information concerning the electronic structure of such complexes.[10g,23] The small deviations of g from the free electron value of $g_e = 2.0023$ may be attributed to the admixture of higher excited states to the (doublet) radical ground state via a relation such as (8),[10g,38] where ξ is the spin–orbit coupling factor and Δ the energy

$$g = g_e \pm \xi/\Delta \qquad (8)$$

separation between the orbital containing the unpaired electron and the orbital with which it may mix by spin–orbit coupling. In its simplified form (8), this equation is usually applied to single paramagnetic metal centers;[38] in its original form, it becomes useful as well for delocalized radicals.[10g,14,23] In the present case as in most other anion radical complexes with group 6 metal carbonyls,[10e,f,h,20] there is a pattern of g corresponding to g(ligand) ~ g(Cr complex) < g(Mo complex) < g(W complex), reflecting the ratio of spin–orbit coupling constants[39] of these metals, $\xi_{Cr(0)} = 223$ cm^{-1}, $\xi_{Mo(0)} = 552$ cm^{-1}, and $\xi_{W(0)} = 2089$ cm^{-1}, and the fact that the energy gap between the highest doubly filled MO (d) and the singly occupied MO (π^*) is smaller than the energetic difference between this singly occupied level and the first empty MO (9). The situation (eq 9) in the anion radical complexes

(9)

of azo-containing ligands tz, bptz, and abpy corresponds to electron spectroscopic results on the neutral complexes,[13] which show one intense MLCT ($\pi^* \leftarrow$ d) transition at very low energies and a wide gap between this and the next major absorption band.

Summary

This study has demonstrated that the azo group in anion radical ligands can be a very effective coordination site for organometallic fragments. These anion radical complexes are formed by reduction at unusually positive potentials, and they exhibit very high stability constants;[13] furthermore, the enhanced nucleophilicity of the nitrogen centers in such anionic ligands also helps in binding metal fragments in a binuclear fashion. The 1,2,4,5-tetrazine systems are particularly noteworthy because they provide unusually favorable conditions to detect metal isotope coupling; statistical advantage (two equivalent coordination sites) as well as the consequences of spin localization at the four tetrazine nitrogen centers is responsible for this extraordinary situation. The tz$^{\bullet-}$ and bptz$^{\bullet-}$ ligands may thus be used as anion radical substrates ("spin labels") to obtain valuable hyperfine information from metal fragments that do not ordinarily exhibit resolved ESR spectra on coordination with anion radical ligands;[40,41] examples include complexes of ruthenium (eq 3),[14] osmium, rhodium, iridium, and the coinage metals.[42]

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A Nickel(III) Complex with a NiO_6 Coordination Sphere

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Constant-potential electrolysis of a solution of tris(2,2'-bipyridine 1,1'-dioxide)nickel(II) perchlorate dihydrate, $[Ni(bpyO_2)_3](ClO_4)_2 \cdot 2H_2O$, in acetonitrile on a platinum electrode at 1.7 V (vs. SCE) affords a violet solution of $Ni(bpyO_2)_3^{3+}$ having the low-spin (d^7, $S = {}^1/_2$) $Ni^{III}O_6$ coordination sphere. In frozen (77 K) acetonitrile solution $Ni(bpyO_2)_3^{3+}$ displays rhombic EPR spectra (fitted to g components: $g_{xx} = 2.220$, $g_{yy} = 2.155$, and $g_{zz} = 2.060$) suggestive of sizable Jahn–Teller distortion and a $(d_{z^2})^1$ ground state. The cation, which shows allowed optical transitions at 370 and 495 nm with a shoulder at 580 nm in acetonitrile solution, is relatively unstable and decomposes, producing a yellow species in which nickel(II) and $bpyO_2$ are present in a 1:2 ratio. The formal potential ($E°_{298}$) of the couple $Ni(bpyO_2)_3^{3+}$–$Ni(bpyO_2)_3^{2+}$ measured cyclic voltammetrically in acetonitrile at platinum with use of solutions of either ion is 1.47 V vs. SCE. The $E°_{298}$ values of the corresponding couples for other 3d elements are as follows (V vs. SCE): Cr, –0.84; Mn, 0.79; Fe, 0.13; Co, 0.87. It is shown that these values vary linearly with the $E°_{298}$ values of the corresponding $M(H_2O)_6^{3+}$–$M(H_2O)_6^{2+}$ couples. From this linear correlation it is estimated that the formal potential of the experimentally inaccessible aquo couple $Ni(H_2O)_6^{3+}$–$Ni(H_2O)_6^{2+}$ is 2.26 ± 0.12 V vs. SCE.

Introduction

This work stems from our interest[1] in the chemistry of higher (>2) oxidation states of nickel. Substantial current activity[2-9] is discernible in this area, which has assumed special significance after the discovery that nickel(III) is present and is probably active

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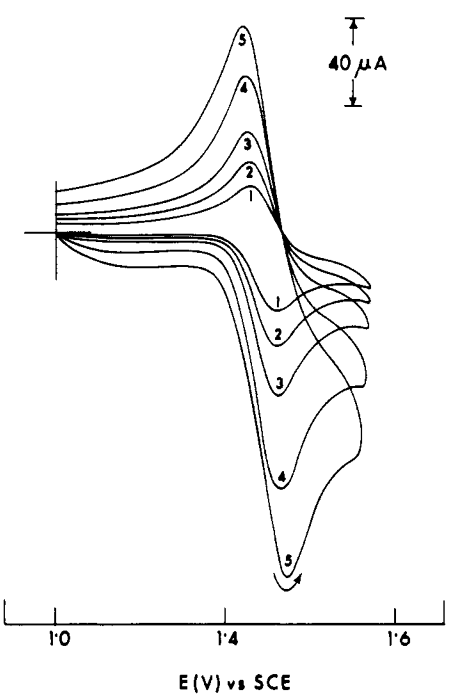

Figure 1. Variable-scan-rate cyclic voltammograms (298 K) of $[Ni(bpyO_2)_3](ClO_4)_2 \cdot 2H_2O$ in acetonitrile (0.1 M TEAP) at platinum (mV s^{-1}): (1) 50; (2) 100; (3) 200; (4) 500; (5) 1000.

Table I. Electrochemical Data[a,b]

complex	$E°_{298}(M^{III}/M^{II})$, V (ΔE_p, mV)
$[Cr(bpyO_2)_3](ClO_4)_3 \cdot 2H_2O$	−0.84 (−)[c]
$[Mn(bpyO_2)_3](ClO_4)_2 \cdot H_2O$	0.79 (60)
$[Fe(bpyO_2)_3](ClO_4)_3 \cdot 3H_2O$	0.13 (70)
$[Co(bpyO_2)_3](ClO_4)_2 \cdot 2H_2O$	0.87 (80)
$[Ni(bpyO_2)_3](ClO_4)_2 \cdot 2H_2O$[d]	1.47 (60)[e]

[a] Conditions are as follows: solvent, acetonitrile (0.1 M in TEAP); electrode, Pt; temperature, 298 K; standard, SCE. [b] Unless otherwise stated, $E°_{298}$ is calculated as the average of anodic and cathodic cyclic voltammetric peak potentials at a scan rate of 50 mV s^{-1}. [c] The anodic response is not observed on scan reversal: the $E°_{298}$ value is a rough estimate (cathodic peak potential + 30 mV). [d] Coulometric data: 9.14 mg of the complex is coulometrically oxidized (278 K) at 1.7 V; *Q*(calcd), 1.03 C; *Q*(found), 0.97 C. [e] The formal potential remains the same at 278 K.

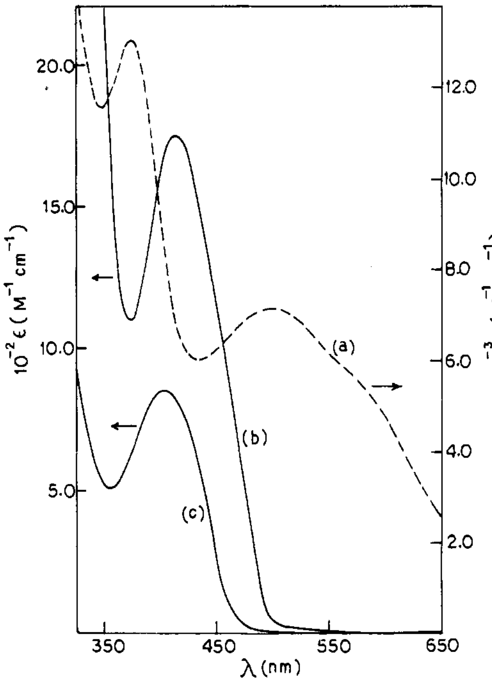

Figure 2. Electronic spectra of (a) $Ni(bpyO_2)_3^{3+}$, (b) $Ni(bpyO_2)_3^{2+}$, and (c) "$Ni(bpyO_2)_2^{2+}$". The solvent is acetonitrile (0.1 M TEAP) in all cases. In (a) the temperature of the study is 278 K, and in (b) and (c) it is 300 K.

in biology.[10] At the present time synthetic species derived from nitrogen donor ligands[1-5,7,8b,e,g,9] constitute the largest single group of known nickel(III,IV) complexes. Discrete molecular coordination spheres of type NiN_6 as well as of type NiF_6 are well-

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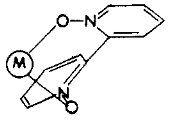
documented, but a similar NiO_6 sphere is missing.[11-13] Herein we report successful electrochemical generation and spectroscopic characterization of a reactive $Ni^{III}O_6$ species in acetonitrile solution. Trischelation by 2,2′-bipyridine 1,1′-dioxide ($bpyO_2$) has been utilized for this purpose. From a systematic correlation of the formal potentials ($E°_{298}$) of $bpyO_2$- and H_2O-ligated MO_6 species a way of estimating the $E°_{298}$ value of the nickel(III)–nickel(II) aquo couple has been devised (M = 3d element).

Results and Discussion

A. Electrochemical Synthesis. The tris chelates $M(bpyO_2)_3^{z+}$ (z = 2, M = Mn, Co, Ni; z = 3, M = Cr, Mn, Fe) have been known for some time.[14,15] The presence of the puckered seven-membered chelate ring **1** in $bpyO_2$ complexes is established by



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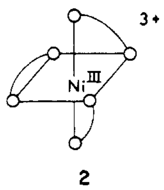

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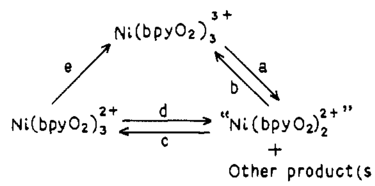
IR data[14c] of various complexes, ^1H contact shift results[16] of $Ni(bpyO_2)_3^{2+}$ and $Co(bpyO_2)_3^{2+}$, and X-ray structure determination[17] of $[La(bpyO_2)_3](ClO_4)_3$. The demonstrated ability of $bpyO_2$ to bind both bivalent and trivalent 3d elements and, in particular, the existence[14] and interconvertibility[18] of $Mn^{II}(bpyO_2)_3^{2+}$ and $Mn^{III}(bpyO_2)_3^{3+}$ encouraged us to explore $bpyO_2$ ligation in designing a discrete $Ni^{III}O_6$ system. All experiments described in this and later sections were performed in acetonitrile solvent.

Yellow solutions (0.1 M in TEAP) of $Ni(bpyO_2)_3^{2+}$ display a cyclic response near 1.5 V (all potentials in this work are referenced to the saturated calomel electrode (SCE)) at platinum as shown in Figure 1 and Table I. The peak-to-peak separation (ΔE_p) is ~60 mV, and the peak heights vary as the square root of scan rate. A one-electron reversible couple is thus operative. Constant-potential coulometry at 1.70 V confirms the one-electron stoichiometry (Table I).

Scheme I



[a] Decomposition. [b] Add 1 mol of $bpyO_2$; electrooxidize. [c] Add 1 mol of $bpyO_2$. [d] Add 0.5 mol of Ni^{2+}. [e] Electrooxidize.

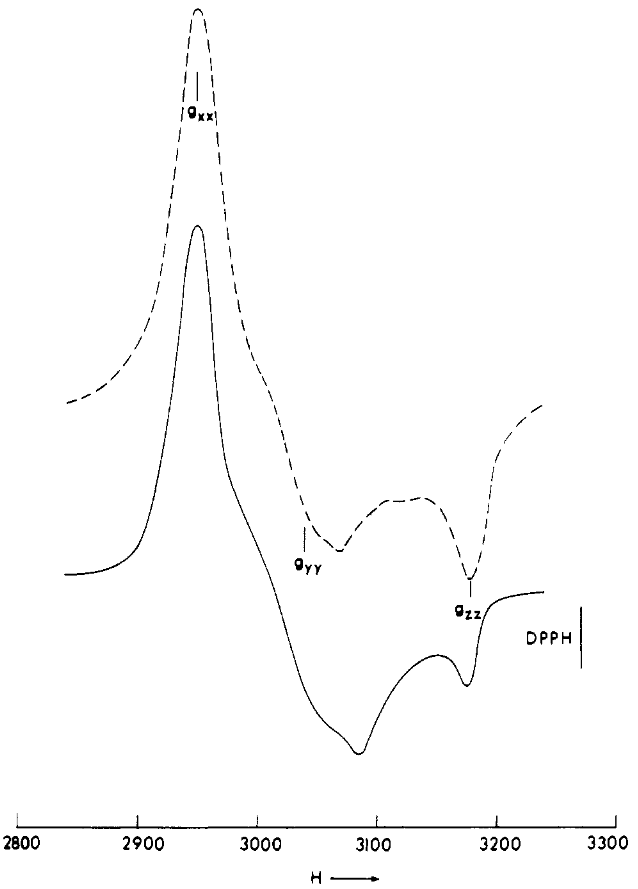


Figure 3. EPR spectrum (77 K) of $Ni(bpyO_2)_3^{3+}$ in frozen acetonitrile (0.1 M TEAP) (—), along with the simulated spectrum (---).

The coulometrically oxidized solution is violet. The cyclic voltammogram of a freshly oxidized (a temperature of 278 K is used for stability reasons; see below) solution is identical[19] with that of $Ni(bpyO_2)_3^{2+}$. This observation coupled with the reversibility of the electrochemical response strongly suggests that there is no major structural reorganization in going from $Ni(bpyO_2)_3^{2+}$ to the violet complex. The EPR data (see below) of the violet complex are compatible with a low-spin d^7 configuration. The violet complex is therefore $Ni^{III}(bpyO_2)_3^{3+}$ (**2**), and its electrochemical synthesis is represented by couple 1 (M = Ni). The formal potential of this couple (Table I) is lower than that of the $Ni(bpy)_3^{3+}$–$Ni(bpy)_3^{2+}$ couple by ~250 mV.

$$M(bpyO_2)_3^{3+} + e^- \rightleftharpoons M(bpyO_2)_3^{2+} \qquad (1)$$

The formal potentials of couple 1 for M = Cr, Mn,[20] Fe, and Co in acetonitrile solution at 298 K were also determined cyclic voltammetrically, and results are in Table I.

B. Stability and Optical Spectra. Though stable on the cyclic voltammetric time scale, solutions of $Ni(bpyO_2)_3^{3+}$ are unsuitable for storing at room temperature (~300 K). Such solutions rapidly turn yellow, and the nature of the yellow species (**3**) is considered

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(19) On scanning at different time intervals the peak heights decrease progressively due to decomposition of oxidized complex (see text).

(20) The $E°_{298}$ value of couple 1 for M = Mn is reported[18] in acetonitrile (0.1 M in tetra-*n*-propylammonium perchlorate) to be 0.87 V. Our result is lower (0.79 V).

in the next section. By generation and storage of $Ni(bpyO_2)_3^{3+}$ at 278 K (slower decomposition) a semiquantitative[21] optical spectrum of the violet complex can be recorded (Figure 2). Characteristic absorption bands, presumably of LMCT origin, occur at 370 nm (extinction coefficient[21] (ϵ) $\sim$13 000 M^{-1} cm^{-1}) and 495 nm (ϵ $\sim$7000 M^{-1} cm^{-1}) with a shoulder at 580 nm (ϵ $\sim$5000 M^{-1} cm^{-1}). The inherent instability of $Ni(bpyO_2)_3^{3+}$ has made its isolation as a pure salt in the solid state unachievable.

C. Nature of Yellow Species 3. This species, formed by the decomposition of $Ni(bpyO_2)_3^{3+}$, has a characteristic absorption band at 403 nm (ϵ 850 M^{-1} cm^{-1} based on nickel); the $Ni(bpyO_2)_3^{2+}$ complex is more intensely yellow (412 nm (ϵ 1750 M^{-1} cm^{-1})) (Figure 2). Complex **3** is EPR-silent and is also electrochemically silent in the voltage range 0.5–1.8 V. Therefore, it is neither a nickel(III) complex nor is it $Ni(bpyO_2)_3^{2+}$. Two observations have helped to clarify the nature of **3**: (i) addition of 1 mol of $bpyO_2$ (for each mole of nickel originally oxidized) to a solution of **3** *quantitatively* regenerates $Ni(bpyO_2)_3^{2+}$, identified by cyclic voltammetry and optical spectra; (ii) addition[22] of 0.5 mol of nickel(II) perchlorate to a solution of $Ni(bpyO_2)_3^{2+}$ affords a species whose optical spectra and electrochemical properties match those of **3**. Thus **3** contains nickel(II) and $bpyO_2$ in the mole ratio 1/2 and we designate it simply[23,24] as "$Ni(bpyO_2)_2^{2+}$". *Stoichiometrically* the decomposition of $Ni(bpyO_2)_3^{3+}$ can be envisaged as effective elimination of 1 mol of ligand with concomitant reduction of the metal center affording 1 mol of **3**. *Mechanistic details* and the fate of the eliminated ligand are unclear at present.[25-28] The observable transformations are summarized in Scheme I.

D. EPR Spectrum and Distorted Geometry. The X-band EPR spectrum of $Ni(bpyO_2)_3^{3+}$ was run after freezing a coulometrically produced solution at 77 K. The observed spectrum is rhombic and could be simulated well with the g components $g_{xx} = 2.220$, $g_{yy} = 2.155$, and $g_{zz} = 2.060$ (Figure 3) having line widths of 30 G (xx, yy) and 25 G (zz). The g values fall in the correct range[5a,7n,8g,9g] for low-spin nickel(III) species. The contact-shifted ^1H NMR spectrum[16] of $Ni(bpyO_2)_3^{2+}$ in solution is compatible with three equivalent chelate rings (D_{3d} symmetry). In this symmetry the octahedral t_{2g} and e_g orbitals transform as a_{1g} + e_g and e_g, respectively. In idealized D_{3d} symmetry the electronic configuration of $Ni(bpyO_2)_3^{3+}$ is $(a_{1g},e_g)^6(e_g)^1$. This configuration, being an orbital doublet with an unpaired electron in an antibonding level, is subject to Jahn–Teller distortion. The nonaxial EPR spectrum of $Ni(bpyO_2)_3^{3+}$ is attributed to the presence of such distortion. The $Ni(bpy)_3^{3+}$ cation is known to be Jahn–Teller distorted[5c] to a considerable extent from X-ray work; its EPR spectrum ($g_{\parallel} = 2.030$; $g_{\perp} = 2.135$) is however reported[5a] to be axial. The nature of the observed spectrum of $Ni(bpyO_2)_3^{3+}$ (Figure 3) strongly suggests that the rhombic field splits the perpendicular absorption of the idealized D_{3d} geometry into overlapping g_{xx} and g_{yy} components, the corresponding parallel absorption being represented by g_{zz}. For the above idealized geometry we can write "$g_{\parallel}$" = 2.060 and "$g_{\perp}$" = $^1/_2(g_{xx} + g_{yy})$ = 2.188. The $g_{\perp} > g_{\parallel}$ result suggests[3a,8g] a $d_{z^2}{}^1$ ground state (axial elongation).

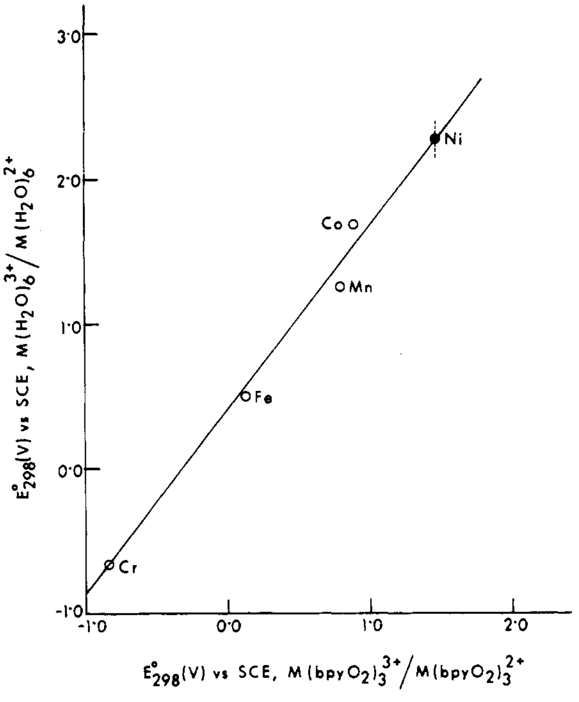

Figure 4. Least-squares plot of formal potentials. The filled circle (Ni) on the least-squares line corresponds to the E°_{298} value of the $Ni(bpyO_2)_3^{3+}$–$Ni(bpyO_2)_3^{2+}$ couple.

E. Relationship with the Nickel(III)–Nickel(II) Aquo Couple. Formal potentials of several aquo couples of type 2 are known.[29-31]

$$M(H_2O)_6^{3+} + e^- \rightleftharpoons M(H_2O)_6^{2+} \qquad (2)$$

However, no direct information on the E°_{298} value of the M = Ni couple is available, presumably because it is too positive to be observable. Such information on aquo species is of inherent interest to chemists. From crystal field considerations disparate estimates like 2.9[32] and 5.2 V[33] have been reported for the E°_{298} value of couple 2 (M = Ni). Using our results on couple 1 (Table

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(21) Since $Ni(bpyO_2)_3^{3+}$ decomposes even as it is being produced coulometrically at 278 K (over a few minutes) and as the oxidized solution is transferred to the optical cell (278 K), exact ϵ values are therefore difficult to obtain. The reported values (average of three independent measurements) were obtained by recording the spectrum immediately after completion of coulometry.

(22) This is part of a systematic study in which the variation of the $\sim$400-nm band is utilized to titrate nickel(II) spectrophotometrically with $bpyO_2$. The $Ni/bpyO_2$ ratio was varied either by adding nickel(II) perchlorate to $Ni(bpyO_2)_3^{2+}$ or by adding $bpyO_2$ to nickel(II) perchlorate. The spectral responses in the two cases are the same for a given $Ni/bpyO_2$ ratio. As $Ni/bpyO_2$ decreases, ϵ increases smoothly on a steeply rising curve that levels off at $Ni/bpyO_2 = 1/3$. Since the absorption maximum also shifts slightly but progressively in the range 385–412 nm, the formation curve is best plotted with a common off-peak wavelength for all compositions. Some representative $Ni/bpyO_2$ ratios and corresponding ϵ (M^{-1} cm^{-1}) values at 420 nm are as follows: 1/0.53, 75; 1/1.04, 213; 1/1.56, 484; 1/2.05, 931; 1/2.38, 1280; 1/3.00, 1700. The concentration of nickel(II) was in the range 2×10^{-3}–3.0×10^{-4} M. The observed ϵ value of **3** fits at $Ni/bpyO_2 = 1/2$ on the general curve.

(23) Coordinated solvent molecules will no doubt be present, and further, **3** could very well be a mobile mixture in which 1/1 and 1/3 complexes are also present as minor equilibrium constituents. These details are however not crucial in the present context.

(24) Attempted crystallization of a nickel(II) complex from solutions of **3** or from mixtures of nickel(II) and $bpyO_2$ (irrespective of composition) always afford salts of $Ni(bpyO_2)_3^{2+}$ (both ClO_4^- and PF_6^- have been tried as anions) only. In the case of **3**, $\sim$33% of the total nickel(II) is left behind in the mother liquor. Evidently salts of the tris chelate have much better lattice energies than those of the lower order chelates.

(25) One possibility is that the oxidation equivalent is actually transferred from the metal to one ligand and the ligand cation radical then rapidly[26] disappears via dimerization or other routes that are well-charted for unstable electrogenerated cation radicals of aromatic compounds.[27] In this context it is significant that $bpyO_2$ itself has a well-formed cyclic voltammetric oxidation peak in acetonitrile at 1.70 V. No reduction peak is however observed on scan reversal, presumably due to rapid disappearance of the cation radical.

(26) Addition of $Ni(bpyO_2)_3^{2+}$ solution to methyl acrylate fails to bring about polymerization of the latter, showing that free radicals do not accumulate to any measurable extent in the decomposition of $Ni(bpyO_2)_3^{3+}$.

(27) Eberson, L. In *Organic Electrochemistry*; Baizer, M. M., Ed.; Marcel Dekker: New York, 1973; pp 447–468. See also other chapters of section D of this book.

(28) Meaningful rate studies of the decomposition of $Ni(bpyO_2)_3^{3+}$ have been beset by the nonavailability of data for the first several minutes.[21] The subsequent rate (followed by measuring the decrease in intensity at 500 nm) is also complex and could not be interpreted in a meaningful way.

(29) The E°_{298} values vs. SCE for the aquo couples are as follows: Cr, −0.68 V;[30] Mn, 1.30 V;[31] Fe, 0.50 V;[30] Co, 1.68 V.[30]

(30) Weaver, M. J.; Yee, E. L. *Inorg. Chem.* **1980**, *19*, 1936.

(31) Zordan, T. A.; Hepler, L. G. Chem. *Rev.* **1968**, *68*, 737.

(32) Jørgensen, C. K. *Acta Chem. Scand.* **1956**, *10*, 1505.

(33) (a) George, P.; McClure, D. S. *Prog. Inorg. Chem.* **1959**, *1*, 381. (b) Buckingham, D. A.; Sargeson, A. M. In *Chelating Agents and Metal Chelates*; Dwyer, F. P.; Mellor, P. D., Eds.; Academic Press: New York, 1964; pp 237–282.

I) and the reported data[29-31] on couple 2, we prescribe a different and more reliable way of estimating this E°_{298} value.

The free energy change (ΔG°) of the cell reaction in which couple 1 is an electrode can be expressed[33b,34] by eq 3, where F is the Faraday constant, I_3 is the 3rd ionization potential of M, ΔG°_f is the difference between the free energies of formation of bivalent and trivalent complexes in the gas phase (in the sense G°_f (bivalent(g)) − G°_f(trivalent(g))), ΔG°_s is the difference between the solvational free energies of bivalent and trivalent complexes in the gas phase, and C is a constant contributed by the reference half-cell. A similar equation will apply for couple

$$-\Delta G^\circ = FE^\circ = I_3 - \Delta G^\circ_f - \Delta G^\circ_s + C \tag{3}$$

2. Both $bpyO_2$ and H_2O are oxygen donor ligands, and the cationic complexes are of the same charge type. Further, the *Dq* values of H_2O and $bpyO_2$ are closely similar[35,36] and a metal will have the same spin state[37] in $M(H_2O)_6^{2+}$ and $M(bpyO_2)_3^{2+}$. The *trend* in the variation of E°_{298} (i.e. of ΔG°_f and ΔG°_s)[38] among the various couples of type 2 should therefore approximately *parallel* the corresponding trend in the case of couples of type 1. The plot of E°_{298} values of one couple against those of the other for M = Cr, Mn, Fe, and Co is indeed found to be linear (Figure 4). The root mean square deviation of the four data points from the least-squares line is ±0.12 V. Considering the inherent approximations of the model used, this deviation is not too disturbing. Extrapolation of the line to the E°_{298} value of couple 1 (M = Ni) affords a formal potential 2.26 ± 0.12 V for the couple $Ni(H_2O)_6^{3+}/Ni(H_2O)_6^{2+}$.

F. Concluding Remarks. The electrochemical generation of the first discrete $Ni^{III}O_6$ species, $Ni(bpyO_2)_3^{3+}$, has been demonstrated. The cation is low spin and rhombic. The presence of chelate rings is no doubt of crucial importance since electrochemical oxidation of $Ni(pyO)_6^{2+}$ to the corresponding nickel(III) species is unachievable[39] even in liquid sulfur dioxide. The nickel(III)–nickel(II) formal potential of $Ni(bpyO_2)^{3+}$ is still quite high (1.47 V), and this no doubt is a factor contributing toward its relative instability. It should be possible to bring the formal potential down by placing electron-donating substituents on $bpyO_2$. The formal potentials of known metal(III)–metal(II) couples of MO_6 species derived from $bpyO_2$ and H_2O ligands display a linear interrelationship from which the potential of the inaccessible hexaaquo nickel(III)–nickel(II) couple has been derived as 2.26 ± 0.12 V. It is clear that oxygen ligands do not stabilize nickel(III) well and the nickel(III)–nickel(II) formal potential is high. Much lower potentials are attainable with nitrogen[1a,e,7d,u,8h] and sulfur[40] donor ligands, and in one case a potential as low as −0.20 V has been reported.[2a] Biological ligands are usually O, N, and S donors. Since biological nickel(III)–nickel(II) couples have to be low potential,[10j] one would expect coordination by one or both of the last two donors to be prevalent. The information available[10k,l,m] thus far is in agreement with this.

Experimental Section

Materials. The ligand 2,2′-bipyridine 1,1′-dioxide ($bpyO_2$) and the complexes $[Cr(bpyO_2)_3](ClO_4)_3\cdot 2H_2O$, $[Mn(bpyO_2)_3](ClO_4)_2\cdot H_2O$, $[Fe(bpyO_2)_3](ClO_4)_3\cdot 3H_2O$, $[Co(bpyO_2)_3](ClO_4)_2\cdot 2H_2O$, and $[Ni(bpyO_2)_3](ClO_4)_2\cdot 2H_2O$ were prepared by following reported methods.[14b] The purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) were done as before.[34]

Electrochemistry. (a) Instrumentation. Electrochemical measurements were done with the help of a PAR Model 370-4 electrochemistry system incorporating the following: Model 174A, polarographic analyzer; Model 175, universal programmer; Model RE0074, X-Y recorder; Model 173, potentiostat; Model 179, digital coulometer; Model 377A, cell system. The three-electrode measurements were carried out with use of a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). For coulometry a platinum-wire-gauze working electrode was used. Measurements were carried out either at 298 K or at 278 K under a dinitrogen atmosphere. The reported potentials are uncorrected for junction contribution.

(b) Synthesis of $Ni(bpyO_2)_3^{3+}$. This was achieved by exhaustive electrolysis of an $\sim 10^{-3}$ M acetonitrile solution (0.1 M in TEAP) of $Ni(bpyO_2)_3^{2+}$ in a thermostated cell (278 K) at a constant potential of 1.7 V. The electrolyzed solution is dark violet.

Spectroscopic Measurements. The X-band EPR spectra were recorded with a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K. The coulometrically produced solution ($\sim 10^{-3}$ M) of $Ni(bpyO_2)_3^{3+}$ was immediately frozen to 77 K, and data were collected. The spectrum was calibrated with the help of DPPH (g = 2.0037). Electronic spectra were obtained with either a Hitachi 330 or a Pye Unicam SP8-150 spectrophotometer fitted with thermostated cell compartments.

Computer simulation of the EPR spectrum of $Ni(bpyO_2)_3^{3+}$ was carried out in the usual manner[41] with use of g values and line widths as input parameters. Both Gaussian and Lorentzian line shapes were tried. The spectrum fitted better when the latter shape was used as in Figure 3.

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Registry No. $[Ni(bpyO_2)_3](ClO_4)_2$, 103620-53-7; $Ni(bpyO_2)_3^{3+}$, 103620-54-8; $Ni(bpyO_2)_2^{2+}$, 84204-86-4; $Cr(bpyO_2)_3^{3+}$, 52730-82-2; $Cr(bpyO_2)_3^{2+}$, 103620-58-2; $Mn(bpyO_2)_3^{2+}$, 103620-55-9; $Mn(bpyO_2)_3^{3+}$, 64939-13-5; $Fe(bpyO_2)_3^{3+}$, 103620-56-0; $Fe(bpyO_2)_3^{2+}$, 103620-59-3; $Co(bpyO_2)_3^{2+}$, 103620-57-1; $Co(bpyO_2)_3^{3+}$, 71498-54-9; $Ni(bpyO_2)_3^{2+}$, 103620-52-6; $Ni(H_2O)_6^{3+}$, 60576-34-3; $Ni(H_2O)_6^{2+}$, 15365-79-4.

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(34) Mukherjee, R. N.; Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 785.

(35) The *Dq* values of the $bpyO_2$ ligand are as follows: Cr(III), 1550 cm^{-1}; Co(II), 1004 cm^{-1}; Ni(II), 857 cm^{-1}. The corresponding *Dq* values[36] of H_2O are as follows: Cr(III), 1740 cm^{-1}; Co(II), 930 cm^{-1}; Ni(II), 850 cm^{-1}.

(36) Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, London, New York, Paris, 1962; Chapter 7.

(37) The spin states of the various ions are as follows: Cr(II), $S = 2$; Cr(III), $S = 3/2$; Mn(II), $S = 5/2$; Mn(III), $S = 2$; Fe(II), $S = 2$; Fe(III), $S = 5/2$; Co(II), $S = 3/2$; Co(III), $S = O$; Ni(II), $S = 1$; Ni(III), $S = 1/2$. We note further that an implicit assumption in the correlation via eq 3 is that structural changes in the various $bpyO_2$ complexes parallel those of the aquo ions. This is justified since the seven-membered chelate ring **1** would have the required flexibility.

(38) A discussion on the various components of ΔG°_f and ΔG°_s can be found elsewhere.[33,34]

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