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Tris(2,2′-bipyrimidine)cobalt(III, II, I). A Cobalt Polyazine Electrochemical System with Large Storage Capabilities

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The preparation of [Co(bpym)$_3$](ClO$_4$)$_2$ where bpym = 2,2′-bipyrimidine, is described. This complex does not undergo the same Co(II) to Co(III) oxidation with H_2O_2 as the 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) analogs. Comparison of the electrochemistry of the bpym, bpy, and phen complexes shows that the Co(II)/Co(III) oxidation is 0.7 volts more positive for the bpym complex. This large difference in potential, along with an increase in the Co(III)/Co(II) to Co(II)/Co(I) separation for the bpym complex, are discussed in terms of potential for use in a storage battery.

Introduction

Recently, we have been interested in the ligand 2,2′-bipyrimidine (bpym), which has the ability to chelate simultaneously to two metal centers [1–4]. In a number of studies [1–8], the properties of this ligand have been compared to 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen).

The preparation of the tris complex of cobalt(II), Co(bpym)$_3^{2+}$, had been reported by Bailar [9] as a potential complex for making highly-cationic polymetallic complexes. In attempting to make the Co(III) analog by the same classical route as for the Co(bpy)$_3^{3+}$ complex [10], (*i.e.*, the addition of H_2O_2 to oxidize Co(II) to Co(III)) peroxide addition did not change the absorption spectrum when bpym was the ligand. This apparent difference in redox potential led us to the study reported herein, which compares and contrasts the spectral and redox properties and chemical reactivity of the Co(AA)$_3^{n+}$ complexes, where AA = bpym, bpy or phen and n = 1, 2 or 3.

Experimental

Materials

The 2,2′-bipyrimidine used in this study was purchased from Alfa Inorganic. The 2,2′-bipyridine and 1,10-phenanthroline was obtained from Fisher Chemicals. The ligands were used without further purification. High purity argon was obtained from Linde and used for deoxygenation of solvents. Water used in spectroscopic and electrochemical studies was deionized and then redistilled from alkaline permanganate in an all-glass apparatus. All other materials used were reagent grade.

Synthesis

The [Co(bpym)$_3$](ClO$_4$)$_2$·H$_2$O complex was prepared by dissolving 0.30 g (1.96×10^{-4} mol) of 2,2′-bipyrimidine (excess) in 75 mL of methanol, followed by bubbling with argon to remove oxygen. A deoxygenated solution containing 0.10 g (4.2×10^{-4} mol) $CoCl_2 \cdot 6H_2O$ in methanol was then added through a separatory funnel. The reddish-pink Co(II) solution immediately turned orange-yellow upon addition to the solution of 2,2′-bipyrimidine. The product was precipitated from solution by the addition of a deoxygenated, saturated, methanolic NaClO$_4$ solution. The pale yellow product was collected by filtration, washed with 200 mL of anhydrous ethanol to remove excess 2,2′-bipyrimidine, and vacuum dried. Yield was 0.28 g (90%). The sample was analyzed by Atlantic Microlab, Inc., Atlanta, Georgia. *Anal.* Calcd for $C_{24}H_{18}N_{12}CoCl_2O_8 \cdot H_2O$: C, 38.38; H, 2.67; N, 22.36. Found: C, 38.80; H, 2.63; N, 22.39. Samples of [Co(bpy)$_3$](ClO$_4$)$_2$ and [Co(phen)$_3$](ClO$_4$)$_2$ were prepared according to the literature procedures [10, 11].

Instrumentation

Cyclic voltammograms were recorded on an IBM Instruments, Inc. Model EC/225 Voltammetric Analyzer. The glassy carbon working electrode (5.0 mm diameter) was polished with alumina prior to each series of scans. A saturated calomel electrode served as a reference electrode (nominally 0.242 V *vs.* NHE). Aqueous scans were recorded in deoxygenated 0.1 *M* KCl solution, with N$_2$ blowing over the top during the scan. Cyclic voltammograms in acetonitrile utilized 0.1 *M* NH$_4$PF$_6$ as a supporting electrolyte. Scan rates were varied from 50–200 mV/s. The potentials

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reported for the oxidation couples are estimates obtained by averaging the anodic and cathodic peak potentials and are referenced to NHE.

Visible absorption spectra were recorded on a Bausch & Lomb Spectronic 2000 spectrophotometer. Near-infrared and ultraviolet spectra were recorded on a Cary 14 with matching quartz cells.

Magnetic susceptibility measurements were made on solid samples using the Faraday method. A Cahn Model RG Automatic Electrobalance and an Alpha Scientific 7500M electromagnet were used. $HgCo(CNS)_4$ was used as a calibrant [12]. Diamagnetic corrections of the molar susceptibilities were made using Pascals constants [13]. Room temperature was controlled at 22.5 ± 0.1 °C.

Kinetics

The rate constant for chelate opening in electrode attached $Co(bpy)_3{}^+$ was approximated voltammetrically. Repetitive cyclic voltammetry scans were recorded in which a variable delay time was used after reduction to Co(I) but before re-oxidation to Co(II). The half-life was approximated as the time (delay + scanning) necessary to generate equal peak areas in the two return peaks (Co(I) → Co(II)).

Results and Discussion

Absorption Spectra

The aqueous, electronic absorption spectrum of $Co(bpym)_3{}^{2+}$ shows ligand field bands quite similar in energy and intensity (Table I) to $Co(bpy)_3{}^{2+}$ and $Co(phen)_3{}^{2+}$ [10, 11]. Large differences which occur between $Co(bpym)_3{}^{2+}$ and $Co(bpy)_3{}^{2+}$ in the internal ligand region (<300 nm) may be attributed to differences in the intra-ligand spectra of the bpym and bpy ligands. The electronic absorption spectrum of $Co(bpym)_3{}^{2+}$ has a broad, low-energy band at 990 nm ($\epsilon = 5\ M^{-1}\ cm^{-1}$), with a higher energy absorption at 472 nm ($\epsilon = 18\ M^{-1}\ cm^{-1}$). These energies and relative intensities correlate closely with ligand field values reported for $Co(bpy)_3{}^{2+}$ [14]. We, therefore, assign the 990 nm peak to the ${}^4T_2(F) \leftarrow {}^4T_1(F)$ and the 472 nm peak to ${}^4T_1(P) \leftarrow {}^4T_1(F)$ transitions, respectively (Table I).

Magnetic Susceptibility

Room temperature magnetic susceptibility for $Co(bpym)_3{}^{2+}$ results in $\mu = 4.6$ B.M. This value compares with $\mu = 4.5$ B.M. for $Co(bpy)_3{}^{2+}$ ($\mu = 4.34$–4.83 B.M. [10, 16]), and $\mu = 4.6$ B.M. for $Co(phen)_3{}^{2+}$ ($\mu = 4.61$ B. M. [17]). Thus, the prepared complex is d^7 Co(II) and has very similar magnetic properties to the bpy and phen analogs.

Cyclic Voltammetry

Aqueous (0.1 *M* KCl) cyclic voltammograms were recorded for $Co(AA)_3{}^{2+}$ complexes (AA = phen, bpy, and bpym). The results appear in Table II. All potentials in Table II are reported *vs.* NHE. Scans included both the Co(III)/Co(II) and Co(II)/Co(I) couples.

The bpy and phen complexes had been the report of some previous cyclic voltammetry studies [18].

TABLE I. Electronic Absorption Spectra $Co(AA)_3{}^{2+}$ and Ligands[a].

Compound	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$	Assignment
$Co(bpym)_3{}^{2+}$	990	5	${}^4T_2(F) \leftarrow {}^4T_1(F)$
	472	18	${}^4T_1(P) \leftarrow {}^4T_1(F)$
	242	47300	Intraligand ($\pi \rightarrow \pi^*$)
$Co(bpy)_3{}^{2+}$	910	6	${}^4T_2(F) \leftarrow {}^4T_1(F)$[b]
	440(sh)	94	${}^4T_1(P) \leftarrow {}^4T_1(F)$[b]
	305	33700	Intraligand ($\pi \rightarrow \pi^*$)
	294	37100	Intraligand ($\pi \rightarrow \pi^*$)
	243	30400	Intraligand ($\pi \rightarrow \pi^*$)
$Co(phen)_3{}^{2+}$	950	5	${}^4T_2(F) \leftarrow {}^4T_1(F)$
	435(sh)	90	${}^4T_1(P) \leftarrow {}^4T_1(F)$
	268	84700	Intraligand ($\pi \rightarrow \pi^*$)
	225	81600	Intraligand ($\pi \rightarrow \pi^*$)
bpym	274	1400	Intraligand ($\pi \rightarrow \pi^*$)
	240	15600	Intraligand ($\pi \rightarrow \pi^*$)
bpy	310	1880	Intraligand ($\pi \rightarrow \pi^*$)[c]
	282	11900	Intraligand ($\pi \rightarrow \pi^*$)[c]
	235	10600	Intraligand ($\pi \rightarrow \pi^*$)[c]
phen	267	28600	Intraligand ($\pi \rightarrow \pi^*$)
	228	35200	Intraligand ($\pi \rightarrow \pi^*$)

[a] Aqueous solution, 25 °C. [b] Assignment from reference 14. [c] Assignment form reference 15.

TABLE II. Electrochemical Data for $Co(AA)_3^{3+/2+/1+}$ Complexes[a].

AA	Co(III)/Co(II)		Co(II)/Co(I)		
	$E_{1/2}$, V	ΔE, mV	$E_{1/2}$, V	ΔE, mV	$\Delta E_{1/2}$, V
phen	0.36	~100	−0.77	~140	1.13
	0.38[e]		−0.8[e]		
	0.524[g]	~180			
bpy	0.31	~170	−0.84	~100	1.15
	0.31[e]–0.35[f]		−0.89[f]		
	0.49[g]	~160			
bpym	1.02	~240	−0.50	~170	1.52
	1.03[g]	~320			

[a] All $E_{1/2}$ values reported *vs.* NHE in 0.1 *M* KCl in H_2O or 0.1 *M* NH_4PF_6 in acetonitrile solution. [b] Estimated from $(E_{pc} + E_{pa})/2$. [c] Estimated from $E_{pc} - E_{pa}$. [d] Estimated from $E_{1/2}(Co(III)/Co(II)) - E_{1/2}(Co(II)/Co(I))$. [e] In 0.5 *M* H_2SO_4, reference 18. [f] Ref. 22. [g] In 0.10 *M* NH_4PF_6/acetonitrile.

The Co(III)/Co(II) couple is chemically reversible and is +0.3 to +0.4 V *vs.* NHE for the two compounds. The Co(II)/Co(I) couple can be approximated at −0.75 to −0.85 V. The uncertainty in the numbers in Table II for the Co(II)/Co(I) couple comes about from surface adsorption of the Co(I) complexes which forms a precipitate at the electrode surface [19].

The $Co(bpy)_3^+$ analog shows a tendency for both chelate opening [19] and substitution (in a coordinating solvent) [20]. Reoxidation of the $Co(bpy)_3^+$ up to Co(III) leads to chelate closure. From cyclic voltammetry studies with various time delays, a rate constant for chelate opening of 6.3×10^{-2} s^{-1} was calculated. Upon periods of >1 minute as $Co(bpy)_3^+$, further unraveling is observed as evidenced by additional oxidation waves in the Co(I) to Co(II) cycle. However, these intermediates lead to an immediate regeneration of the tris(chelate) complex upon reoxidation to Co(III).

There is positive evidence that the Co(I) complex, at least the tris species, is absorbed on the electrode surface. After reduction to Co(I), the electrochemical experiment was terminated and the cobalt solution was replaced with a solution containing only electrolyte. The potential was initiated in the Co(I) region and the cycle Co(I) Co(II) → Co(I) gave an oxidation and reduction wave, even if at approximately one-third the amplitude and slightly shifted from the voltammogram in the solution containing the cobalt complex.

The cyclic voltammogram of $Co(phen)_3^{3+/2+/1+}$ is more straightforward than the bpy analog. Table II summarizes the results obtained for this complex. This system, like the bpy analog, is chemically reversible in the 3+/2+ region but shows a 100 mV peak-to-peak separation at a 100 mV/s scan rate. Reduction of $Co(phen)_3^{2+}$ to $Co(phen)_3^+$ leads to the formation of a blue precipitate. However experiments varying delay time between reduction to Co(I) and reoxidation to Co(II) show only one peak [21] and thus no evidence of a monodentate phen ligand. The electrode attachment of the Co(I) complex was confirmed by analogous experiments as described above for the bpy analog.

The electrochemistry of the $Co(bpym)_3^{3+/2+/1+}$ complex is very interesting and although qualitatively similar is quantitatively much different than the bpy or phen analogs. The bpym complex still has a chemically reversible 3+/2+ couple ($E_{1/2} = 1.02$ V; ΔE = 240 mV) and forms some precipitate with the formation of $Co(bpym)_3^+$. There is a qualitative difference between the bpym and bpy complexes. In the oxidation of $Co(bpym)_3^+$, the first peak is much smaller than the second peak. This is in direct contrast with the results obtained for $Co(bpy)_3^+$. In addition, there is no change in peak ratio for the bpym complex when the delay time is increased. Since cycling through the Co(III) species regenerated all of the electroactive species, any intermediates formed must not involve total loss of any ligand.

More interestingly, there is another qualitative difference between the bpym complex and its bpy and phen analogs. The Co(III)/Co(II) couple for bpym is shifted ~0.7 V more positive than the bpy and phen complexes. This represents a 68 kJ difference in potential from a small modification in ligand. This 0.7 V potential shift explains why $Co(bpym)_3^{2+}$ is not chemically oxidized by H_2O_2.

One of the reasons Bard and coworkers [18, 22] have been looking at the phen and bpy complexes of iron and cobalt is their potential use for a redox flow battery system. A number of different redox couples have been proposed for such a system. However, a difficulty in the storage cell is the possible intermixing of the components of the two half-cells. One approach which minimizes this problem is the use of a single element, three oxidation state system

[22]. Some of the problems encountered with the use of $Co(bpy)_3^{3+/2+/1+}$ and $Co(phen)_3^{3+/2+/1+}$ systems are that the Co(III)/Co(II) couple is not very positive, the Co(I) complex forms a precipitate, and difference between the Co(III)/Co(II) and Co(II)/Co(I) redox couples in not very large (~1.1 V). On the other hand, the Co(III)/Co(II) couple for bpym is 0.7 V more positive than previous analogs, shows a greater solubility of Co(I) complex, and more importantly, shows a 1.5 V difference between Co(III)/Co(II) and Co(II)/Co(I) couples. These qualities suggest that the bpym series and its derivatives may warrant further study as solutions for use in storage batteries.

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References

1 R. R. Ruminski and J. D. Petersen, *Inorg. Chem., 21,* 3706 (1982).
2 R. R. Ruminski and J. D. Petersen, *Inorg. Chim. Acta, 65,* L177 (1982).
3 K. J. Moore and J. D. Petersen, *Polyhedron, 2,* 279 (1983).
4 R. R. Ruminski and J. D. Petersen, *Inorg. Chem.* submitted for publication.
5 E. V. Dose and L. J. Wilson, *Inorg. Chem. 17,* 2260 (1978).
6 M. Hunziker and A. Ludi, *J. Am. Chem. Soc., 99,* 7370 (1977).
7 D. P. Rillema, R. W. Callahan and K. B. Mack, *Inorg. Chem., 21,* 2589 (1982).
8 D. P. Rillema and K. B. Mack, *Inorg. Chem., 21,* 3849 (1982).
9 J. C. Bailar, Jr., D. J. Baker and R. A. Bauer, *U.S. NTIS, AD Rep.,* AD-A015508 (1975).
10 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.,* 3570 (1952).
11 V. P. Pfeiffer and B. Werdelmann, *Z. anorg. Chem., 261,* 197 (1950).
12 S. Sullivan, A. N. Thorpe and P. Hambright, *J. Chem. Ed., 48,* 345 (1971).
13 A. Earnshaw, 'Introduction to Magnetochemistry', Academic Press, New York, 1968.
14 R. A. Palmer and T. S. Piper, *Inorg. Chem., 5,* 864 (1966); R. D. Hancock and G. J. McDougall, *J. Chem. Soc., Dalton,* 67 (1977).
15 Y. Gondo, *J. Chem. Phys., 41,* 3928 (1964); J. E. Fergusson and G. M. Harris, *J. Chem. Soc., A,* 1293 (1966).
16 E. Paglia and C. Sironi, *Gazz. chim. ital., 87,* 1125 (1957); G. Favini and E. Paglia, *J. Inorg. Nucl. Chem., 8,* 155 (1958); B. N. Figgis M. Gerloch, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc. A,* 2086 (1968).
17 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.,* 338 (1958).
18 Y.-W. D. Chen, K. S. V. Santhanam and A. J. Bard, *J. Electrochem. Soc., 129,* 61 (1982).
19 G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem., 8,* 551 (1958).
20 S. Margel, W. Smith and F. C. Anson, *J. Electrochem. Soc., 125,* 241 (1978).
21 A broadening of the peak in going from $Co(phen_3^+)$ to $Co(phen)_3^{2+}$ is sometimes observed as in reference 23. However, the shoulder or broadening occurred in very few experiments, was not reproducible, and possibly can be attributed to a non-uniform coating of $Co(phen)_3^+$ on the electrode surface.
22 Y.-W. D. Chen, K. S. V. Santhanam and A. J. Bard, *J. Electrochem. Soc., 128,* 1640 (1981).
23 C. V. Krishnan, C. Creutz, D. Mahajan, H. A. Schwartz and N. Sutin, *Isr. J. Chem., 22,* 98 (1982).