

$s^{-1}$ , demonstrating a weak Ru-Ru interaction between the ruthenium(II) ions.

Less than 50% of the Ru(II) sites were excited to the phosphorescent state of the biruthenium(II) compound,  $[\text{Ru}(\text{bpy})_2]_2(\text{dpbime})^{4+}$ , as is shown in Figure 9. The laser intensity was large enough to convert the majority of the mononuclear compounds to the excited state. The low excitation efficiency of the biruthenium compounds, therefore, implies that the excitation of both of Ru(II) ions in the biruthenium compounds leads to annihilation of excited states.

The annihilation of the excited Ru(II) ions can be initiated by electron transfer to form a Ru(III) ion and a reduced bpy which are separated by the bridging ligand. The rapid back-electron-transfer may prevent detection ( $>10^7 \text{ s}^{-1}$ ). This speculation is more probable because intramolecular electron transfer in a mixed-metal (Ru(III) and Rh(II)) compound,  $(\text{bpy})_2\text{Ru}(\text{bpimH}_2)\text{Rh}(\text{bpy})^{5+}$ , was too fast to be detected by means of picosecond laser photolysis.<sup>28</sup> The electron transfer as the initial process of the annihilation is allowed from an energetic point of

view. That is, the ergonicity of electron transfer is calculated to be  $-(2 \times 2.0 - 0.83 - 1.71) \text{ eV}$  from the excitation energy and the redox potentials. Annihilation of excited states was postulated to occur between  $\text{Cr}(\text{CN})_6^{3-}$  moieties linked by  $\text{Ru}(\text{bpy})_2^{2+}$ .<sup>32</sup>

**Registry No.** bpimH, 1137-68-4; dpbime, 102948-77-6; Ru-(pbimH)<sub>3</sub><sup>2+</sup>, 80634-41-9; Ru(bpy)<sub>2</sub>(dpbime)<sup>2+</sup>, 137744-52-6; Ru(bpy)<sub>2</sub>-(bpimH)<sub>2</sub><sup>2+</sup>, 137729-41-0; Ru(dmpby)<sub>2</sub>(bpimH)<sub>2</sub><sup>2+</sup>, 137744-53-7; Ru(phen)<sub>2</sub>(bpimH)<sub>2</sub><sup>2+</sup>, 137744-54-8; [Ru(bpy)<sub>2</sub>]<sub>2</sub>(dpbime)<sup>4+</sup>, 137744-55-9; [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpimH)<sub>2</sub><sup>4+</sup>, 137744-56-0; [Ru(dmpby)<sub>2</sub>]<sub>2</sub>-(bpimH)<sub>2</sub><sup>4+</sup>, 137744-57-1; Ru(dmpby)<sub>2</sub>(bpimH)<sub>2</sub>Ru(phen)<sub>2</sub><sup>4+</sup>, 137744-58-2; Ru(bpy)<sub>3</sub><sup>2+</sup>, 15158-62-0; Ru(dmpby)<sub>3</sub><sup>2+</sup>, 32881-03-1; Ru(phen)<sub>3</sub><sup>2+</sup>, 22873-66-1; [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpimH)<sub>2</sub><sup>2+</sup>, 137744-59-3; [Ru-(bpimH)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, 80634-42-0; [Ru(bpy)<sub>2</sub>(dpbime)](ClO<sub>4</sub>)<sub>2</sub>, 137744-61-7; [Ru(bpy)<sub>2</sub>]<sub>2</sub>(dpbime)(ClO<sub>4</sub>)<sub>2</sub>, 137744-62-8; RuCl<sub>3</sub>, 10049-08-8; NaClO<sub>4</sub>, 7601-89-0; *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, 19542-80-4; HClO<sub>4</sub>, 7601-90-3; CF<sub>3</sub>COOH, 76-05-1; glycerol, 56-81-5; anthracene, 120-12-7.

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## Electronic Absorption Spectra of the Iron(II) Complexes of 2,2'-Bipyridine, 2,2'-Bipyrimidine, 1,10-Phenanthroline, and 2,2':6',2''-Terpyridine and Their Reduction Products

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The iron(II) complexes  $[\text{Fe}(\text{bpy})_3]^{2+}$  (I),  $[\text{Fe}(\text{bpym})_3]^{2+}$  (II),  $[\text{Fe}(\text{phen})_3]^{2+}$  (III), and  $[\text{Fe}(\text{terpy})_2]^{2+}$  (IV) (bpy, 2,2'-bipyridine; bpym, 2,2'-bipyrimidine; phen, 1,10-phenanthroline; terpy, 2,2':6',2''-terpyridine) were subjected to two (for IV) or three (for I-III) stepwise one-electron electrochemical reductions; the products were studied in situ by solution UV-vis-near-IR spectroscopy. Bands of the reduced species in the UV-vis-near-IR region were observed and assigned to anion radical ligands. The reductions took place in all cases on individual ligands, the spectra of IV<sup>-</sup> as well as IV<sup>2-</sup> showing equivalent features similar to those of  $[\text{Li}^+[\text{terpy}]^-]$ .

### Introduction

Polydentate ligands containing N-donor heterocyclic rings have played an important role in the development of coordination chemistry and continue to be of widespread interest, particularly centered upon complexes of diimine-type ligands,<sup>1</sup> such as 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpym), 1,10-phenanthroline (phen), and 2,2':6',2''-terpyridine (terpy). Although the coordination chemistry of phen and bpym, as well as terpy is well studied,<sup>1d-k</sup> there have been few spectroelectrochemical studies of these metal complexes.<sup>1g,2</sup> A preliminary account of our results for III has appeared<sup>1b</sup> (we have ourselves published such studies for Kaim's<sup>3</sup>  $\mu$ -bpym complexes, while Berger and McMillin<sup>2c</sup> have independently investigated  $[\text{Ru}(\text{terpy})_2]^{2+}$ ). In this paper we describe spectroscopic results for I-IV and their reduced species.

### Experimental Section

**Materials.** Spectrol grade dimethylformamide (DMF) was purchased from BDH and stored over molecular sieves.  $\alpha$ -Diimine ligands were used as received from Aldrich (2,2'-bipyridine and anhydrous 1,10-phenanthroline) or Lancaster Synthesis (2,2'-bipyrimidine). 2,2':6',2''-Terpyridine was prepared by literature methods.<sup>1j</sup> Tetra-*n*-butylammonium tetrafluoroborate (TBA)BF<sub>4</sub> as a supporting electrolyte was prepared by metathesis of tetra-*n*-butylammonium hydroxide and HBF<sub>4</sub> in water, washed repeatedly with water, and purified by successive recrystallizations from ethyl acetate/pentane followed by drying in vacuo at 80 °C. Microanalyses were performed in the Microanalysis Lab, University of Glasgow, Scotland, for Fe(II) complexes. The complexes were prepared as well-formed crystalline materials by reaction between ferrous sulfate and the appropriate ligand in a 1:3 mole ratio (1:2 mole

ratio for IV) in aqueous solution<sup>1f,4</sup> and precipitated by addition of ammonium tetrafluoroborate (under these conditions, II is known<sup>1f</sup> to precipitate with seven molecules of water per formula unit, while the other salts prepared are known to be anhydrous<sup>1j,4b</sup>).  $[\text{Li}^+[\text{terpy}]^-]$  was synthesized by direct reaction between lithium metal and terpy in ether at room temperature using an ultrasonic bath.

**Instrumentation.** Cyclic voltammetric and spectroelectrochemical experiments were performed in DMF (Metrohm cell for cyclic voltam-

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**Table I.** Oxidation and Reduction Potentials (V) of Fe(II) Complexes in DMF<sup>a</sup>

complexes	oxidn	redn		
	$E_{1/2}$	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$
I	+0.802 (65) <sup>b</sup>	-1.537 (62)	-1.720 (67)	-1.900 (71)
II <sup>c</sup>	+1.036 (70)	-1.276 (69)	-1.435 (79)	-1.617 (102) (inc) <sup>d</sup>
III	+0.785 (67)	-1.570 (65)	-1.762 (70)	-1.848 (78)
IV	+0.895 (69)	-1.477 (65)	-1.661 (70)	

<sup>a</sup>Measurements taken vs Ag/0.01 M AgNO<sub>3</sub>/0.09 M (TBA)BF<sub>4</sub> in stated solvent, but referred to ferrocene/ferrocenium/0.1 M (TBA)BF<sub>4</sub> in solvent/cell combination used. <sup>b</sup> $E_{pa} - E_{pc}$  (mV). <sup>c</sup>at -40 °C. <sup>d</sup>Denotes incomplete chemical reversibility (scan rate 200 mV s<sup>-1</sup>)

metry and 1-mm quartz UV cell for spectroelectrochemistry), with cross-sections of a 0.1-mm-diameter Pt wire as working and counter electrodes. The reference electrode was Ag/0.01 M Ag<sup>+</sup> + 0.09 M (TBA)BF<sub>4</sub>, but potentials are referred to the ferrocene/ferrocenium potential obtained under identical conditions. Solutions were typically 0.005 M for cyclic voltammetry and 0.001 M for spectroelectrochemistry. Cyclic voltammetry was performed at potentials from 20 to 200 mV s<sup>-1</sup>, using a Princeton Applied Research (PAR) Model 173 potentiostat, in conjunction with a PAR Model 175 signal generator, with provision (PAR 170) for *iR* compensation, results being recorded on a JJ X-Y recorder, Model 151 (the same potentiostat was then used for controlled-potential electrolysis in the spectroelectrochemistry experiments).  $E_{1/2}$  values were calculated from the average of the cathodic and anodic peak potentials. Prior to each measurement, the solution was purged with dried argon that had been passed through a silica gel column and saturated with DMF. Solutions of II at room temperature showed a shoulder at around -1.2 V, probably due to reduction of the water present in this salt. No features due to water were observed in any other case. Spectra were collected on a Perkin-Elmer Lambda 9 spectrophotometer.

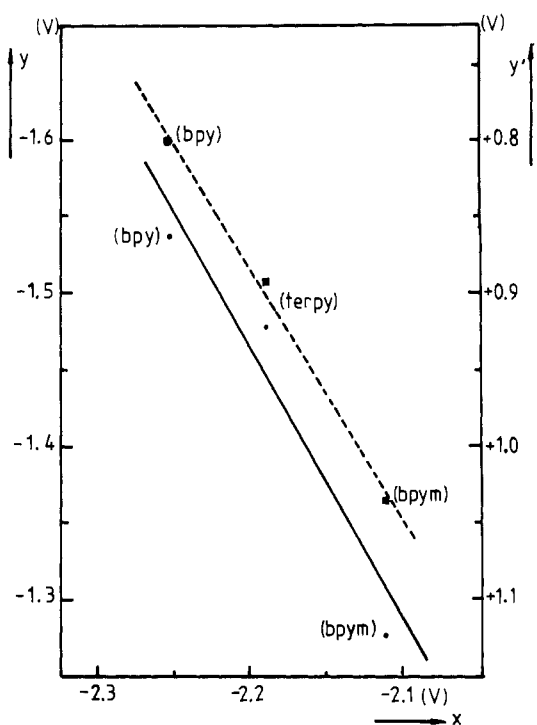
Controlled-potential electrolysis experiments were performed in an optically transparent thin-layer electrode (OTTLE) cell, which consisted of a special 1 mm path length quartz cell with a platinum gauze working electrode which was placed in the cell, as described previously.<sup>2a,2b,5</sup> (The short path length helps to ensure quantitative electrolysis of the interrogated material, while minimizing convective mixing with material in the barrel of the cell). Applied potentials were nominally around 50 mV more negative than the mean of CV forward and return waves, thus ensuring approximately 95% conversion of all the material in the optical path length. Essential features of the experiment are that the working electrode covers the area sampled by the light beam, and that the counter electrode compartment is isolated by a porous Vycor frit from the main bulk of the solution in order to prevent interference by oxidized species. The reference electrode used was the same as that used in the cyclic voltammetry work.

Low-temperature (-40 °C) spectroelectrochemistry experiments were performed by mounting the OTTLE cell in a Teflon block which was divided into three compartments by four strain-free quartz windows. The OTTLE cell was inserted into the central compartment, and cold, dry nitrogen which had been passed through a liquid-nitrogen bath was blown through this compartment. Dry room-temperature nitrogen was passed through the outer compartments to prevent condensation of ice on the quartz windows. The temperature inside the cell was monitored at all times using a thermocouple which was inserted into the solution.

## Results and Discussion

**Electrochemistry.** The oxidation and reduction potentials of the Fe(II) complexes studied are shown in Table I. All of the complexes exhibit a single one-electron reversible oxidation between +0.785 and +1.036 V and several reversible one-electron reduction processes at potentials between -1.276 and -1.970 V, which we assign to the usual<sup>2e,5</sup> ligand-based reduction. Thus IV undergoes two reversible one-electron reduction, one for each  $\alpha$ -diimine ligand, while I-III undergo three such steps. The oxidation of all the complexes is assigned as metal-based. Potentials are, however, strongly dependent on the nature of the ligands (Figure 1).

In the cyclic voltammogram of II at room temperature, no reversible steps were observed other than that<sup>6,7</sup> for the free ligand, presumably liberated by solvolysis or by reaction with the water present in the salt used. However, at -40 °C, the expected series of three narrowly spaced reversible reductions appeared.



**Figure 1.** Oxidation and reduction potentials (V vs ferrocene/ferrocenium) of complexes as function of the free ligand values (dashed line with ■ = oxidation; full line with ● = reduction): x, First reduction potential of free ligands; y, First reduction potential of complexes, y', First oxidation potential of complexes.

The order of decreasing ease of reduction and increasing ease of oxidation in the complexes follows the order  $bpym > terpy > bpy \geq phen$ , and the potential differences are closely parallel (see Figure 1) to the reduction potential differences of the free ligands.<sup>8</sup> The greater ease of reduction of the terpy complex compared to that of bpy is presumably due to the more extended ligand  $\pi$ -system. For phen, the reduction potential of the free ligand is not available, since the cathodic wave at -2.040 V corresponds to a chemically irreversible process (our observation, room temperature at -40 °C, scan rate up to 2 V s<sup>-1</sup>, using nominally anhydrous material; no reduction peak for water detectable). However, extrapolation from the oxidation and reduction potentials of III gives values of -2.270 and -2.275 V respectively for this potential.

**Spectra of Parent Fe(II) Complexes.** The UV-vis-near-IR spectra of the parent complexes of [Fe(L)<sub>3</sub>]<sup>2+</sup> (L = bpy, bpym, phen) contain three main absorption bands (Table II). The highest energy absorption at approximately 33 000 cm<sup>-1</sup> in each complex is associated with a  $\pi \rightarrow \pi^*$  transition of the coordinated diimine ligand. There are also intense bands around 20 000 cm<sup>-1</sup> which have been assigned<sup>4a</sup> to MLCT transitions. These MLCT transition bands are dependent upon the LUMO energy of the coordinated diimine ligands, occurring at lower energy in II compared to complexes I and III. However, the observed MLCT band

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Table II. Main Absorption Bands and Assignments in DMF-(TBA)BF<sub>4</sub> at 25 °C [ $\nu/10\text{ cm}^{-1}$  ( $10^{-3}\epsilon/\text{M}^{-1}\text{ cm}^{-1}$ )]

a. Parent and Reduced I and II					
	$\pi(6) \rightarrow \pi(7)$ of L <sup>a</sup>	$\pi(6) \rightarrow \pi(7)$ of [L] <sup>-</sup>	MLCT	$\pi(7) \rightarrow \pi(10)$ of [L] <sup>-</sup>	$\pi(7) \rightarrow \pi(8,9)$ of [L] <sup>-</sup>
I	32.9 (58.0)		19.2 (11.2)		
I <sup>-</sup>	32.7 (39.5)	27.4 (12.2)	19.5 (sh) <sup>b</sup>	18.3 (10.2)	10.7 (2.7)
I <sup>2-</sup>	32.2 (24.5)	27.0 (19.8)	20.1 (sh) <sup>b</sup>	18.2 (10.7)	10.5 (3.0)
I <sup>3-</sup>		26.4 (28.0)		17.8 (11.0)	10.2 (3.2)
II	32.7 (55.0)		18.2 (12.3)		
II <sup>-c</sup>	32.9 (37.5)	27.0 (11.2)	17.7 (sh) <sup>b</sup>	19.6 (9.5)	9.8 (2.5)

b. III <sup>0/-2-/3-</sup>					
	$\pi \rightarrow \pi^*$ (L <sup>-</sup> )	MLCT	MLCT	$\pi^* \rightarrow \pi^*$ (L <sup>-</sup> )	$\pi^* \rightarrow \pi^*$ (L <sup>-</sup> )
III		23.0 (7.3)	19.4 (11.2)		
III <sup>-</sup>	26.0 (4.2)	23.2 <sup>b</sup> (5.9)	19.7 (7.7)	16.9 (3.9)	11.7 (2.4)
III <sup>2-</sup>	25.7 (6.3)		19.9 <sup>b</sup> (5.1)	16.7 (5.0)	11.5 (2.5)
III <sup>3-</sup>	25.3 (7.9)			16.5 (7.1)	11.2 (2.6)

<sup>a</sup>L = bpy, bpym. <sup>b</sup>Shoulder. <sup>c</sup>At -40 °C.

in III appears very wide and shows vibrational structure. Because the phen system is characterized by two low-lying unoccupied molecular orbitals of comparable energies,<sup>9</sup> the visible MLCT absorption of III should contain two kinds of very closely located MLCT transitions,  $d \rightarrow \pi(8)$  and  $d \rightarrow \pi(9)$ , and the order of these in the complex relative to the free ligand is a matter of some interest.<sup>10</sup>

The absorption spectrum of IV shows four main absorptions. The two high-energy absorption bands at 36 500 and 31 400  $\text{cm}^{-1}$  are associated with ligand-localized  $\pi \rightarrow \pi^*$  transitions of coordinated terpy. There is an intense band at 17 800  $\text{cm}^{-1}$  which has been assigned<sup>11</sup> as MLCT transition. This main MLCT transition band of IV is remarkably narrow, and a shoulder appears at approximately 1500  $\text{cm}^{-1}$  higher energy. This shoulder is less pronounced than the one observed for the spectra of the Fe(II) complexes of bpy ligands and has been tentatively assigned to a transition to higher orbital(s) on the ligand.<sup>11</sup> The shift of MLCT band to lower frequency for IV compared with that for I is attributed to the lower LUMO energy of the terpy ligands. A very weak ( $\epsilon = 4 \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ ) absorption around 12 000  $\text{cm}^{-1}$  could be assigned to a  $d \rightarrow d$  transition<sup>12</sup> of the central metal ion.

**Spectra of the Reduced Fe(II) Species.** The band energies and assignments of I-III and their reduced species are collected in Table II. Comparison of the spectra of I-IV<sup>4b</sup> and their reduction products shows ligand-based reductions rather than metal-based ones. The spectra of the reduced Fe(II) complexes exhibit [L]<sup>-</sup> intraligand  $\pi \rightarrow \pi^*$  and  $\pi^* \rightarrow \pi^*$  transitions in the UV-vis-near-IR regions,<sup>8d</sup> the added electrons being localized on separate ligands.

The typical<sup>13</sup>  $\pi(6) \rightarrow \pi(7)$  (26 400  $\text{cm}^{-1}$ ),  $\pi(7) \rightarrow \pi(10)$  (17 800  $\text{cm}^{-1}$ ), and  $\pi(7) \rightarrow \pi(8,9)$  (10 200  $\text{cm}^{-1}$ ) bands of coordinated [bpy]<sup>-</sup> in I<sup>-</sup> (Figure 2) appear on the addition of the first electron and increase in intensity at each further step, as in the related Ru(II) complexes.<sup>2a,2b</sup> In the region around 16 000–20 000  $\text{cm}^{-1}$ ,  $\pi(7) \rightarrow \pi(10)$  overlaps the MLCT band. In I, the MLCT band alone is present, while I<sup>3-</sup> can only show the  $\pi(7) \rightarrow \pi(10)$  band in this region, since there is no [Fe<sup>II</sup>(bpy)<sup>0</sup>] chromophore. The MLCT band of the [Fe<sup>II</sup>(bpy)<sup>0</sup>] chromophore should occur at around 0.6 eV higher energy, corresponding to the difference between the first and second reduction potentials of bpy.<sup>8a,d</sup> This would place the band beneath  $\pi(6) \rightarrow \pi(7)$  of bpy<sup>-</sup> and would contribute to the observed absorption intensity around 25 000  $\text{cm}^{-1}$ . Similar considerations presumably apply to the spectra of [Ru(bpy)<sub>3</sub>]<sup>+0/-</sup>.<sup>2a</sup> Similar assignments apply to the spectrum of II<sup>-</sup>

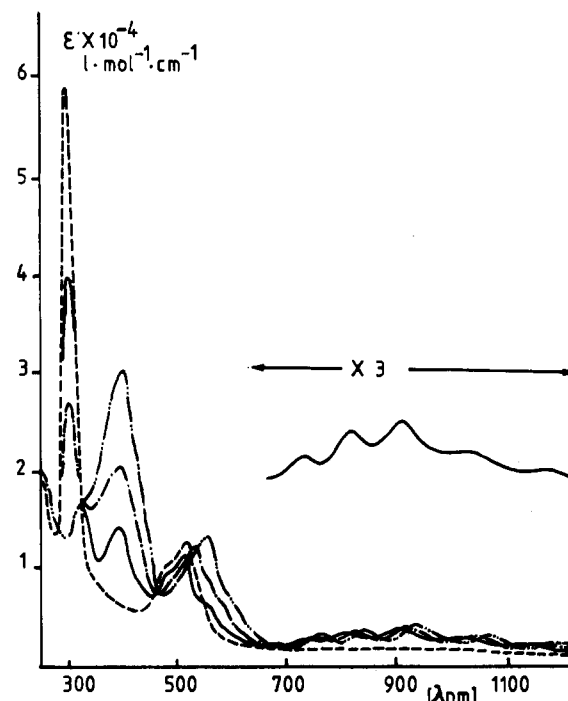


Figure 2. Absorption spectra of [Fe(bpy)<sub>3</sub>]<sup>2+/+0/-</sup> in DMF-TBAPF<sub>4</sub> solution at 25 °C (V vs ferrocene/ferrocenium): (---) parent; (—) singly reduced species at -1.587 V; (-·-) doubly reduced species at -1.770 V; (- - -) triply reduced species at -1.850 V.

(Figure 3), but the spectra of the doubly and triply reduced species are not available because, even at -40 °C, these species are unstable in our time scale. The assignments of the corresponding bands for the free ligand anion radicals and the relevant selection rules and factors affecting relative intensity have been discussed at some length in earlier work.<sup>2a,8d,13</sup>

The assignments of the spectrum of reduced III are more difficult than those of I, although a pseudoisobestic point occurs for the series III<sup>0/-2-/3-</sup> (Figure 4). The band at around 25 300  $\text{cm}^{-1}$  is presumably associated with the intraligand HOMO[ $\pi(7)$ ]  $\rightarrow$  LUMOs [ $\pi(8)$  and  $\pi(9)$ ]  $\pi \rightarrow \pi^*$  transitions of the coordinated [phen]<sup>-</sup>. Transitions between the LUMOs and higher orbitals (presumably  $\pi(10)$  through  $\pi(14)$ ) are observed in the near-IR and vis regions. Further studies are required for precise assignments of these bands, but the stepwise increase in intensity of the [phen]<sup>-</sup>  $\pi^* \rightarrow \pi^*$  transition and, especially, the  $\pi \rightarrow \pi^*$  transition on progressive reduction is characteristic of localization of the added electrons. The bands that we assign to coordinated phen<sup>-</sup> in this complex agree well with those reported by Shida,<sup>14</sup> in his

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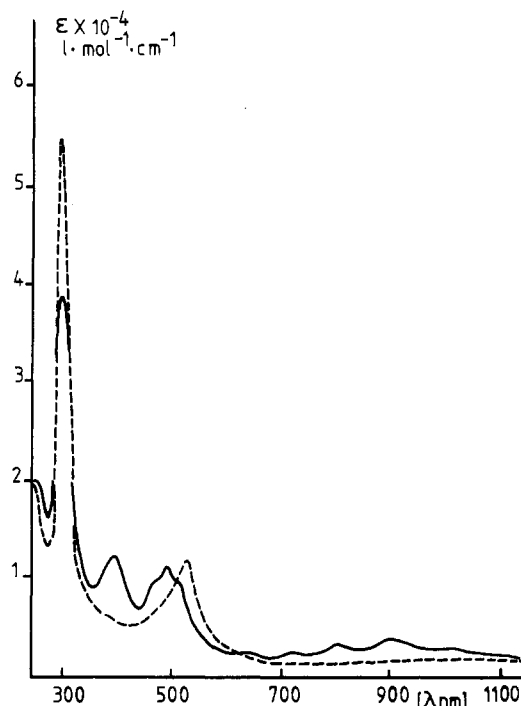
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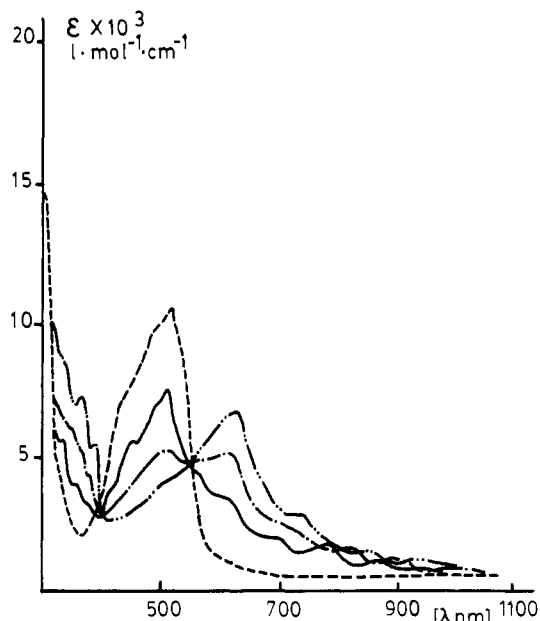
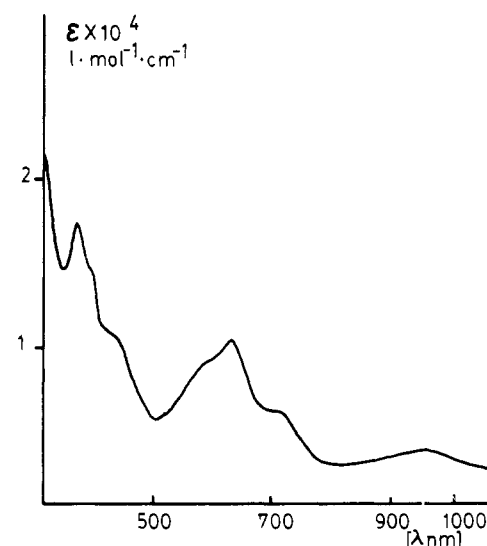
**Table III.** Main Absorption Bands and Assignments of [terpy]<sup>0/-</sup> and IV<sup>0/-/2-</sup> in DMF-(TBA)BF<sub>4</sub> at 25 °C [ $\nu/10\text{ cm}^{-1}$  ( $10^{-3}\epsilon/M^{-1}\text{ cm}^{-1}$ )]

	$\pi \rightarrow \pi^*(\text{terpy})$	$\pi \rightarrow \pi^*(\text{terpy}^-)$	$\pi \rightarrow \pi^*(\text{terpy})$	$\pi \rightarrow \pi^*(\text{terpy}^-)$	MLCT	$\pi^* \rightarrow \pi^*(\text{terpy}^-)$
[terpy] [terpy] <sup>-a</sup>	37.0 (18.5)		31.8 (17.7)			
				26.5 (16.0)		22.4 (10.0) 16.1 (12.5) 14.2 (7.5) 10.6 (3.5)
IV	36.5 (40.5)	36.0 (38.5)	31.4 (38.0) 31.2 (26.5)	27.3 (16.5) 22.5 (9.8) <sup>b</sup>	17.8 (12.0) 18.1 (sh) <sup>b</sup>	17.9 (8.5) 13.8 (6.5) 11.2 (3.8) 16.8 (9.2) 13.2 (7.7) 10.7 (4.2)
IV <sup>2-</sup>		35.2 (39.0) 33.3 (sh) <sup>b</sup>		27.0 (30.0) 22.1 (13.2) <sup>b</sup>		

<sup>a</sup>In ether. <sup>b</sup>Shoulder.**Figure 3.** Absorption spectra of [Fe(bpy)<sub>3</sub>]<sup>2+/+</sup> in DMF-(TBA)BF<sub>4</sub> solution at -40 °C (V vs ferrocene/ferrocenium): (---) parent; (—) singly reduced species at -1.326 V.

important compilation of radical ion spectra, for free [phen]<sup>-</sup> in MTHF. The strong visible  $\pi^* \rightarrow \pi^*$  band, at around 16 500 cm<sup>-1</sup>, is significantly shifted from that reported around 21 000 cm<sup>-1</sup> in aqueous solution in the pulse radiolysis data of Simic and co-workers<sup>15</sup> and Atherton.<sup>16</sup> We do not claim to understand this difference, but note that Shida reports comparable solvent sensitivity for [phen]<sup>+</sup>. We can, however, conclude that (despite speculation to the contrary)<sup>17</sup> the energies and ordering of LUMO orbitals in [phen]<sup>-</sup> are not much affected by complexation.

Figure 5 shows the spectrum of the terpy anion synthesized in solution as the lithium salt. The terpy has 18  $\pi$  orbitals, by the exact assignments of the  $\pi \rightarrow \pi^*$  and  $\pi^* \rightarrow \pi^*$  transitions of both terpy and [terpy]<sup>-</sup> are unidentified. The spectrum of [terpy]<sup>-</sup> has been reported in the range between 450 nm and 600 nm,<sup>18</sup> the results are in broad agreement with those reported here. The observed absorption bands of [terpy]<sup>-</sup> and IV<sup>0/-/2-</sup> are collected in Table III. The strong absorption band at 26 500 cm<sup>-1</sup> in [terpy]<sup>-</sup> may correlate with the band at 31 300 cm<sup>-1</sup> in the neutral species, although we cannot assume the same ligand conformation in Li<sup>+</sup>[terpy]<sup>-</sup> as in IV<sup>-/2-</sup>.

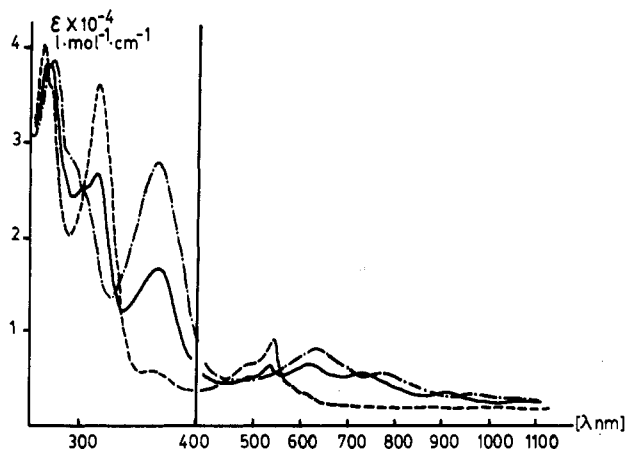
**Figure 4.** Absorption spectra of [Fe(phen)<sub>3</sub>]<sup>2+ / + / 0 / -</sup> in DMF-TBABF<sub>4</sub> solution at 25 °C (V vs ferrocene/ferrocenium): (---) parent; (—) singly reduced species at -1.620 V; (-·-) doubly reduced species at -1.812 V; (- - -) triply reduced species at -1.898 V.**Figure 5.** Absorption spectrum of [Li]<sup>+</sup>[terpy]<sup>-</sup> in ether at 25 °C.

The spectra of singly and doubly reduced IV show five main absorptions in the regions from 38 500 to 9000 cm<sup>-1</sup> with two pseudoisobestic points at 33 200 and 29 300 cm<sup>-1</sup> (Figure 6). The bands at 36 500 and 31 400 cm<sup>-1</sup> are assigned to the intraligand  $\pi \rightarrow \pi^*$  transitions of the coordinated neutral terpy, the energy

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**Figure 6.** Absorption spectra of  $[\text{Fe}(\text{terpy})_2]^{2+/\pm/0}$  in DMF-TBAPF<sub>4</sub> solution at 25 °C (V vs ferrocene/ferrocenium): (---) parent; (—) singly reduced species at  $-1.527$  V; (-·-) doubly reduced species at  $-1.711$  V.

difference between these two bands being approximately  $5000\text{ cm}^{-1}$  ( $0.63\text{ eV}$ ). The band at  $31\,400\text{ cm}^{-1}$  has slightly shifted to lower energies and has lost about half its intensity on going to the reduced species. The loss of intensity in this absorption band is due to the loss of neutral terpy function. The new band at  $27\,000$

$\text{cm}^{-1}$  in singly reduced IV then correlates with the  $26\,500\text{ cm}^{-1}$  band of free  $[\text{terpy}]^-$ . Another  $\pi \rightarrow \pi^*$  transition of  $[\text{terpy}]^-$  appears at  $35\,200\text{ cm}^{-1}$ . The band at  $17\,800\text{ cm}^{-1}$  of IV, assigned as MLCT, is apparently moved slightly to higher energy and loses intensity when the complex becomes singly reduced. More  $\pi \rightarrow \pi^*$  transitions appear at around  $16\,800$ ,  $13\,200$ , and  $10\,700\text{ cm}^{-1}$  and shift to lower energy on going to the doubly reduced species. The spectra of IV<sup>-</sup> shows  $\pi \rightarrow \pi^*$  transitions of both neutral terpy and  $[\text{terpy}]^-$  ligands in the same complex ion. This shows that when the IV is singly reduced, the added electron is localized (on the UV timescale) on one of the coordinated terpy ligands. Similar results have been reported<sup>2a</sup> for  $[\text{Ru}(\text{terpy})_2]^{2+}$ , but the extension to IV, with its smaller central metal ion, is not obvious.

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**Registry No.** I, 15025-74-8; I<sup>+</sup>, 18661-69-3; I<sup>-</sup>, 51383-17-6; I<sup>2-</sup>, 15388-61-1; I<sup>3-</sup>, 19709-86-5; II, 70529-75-8; II<sup>+</sup>, 96042-46-5; II<sup>-</sup>, 138355-71-2; II<sup>2-</sup>, 138355-72-3; II<sup>3-</sup>, 138355-73-4; III, 14708-99-7; III<sup>+</sup>, 13479-49-7; III<sup>-</sup>, 134587-89-6; III<sup>2-</sup>, 15187-23-2; III<sup>3-</sup>, 134961-06-1; IV, 17455-70-8; IV<sup>+</sup>, 47779-99-7; IV<sup>-</sup>, 75324-87-7; IV<sup>2-</sup>, 20515-11-1; DMF, 68-12-2; TBA(BF<sub>4</sub>), 429-42-5; terpy, 1148-79-4;  $[\text{terpy}]^-$ , 138384-34-6; bpy, 366-18-7; bpym, 34671-83-5.

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## Influence of Coligands on the $\eta^1$ -Coordination Mode of $\text{SO}_2$ in $\text{L}_3\text{NiSO}_2$ Complexes. A Pseudopotential ab Initio Study

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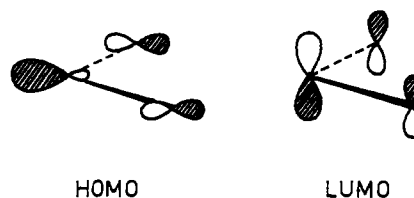
In tris(phosphine)(sulfur dioxide)nickel(0) complexes the mode of  $\eta^1$ -coordination of  $\text{SO}_2$  depends in a very sensitive way on the nature of the phosphine coligands, i.e., their electronic and steric influences. MO calculations on the pseudopotential ab initio level show that the experimental structure ( $\eta^1$ -pyramidal vs  $\eta^1$ -coplanar coordination of  $\text{SO}_2$ ) is a consequence of various different and partially counteracting influences of the coligands. The recently found unusual  $\eta^1$ -pyramidal mode as compared to the usual  $\eta^1$ -coplanar one can be expected to be obtained by coligands which are small and have strong donor power as well.

### Introduction

In recent years the coordination chemistry of sulfur dioxide has received considerable attention. Due to the growing environmental problems the need for detailed knowledge of all aspects of  $\text{SO}_2$  chemistry is obvious. In addition, however, the investigation of structure and bonding of transition-metal sulfur dioxide complexes is a fascinating topic of modern coordination chemistry.  $\text{SO}_2$  seems to be the ligand with the greatest variety of coordination modes. Due to its ability to behave either as a Lewis base or as a Lewis acid, it can attain  $\eta^1$ -coplanar,  $\eta^1$ -pyramidal or  $\eta^2$ -bonding to transition-metal fragments. Moreover, there exist various polynuclear  $\text{SO}_2$ -bridged species. Reviews about the coordination variety have been published by Ryan et al.<sup>1</sup> and Schenk.<sup>2</sup>

Depending on its coordinate bond nature, the  $\text{SO}_2$  ligand is more or less activated and shows a different reaction behavior. As an important example the oxidation of the  $d^{10}$ -metal complexes  $\text{L}_3\text{NiSO}_2$  with  $\text{O}_2$  leading to bidentate coordinated sulfate seems to be typical for the  $\eta^1$ -pyramidal coordination mode, whereas in the case of  $\eta^1$ -coplanar  $\text{SO}_2$  an unspecific destruction of the complex moiety is observed.<sup>1,3</sup> In general, in the case of  $\text{M} = \text{Ni}$  the coplanar coordination is preferred, and in the case of  $\text{M}$

Chart I



= Pd and Pt, the pyramidal coordination is preferred.

The frontier orbitals of sulfur dioxide are shown in Chart I. Sakaki et al.<sup>4</sup> have extensively investigated the bonding in  $d^{10}$ -metal sulfur dioxide complexes using ab initio molecular orbital methods. They found for  $(\text{PH}_3)_3\text{NiSO}_2$  that due to electronic reasons the  $\eta^1$ -pyramidal structure should be favored (see Chart II). In the coplanar coordination mode the  $\text{SO}_2$  lone-pair orbital strongly overlaps with the occupied  $d_\sigma$  orbital of the  $d^{10}$  transition metal to cause a large four-electron destabilization. In the pyramidal mode the lone-pair orbital overlaps with a Ni  $d_x$  orbital, causing

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