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Complex Formation of Lanthanide Polyaminopolycarboxylates

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Methods to synthesize bis(3-aminopropyl) ether *N,N,N′,N′*-tetraacetic acid and (bis(3-(bis(carboxymethyl)amino)-propyl)methylammonio)acetate are reported. The complex formation constants of their anions with lanthanide ions are also measured. The effects of ring size on the stability constants of the complexes and the selectivity of Ln–Ac separation are discussed.

Introduction

Polyaminopolycarboxylic acids have long been known to be effective chelating agents in lanthanide and actinide separations,[1] and in the area of cation-exchange separations, certain polyaminopolycarboxylic acids (EDTA, DTPA, EEDTA)[2,3] surpass most other reagents (e.g., phosphoric acids, hydroxycarboxylic acids, and amines) in effectiveness. In the past, the study of polyaminopolycarboxylic acids has been concentrated mainly on reagents with an ethylene (EDTA) or diethylene (DTPA and EEDTA) backbone. Such compounds form multiple five-membered rings with metal ions in their complexes. To establish ring-size influence on the selectivity of such complex-forming reagents, an investigation of other than five-membered rings became necessary. Therefore, a study of the synthesis of bis(3-aminopropyl) ether *N,N,N′,N′*-tetraacetic acid (BPETA) and (bis(3-(bis(carboxymethyl)amino)propyl)methylammonio)acetate (BCPA) and the affinities of their anions for lanthanide metal ions was undertaken. The performance of these ligands as selective eluants in lanthanide–actinide separations was also examined.

Experimental Section

Starting Materials. Bis(3-aminopropyl)methylamine was purchased from Alfa Products. Bis(2-cyanoethyl) ether was obtained from Pfaltz and Bauer, Inc., and chloroacetic acid was obtained from Aldrich Chemical Co. These chemicals were used without further purification. Tetrahydrofuran was dried over calcium hydride, distilled under dry nitrogen at 64–65 °C, and used immediately. Approximately 0.1 M $Ln(NO_3)_3$ solutions were made by dilution of stock solutions previously prepared from corresponding oxides (greater than 99.9% purity) with use of the method described by Adolphson.[4] Lanthanide tracers, $^{241}Am(NO_3)_3$ and $^{155}Eu(NO_3)_3$, were purchased from New England Nuclear and diluted to provide convenient activity levels. Generally, reagent-grade solvents were used without additional purification.

Physical Measurements. Mass spectra were recorded on a Finnigan 400 GC MS DS instrument. Nuclear magnetic resonance spectra were obtained by using either the JEOL FX 90Q Fourier transform NMR spectrometer or the Bruker WM300. All the elemental analyses were performed by Galbreath Laboratories, Inc., Knoxville, TN. Molecular weights of product acids were determined by the potentiometric titration method, with standardized carbonate-free potassium hydroxide used as the titrant.

Bis(3-aminopropyl) Ether. A 3-L, three-necked flask was equipped with a reflux condenser, a mechanical stirrer, and a dropping funnel. The reaction was carried on under dry N_2. The flask in which 0.70 mol (26.6 g) of lithium aluminum hydride was suspended in 1 L of dry THF was placed in an ice bath. Then, 0.35 mol (34.3 g) of 100% H_2SO_4 was slowly added to the solution with vigorous stirring over a period of 30 min. Hydrogen gas was evolved during this time. To this aluminum hydride solution was slowly introduced 0.25 mol (31.0 g) of bis(2-cyanoethyl) ether in 70 mL of dry THF over 45 min through a dropping funnel. During the addition of the ether solution, hydrogen gas was not evolved. After completion, the solution was stirred vigorously for 3 h. The solution color changed to light yellow during this time. Excess NaOH solution was added carefully to destroy any excess hydride and to coagulate the precipitated aluminum hydroxide. The precipitate was then separated by filtration, and the light yellowish filtrate was concentrated and treated with 140 mL of HCl/H_2O (1:1). The aqueous layer was then concentrated to a viscous mass. Ethyl ether was added, followed by saturated potassium hydroxide solution. The light yellowish ether extract obtained was dried over anhydrous potassium carbonate, potassium hydroxide pellets, and then sodium metal. The product was finally distilled at a temperature of 83–85 °C and 5 torr, and the distillation yielded 20.0 g (0.151 mol, 60.5%) of product. Mass spectrum: m/e 133 (M + H), 103, 76 (100) 74, 59, and 57. NMR: ^1H (90 MHz, $CDCl_3$) δ 3.49 (4 H, t), 2.78 (4 H, t), 1.70 (4 H, p) 1.38 (4 H, s); ^{13}C δ 68.72, 39.30, 33.23.

$$2LiAlH_4 + H_2SO_4 \rightarrow Li_2SO_4 + 2AlH_3 + 2H_2$$

$$2AlH_3 + O(CH_2CH_2CN)_2 \xrightarrow{OH^-/H_2O} 2Al(OH)_3 + O(CH_2CH_2CH_2NH_2)_2$$

Bis(3-aminopropyl) Ether *N,N,N′,N′*-Tetraacetic Acid Monohydrate (BPETA). This compound had been prepared by Schwarzenbach et al.;[5] however, no detailed experimental preparation method was reported.

BPETA was prepared in a manner similar to that used to prepare EEDTA[3] and BEATA by treating 19 g (0.144 mol) of bis(3-aminopropyl) ether with 1 mol excess chloroacetic acid. The white product was recrystallized from H_2O/absolute ethanol and dried in an oven at 80 °C overnight. The pure compound decomposed at about 99 °C and weighed 47.6 g (0.125 mol, 86.6%). The determined molecular weight was 385.4, which was quite close to the calculated 382.4.

$$O(CH_2CH_2CH_2NH_2)_2 + 4ClCH_2COOH \rightarrow O[CH_2CH_2CH_2N(CH_2COOH)_2]_2 + 4HCl$$

Anal. Calcd for $C_{14}H_{24}N_2O_9{\cdot}H_2O$: C, 43.98; H, 6.85; N, 7.33; O, 41.84. Found: C, 43.82; H, 6.91; N, 7.20; O, 41.94. The result of NMR analysis was as follows: ^1H (300 MHz D_2O/Me_4Si) δ 4.01 (8 H, s), 3.72 (4 H, t), 3.44 (4 H, t), 2.06 (4 H, p); ^{13}C (90 MHz, D_2O/CD_3CN) 169.80, 70.04, 56.71, 56.38, 24.58.

(Bis(3-(bis(carboxymethyl)amino)propyl)methylammonio)acetate Monohydrate (BCPA). The procedure for preparation of BCPA was the same as for EEDTA[3] with 25.0 g (0.172 mol) of bis(3-aminopropyl)methylamine and 97.6 g (1.03 mol) of chloroacetic acid yielding 66.5 g (0.147 mol, 85.5%) of pure product after drying in an oven at 100 °C for 5 h. In a melting-point tube, the white powder decomposed at 120 °C. Its experimental molecular weight was 451.8, which agreed well with the calculated 453.4 for the monohydrate.

$$H_3CN(CH_2CH_2CH_2NH_2)_2 + 5ClCH_2COOH \rightarrow {}^-OOCCH_2N^+(CH_3)[CH_2CH_2CH_2N(CH_2COOH)_2]_2 + 5HCl$$

Anal. Calcd for $C_{17}H_{29}N_3O_{10}{\cdot}H_2O$: C, 45.05; H, 6.98; N, 9.27. Found: C, 44.98; H, 7.01; N, 9.42. NMR: ^1H (300 MHz, D_2O/Me_4Si) δ 4.04 (8 H, s), 4.00 (2 H, s), 3.71 (4 H, t) 3.43 (4 H, t),

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Table I. Protonation Constants of $O[CH_2CH_2CH_2N(CH_2COOH)_2]_2$ at 25 °C and Ionic Strength (I) 0.1

		log α(20 °C)	
		ref 5	ref 7
$\alpha_1 = [HL]/([H][L]) = 0.108 \times 10^{11}$	$\log [HL]/([H][L]) = 10.03$	10.17	10.14
$\alpha_2 = [H_2L]/([H]^2[L]) = 0.817 \times 10^{20}$	$\log [H_2L]/([H][HL]) = 9.88$	9.67	9.64
$\alpha_3 = [H_3L]/([H]^3[L]) = 0.366 \times 10^{23}$	$\log [H_3L]/([H][H_2L]) = 2.65$	2.7	2.74
$\alpha_4 = [H_4L]/([H]^4[L]) = 0.767 \times 10^{25}$	$\log [H_4L]/([H][H_3L]) = 2.32$	2.1	2.0

3.24 (3 H, s), 2.27 (4 H, p); ^{13}C (90 MHz, D_2O/CD_3CN) δ 169.86, 168.24, 61.78, 60.15, 57.10, 53.52, 49.94, 18.79.

Anion Protonation Constants. In each case, the anions' protonation constants were obtained from pH_c measurements on a series of independently prepared chelating agent solutions, each containing a different amount of KOH or HNO_3 and enough KNO_3 to adjust the ionic strength to 0.1 M.

Lanthanum Polyaminopolycarboxylate Stability Constants. The stability constants for the ML^- ($\beta_1 = [ML]/[M][L]$) and MHL ($\beta_H = [MHL]/[M][HL^-]$) complexes formed by the various lanthanides were determined potentiometrically at 25.00 ± 0.05 °C and ionic strength (KNO_3) 0.1 M. These values were calculated from pH_c measurements on a series of independently prepared solutions of chelating agent, $M(NO_3)_3$, KNO_3, and KOH. The nonlinear calculation method that was employed has been described in detail elsewhere.[6]

Cation Elution. Approximately 3–5 μL of well-mixed tracers were injected into the top of the ion-exchange column (2 by 500 mm bed of Dowex 50W-8, 200–400 mesh), which was presaturated with the eluant. Each eluant was prepared by dissolution of the pure polyaminopolycarboxylic acid, followed by pH adjustment with NH_4OH. To ensure a constant ionic strength of 0.1 M, an appropriate amount of NH_4NO_3 was added. The effluent from the elution experiments was collected, and the individual samples were counted by means of a Ge-Li detector.

Results and Discussion

BPETA. The protonation constants of BPETA have been determined before by two other groups[5,7] under different conditions. The verified values of these constants are shown in Table I. Even though the conditions differ by 5 °C, the values obtained in this work agree well with the earlier data. The pK values of EEDTA are 9.47, 8.84, 2.76, and 1.8.[8] Comparison of pK values of BPETA and EEDTA indicates that bis(3-aminopropyl) ether *N,N,N′,N′*-tetraacetic acid is a more basic compound due to the reduced inductive effect of the ether oxygen atom when it is in a less proximate location (i.e., the 3-position rather than the 2-position of the chain which connects the iminodiacetate moieties).

The stability constants of BPETA chelates involving lanthanide ions are displayed in Table II, and a plot of log β_1 values vs. the metal ionic radius is shown in Figure 1. The ligand–cation affinity rises to a maximum at samarium, falls to a minimum at terbium, and then increases again. The stability constants of BPETA chelates with lanthanons are about 10^6-fold less than those of EEDTA.[9] The great difference of stability constants between homologues may be caused by two factors: the inductive effect and the influence of ring size. Upon replacement of the ethylene linkages of EEDTA by propylene in BPETA, the acidity of the chelating agent is lessened (Table I) because the inductive effect of the ether oxygen atom is attenuated.[10] Secondly, with EEDTA, a heptadentate ligand, six five-membered chelating rings involve the metal ion. With BPETA, one more methylene group is present in each connection between ether O and amino N donor atoms. Therefore, two of the six five-membered chelating rings are converted to six-membered chelating rings. Experimental results[11] have shown that, in metal-chelating complexes, a five-membered ring provides higher stability than any other size of chelating ring. Combination of the two effects above renders BPETA a much less effective chelate for lanthanide ions than EEDTA.

Table II. Stability Constants of Lanthanides with $O[CH_2CH_2CH_2N(CH_2COOH)_2]_2$ at 25 °C and $I = 0.1$

M	β_H	log β_H	β_1	log β_1	α_Z^{Z+1} [b]
La	0.391×10^7	6.59	0.474×10^{11}	10.68[a]	La–Ce = 3.93
Ce	0.680×10^7	6.83	0.186×10^{12}	11.27	Ce–Pr = 1.85
Pr	0.967×10^7	6.99	0.345×10^{12}	11.54	Pr–Nd = 1.32
Nd	0.108×10^8	7.03	0.458×10^{12}	11.66	Nd–Sm = 1.63
Pm					
Sm	0.159×10^8	7.20	0.744×10^{12}	11.87	Sm–Eu = 0.88
Eu	0.198×10^8	7.30	0.655×10^{12}	11.82	Eu–Gd = 0.83
Gd	0.195×10^8	7.30	0.545×10^{12}	11.74	Gd–Tb = 0.91
Tb	0.364×10^8	7.56	0.498×10^{12}	11.70	Tb–Dy = 1.05
Dy	0.507×10^8	7.71	0.524×10^{12}	11.72	Dy–Ho = 1.07
Ho	0.625×10^8	7.80	0.561×10^{12}	11.75	Ho–Er = 1.31
Er	0.700×10^8	7.85	0.735×10^{12}	11.87	Er–Tm = 1.32
Tm	0.847×10^8	7.93	0.972×10^{12}	11.99	Tm–Yb = 1.23
Yb	0.123×10^9	8.09	0.119×10^{13}	12.08	Yb–Lu = 1.17
Lu	0.135×10^9	8.13	0.139×10^{13}	12.14	

[a] Values are estimated to be reliable to ±0.05. [b] Separation factor.

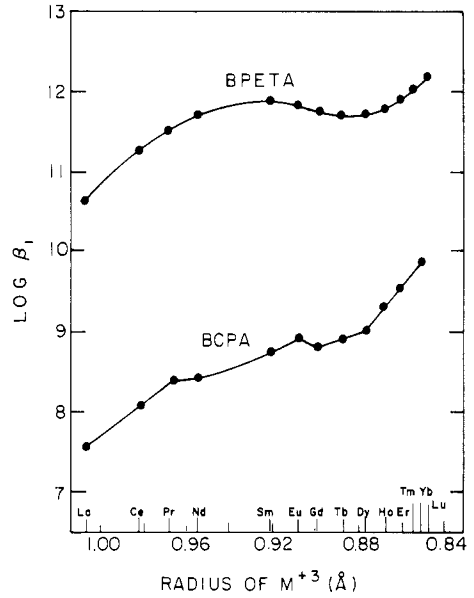

Figure 1. Plots of log β_1 vs. radius of M^{3+} of BPETA and BCPA.

The stability constant curve of BPETA in Figure 1 resembles those of the lanthanide hydroxycarboxylates, which were studied by Powell et al.[12,13] As the metal ion becomes smaller, the steric stress becomes more pronounced and affects the stability constants of the complexes. The gradual decrease in stability constant starting at samarium and continuing until terbium suggests a progressive change of coordination within

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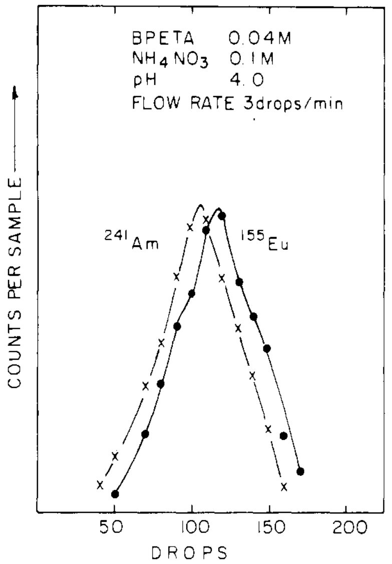

Figure 2. Cation-exchange elution of ^{241}Am and ^{155}Eu with BPETA.

Table III. Protonation Constants of $^-OOCCH_2N^+(CH_3)[CH_2CH_2CH_2N(CH_2COOH)_2]_2$ at 25 °C and $I = 0.1$

$\alpha_1 = [HL]/([H][L]) = 0.690 \times 10^9$	$\log [HL]/([H][L]) = 8.84$
$\alpha_2 = [H_2L]/([H]^2[L]) = 0.617 \times 10^{17}$	$\log [H_2L]/([H][HL]) = 7.95$
$\alpha_3 = [H_3L]/([H]^3[L]) = 0.410 \times 10^{20}$	$\log [H_3L]/([H][H_2L]) = 2.82$
$\alpha_4 = [H_4L]/([H]^4[L]) = 0.569 \times 10^{23}$	$\log [H_4L]/([H][H_3L]) = 2.14$

the metal complex. One of the seven attachments of the chelating agent to the metal (via electron-donor atoms) is gradually compromised and eventually broken. After terbium, the continued increasing charge density of the lanthanons (whose size is diminishing) results again in an increasing affinity for those donor atoms that can be accommodated with little stress. Note that while even the smallest lanthanon, Lu^{3+}, can accommodate at least eight oxygen atoms from water molecules, not all the donor atoms of a polydentate ligand can be forced into an array that will replace such H_2O molecules on a one to one basis. Accommodation of the potential donor O's and N's of a polydentate ligand is less constrained in the case of larger cations, where the coordination sphere is larger and close packing of a greater number of donor atoms, of whatever origin, is more flexible. In reduction of dentate character from heptadentate to hexadentate it is more likely that a terminal (carboxylate) O detaches rather than either the ether O or a tertiary amine N because ruination of fewer rings occurs. The destruction of two chelate rings would decrease the stability of a complex tremendously.[3] Therefore, it appears to be more reasonable to assume that one of the carboxylate groups is released rather than an atom associated with a greater number of rings.

The experimental conditions and results of the BPETA elution of Am^{3+} and Eu^{3+} are displayed in Figure 2. ^{241}Am eluted slightly ahead of ^{155}Eu, and the Eu–Am separation factor is 1.10. If this calculated Eu–Am separation factor is employed, the stability constant ($\log \beta_1$) of Am is estimated to be 11.86, which interposes it between Sm and Eu, as well as between Ho and Er. Am, therefore, cannot be separated easily from the lanthanide family by elution with BPETA. The ligand, however, exhibits a good separation factor for Am from any light lanthanide (La–Nd). Besides that, BPETA is very soluble in water at room temperature, allowing the use of hydrogen ion as a retaining ion in displacement cation-exchange schemes.

Table IV. Stability Constants of Lanthanide–BCPA Complexes at 25 °C and $I = 0.1$

M	β_H	$\log \beta_H$	β_1	$\log \beta_1$	$\alpha_Z{}^{Z+1}$ [a]
La	0.129×10^6	5.11	0.379×10^8	7.58	La–Ce = 3.20
Ce	0.216×10^6	5.33	0.121×10^9	8.08	Ce–Pr = 1.93
Pr	0.274×10^6	5.44	0.234×10^9	8.37	Pr–Nd = 1.16
Nd	0.313×10^6	5.50	0.271×10^9	8.43	Nd–Sm = 1.90
Pm					
Sm	0.462×10^6	5.67	0.516×10^9	8.71	Sm–Eu = 1.55
Eu	0.456×10^6	5.64	0.802×10^9	8.90	Eu–Gd = 0.77
Gd	0.471×10^6	5.67	0.618×10^9	8.79	Gd–Tb = 1.21
Tb	0.606×10^6	5.78	0.744×10^9	8.87	Tb–Dy = 1.34
Dy	0.102×10^7	6.02	0.995×10^9	9.00	Dy–Ho = 2.24
Ho	0.130×10^7	6.12	0.223×10^{10}	9.35	Ho–Er = 1.56
Er	0.160×10^7	6.20	0.348×10^{10}	9.54	Er–Tm = 1.42
Tm	0.216×10^7	6.34	0.494×10^{10}	9.69	Tm–Yb = 1.42
Yb	0.257×10^7	6.41	0.701×10^{10}	9.85	Yb–Lu = 0.97
Lu	0.271×10^7	6.43	0.680×10^{10}	9.83	

[a] Separation factor.

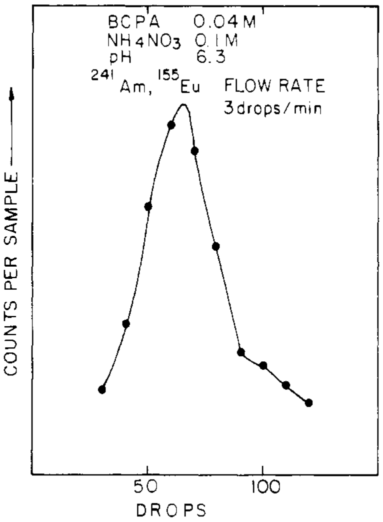

Figure 3. Cation-exchange elution of ^{241}Am and ^{155}Eu with BCPA.

BCPA. The protonation constants of BCPA are shown in Table III. The values for this compound are lower than those of bis(2-aminoethyl)methylamine-*N*,*N*,*N'*,*N'*-tetraacetic acid ($pK_1 = 10.89$, $pK_2 = 7.39$, $pK_3 = 3.65$, $pK_4 = 2.8$ at 20 °C, $I = 0.1$),[5] which indicates that this acid is more acidic than $CH_3N[CH_2CH_2N(CH_2COOH)_2]_2$. Its acidic properties are also much different from those of EEDTA and BPETA. The difference is apparently due to the introduction of a carboxylate group on the central nitrogen atom. The electron-withdrawing effect of the carboxylate group at the middle nitrogen atom causes protons on the terminal carboxylate groups and at the terminal amines to be more acidic.

The stability constants of complexes formed by BCPA with lanthanide ions are much lower than those formed by other polyaminopolycarboxylates that have been reported, and the values are listed in Table IV. When the β_1 values of BCPA and PMDTA[3] are compared, it is seen that the stability constants of BCPA are about 10 times lower than those of PMDTA, which is a hexadentate ligand. That the dipolar ligand, BCPA, exhibits properties similar to PMDTA indicates that BCPA is also a hexadentate ligand. This is not surprising because the central nitrogen atom is a quaternary ammonium atom and is without a lone pair of electrons. One would expect that the carboxylate group of the acetate attached to the central N atom could play a major role in bonding to lanthanons as does a comparable group in DTPA. However, experimental results suggest that this is not the case. If that carboxylate bonded to the metal ion, BCPA would become a heptadentate (instead of hexadentate) ligand and chelation would result in additional (albeit nine-membered) rings. Although the effect of nine-membered rings on the stability of the metal complex might be small, it should be positive. BCPA would obviously bond to lanthanons more tenaciously than PMDTA if its fifth carboxylate O were involved in chelation. This is apparently not the case since the lanthanide–BCPA stability constants are approximately 10-fold less stable than their PMDTA counterparts. The trend of stability with BCPA complexes mimics the trend observed with PMDTA rather than that characteristic of EEDTA[9] and BPETA chelates, in which additional rings are formed, making the structure less flexible.

The experimental conditions for BCPA are different from those of BPETA. Both ^{241}Am and ^{155}Eu were eluted, coincidentally, under necessarily more basic conditions. The results are shown in Figure 3. Preliminary elutions with 25 column volumes of 0.04 M BCPA solution at pHs of 3.0, 4.0, 5.0, and 6.0 were insufficient to remove the Am and Eu tracers from the resin bed. The higher pH requirements reflect the 1000-fold lower affinity of BCPA (compared to BPETA) for trivalent cations.

Registry No. $H_3CN(CH_2CH_2CH_2NH_2)_2$, 105-83-9; $O(CH_2CH_2CN)_2$, 1656-48-0; $O(CH_2CH_2CH_2NH_2)_2$, 2157-24-6; BPEDTA, 87720-52-3; BCPA, 89378-46-1.

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Photosubstitution Reactions of $Ru(bpy)_2XY^{n+}$ Complexes

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The quantum yields for the photosubstitution of a series of $Ru(bpy)_2XY^{n+}$ complexes have been measured. The ligands X and Y span the range of the spectrochemical series from Cl^- to CO. The correlation between the energy of the lowest energy charge-transfer transition and the quantum yield is discussed in terms of the energies of MLCT and d–d excited states.

Introduction

The photoreactivity of ruthenium(II) complexes of the type $Ru(bpy)_2XY^{n+}$, where bpy = 2,2′-bipyridine and X and Y = any monodentate ligand, has been noted since the publication of a series of synthetic papers by Bosnich, Dwyer, and coworkers.[1] The photoreactions usually involve loss of the monodentate ligands according to reactions 1 and 2. In

$$Ru(bpy)_2XY^{n+} + S \xrightarrow{h\nu} Ru(bpy)_2YS^{p+} + X \quad (1)$$

$$Ru(bpy)_2YS^{p+} + S \xrightarrow{h\nu} Ru(bpy)_2S_2^{q+} + Y \quad (2)$$

coordinating solvents S will usually be a solvent molecule, while in poor coordinating, low dielectric constant solvents S may be the counterion, added anions, or residual water in the solvent.[2,3] These reactions have proven to be of some synthetic utility.[3]

The $Ru(bpy)_3^{2+}$ ion may also be placed in this series of complexes. The $Ru(bpy)_3^{2+}$ ion, however, is substantially less photoreactive, and this has been shown to be a result of efficient ring reclosure after the primary photochemical event.[4] Numerous studies[5] have resulted in a reasonably well-defined description of the excited-state manifold of $Ru(bpy)_3^{2+}$. This description has been successfully extended[6-8] to some $Ru(bpy)_2XY^{n+}$ complexes to explain the temperature dependence of the emission lifetime.

With this description in mind we have embarked on a study of those aspects of the excited-state manifold that play an important role in the photochemical reactions in the series of complexes $Ru(bpy)_2XY^{n+}$. The following is a report of an interesting correlation between quantum yield for photosubstitution and the energy of the major visible charge-transfer transition.

Experimental Section

Materials. All of the ruthenium complexes except those containing carbon monoxide were prepared as PF_6^- salts from *cis*-$Ru(bpy)_2Cl_2$ by standard literature procedures.[1,9] The complexes were purified by column chromatography on alumina. Purity was judged by cyclic voltammetry and NMR and visible spectroscopy. Dichloromethane was dried over molecular sieves. Tetrabutylammonium chloride and all other reagents were used as received.

$[Ru(bpy)_2(CO)_2](PF_6)_2$. This complex was prepared by a slight modification of the procedure described by Choudhury and coworkers.[10] A solution of dichloromethane containing 0.38 g of $Ru(bpy)_2Cl_2$ (0.78 mmol) and 0.6 g of $AgSbF_6$ (1.75 mmol) was heated to 80 °C in an an autoclave pressurized with carbon monoxide (4 atm). After 48 h the solid material obtained by filtration of the reaction mixture was extracted with acetone. The volume of acetone was reduced to less than 5 mL in a rotary evaporator and the product recovered by adding the acetone solution dropwise to ethyl ether followed by filtration and air drying. The product was further purified

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