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Tris(2,2′-Bipyrimidine)Cu(II) Hexafluorophosphate. Synthesis and Spectroscopic Properties for Precursor Complexes in the Preparation of Polymetallic Systems

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Abstract

The synthesis, electronic spectrum, magnetic susceptibility and electrochemistry of the d^9 metal complex $[Cu(bpym)_3](PF_6)_2$(bpym = 2,2′-bipyrimidine) are reported here. Ligand field electronic spectral assignments are made by comparison to the analogous $Cu(bpy)_3^{2+}$(bpy = 2,2′-bipyridine) complex. Cu(II) d orbitals are shown to have less $d_M \rightarrow \pi^*_L$ interaction than other $M(bpym)_3^{2+}$ (M = Co, Ni) complexes from the position of the MLCT absorption. Cyclic voltammetry of $Cu(bpy)_3^{2+}$ in acetonitrile shows the reduction potential ($E_{1/2}$(2+/1+)) is +0.27 V more positive than $Cu(bpy)_3^{2+}$.

Introduction

Many recent studies have focused on the synthesis, spectroscopy and use of nitrogen donor 2,2′-bipyridine (bpy) analog ligands coordinated to transition metal complexes [1–6]. The effective use of 2,2′-bipyrimidine (bpym) as an effective bpy analog, and as a bridging ligand between metal centers has been demonstrated in the preparation of monometallic and bimetallic complexes [7–18]. We have previously prepared, characterized and reported the series of $M(bpym)_3^{2+}$ (M = Fe(II), Co(II), Ni(II)) complexes, and their potential use as synthetic precursor complexes [16–18].

The continuation of the study of $M(bpym)_3^{2+}$ complexes to include Cu(II) is of particular interest because spectroscopically, $Cu(bpym)_3^{2+}$ may provide another example of a Cu(II) complex that might be forced to undergo minimum tetragonal distortion due to ligand rigidity [19–24]. $Cu(bpym)_3^{2+}$ is of synthetic interest owing to uncoordinated peripheral nitrogen opposite the metal center, which might allow $Cu(bpym)_3^{2+}$ to serve as a building block in the synthesis of polymetallic systems. Some Cu(bpym) chelated complexes have been prepared and are being studied as synthetic models for the Fe/Cu binuclear active site of cytochrome oxidase [14].

We now wish to report the preparation, spectroscopy, magnetic susceptibility and electrochemistry of d^9 $[Cu(bpym)_3](PF_6)_2$. Assignment of the metal d–d ligand field and metal to ligand charge transfer (MLCT) transitions will be made by comparison to the analogous $Cu(bpy)_3^{2+}$ and other $M(bpym)_3^{2+}$ (M = Co(II), Ni(II)) complexes. Electrochemical results for the comparison of $Cu(bpym)_3^{2+}$ *vs.* $Cu(bpy)_3^{2+}$ will be used to assess the comparative amount of electron delocalization over the nitrogen heterocyclic rings.

Experimental

Materials

The 2,2′-bipyrimidine used in this study was purchased from Lancaster Synthesis LTD, Lancaster, England, and used without purification. 2,2′-Bipyridine was purchased from Alfa Inorganics. Argon was obtained from Linde, passed through a chromous solution, then dried by passing through $CaCl_2$ before use in solvent deoxygenation. All other materials used were reagent grade.

Synthesis

$[Cu(bpym)_3](PF_6)_2$ was prepared by dissolving 0.16 gm 1.01×10^{-3} mol) of bpym with stirring in 10 mL methanol, followed by bubbling with argon to remove oxygen. Above the 3 neck flask containing the bpym solution was a separatory funnel containing a deoxygenated solution of 0.04 gm (3.0×10^{-4} mol) $CuCl_2$ in 10 mL methanol. Upon reduction of argon flow into the flask, the green Cu(II) dripped into the bpym and immediately turned blue. After 15 min the product was precipitated by the addition of solid NH_4PF_6 or KPF_6. The blue precipitate was collected by filtration, washed with methanol and vacuum dried. The recrystallized product was obtained by dissolving the blue powder in a minimum of CH_3CN, followed by the addition of NH_4PF_6 or KPF_6 then addition of methanol to induce precipitation. The final product was washed quickly with a minimum of cold water, followed by methanol and ether. The pale blue powder was vacuum dried. Yield (0.041 gm, 4.8×10^{-5} mol) 20%. The sample was analyzed by Atlantic Microlab Inc., Atlanta, Ga. Calcd for

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TABLE I. Electronic Absorption, Electrochemical and Magnetic Susceptibility Data for $Cu(bpym)_3^{2+}$ and $Cu(bpy)_3^{2+}$ Complexes.

Complex	λ (nm) ε (M^{-1} cm^{-1})	Assignment	$E_{1/2}$ (V) *vs.* SCE	μ (BM)
$Cu(bpym)_3^{2+}$	300, 4.4 × 10^3 [a]	MLCT	+0.243 [f]	1.85 [b]
	682, 81.0	$^2E \leftarrow {}^2E$		
	1320, 37.4	$^2A \leftarrow {}^2E$		
$Cu(bpy)_3^{2+}$	671, 56.5 [c]	$^2E \leftarrow {}^2E$ [c]	−0.03 [f]	1.95 [d]
	1300, 28.2	$^2A \leftarrow {}^2E$	−0.21 [g]	1.91 [e]
			−0.20 [h]	

[a] This work, in CH_3CN. [b] This work, $[Cu(bpym)_3](PF_6)_2 \cdot H_2O$. [c] Ref. 21, in CH_3NO_2. [d] This work. [e] Ref. 28, 29. [f] Recorded in CH_3CN, 0.1 M tetraethylammonium perchlorate and excess ligand. [g] Recorded in H_20 0.1 M KCl and saturated with excess ligand. [h] Ref. 30, 31, recorded in H_20 0.1 M KCl and saturated with excess ligand.

$C_{24}H_{18}N_{12}CuP_2F_{12} \cdot H_2O$: C, 34.03; H, 2.36; N, 19.85%. Found C, 33.98; H, 2.36; N, 19.83%. The room temperature magnetic susceptibility was measured at $\mu = 1.85$ B.M. which is typical for the paramagnetic d^9 species (Table I).

$Cu(bpy)_3^{2+}$ was prepared according to literature procedures [27].

Instrumentation

Cyclic voltammograms were recorded on a Bioanalytical Systems CV-18 Cyclic Voltammograph with a Hewlett Packard 7044A XY recorder. The glassy carbon (3.0 mm diameter) working electrode was polished with alumina prior to each scan. An Ag|AgCl (3 M KCl, nominally −0.044 V *vs.* SCE) reference electrode was used. All potentials are reported *vs.* SCE and remain uncorrected for junction potential. The potentials reported for oxidation couples, $E_{1/2}$, are estimates obtained by averaging the anodic and cathodic peak potentials. Cyclic voltammograms were recorded in CH_3CN and utlized 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Scan rates were varied from 50–300 mV/s.

Utraviolet visible and near infrared spectra were recorded on a Beckman Model 5240 Spectrophotometer, with matching quartz cells.

Magnetic susceptibility measurements were made on solid samples, as described previously [18].

Results and Discussion

The electronic absorption spectrum of $Cu(bpym)_3^{2+}$ (Fig. 1) was recorded in acetonitrile and has ligand field absorptions similar in wavelength and intensity to those for $Cu(bpy)_3^{2+}$ (Table I). The shift towards longer wavelength for $Cu(bpym)_3^{2+}$ *vs.* $Cu(bpy)_3^{2+}$ is consistent with longer wavelength changes observed for other $M(bpym)_3^{2+}$ *vs.* $M(bpy)_3^{2+}$ (M = Co(II), Ni(II)) comparisons [18]. While six coordinate octahedral Cu(II) complexes undergo Jahn–Teller distortion, the interaction for tris chelated bidentate Cu(II) is less well defined [19–24]. Solution studies have proposed that bidentate ligand rigidity restricts Jahn–Teller distortion and assigned ligand field absorptions for $Cu(bpy)_3^{2+}$ and $Cu(phen)_3^{2+}$ on the basis of trigonally distorted pseudo D_3 symmetry [22–24]. Single crystal polarization studies may indicate a more tetragonally distorted octahedron for some Cu(II) complexes [19, 20, 22]. Owing to the similarity of bpym with the nitrogen donor aromatic ligands bpy and phen, by analogy we assign ligand field absorptions for $Cu(bpym)_3^{2+}$ in solution as $^2E \leftarrow {}^2E(\lambda_{max} = 682$ nm, $\epsilon = 81.9$ M^{-1} $cm^{-1})$ and $^2A \leftarrow {}^2E(\lambda_{max} = 1320$ nm, $\epsilon = 37.4$ M^{-1} $cm^{-1})$. Addition of excess bpym did not change the spectrum.

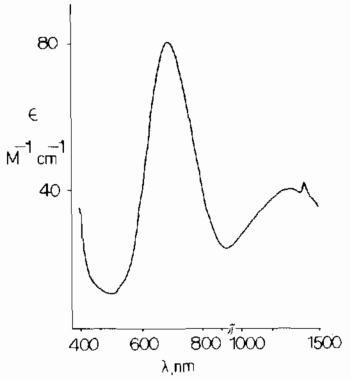

Fig. 1. Electronic Absorption Spectrum of $Cu(bpym)_3^{2+}$ in CH_3CN. Water overtone appears on the low energy absorption. Wavelength scale change at 850 nm.

The aqueous absorption spectrum of $Cu(bpym)_3^{2+}$ was found to be wavelength and intensity dependent on the addition of excess bpym ligand. While a 5.00 mL aqueous solution made up to be 1.4 × 10^{-3} M (7.1 × 10^{-6} mol) $Cu(bpym)_3^{2+}$ had $\lambda_{Max} = 700$nm ($\epsilon = 31.9$ M^{-1} cm^{-1}), addition of 1.3 × 10^{-3} mol solid bpym shifted the wavelength to $\lambda_{max} = 682$ nm ($\epsilon = 81.4$ M^{-1} cm^{-1}). These results indicate the ring opening or dissociation, of at least one bpym in aqueous solution from $Cu(bpym)_3^{2+}$. Ligand dissociation in dilute aqueous $Fe(bpym)_3^{2+}$ solution has been attributed to solvent ligand interaction through the non-coordinated bpym nitrogens [16–18]. Attempts to measure wavelength maxima and extinction coefficients of $Cu(bpym)_3^{2+}$ in organic non-coordinating solvents such as propylene carbonate (1,2 propanediol cyclic carbonate) produced a green solution (λ_{max} = 715 nm, ϵ = 104 M^{-1} cm^{-1}) without low energy absorptions in the near infrared. Addition of excess bpym did not shift λ_{max}, and the complex in solution may be $Cu(bpym)_2^{2+}$. Similar results were obtained in DMF.

The ultraviolet spectrum of $Cu(bpym)_3^{2+}$ in CH_3CN is characterized by a metal to ligand charge transfer (MLCT) absorption shoulder at 300 nm, which appears on the low energy side of a more intense bpym π–π^* intraligand transition. The MLCT energy is slightly higher than for $Ni(bpym)_3^{2+}$(λ = 370 nm), and other M(bpym) complexes [17, 18]. Assuming a highest occupied molecular orbital (HOMO) principally metal $d\sigma^*$ in character, the higher energy transition may be understood as an increase of $d\sigma^*$–$p\pi^*$ separation as metal d orbitals are stabilized across the periodic table, while ligand $p\sigma$ and $p\pi$ remain unchanged [18].

The cyclic voltammetry of $Cu(bpym)_3^{2+}$ was recorded in acetonitrile with excess bpym present. The results show a single irreversible wave with peak to peak separation of 110–130 mV at v = 0.050 (v = scan rate in V/s) when scanned from +1.0 V to −0.30 V *vs.* SCE. Plots of $v^{1/2}$ *vs.* anodic wave height are nonlinear and indicate irreversibility [25]. The asymmetrical shape of the voltammogram following Cu(I)/Cu(II) oxidation suggest chemical reaction occurred during reduction to the Cu(I) complex. The $E_{1/2}$ couple for $Cu(bpym)_3^{2+}$ of +0.24 V *vs.* SCE is 0.27 V more positive than $E_{1/2}$ = −0.03 V for $Cu(bpy)_3^{2+}$. The shift to more positive reduction potential has also been observed for $M(bpym)_3^{2+}$ *vs.* $M(bpy)_3^{2+}$ (M = Fe(II), Co(II), Ni(II)) and other systems [4, 7, 16–18]. We attribute this to an increased amount of delocalization of electron density over bpym *vs.* bpy ligand orbitals as the electron withdrawing N replaces the C–H group.

Exhaustive electrolysis of a solution of $Cu(bpym)_3^{2+}$ in acetonitrile at 0.0 V *vs.* SCE results in a visible wavelength maxima change from 682 nm to 715 nm. While the product has not been conclusively determined, ligand loss followed by solvent substitution seems probable. The formation of a stable Cu(I) d^{10} complex is tentatively ruled out since Cu(I) complexes exhibit characteristic MLCT absorptions of 440–460 nm (ϵ = 2400–5000 M^{-1} cm^{-1}) [26].

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