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Jerzy B. Chlistunoff, and Allen J. Bard

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Electrochemistry in Liquid SO₂. 11. Oxidation of Ni(bpy)₃²⁺ and Spectroscopy and Isolation of Products

Jerzy B. Chlistunoff[†] and Allen J. Bard*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

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The electrochemical oxidations of Ni(bpy)₃²⁺ (bpy = 2,2'-bipyridine) in 0.1 M tetrabutylammonium hexafluoroarsenate solution in liquid sulfur dioxide was studied by cyclic voltammetry and spectroscopic (UV-vis and ESR) techniques. Within the accessible potential range four successive oxidations could be observed. The first one-electron reversible oxidation, at about +1.3 V vs a silver quasireference electrode (AgQRE), corresponds to the oxidation of the metal center. The second oxidation, at about +2.0 V vs AgQRE, produces Ni(bpy)₃⁴⁺, which exhibits thermochromic properties. The thermochromism of the Ni(bpy)₃⁴⁺ is attributed to the dependence of the degree of charge transfer interactions between the Ni(IV) center and bpy ligands on temperature. The third, reversible oxidation, at +3.2 V, is attributed to the oxidation of a coordinated bpy, and the fourth, totally irreversible oxidation at +3.5 V, is a multielectron process. The procedure of separation and purification of a new very strong, solid oxidant, Ni(bpy)₃(AsF₆)₄ (*E*^o = 2.5 V vs SCE), is presented.

Introduction

Previous reports¹⁻⁴ described the utility of liquid SO₂ as a solvent for electrochemical generation of highly oxidized species. For example, the oxidation of 2,2'-bipyridyl (bpy) complexes of Fe(II), Ru(II), and Os(II), up to the 6+ ions, can be carried out.^{1a} In these cases, however, the oxidation state of the metal center did not exceed 3+ (Fe, Ru) or 4+ (Os). While all of the 6+ forms were unstable, even at the low temperature (-70 °C) usually employed when using liquid sulfur dioxide as a solvent, 5+ forms were stable at least on the time scale of the typical electrochemical experiment, and 4+ forms were stable enough to be produced quantitatively by controlled potential electrolysis.^{1a} These highly oxidized species provided new chemical oxidants for 1 e⁻ oxidations at potentials beyond those usually available. Although Ru(bpy)₃³⁺(AsF₆)₄ could be easily isolated and applied as a very strong oxidant, its practical application may be limited because of its high cost.

In this paper we report the electrochemical oxidation of Ni(bpy)₃²⁺ in liquid sulfur dioxide along with spectroscopic and ESR studies. We also show an easy separation and purification procedure for the very strong oxidant, solid Ni(bpy)₃(AsF₆)₄, and discuss its thermochromic properties.

Experimental Section

Measurements. Electrochemical experiments were made with a PAR Model 173 potentiostat, a Model 175 universal programmer, and a Model 179 digital coulometer (Princeton Applied Research Corp., Princeton, NJ) employing positive feedback for *iR* compensation. The voltammograms were recorded with a Model 2000 X-Y recorder (Houston Instruments Inc., Austin, TX). The working electrodes were Pt disk (diameter 0.5 mm) and Pt gauze for voltammetric and coulometric experiments, respectively. Platinum gauze and reticulated vitreous carbon (RVC) served as counter electrodes in respective experiments. The silver quasireference electrode (AgQRE) was separated from the working electrode compartment by a fine porosity glass frit. Ferrocene, added

as an internal standard at the end of experiments, was used to calibrate the potential scale. Electronic spectra were recorded on a Hewlett-Packard Model 8450A UV-vis diode-array spectrophotometer. ESR spectra were obtained on an IBM Instruments Inc. Model ER 300 spectrometer.

Chemicals. Tetra-*n*-butylammonium hexafluoroarsenate ((TBA)-AsF₆) was prepared by mixing aqueous solutions of LiAsF₆ (Johnson Matthey Electronics, Ward Hill, MA) and (TBA)Br (Aldrich, Milwaukee, WI). The resulting precipitate was dissolved in acetone and reprecipitated with water four times. Finally, the compound was recrystallized three times from an ethyl acetate/ether mixture and dried at 120 °C under vacuum for 72 h.

Ni(bpy)₃(AsF₆)₂ was obtained by a procedure analogous to that used by Burstall and Nyholm⁵ for the synthesis of Ni(bpy)₃(ClO₄)₂, i.e., by mixing aqueous NiCl₂ and bpy, in a mole ratio of 1:3.1, and LiAsF₆ solutions. The pink precipitate was filtered off, rinsed with water, and dried under vacuum at 70 °C. It was recrystallized twice by slow evaporation of the acetone solution and finally dried at 70 °C under vacuum for 72 h. SO₂ anhydrous (Matheson Gas Co., Houston, TX) was purified as described previously.^{1a} Ferrocene (Strem Chemicals, Inc., Newburyport, MA) was used as received.

Procedures. The general experimental procedures for electrochemical studies in liquid sulfur dioxide have been reported previously.¹ Electronic spectra of SO₂ solutions at ambient temperature were recorded using a homemade high-pressure cuvette. The compounds generated electrochemically were transferred directly into the cuvette attached to the electrochemical cell (both immersed in a dry ice/2-propanol mixture). The cuvette was then sealed off and allowed to warm up. A similar procedure was used when measuring the electronic spectra at -70 °C, but with a Dewar-type Pyrex glass cuvette (Figure 1). The samples for ESR experiments were prepared in an analogous manner. The procedure used for separation and purification of Ni(bpy)₃(AsF₆)₄ is described below.

Results

Electrochemistry. Electrode processes of Ni(bpy)₃²⁺ were studied employing a Ni(bpy)₃(AsF₆)₂ concentration ranging from 1.9 to 12 mM in 0.1 M (TBA)AsF₆. Typical cyclic voltammograms are shown in Figure 2. The first two oxidations (1, 2) seen on the voltammograms were near-Nernstian one-electron processes for scan rates between 0.03 and 0.5 V s⁻¹ (see Table I). Sometimes, however, the first oxidation, at about 1.3 V vs AgQRE, appeared to be quasireversible, probably because of adsorption of impurities on the electrode. The lack of similar effects for the 4+/3+ couple suggests that either the intrinsic rate of the electron exchange in the 3+/2+ couple is lower than that of the 4+/3+

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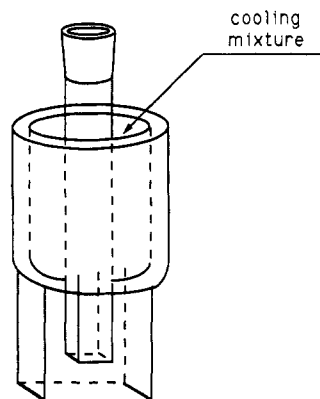


Figure 1. Cuvette for low-temperature spectrophotometry. The cooling mixture used was dry ice/2-propanol (-70°C).

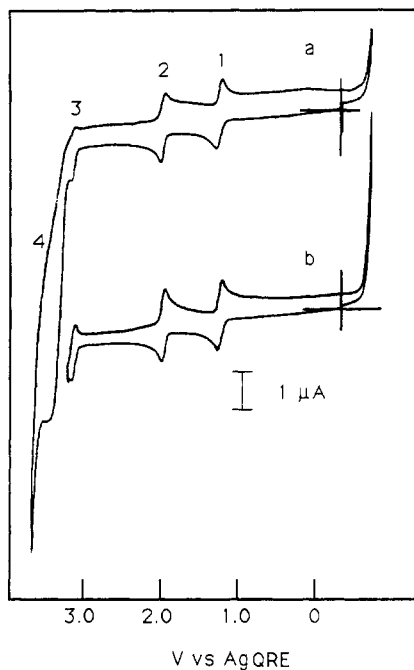


Figure 2. Cyclic voltammograms of 1.92 mM $\text{Ni}(\text{bpy})_3^{2+}$ in 0.1 M (TBA)- AsF_6 solution in liquid SO_2 at -70°C . Scan rate: 0.2 V s^{-1} . Anodic reversal potential: (a) 3.7 V; (b) 3.25 V.

couple or the possible inhibitor desorbs or is oxidized at potentials corresponding to $\text{Ni}(\text{bpy})_3^{3+}$ oxidation.

Controlled-potential coulometry of the pale pink $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_2$ solution at potentials more positive than the potential of the first anodic peak and then at potentials more positive than the potential of the second anodic peak confirmed that both oxidations are one-electron processes (Table I) and that both the 3+ and 4+ ions are stable in liquid SO_2 at -70°C for at least the 2–3 h time period of the coulometric electrolysis. Unfortunately, it was impossible to perform a coulometric experiment for the third oxidation because of the close proximity of the fourth, totally irreversible, oxidation. The voltammetric results (Figure 2 and Table I), however, suggest that the third oxidation ($+3.2\text{ V vs AgQRE}$) is also a reversible one-electron process. The diffusion coefficients of the 2+, 3+, and 4+ ions were determined from voltammograms recorded for $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_2$ solutions both before and after the exhaustive electrolyses. Their values are listed in Table I and are similar to those of the corresponding Ru, Fe, and Os complexes determined previously.⁶

The position and height of the fourth anodic peak, at about $+3.5\text{ V vs AgQRE}$, were not very reproducible from experiment

to experiment. The probable reason for this behavior was the presence of an adsorption effect that inhibited the reaction and produced a resistive film on the electrode. These effects were manifested on the cathodic scans of the voltammograms recorded at higher scan rates as a decrease of the cathodic peak currents and a negative shift of the peak potentials for the remaining electrode processes (Figure 2). Although fast chemical reactions between products of the fourth oxidation and $\text{Ni}(\text{II})$, $\text{Ni}(\text{III})$, and $\text{Ni}(\text{IV})$ may exert a similar influence on the cathodic scan of the voltammogram, the negative shift of the potential of the totally irreversible solvent reduction (Figure 2) favors the former explanation. Within experimental error, the fourth anodic peak showed the characteristics of a simple electrochemically irreversible multielectron oxidation; i.e., the peak current was directly proportional to the square root of the scan rate, and the peak potential shifted with an increase of the scan rate as predicted theoretically from the Tafel slope. The peak current was proportional to $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_2$ concentration, but because of the above-mentioned irreproducibilities, the ratio of the fourth to the first anodic peak currents varied in a random way between 8 and 10.

Associated with the fourth anodic peak was a corresponding cathodic peak at about $+0.2\text{ V vs AgQRE}$. It was poorly defined and could be easily overlooked at lower scan rates (Figures 2 and 3). The height of this peak depended strongly on the scan rate (Figure 3). When employing a single scan rate and varying the anodic reversal potential in the range corresponding to the fourth oxidation process, an approximate proportionality between the cathodic peak current and the faradaic charge corresponding to the fourth oxidation was found (Figure 4). This cathodic peak probably represents either the reduction of H^+ released during the multistep oxidation of the Ni complex or the reduction of the previously mentioned adsorbate. The presence of a similar cathodic peak when extending the anodic scan up to potentials corresponding to the anodic background processes in pure supporting electrolyte solution (Figure 3) suggests that the cathodic peak is due to the hydrogen reduction.^{1b} In either case, however, the species reduced at $+0.2\text{ V}$ is unstable in this solution and undergoes either a chemical reaction or desorption process.

UV-Vis Spectroscopic Results. The spectra of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_2$ recorded at ambient temperature (20°C) in sulfur dioxide at a pressure of 3 atm (Figure 5) agree well with those obtained in other solvents.^{7–10} The values of molar absorptivities (a) and band positions are listed in Table II.

The spectra of $\text{Ni}(\text{bpy})_3^{3+}$ were obtained under different conditions. The spectra for relatively concentrated (millimolar) green solutions of electrochemically generated 3+ ion in the presence of the supporting electrolyte were measured at ambient temperature. Under these conditions only a relatively weak band ($a = 259\text{ M}^{-1}\text{ cm}^{-1}$) at 600 nm and a strong increase of the absorbance at shorter wavelengths are seen (Figure 6). The band in the near-UV region was measured for less concentrated $\text{Ni}(\text{bpy})_3^{3+}$ solutions at -70°C . These solutions were obtained by distilling sulfur dioxide into the low-temperature cuvette containing a solid sample of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ and $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_2$ in a mole ratio slightly less than 1:1 to ensure complete reduction of $\text{Ni}(\text{bpy})_3^{4+}$. This procedure minimizes the influence of nonreacted species on the absorption spectrum of $\text{Ni}(\text{bpy})_3^{3+}$, because the 4+ species shows a much stronger absorption in the near-UV region than the 2+ species does. The band positions agree well with those in other solvents,^{10–12} but the UV band

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Table I. Electrochemical Properties of Tris(2,2'-bipyridine) Complexes of Nickel in Liquid Sulfur Dioxide at $-70\text{ }^\circ\text{C}^{a,b}$

reaction	$10^6 D$, $\text{cm}^2 \text{s}^{-1}$	$E_{pa} - E_{pc}$, ^c mV	i_{pc}/i_{pa}	n_{app}	E° , ^d V vs Fc/Fc ⁺
$\text{Ni}(\text{bpy})_3^{3+/2+}$	$2.4 (\pm 0.2)$	$47 (\pm 5)$	$0.93 (\pm 0.03)$	0.98	$1.325 (\pm 0.004)$
$\text{Ni}(\text{bpy})_3^{4+/3+}$	$2.1 (\pm 0.2)$	$40 (\pm 3)$	$1.02 (\pm 0.06)$	0.96	$2.064 (\pm 0.011)$
$\text{Ni}(\text{bpy})_3^{5+/4+}$	$1.9 (\pm 0.2)$	$45 (\pm 3)$	~ 1		$3.219 (\pm 0.015)$

^a Errors are population standard deviations. ^b D is the diffusion coefficient of the reduced form, $E_{pa} - E_{pc}$ is the difference of the anodic and cathodic peak potentials, i_{pc}/i_{pa} is the ratio of cathodic to anodic peak currents, and n_{app} is the coulometrically determined apparent number of electrons involved when oxidizing the complex. ^c For a Nernstian 1 e^- process at $-70\text{ }^\circ\text{C}$, 40 mV. ^d The standard potential corresponding to the redox process vs the ferrocenium/ferrocene couple (Fc⁺/Fc). This can roughly be converted to V vs aqueous SCE by adding 0.4 V.

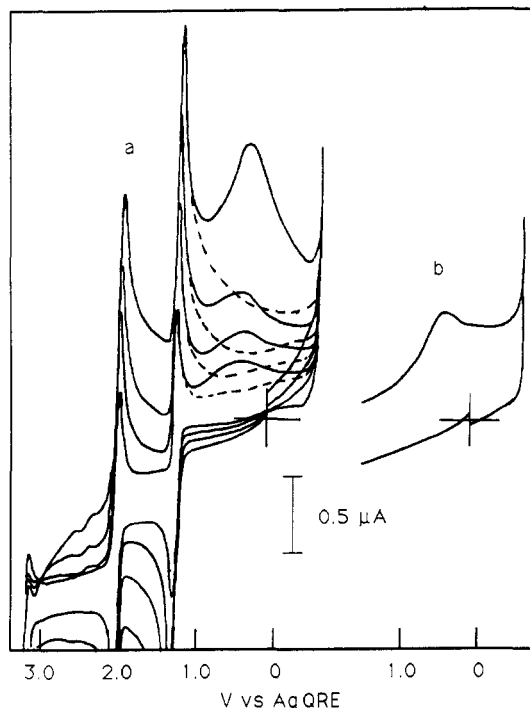


Figure 3. Cathodic portions of the voltammograms recorded at $-70\text{ }^\circ\text{C}$ for (a) $7.1\text{ mM Ni}(\text{bpy})_3^{2+}$ in 0.1 M (TBA)AsF_6 and (b) 0.1 M (TBA)AsF_6 . Anodic reversal potentials: (a) 3.7 V , solid lines; 3.0 V , dashed lines; (b) 4.1 V .

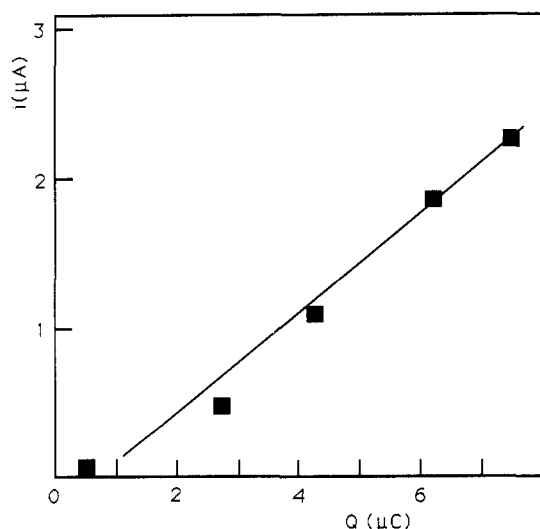


Figure 4. Current of the cathodic peak associated with the fourth $\text{Ni}(\text{bpy})_3^{2+}$ oxidation plotted versus the anodic charge passed during this oxidation. Concentration of $\text{Ni}(\text{bpy})_3^{2+}$: 7.1 mM . Scan rate: 0.5 V s^{-1} .

observed here is resolved better than that in acetonitrile¹² or aqueous perchloric acid¹¹ solutions at ambient temperatures. The molar absorptivities (Table II) are close to those reported by

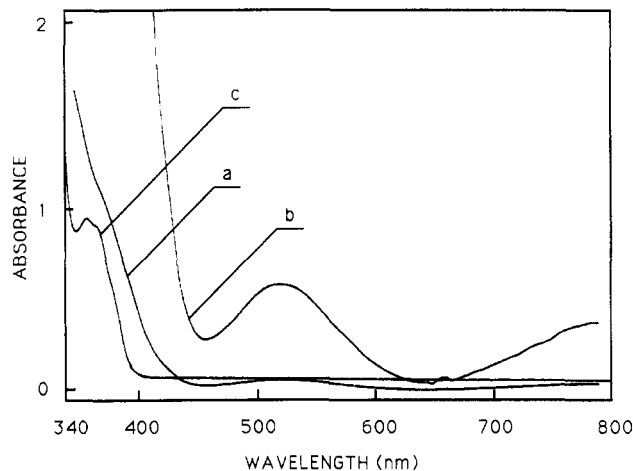


Figure 5. Electronic spectra of $\text{Ni}(\text{bpy})_3^{2+}$ in liquid SO_2 at ambient temperature ($20\text{ }^\circ\text{C}$) corrected for absorption of the solvent: (a) spectrum of $4.9\text{ mM Ni}(\text{bpy})_3^{2+}$ in the presence of $0.093\text{ M (TBA)AsF}_6$; (b) spectrum as in part a but absorbance multiplied by 10; (c) spectrum of pure $0.093\text{ M (TBA)AsF}_6$.

Table II. UV-Vis Spectral Data for Tris(2,2'-bipyridine) Complexes of Nickel in Liquid Sulfur Dioxide

complex	T , $^\circ\text{C}$	band max, nm	molar absorptivity, ^a $\text{M}^{-1} \text{cm}^{-1}$	assign ^t
$\text{Ni}(\text{bpy})_3^{2+}$	20	516	11.1	$^3\text{A}_2\text{-}^3\text{T}_1(\text{F})^b$
		788	6.7	$^3\text{A}_2\text{-}^1\text{E} + ^3\text{A}_2\text{-}^3\text{T}_2^b$
$\text{Ni}(\text{bpy})_3^{3+}$	20 ^c	600	259	LMCT ^d
	-70	376	1850	LMCT
$\text{Ni}(\text{bpy})_3^{4+}$	20 ^c	~ 400	>2500	LMCT
	20 ^c	794	378	LMCT
	-70	406	3190	LMCT
	-70 ^c	785	554	LMCT

^a Corrections for the blank (pure liquid sulfur dioxide) and for the temperature concentrations changes were applied. ^b Reference 9. ^c In the presence of dissolved (TBA)AsF₆. ^d d-d transition may overlap.

Brown et al.¹¹ and Brodovitch et al.,¹² but they are considerably higher than the values quoted by Prasad and Scaife.¹⁰

The first attempt to measure the optical spectrum of the relatively concentrated greenish-brown solution of $\text{Ni}(\text{bpy})_3^{4+}$ at ambient temperature revealed that $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ precipitated at room temperatures, and the color of the solution changed from greenish-brown to brown on heating from $-70\text{ }^\circ\text{C}$. Both the solubility and the color changes with temperature were reversible. This decrease in the solubility of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ was employed in separation and purification of this salt, as described below. Because the precipitation was slow, it was possible to measure the spectra of both supersaturated and saturated solutions at ambient temperature (Figure 7) and to estimate from the spectra that the solubility of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ at $20\text{ }^\circ\text{C}$ was $\sim 0.6\text{ mM}$ in the presence of 0.093 M tetrabutylammonium hexafluoroarsenate. The spectra of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ exhibit two bands, one in the red region of the spectrum and one in the blue near-ultraviolet region (Table II, Figure 7). A temperature decrease causes an increase in the molar absorptivities for both bands, and a small blue shift of the lower energy band is accompanied by a decrease in its half-width. The higher energy band probably

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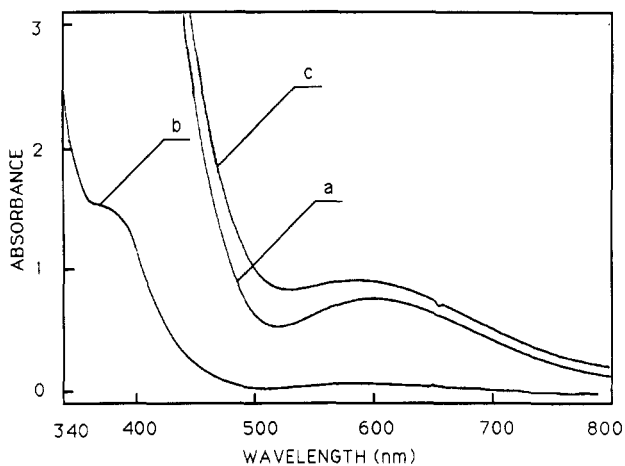


Figure 6. Electronic spectra of $\text{Ni}(\text{bpy})_3^{3+}$ in liquid SO_2 corrected for absorption of the solvent: (a) 2.9 mM $\text{Ni}(\text{bpy})_3^{3+}$ in the presence of 0.093 M $(\text{TBA})\text{AsF}_6$ at 20 °C; (b) 0.158 mM $\text{Ni}(\text{bpy})_3^{3+}/0.044$ mM $\text{Ni}(\text{bpy})_3^{2+}$ at -70 °C; (c) solution obtained by the decomposition of 3.8 mM $\text{Ni}(\text{bpy})_3^{4+}$ in the presence of 0.093 M $(\text{TBA})\text{AsF}_6$ at 20 °C.

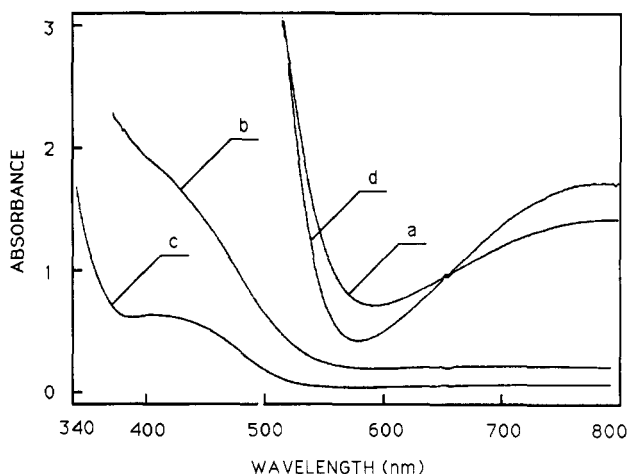


Figure 7. Electronic spectra of $\text{Ni}(\text{bpy})_3^{3+}$ in liquid SO_2 corrected for absorption of the solvent: (a) supersaturated 3.8 mM $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ solution in the presence of 0.093 M $(\text{TBA})\text{AsF}_6$ at 20 °C; (b) saturated, approximately 0.6 mM, $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ solution in the presence of 0.093 M $(\text{TBA})\text{AsF}_6$ at 20 °C; (c) 0.194 mM $\text{Ni}(\text{bpy})_3^{4+}$ solution at -70 °C; (d) 3.07 mM $\text{Ni}(\text{bpy})_3^{4+}$ in the presence of 0.1 M $(\text{TBA})\text{AsF}_6$ at -70 °C.

shifts to the red (Figure 7), but a quantitative estimate of this effect was not possible, because at higher temperatures the overlap between this band and the bands corresponding to transitions within the bpy ligand is increased, making the determination of the band position difficult. A more striking change of the color was seen when the glass ampule containing brown crystals of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ (prepared as described below) was immersed in liquid nitrogen. At liquid N_2 temperature $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ has a pure dark green color. The color change of the solid $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ is reversible.

A solution of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ in the presence of the solid phase held at ambient temperature decomposed after 4 days to produce a green solution with a spectrum nearly identical to the spectrum of the trivalent nickel complex (Figure 6).

ESR Experiments. Freshly-prepared $\text{Ni}(\text{bpy})_3^{4+}$ solutions in both liquid (-60 °C) and solid (-168 °C) states did not produce a detectable ESR signal, so that the 4+ ion can be regarded, to a first approximation, as a complex of tetravalent nickel (d^6). After this solution was stored for 3 days at ambient temperature, an isotropic spectrum with $g = 2.098$ for the liquid sample and an axial spectrum for the solid sample at -168 °C were observed (Figure 8). These signals were attributed to the presence of the tris(2,2'-bipyridine) complex of trivalent nickel.^{11,12} The lack of any splitting of the signal recorded at -168 °C could be

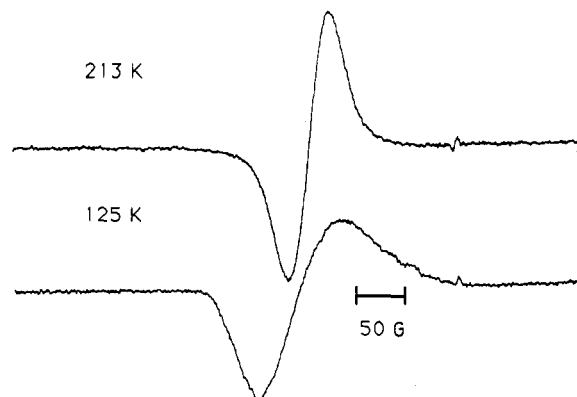


Figure 8. ESR spectra of the decomposed $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ solution.

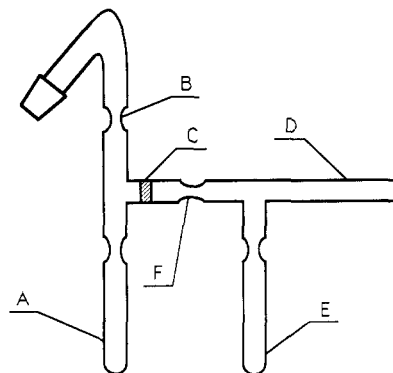


Figure 9. High pressure vessel used for separation and purification of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$.

qualitatively explained, as suggested by Brodovitch et al.,¹² by assuming that the frozen $\text{SO}_2/(\text{TBA})\text{AsF}_6$ solution has an inhomogeneous polycrystalline structure that leads to a variable environment for each paramagnetic center and thus only to broadening of the ESR signal.

Separation and Properties of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$. Separation of the $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ was performed using the Pyrex glass high-pressure vessel shown in Figure 9. The solution was transferred from the electrolytic cell to part A of the vessel with both the cell and the vessel immersed in a dry ice/2-propanol bath. The high-pressure vessel was then sealed off at constriction B and allowed to warm up, resulting in the precipitation of a solid in compartment A. The crystals of this solid were then filtered through the medium-porosity glass frit C by immersing part D in the cooling bath. These were washed by allowing the vessel to warm up so that part of the liquid sulfur dioxide in D distilled under high pressure into compartment A again, by holding part A under a stream of water. The crystals were redissolved again by immersing the whole vessel in the cooling bath (to prevent the condensation of the additional amounts of sulfur dioxide in compartment A). Then the compound was precipitated again by warming and the remaining traces of $(\text{TBA})\text{AsF}_6$ were removed as a solution in SO_2 from compartment A. After the distillation of SO_2 to compartment A was repeated and the compound was dissolved (see above), the vessel was left in the cooling mixture and allowed to warm up very slowly so that the temperature of the bath increased (over several hours) to about 0 °C. The first crystals formed at about -15 °C. In this way we were able to obtain flat square crystals as large as 3 × 3 mm. The crystals were filtered off and dried (by immersing part D in liquid nitrogen), and finally part A was sealed off at constriction F.

The crystals prepared in this way were used for X-ray studies. However, our attempts to determine the crystal structure of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ were unsuccessful, because most of the crystals, especially the bigger ones, showed many internal cracks that could be seen clearly under a microscope (Figure 10). The crystals

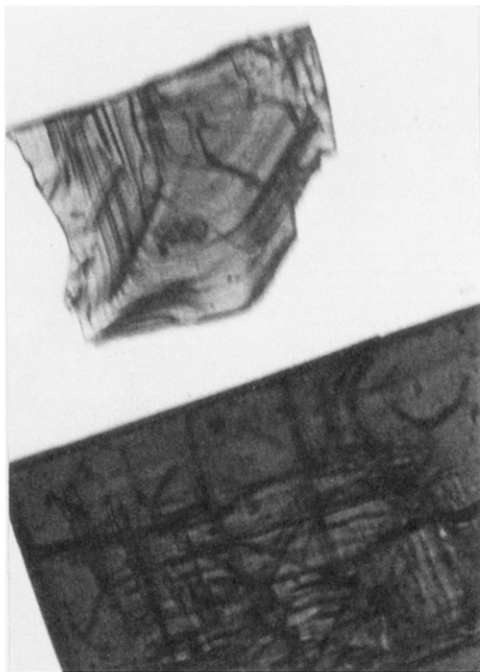


Figure 10. Photograph of the single $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ crystal obtained as described in the text.

were also extremely delicate; even the small ones broke very easily. Although we were able to select several small crystals and place them in 0.5-mm glass capillaries, the X-ray images of these were poor and resembled weak intensity images of a polycrystalline solid. These facts suggested inherent instability of the crystal structure of $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$.

$\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ was not soluble in solvents like aliphatic hydrocarbons (pentane, hexane), methylene chloride, or benzene. It turned green (to $\text{Ni}(\text{III})$) slowly in hydrocarbon solvent and more quickly in CH_2Cl_2 , perhaps because of traces of water present in them. A similar reaction occurred in a silicone oil, when this was used as a matrix to suspend $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ crystals for the X-ray studies.

$\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ readily dissolved in acetone but also reacted very quickly with the solvent, turning green and eventually pale pink, i.e., to the $\text{Ni}(\text{III})$ and $\text{Ni}(\text{II})$ forms, respectively. In anhydrous acetonitrile the reaction was slower (a few minutes), and the resulting green solution of $\text{Ni}(\text{III})$ was relatively stable, in agreement with previous studies.^{10,12} Water reacted in seconds with $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ to form a $\text{Ni}(\text{III})$ species which was stable for several seconds and eventually produced the pale pink $\text{Ni}(\text{II})$ species. No oxygen bubbles were seen during the reaction. $\text{Ni}(\text{bpy})_3(\text{AsF}_6)_4$ could be stored for approximately 6 weeks in a drybox, but after this time it decomposed partially, probably due to the reactions with the organic solvent vapors in the box. On the other hand, it could be stored indefinitely in a closed glass ampule under an inert (vacuum or He) atmosphere.

Discussion

The first synthesis of the relatively stable $\text{Ni}(\text{bpy})_3^{3+}$ complex, as well as the determination of the 3+ oxidation state of nickel in the complex, was reported more than a decade ago.¹⁰⁻¹² The present results show that the $\text{Ni}(\text{bpy})_3^{4+}$ and $\text{Ni}(\text{bpy})_3^{5+}$ complexes are also quite stable. The oxidation state of the metal in the $\text{Ni}(\text{bpy})_3^{4+}$ complex seems to be 4+ on the basis of the ESR experiments. There are a number of known complexes of $\text{Ni}(\text{IV})$,¹³ and the existence of a stable $\text{Ni}(\text{V})$ complex seems possible.

Although we were not able to perform direct ESR measurement with the $\text{Ni}(\text{bpy})_3^{5+}$, information on the oxidation state of Ni in

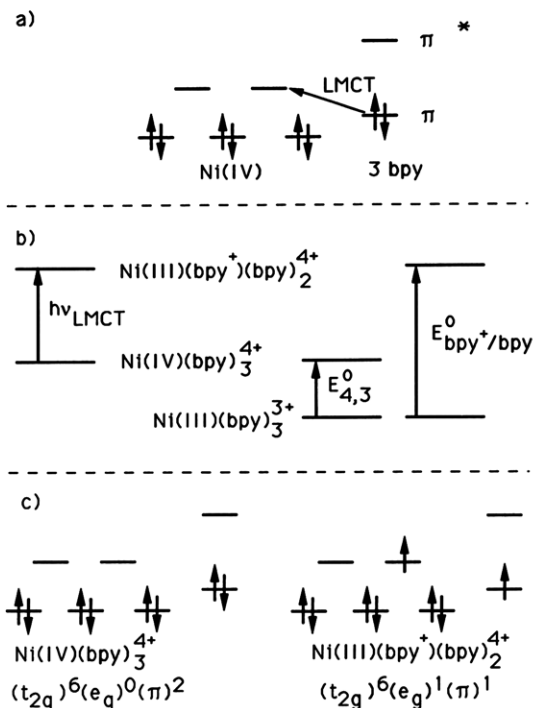


Figure 11. (a) Scheme of energy levels of $\text{Ni}(\text{bpy})_3^{4+}$. (b) Graphical presentation of eq 1. (c) Lowest singlet and triplet localized configurations of $\text{Ni}(\text{bpy})_3^{4+}$.

$\text{Ni}(\text{bpy})_3^{5+}$ and also in $\text{Ni}(\text{bpy})_3^{4+}$ can be obtained from a combined analysis of the spectroscopic and electrochemical results.

In an ideal octahedral symmetry of the $\text{Ni}(\text{bpy})_3^{4+}$ ion, the six d electrons would occupy the triply degenerate t_{2g} orbitals, while the e_g orbitals would remain empty (Figure 11a). For the highly charged metal ion surrounded by the strong-field bipyridine ligands, the energy difference between the split d-orbitals is expected to be higher than the energy of the low energy band seen on the $\text{Ni}(\text{bpy})_3^{4+}$ spectrum (Figure 7). Moreover, the intensity of this band seems too high for a d-d electronic transition. Although significant deviations from octahedral or trigonal symmetry of the ion may produce a complicated orbital splitting pattern, we suggest that the band at 785 nm (-70°C) is due to a ligand-to-metal charge transfer (LMCT) transition. This assignment is supported by the voltammetric results. Using a simple thermodynamic cycle,^{6a} the following relation holds (Figure 11b)

$$E^\circ_{\text{bpy}^{\bullet+}/\text{bpy}} = E^\circ_{4,3} + h\nu_{\text{LMCT(IV)}} \quad (1)$$

where $E^\circ_{\text{bpy}^{\bullet+}/\text{bpy}}$ is the standard potential of the reduction of the bipyridine cation radical when coordinated to nickel(III), $E^\circ_{4,3}$ is the standard potential for the $\text{Ni}(\text{bpy})_3^{4+/3+}$ couple (metal-centered reduction), and $h\nu_{\text{LMCT(IV)}}$ is the energy of the lowest ligand-to-metal charge transfer transition in the complex ion $\text{Ni}(\text{bpy})_3^{4+}$. The above relation holds as long as the distortions between ground and excited states are small. Because oxidation of bipyridine in the coordination sphere of the cation is probably not strongly affected by the charge of the metal ion,^{1a,6a} we can take $E^\circ_{\text{bpy}^{\bullet+}/\text{bpy}}$ to be the potential of the $\text{bpy}^{\bullet+}/\text{bpy}$ half-reaction for bpy coordinated to a metal ion of any charge. From eq 1, the energy of the LMCT transition in the 4+ species (1.58 eV), and $E^\circ_{4,3}$ (2.06 V vs Fc^+/Fc), we obtain $E^\circ_{\text{bpy}^{\bullet+}/\text{bpy}} = 3.64$ V vs Fc^+/Fc .

We now consider the oxidation of $\text{Ni}(\text{bpy})_3^{4+}$. If this is considered as removal of an electron from a coordinated bpy, the potential $E^\circ_{5,4}$ should approximately equal $E^\circ_{\text{bpy}^{\bullet+}/\text{bpy}}$. The value found (Table I), 3.22 V vs Fc^+/Fc , is somewhat smaller. Although there is some discrepancy between these values we show below that the observed difference is generally consistent with our

assignment of the LMCT transition. The relatively low intensity of the low-energy transition also does not contradict the above assignment, since the band considered most probably corresponds to the transfer of an electron from the ligand π to the metal σ (e_g) orbital. The second band in the spectrum of Ni(bpy)₃⁴⁺ is probably also a LMCT band, but corresponds to the transfer of the electron from one of the lower lying filled bipyridine orbitals. This band cannot be the lowest CT transition because such an assignment would imply that the first oxidation of the coordinated bpy unit would be observed at potentials as positive as 5 V vs Fc⁺/Fc, while this process usually occurs at much less positive potentials.^{1a} Additionally, not only Ni(V) but also Ni(VI) would be stabilized in bpy complexes, while only the 3+, or at most the 4+, oxidation state is stabilized in complexes of Fe, Ru, and Os, which generally exhibit lower ionization potentials than nickel.¹⁴ Consequently, we believe that the third oxidation wave of Ni(bpy)₃²⁺ corresponds to the oxidation of the ligand and not the metal center. Possible d-d transitions are not seen in the spectrum of Ni(bpy)₃⁴⁺, because they are hidden under much stronger CT bands.

The spectral transition for the Ni(bpy)₃³⁺ species and the potential of the second wave ($E^{\circ}_{3,2}$) can be analyzed in a similar way, yielding

$$E^{\circ}_{\text{bpy}^+/ \text{bpy}} = E^{\circ}_{3,2} + h\nu_{\text{LMCT(III)}} \quad (2)$$

To our knowledge, no detailed analysis of the spectrum of Ni(bpy)₃³⁺ has been performed. The weak absorption around 600 nm in numerous Ni(III) complexes is believed to originate from d-d transitions.¹⁵ However, as with Ni(bpy)₃⁴⁺, the bands observed for the 3+ species may originate from LMCT transitions, with weaker d-d transitions hidden. From the energy of the 600-nm transition (2.07 eV) and $E^{\circ}_{3,2}$ (1.32 V vs Fc/Fc⁺), eq 2 yields 3.39 V vs Fc⁺/Fc for $E^{\circ}_{\text{bpy}^+/ \text{bpy}}$, again compared to $E^{\circ}_{5,4} = 3.22$ eV. In this case the analysis is even better than that based on eq 1 and the assignment of the band in the 4+ species. Note that some deviations from the simplified analysis implied by eqs 1 and 2 are expected. The Ni(bpy)₃³⁺ ($t_{2g}^6 e_g^1$) ion is a tetragonally distorted octahedron with shorter axial bonds due to the Jahn-Teller effect.¹⁶ Ni(bpy)₃⁴⁺ should not undergo this type of distortion. According to the Franck-Condon principle, transfer of an electron from the ligand π orbital to the empty e_g level of Ni(IV) would produce a Ni(III) state with at least the equatorial bonds significantly shorter than in equilibrium Ni(III) configuration. The excess of energy of this nonequilibrium configuration gives rise to higher energy of the LMCT band in Ni(IV) species than one could expect from measurements of equilibrium standard potentials. A similar effect for the CT energy in the Ni(III) complex is probably smaller, because the electron is transferred to the already occupied e_g level. The differences in the equilibrium Ni-N bond lengths in Ni(III) and Ni(II) species would still be significant^{16,17} with the energy of the LMCT transition slightly higher than predicted from equilibrium electrode potentials.

Although the agreement between the spectral and electrochemical data supports our assignments of the UV-visible spectra and electrochemical processes, it does not explain the thermochromic properties of Ni(bpy)₃⁴⁺. We suggest that the thermochromism of this complex ion is caused by the partial charge transfer bonding between the Ni center and the bipyridine ligands. The energy of the lowest LMCT transition in the Ni(bpy)₃⁴⁺ corresponds to a first approximation to the energy difference

between the limiting localized singlet configurations ($t_{2gNi}^6(e_{gNi})^0(\pi_{bpy})^2$ and ($t_{2gNi}^6(e_{gNi})^1(\pi_{bpy})^1$). This energy is relatively low (1.58 eV) and the energy difference between the singlet state corresponding to the approximate ground state configuration ($t_{2gNi}^6(e_{gNi})^0(\pi_{bpy})^2$ and the triplet state corresponding to the excited configuration ($t_{2gNi}^6(e_{gNi})^1(\pi_{bpy})^1$) is even smaller (Figure 11c). Consequently, both the ground and the excited states of Ni(bpy)₃⁴⁺ may be mixtures of these close-lying electronic states. The degree of mixing depends in a simple way on temperature. The entropy changes associated with the changes in bond lengths will favor a more significant participation of the "long-bond" ($t_{2g}^6 e_g^1$) limiting configuration [Ni^{III}(bpy)₂(bpy⁺)]⁴⁺ at higher temperature and of the "short-bond" ($t_{2g}^6 e_g^0$) configuration [Ni(bpy)₃]⁴⁺ at lower temperatures (there is also a shift of the low-energy CT band in the [Ni(bpy)₃]⁴⁺ spectrum). Consequently, temperature exerts a strong influence on both the spectra and the bond lengths in Ni(bpy)₃⁴⁺. This may also explain the instability of the Ni(bpy)₃(AsF₆)₄ crystals, as well as the atypical temperature dependence of the solubility of Ni(bpy)₃(AsF₆)₄ in liquid SO₂. Ni(bpy)₃(AsF₆)₄ may also exhibit piezochromic properties, because a high pressure should also lead to a lowering of the contribution of the radical configuration [Ni^{III}(bpy)₂(bpy⁺)]⁴⁺, and a similar change of color from brown to green would then occur.

The only experimental finding that seems to contradict our interpretation of the results is the lack of ESR activity of Ni(bpy)₃⁴⁺. In fact, participation of the triplet state in the ground electronic state of Ni(bpy)₃⁴⁺ should produce, as with other CT complexes,^{18,19} an ESR signal. Perhaps the ESR signal could not be detected by us because of its low intensity and extreme broadening of the line, as found with other metal complexes in the triplet state, where one unpaired electron is localized on the metal and the other on the ligands.²⁰

Conclusions

The present results show that the oxidation state of Ni in Ni(bpy)₃⁴⁺ is close to 4+, but an increase in temperature leads to a lowering of the contribution of this oxidation state of Ni due to increased participation of the excited configuration [Ni^{III}(bpy)₂(bpy⁺)]⁴⁺ in the ground state of the ion. Higher oxidized forms of complexes of Ni with 2,2'-bipyridyl with charges of 5+ and 6+ (extremely unstable) are best represented as complexes of Ni(IV) containing one or two bpy cation radicals in the coordination sphere.

Ni(bpy)₃⁴⁺ is a very strong oxidant. Its standard potential at -70 °C is 2.064 V vs Fc⁺/Fc or approximately 2.5 V vs an aqueous saturated calomel electrode. Though not as powerful an oxidant as Ru(bpy)₃⁴⁺ ($E^{\circ} = 3.28$ V vs SCE),^{1a} its cost is much lower. The preparation, separation, and purification of Ni(bpy)₃(AsF₆)₄ is straightforward, so that this material should be useful in laboratory applications as a very strong oxidant.

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Registry No. Ni(bpy)₃(AsF₆)₂, 143546-49-0; Ni(bpy)₃(AsF₆)₃, 143546-50-3; Ni(bpy)₃²⁺, 21595-29-9; Ni(bpy)₃³⁺, 64592-13-8; Ni(bpy)₃⁴⁺, 143546-51-4; Ni(bpy)₃⁵⁺, 143546-52-5; (TBA)AsF₆, 3109-63-5; SO₂, 7446-09-5; Pt, 7440-06-4.

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