemical shift variation ($\Delta\delta$ = +0.34) could be substantially due to back-bonding effects.

This behavior was not observed for the corresponding $[Ru(CN)_5DTDP]^{3-}$ complex. The chemical shifts for the 3,5-protons $H_3$, $H_5$ and $H_3'$, $H_5'$, occur at 7.64 and 7.49 ppm, respectively. This observation suggests that the anisotropic effect of Ru(II), deshielding the protons in the coordinated pyridine ring ($\Delta\sigma$ = –0.22), probably overcomes the electron density increase due to the $4d_\pi \rightarrow p_\pi$ back-bonding effect. This effect has also been observed for the $[Ru(NH_3)_5DTDP]^{3+}$ system, where the Ru(II) → DTDP back-bonding is greater than in $[Ru(CN)_5DTDP]^{3-}$.

**Table 4.** Near-IR Absorption Data and Comproportionation Constants[a]

| Metal system | Ligand | λ (nm) | ε ($M^{-1}cm^{-1}$) | $H_{AB}$ ($cm^{-1}$) | $K_c$ |
|---|---|---|---|---|---|
| $[Ru(NH_3)_5]_2$ |  | 1,570 | 5,000 | 3,300 | $4 \times 10^6$ |
| |  | 1,500 | 4,260 | 855 | $8 \times 10^4$ |
| |  | 920 | 1,010 | 500 | $5 \times 10^2$ |
| |  | 960 | 760 | 305 | 2 x 10 |
| |  | 920 | 640 | 285 | 14 |
| |  | 855 | 70 | 150 | |
| |  | 1,030 | 920 | 390 | 2 x 10 |
| |  | 810 | 30 | 100 | 9.8 |
| $[Fe(CN)_5]_2$ |  | 1,200 | 2,200 | 900 | $5 \times 10^2$ |
| |  | 1,195 | 900 | 466 | $1 \times 10^2$ |
| |  | 1,300 | 600 | 220 | 4 |
| |  | 1,200 | 1,100 | 390 | 4 |

[a] Data collected from ref 34 except for L = DTDP.

The relevance of the second sulfur atom bridging the two pyridine rings can be evaluated comparing the chemical characteristics of bis(4-pyridyl) sulfide (DPS)[31] and DTDP as ligand on Ru(II). The $\lambda_{max}$ values of the MLCT band for both acids $[Ru(NH_3)_5DPSH]^{3+}$ are experimentally the same (474 nm), and the molar absortivity for the $DTDPH^+$ species (1.4 × $10^4$ $M^{-1}$ $cm^{-1}$) is only 2.2 times bigger than the observed[31] values for the $DPSH^+$ species (6.3 × $10^3$ $M^{-1}$ $cm^{-1}$).

The voltammetric spectra for the $[\{Ru(NH_3)_5\}_2DTDP]^{4+}$ species exhibit two well-defined one electron reversible electrochemical processes $(E_{1/2})_1$ = –0.130 V, $(E_{1/2})_2$ = 0.160 V) and an intervalence band (see Figure 2) at 1500 $cm^{-1}$ ($\epsilon$ = 4.3 × $10^3$ $M^{-1}$ $cm^{-1}$). For the $[II,III]^{5+}$ species, the band width at half-height (1.24 × $10^3$ $cm^{-1}$) is significantly narrower than that calculated by Hush's equation (3.92 × $10^3$ $cm^{-1}$) and the electronic coupling values $H_{AB}$ = 855 $cm^{-1}$ indicates a strong coupling between the two ruthenium centers. The high values of the comproportionation constant $K_c$ = 8 × $10^4$, for the reaction

$$[2,2]^{4+} + [3,3]^{+6} \overset{K_c}{\rightleftarrows} 2[3,2]^{5+}$$

calculated from the $E_{1/2}$ data above, strongly supports our conclusions based on the near-infrared data.

The $[\{Ru(NH_3)_5\}_2DPS]^{4+}$ complex ions exhibit[31] only a one stage redox process ($E_{1/2} \cong 0.12$ V), with a peak-to-peak separation larger than the expected for a reversible one electron process. This voltammetric spectrum was interpreted[31] assuming the existence of two stages [2,2]–[2,3]–[3,3] with very close values of half-wave potentials. The intervalence transition for the

(31) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512.

$[\{Ru(NH_3)_5\}_2DPS]^{5+}$ species was observed at 855 nm ($\epsilon$ = 70 $M^{-1}$ $cm^{-1}$), $\Delta\nu_{1/2}$ = 7.3 × $10^3$ $cm^{-1}$, and $H_{AB}$ = 150 $cm^{-1}$). These data[31] are consistent with the voltammetric spectra for the binuclear $[\{Ru(NH_3)_5\}_2DPS]^{4+}$ species and taken together unambiguously indicate a weak coupling between the two ruthenium centers. Indeed, only weak coupling has been reported for a series of binuclear ruthenium complexes containing two separated sulfur atoms in the bridging ligand.

Experimental data collected for the $[\{Fe(CN)_5\}_2DTDP]^{6-}$ species also provide strong evidence for the electron delocalization through the "S–S" bridge. The half-wave potentials for the two reversible electrochemical process ($(E_{1/2})_1$ = 0.155 and $(E_{1/2})_2$ = 0.275 V) allows us to calculate $K_c$ as equal to 1 × $10^2$. The near-infrared band for the $[Fe^{II}, Fe^{III}]^{5-}$ ions, (see Figure 3), occurs at 1.195 nm ($\epsilon$ = 9.0 × $10^2$ $M^{-1}$ $cm^{-1}$), with $\Delta\nu_{1/2}$ = 4.02 × $10^3$ $cm^{-1}$ and $H_{AB}$ = 466 $cm^{-1}$.

Table 4 gives near-infrared characteristics and comproportionation constants[32,33] $K_c$ for related complexes of ruthenium and iron.

A noteworthy feature of the disulfide ligand came out when comparing the coupling between ruthenium centers and between iron centers on closely related bipyridine complexes.[32,33] As judged from near-infrared and voltammetric data, the "S–S" bridge provides more efficient electron delocalization than NH methylene, ethylene, and acetylene groups.

Another point that deserves some comments is the stability of the sulfur–sulfur bridge of the DTDP molecule. The free ligand is easily reduced by ascorbic acid or zinc amalgam yielding 4-mercaptopyridine.[34,35] However, when DTDP is coordinated to the Fe(II) or Ru(II) centers, the –S–S– bridge is quite stable and does not yield cleavage products in the reaction with reducing agents such as $N_3^-$, ascorbic acid, or zinc amalgam or by controlled potential electrolysis.

The change in the DTDP chemical reactivity upon coordination, as shown here clearly indicates electron delocalization through the –S–S– bridge and its relevance in electron transfer processes.

Binuclear complexes of Ru(II), Os(II), and Fe(II) with DTDP as bridging ligand are currently under investigation[36,37] at our laboratory. The results will be reported in a forthcoming paper.

**Acknowledgment.** The authors are thankful to the Brazilian agencies FAPESP, CAPES, and CNPq, for financial support and to Profs. Milan Trsic, Rudi van Eldik, and Augusto Coelho for reading the English manuscript.

(32) Creutz, C. *Prog. Inorg. Chem.* **1993**, *30*, 1 and references therein.
(33) Isied, S. S., *Metal Ions in Biological Systems*; Marcel Dekker: New York, 1991; Vol. 27, pp 1–56 and references therein.
(34) Bensk, K. G.; Koener, O.; Lohmann, W. *Biochem. Biophys. Res. Commun.* **1981**, *101* (1), 312.
(35) Fleming, J. E.; Bensch, K. G.; Sheiber, J.; Lohmann, W. *Z. Naturforsch., C: Biosci.* 1983, *38C*, 9, 859.
(36) Moreira, I. S.; Franco, D. W. *J. Chem. Soc., Chem. Commun.* **1992**, 5, 450.
(37) Moreira, I. S.; Franco, D. W. Manuscript in preparation.