Inorganic Chemistry

ARTICLE

pubs.acs.org/IC

Complexation of Metal Ions, Including Alkali-Earth and Lanthanide(III) Ions, in Aqueous Solution by the Ligand 2,2′,6′,2″-Terpyridyl

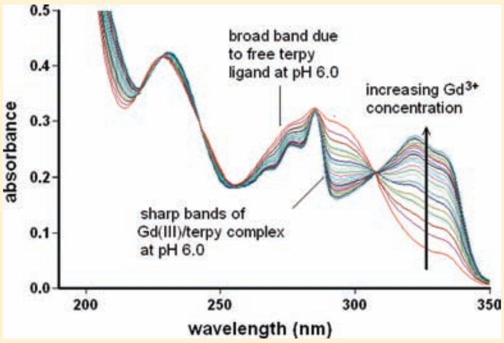
Joanna M. Hamilton,[†] Michael J. Anhorn,[†] Karen A. Oscarson,[†] Joseph H. Reibenspies,[‡] and Robert D. Hancock*,[†]

[†]Department of Chemistry and Biochemistry, University of North Carolina at Wilmington, Wilmington, North Carolina 28403, United States

[‡]Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

S *Supporting Information*

ABSTRACT: Some metal-ion-complexing properties of the ligand 2,2′,6′,2″-terpyridyl (terpy) in aqueous solution are determined by following the $\pi-\pi^*$ transitions of 2×10^{-5} M terpy by UV—visible spectroscopy. It is found that terpy forms precipitates when present as the neutral ligand above pH ~5, in the presence of electrolytes such as $NaClO_4$ or NaCl added to control the ionic strength, as evidenced by large light-scattering peaks. The protonation constants of terpy are thus determined at the ionic strength (μ) = 0 to avoid precipitation and found to be 4.32(3) and 3.27(3). The log K_1 values were determined for terpy with alkali-earth metal ions Mg^{II}, Ca^{II}, Sr^{II}, and Ba^{II} and Ln^{III} (Ln = lanthanide) ions La^{III}, Gd^{III}, and Lu^{III} by titration of 2×10^{-5} M free terpy at pH >5.0 with solutions of the metal ion. Log K_1(terpy) was determined for Zn^{II}, Cd^{II}, and Pb^{II} by following the competition between the metal ions and protons as a function of the pH. Complex formation for all of these metal ions was accompanied by marked sharpening of the broad $\pi-\pi^*$ transitions of free terpy, which was attributed to complex formation affecting ligand vibrations, which in the free ligand are coupled to the $\pi-\pi^*$ transitions and thus broaden them. It is shown that log K_1(terpy) for a wide variety of metal ions correlates well with log $K_1(NH_3)$ values for the metal ions. The latter include both experimental log $K_1(NH_3)$ values and log $K_1(NH_3)$ values predicted previously by density functional theory calculation. The structure of $[Ni(terpy)_2][Ni(CN)_4] \cdot CH_3CH_2OH \cdot H_2O$ (**1**) is reported as follows: triclinic, $P\bar{1}$, $a = 8.644(3)$ Å, $b = 9.840(3)$ Å, $c = 20.162(6)$ Å, $\alpha = 97.355(5)°$, $\beta = 97.100(5)°$, $\gamma = 98.606(5)°$, $V = 1663.8(9)$ Å^3, $Z = 4$, and final $R = 0.0319$. The two Ni—N bonds to the central N donors of the terpy ligands in **1** average 1.990(2) Å, while the four peripheral Ni—N bonds average 2.107(10) Å. This difference in the M—N bond length for terpy complexes is typical of the complexes of smaller metal ions, while for larger metal ions, the difference is reversed. The significance of the metal-ion size dependence of the selectivity of polypyridyl ligands, and the greater rigidity of ligands based on aromatic groups such as pyridyl groups, is discussed.



INTRODUCTION

2,2′,6′,2″-Terpyridyl (terpy) and terpy-like ligands (Figure 1) have become of considerable interest in relation to the selective separation of Am^{III} and Cm^{III} from Ln^{III} (Ln = lanthanide) ions in the treatment of nuclear waste.[1] Musikas[2] pioneered the use of such ligands with studies on the selective extraction of Am^{III} from Ln^{III} ions by N-donor ligands. Other N-donor ligands of interest in such separations are BTP,[3] TPEN,[4] 4,7-diphenylphen,[5] as well as TPTZ.[2,6−9] The use[2] of N-donor ligands for the proposed separation of Am^{III} and Cm^{III} from Ln^{III} ions arises because the main difference in the ligand affinity between the similarly sized An^{III} (An = actinide) and Ln^{III} ions is due to the fact that An ions are slightly softer in the hard and soft acids and bases (HSAB) sense than the analogous Ln ions.[2,10,11] Thus, the N donors of BTP or TPTZ, for example, are softer than the usual O donors used as solvent extractants for Ln^{III} or An^{III} ions such as tributylphosphate. The greater affinity of Am^{III}, and some other An ions of interest, for N-donor ligands is supported by density functional theory (DFT) calculations that suggest[12,13] the following log K_1 (formation constant) values for NH_3 complexes in aqueous solution:

Metal ion :	La^{3+}	Gd^{3+}	Lu^{3+}	Am^{3+}	Y^{3+}	Sc^{3+}	Th^{4+}	Pu^{4+}	UO_2^{2+}
log $K_1(NH_3)$:	0.3	0.7	1.0	2.3	0.1	0.9	0.1	2.7	2.0

Ligands containing pyridyl groups, such as 2,2′-bipyridyl (bipy), have been extensively studied, as evidenced by 2003 structures for complexes of bipy with metal ions reported in the Cambridge Structural Database (CSD)[14] and 84 papers reported on the thermodynamic stabilities of complexes of bipy with metal ions in aqueous solution.[15] Although 873 structures of terpy complexes

Received: August 26, 2010
Published: March 02, 2011

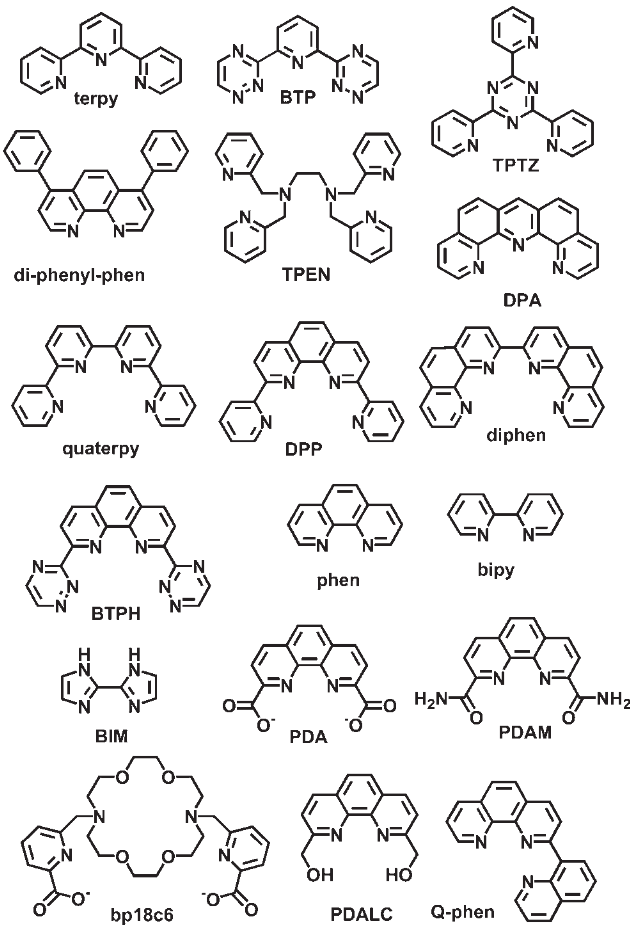


Figure 1. Ligands discussed in this paper.

have been reported,[14] there are only 14 papers on the thermodynamic stability of complexes of terpy in aqueous solution,[15] and these do not cover complexes with "hard" (in the HSAB sense[16]) metal ions such as alkali-earth metal ions or, in particular, Ln ions.

In this paper, an attempt is made to extend knowledge of the affinity of polypyridyl ligands for hard metal ions by a spectrophotometric study of the complexes of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}, Gd^{3+}, and Lu^{3+} with terpy. In addition, because some previously reported[17] log K_1 values for Zn^{II} and Cd^{II} with terpy appeared to be rather low and log K_1(terpy) has not been reported[14] for Pb^{II} ion, log K_1 values for terpy with these ions are presented. Because the five-membered chelate rings formed by terpy are predicted[18] to lead to steric preference for large metal ions of ionic radii[19] in the vicinity of 1.0 Å, an effort was made to grow crystals of terpy complexed with the very small[19] low-spin Ni^{II} ion in order to examine the distortion of the terpy ligand by a too-small metal ion. The aim was to produce a crystal of a low-spin square-planar complex of the type $[Ni(terpy)CN]^+$. The complex produced was not square-planar, but the structure is reported here as being of some interest.

■ EXPERIMENTAL SECTION

Materials and Methods. The terpy ligand was obtained from Alfa Aesar in 98% purity and used as received. The metal perchlorates were obtained from VWR or Strem in 99% purity or better and used as received. All solutions were made up in deionized water (Milli-Q, Waters Corp.) of >18 MΩ·cm^{-1} resistivity.

Table 1. Crystal Data and Structure Refinement for 1

empirical formula	$C_{36}H_{30}N_{10}Ni_2O_2$
fw	752.08 g·mol^{-1}
temperature	110(2) K
wavelength	0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	a = 8.644(3) Å
	b = 9.840(3) Å
	c = 20.162(6) Å
	α = 97.355(5)°
	β = 97.100(5)°
	γ = 98.606(5)°
volume	1663.8(9) Å^3
Z	4
final R indices [$I > 2\sigma(I)$]	R1 = 0.0319, wR2 = 0.0798
R indices (all data)	R1 = 0.0375, wR2 = 0.0900

Table 2. Selected Bond Lengths and Angles for 1

Bond Lengths (Å)			
Ni1−N5	1.990(2)	Ni1−N2	1.990(2)
Ni1−N4	2.099(2)	Ni1−N3	2.101(2)
Ni1−N6	2.106(2)	Ni1−N1	2.121(2)
Ni2−C32	1.865(3)	Ni2−C31	1.873(3)
Ni3−C33	1.867(3)	Ni3−C34	1.869(3)
Bond Angles (deg)			
N5−Ni1−N2	174.50(9)	N5−Ni1−N4	78.56(9)
N2−Ni1−N4	106.92(9)	N5−Ni1−N3	101.06(9)
N2−Ni1−N3	78.42(9)	N4−Ni1−N3	92.92(9)
N5−Ni1−N6	78.15(9)	N2−Ni1−N6	96.37(9)
N4−Ni1−N6	156.71(9)	N3−Ni1−N6	91.84(9)
N5−Ni1−N1	102.42(9)	N2−Ni1−N1	78.30(9)
N4−Ni1−N1	90.79(9)	N3−Ni1−N1	156.50(9)
N6−Ni1−N1	93.87(8)		

Synthesis of $[Ni(terpy)_2][Ni(CN)_4]\cdot CH_3CH_2OH\cdot H_2O$ (1). A 1:1:1 solution of Ni^{II}/terpyridine/CN^-, each 0.0038 M, was prepared as follows: 0.15 g of terpyridine was dissolved in 25 mL of acetone. In another beaker, 0.09 g of $NiCl_2\cdot 6H_2O$ was dissolved in 25 mL of ethanol and stirred to dissolve. In a separate beaker, 0.019 g of NaCN was dissolved in 50 mL of ethanol. The solutions were combined and allowed to stand for 24 h. Pale-green crystals were deposited and analyzed as follows. Calcd for $C_{36}H_{30}N_{10}Ni_2O_2$: C, 57.49; H, 4.02; N, 18.62. Obsd: C, 57.37; H, 3.93; N, 18.42.

Molecular Structure Determination. A mounted crystal of **1** was placed in a cold nitrogen stream maintained at 110 K. A Bruker APEXII four-circle diffractometer was employed for crystal screening, unit cell determination, and data collection. The structures were solved by Patterson synthesis and refined to convergence.[20] Details of the structure determination of **1** are shown in Table 1, and these together with the crystal coordinates have been deposited with the CSD.[14] Some more important bond lengths and angles for **1** are given in Table 2. The structure of **1** is shown in Figure 2.

Formation Constant Determination. Protonation and formation constants with a variety of metal ions were determined for terpy by utilizing the intense $\pi \rightarrow \pi^*$ transitions present in the UV spectrum.[21]

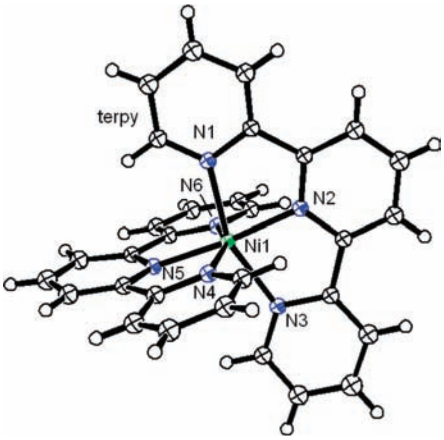


Figure 2. Structure of the $[Ni(terpy)_2]^{2+}$ cation from **1** showing numbering of the donor atoms. Drawing made with ORTEP.[23]

UV−visible spectra were recorded using a Varian 300 Cary 1E UV−visible spectrophotometer controlled by Cary Win UV Scan Application version 02.00(5) software. A VWR sympHony SR60IC pH meter with a VWR sympHony gel epoxy semimicrocombination pH electrode was used for all pH readings, which were made in the external titration cell, with N_2 bubbled through the cell to exclude CO_2. The pH meter was calibrated prior to each titration by means of titration of a standard acid with a standard base: the value of $E°$ for the cell, as well as the Nernstian slope, was obtained from a linear plot of the measured values of E versus the calculated pH. The cell containing 50 mL of a ligand/metal solution was placed in a bath thermostatted to 25.0 ± 0.1 °C. With previous studies of pyridine-based ligands,[22] a peristaltic pump was used to circulate the solution through a 1.0 cm quartz flow cell situated in the spectrophotometer. It was found upon circulation of solutions of terpy in this manner that the peak intensity steadily decreased with time even at constant pH, suggesting that terpy was depositing on the Tygon tubing used to connect the external cell with the flow cell in the spectrophotomer. The titrations were thus carried out in an external jacketed cell as before, but a glass Pasteur pipet was used to transfer the solution to a standard quartz cell in the spectrophotometer, which was not moved during the course of the titration. This was important because movement of the quartz cell in the spectrophotometer is a main cause of displacement of the baseline, and hence of irreproducibility of the spectra. The pH was altered in the range 2−8 by additions to the external titration cell of small amounts of standard $HClO_4$ or NaOH as required using a micropipet. After each adjustment of the pH, the Pasteur pipet was used to transfer a suitable quantity of the solution in the external cell to the flow cell back and forth to the cell in the spectrophotometer several times to ensure adequate mixing prior to recording of the spectrum, and to further promote mixing, the solution in the external cell was stirred with a magnetic stirrer.

Experimentation with terpy shows that the solubility in aqueous solution, particularly of the nonprotonated form of the ligand, is sensitive to salts added to control the ionic strength. This was evidenced for 2×10^{-5} M solutions of terpy at about pH 7.0, where terpy is not protonated, by a rising baseline and an intense broad "peak" due to light scattering observed near 200 nm in, for example, 0.1 M NaCl or $NaClO_4$. This intense peak can only be avoided in solutions with no added Na^+ or K^+ salts aimed at controlling the ionic strength. We thus determined the pK_1 and pK_2 (protonation constants) for terpy at effectively μ (ionic strength) = 0, with the only added electrolytes being the small amounts of acid or base required to adjust the pH in the vicinity of the protonation constants measured as $pK_1 = 4.32$ and $pK_2 = 3.27$ at $\mu = 0$. The spectra of terpy in aqueous solution in the pH ranges 2.15−3.68 and 3.78−6.0 are shown in parts a and b of Figure 3, with the ranges being separated so as not to jumble the two sets of spectra on top of each other. In Figure 4 is shown variation of the absorbance for 2×10^{-5} M terpy at six wavelengths as a function of the pH. The solid lines, which are theoretical curves of absorbance versus pH, were fitted to the experimental data using the *SOLVER* function of *EXCEL*.[24] The standard deviations in the p*K* values given in Table 3 were calculated using the *SOLVSTAT* macro provided with ref 24.

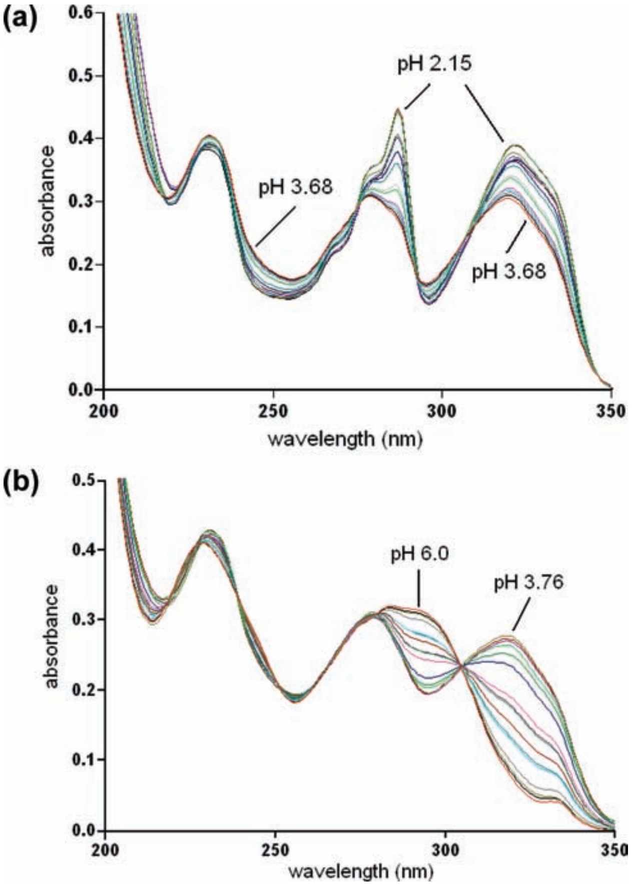


Figure 3. Spectra of 2×10^{-5} M terpy in aqueous solution (a) from pH 2.15 to 3.68 and (b) from pH 3.76 to 6.0.

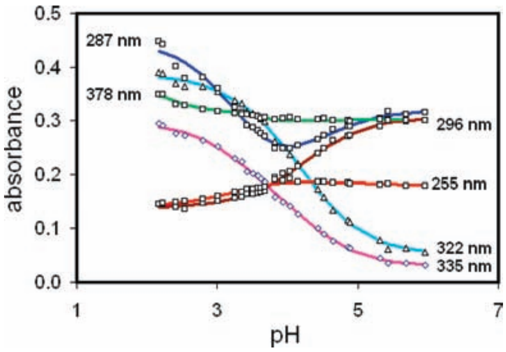


Figure 4. Variation of the absorbance of 2×10^{-5} M terpy as a function of the pH at six different wavelengths. Points are experimental values, and solid lines are theoretical curves generated from $pK_1 = 4.32$ and $pK_2 = 2.37$.

The metal-ion complexes of terpy of stability greater than log $K_1 = 5.0$, which turn out to be Zn^{II}, Cd^{II}, and Pb^{II}, were studied by conventional spectroscopic methods,[25] where the equilibrium (1) was followed spectroscopically in solutions 2×10^{-5} M in both terpy and

Table 3. Protonation and Formation Constants Determined Here for Complexes of terpy at the Ionic Strengths (μ) Indicated

metal ion	equilibrium	log K	μ	ref
H^+	$H^+ + OH^- \leftrightarrows H_2O$	13.997	0	15
	H^+ + terpy $\leftrightarrows$ terpyH^+	4.32(3)	0	this work
	terpyH^+ + H^+ $\leftrightarrows$ terpyH_2^{2+}	3.27(3)	0	this work
	H^+ + terpy $\leftrightarrows$ terpyH^+	4.70	0.1	15
	terpyH^+ + H^+ $\leftrightarrows$ terpyH_2^{2+}	3.60	0.1	15
Mg^{2+}	Mg^{2+} + terpy $\leftrightarrows$ [Mg(terpy)]$^{2+}$	0.74(1)	0.4	this work
Ca^{2+}	Ca^{2+} + terpy $\leftrightarrows$ [Ca(terpy)]$^{2+}$	0.85(1)	0.5	this work
Sr^{2+}	Sr^{2+} + terpy $\leftrightarrows$ [Sr(terpy)]$^{2+}$	−0.5(1)	1.0	this work
Ba^{2+}	Ba^{2+} + terpy $\leftrightarrows$ [Ba(terpy)]$^{2+}$	−0.6(2)	1.0	this work
La^{3+}	La^{3+} + terpy $\leftrightarrows$ [La(terpy)]$^{3+}$	2.08(2)	0.05	this work
Gd^{3+}	Gd^{3+} + terpy $\leftrightarrows$ [Gd(terpy)]$^{3+}$	2.60(2)	0.05	this work
Lu^{3+}	Lu^{3+} + terpy $\leftrightarrows$ [Lu(terpy)]$^{3+}$	2.80(2)	0.05	this work
Zn^{2+}	Zn^{2+} + terpy $\leftrightarrows$ [Zn(terpy)]$^{2+}$	7.58(2)	0	this work
		6.0	0.1	17
Cd^{2+}	Cd^{2+} + terpy $\leftrightarrows$ [Cd(terpy)]$^{2+}$	6.33(3)	0	this work
		5.1	0.1	17
Pb^{2+}	Pb^{2+} + terpy $\leftrightarrows$ [Pb(terpy)]$^{2+}$	6.0(1)	0	this work

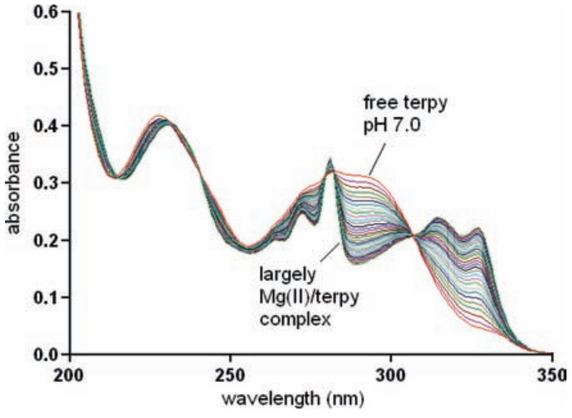


Figure 5. Spectra of 2 × 10^{-5} M terpy at pH 7.0 as a function of the Mg^{2+} concentration. The initial spectrum is that of free terpy, while the final spectrum, exhibiting sharp peaks typical of the complex formation of metal ions with terpy, is that of terpy in the presence of 0.145 M Mg^{2+}.

metal ion.

$$[M(terpy)]^{2+} + 2H^+ \leftrightarrows M^{2+} + [terpyH_2]^{2+} \qquad (1)$$

It is then a simple matter to combine the equilibrium quotient for eq 1 with the protonation constants of the ligand to obtain the log K_1 values for the metal ions. For more weakly bound metal ions, a solution of terpy at about pH 6.0, where terpy is not significantly protonated, was titrated with a solution of the metal perchlorate. This produced excellent sets of spectra, as seen for Mg^{II}, La^{III}, and Lu^{III} in Figures 5−7. Analysis of these sets of spectra was achieved using the solver module of *EXCEL*,[24] and the standard deviations given in Table 3 for the log K_1 values determined were calculated using *SOLVSTAT*.[24] The fitting procedures followed were those used in previous studies of polypyridyl-type ligands.[26−31] The ionic strengths given for each log K_1 value in Table 1 are those generated by the added metal salts complexing terpy in the vicinity of nbar = 0.5 (nbar = average number of ligands bound to the metal ion). It should be noted that, for titrations involving Ln^{III} ions, there were very small drops in the pH as the Ln^{III} solution was added, and the pH was kept at pH 6.0 by the addition of small quantities of a NaOH solution.

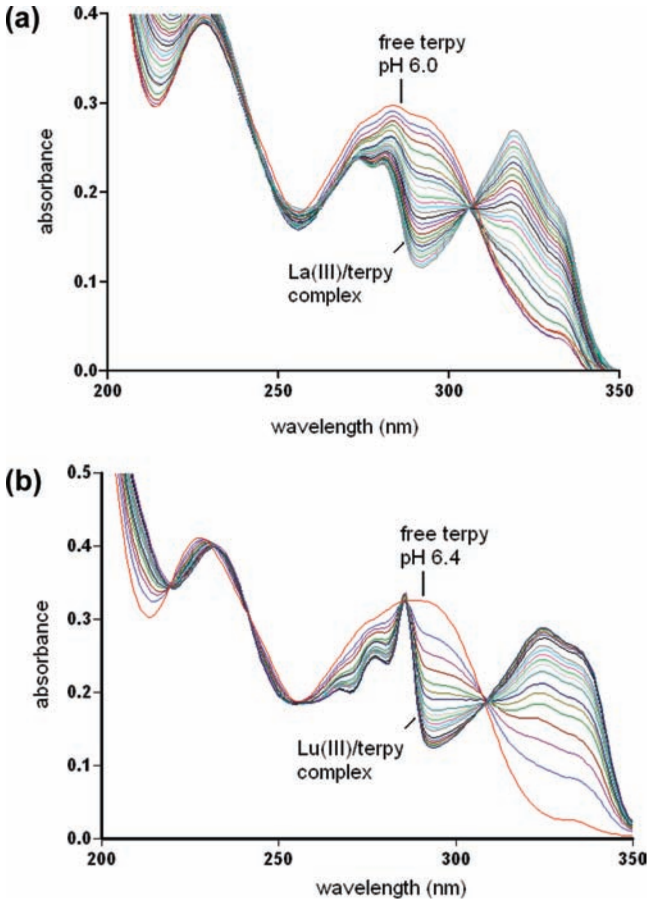


Figure 6. Spectra of 2 × 10^{-5} M terpy at pH 6.0 as a function of the (a) La^{3+} and (b) Lu^{3+} concentrations. The upper spectra are those of free terpy, while the spectra exhibiting sharp peaks are those of terpy in the presence of (a) 0.0089 M La^{3+} and (b) 0.0043 M Lu^{3+}.

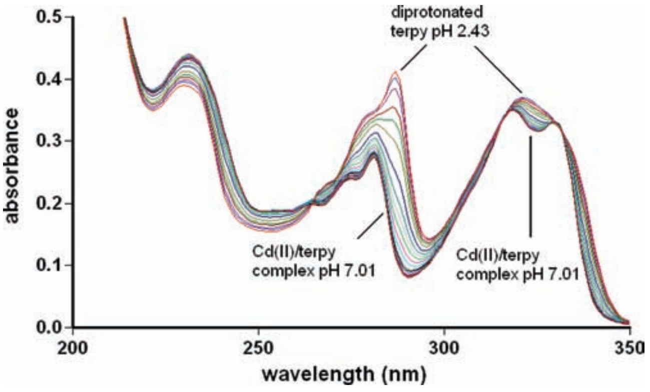


Figure 7. Variation of the absorbance of 1:1 solutions (2 × 10^{-5} M) of $Cd(ClO_4)_2$ and terpy in the pH range 2.43−7.01.

■ RESULTS AND DISCUSSION

Formation Constants. The protonation and formation constants reported here for terpy with a variety of metal ions are seen in Table 3. As mentioned above, with 0.1 M electrolytes such as

$NaClO_4$ or NaCl added to control the ionic strength, 2×10^{-5} M terpy shows a large (absorbance ≥2.5) light-scattering "peak" in aqueous solution in the vicinity of 220 nm at higher pH values, where the free ligand is present. The light-scattering peaks are not present in water if the only electrolytes are the small amounts of acid or base required to adjust the pH, suggesting that terpy is salted out by higher concentrations of electrolytes. The excellent isosbestic points observed for the sets of spectra for terpy and terpy complexes in Figures 3 and 5−7 suggest that the approach adopted here produces reliable results, where plastic tubing was avoided because of deposition of terpy on the tubing, and electrolytes such as $NaClO_4$ were avoided because of precipitation. The spectra of terpy with no added electrolytes, apart from the small amounts of acid or base needed to adjust the pH, are shown in Figure 3a,b and kept separate so as not to jumble them on top of each other. The two sets of spectra correspond to the two protonation equilibria of terpy; the pH range 2.15−3.68 in Figure 3a represents pK_2, while in Figure 3b, the pH range 3.76−6.0 corresponds to pK_1.

The presence of light scattering is not serious if it represents only a tiny fraction of the ligand forming suspended particulates because the calculations can be performed using wavelengths well away from the region of light scattering, typically above 250 nm. However, in the case of terpy, the spectra at higher pH in the presence of higher concentrations of $NaClO_4$ or NaCl are less intense than those with no electrolyte present, and the isosbestic points seen in Figure 3b are not well-defined. A reviewer has queried the possibility of precipitates affecting our mass balance equations and calculated log K values. It should be emphasized that no calculations were carried out using results from solutions where light scattering indicated the presence of precipitates. A reviewer has also questioned whether hydrolyzed species such as $LnOH^{+}$ should be important at pH 6.0 in our titrations of La^{III} and Lu^{III} shown in Figure 6a.b. In fact, pH 6.0 was chosen for titration of the Ln^{III} ions with terpy because hydrolysis of the Ln^{III} ions should be negligible at this pH. The protonation constants determined here at $\mu = 0$ for terpy in Table 3 are lower than those selected[15] at ionic strength 0.1, as would be expected for a neutral ligand. The good fit for the theoretical values of absorbance versus pH calculated for terpy to the observed values is shown in Figure 4.

The formation of complexes by terpy in aqueous solution is accompanied by the formation of sharp peaks in the UV spectrum of terpy that are useful diagnostically at confirming complex formation. This is seen in Figure 5 for formation of the Mg^{II} complex of terpy. This type of band sharpening accompanying complex formation has been observed for complexes of DPP,[26] PDA,[27−29] PDAM,[30] and BIM.[31] It was proposed[26] that the sharpening of the peaks was caused by rigidification of the ligand on complex formation, which alters ligand vibrations coupled to the $\pi-\pi^*$ transitions of the ligand, the vibrations of which characteristically cause electronic band broadening in solution. In Figure 6a is seen the set of spectra of terpy as a function of the La^{3+} concentration, which shows band sharpening that is less than that produced by Mg^{II} [ionic radius[19] (r^{+}) for coordination number (CN) 6 = 0.74 Å], which may reflect the larger size of the La^{III} ion (r^{+} for CN 9 = 1.22 Å). The smaller Lu^{III} ion (r^{+} for CN 9 = 1.11 Å) produces (Figure 6b) sharp bands in its terpy complex, resembling those of Mg^{II}. In Figure 7 is shown the set of spectra for a 1:1 mixture of $Cd(ClO_4)_2$ and terpy, both at 2×10^{-5} M, as a function of the pH between 2.43 and 7.01. One sees the sharpening of the bands in the UV spectrum upon complex formation found with other metal ions, but the sharpened bands also shift to shorter wavelengths, which may reflect the more covalent interaction of the softer[16] Cd^{II} ion with the π system of terpy. One notes in Figures 3a and 7 that the same peaks that are sharper in the complexes of terpy with metal ions are also sharper in the diprotonated form of the ligand ($terpyH_2^{2+}$) at low pH, although the sharpening is somewhat less in $terpyH_2^{2+}$ than in the metal complexes. It seems probable that the sharpening arises from constraint of terpy[21] in the cis−cis form, which is found in the crystal structure[32] of $terpyH_2^{2+}$, as well as in complexes of metal ions with terpy. In contrast, the free ligand has[33,34] the trans−trans conformation, while the monoprotonated form is[35] cis−trans. It seems possible that complex formation, or internal hydrogen-bonding in cis−cis $terpyH_2^{2+}$, limits motions around the C−C bonds connecting the pyridyl groups of terpy and so removes rocking vibrations involving these bonds, which otherwise couple to the electronic transitions and broaden them.

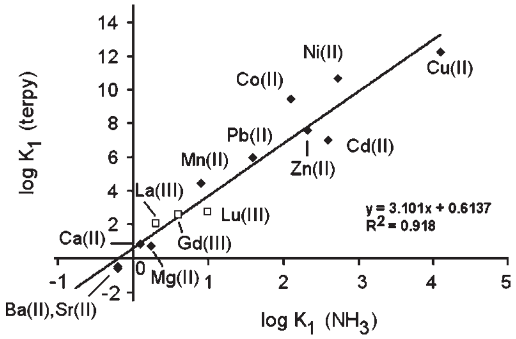


Figure 8. Relationship between log K_1(terpy) and log $K_1(NH_3)$ values for divalent (♦) and trivalent (□) metal ions. log K_1(terpy) values from this work and ref 2 and log $K_1(NH_3)$ values from ref 2 and (Ln^{III} ions) refs 15, 16, and 18. The equation on the diagram is for the least-squares best-fit line relating log K_1(terpy) values to log $K_1(NH_3)$ values, with the correlation coefficient R^2 also given. Plot made with *EXCEL*.[25].

The log K_1(terpy) values correlate quite well with the log $K_1(NH_3)$ values, as seen in Figure 8. The log $K_1(NH_3)$ value for any metal ion is[18] an important piece of ligand design information because it indicates the relative affinity of any metal ion for N donors when N donors are incorporated in polydentate ligands. It is important to note that no experimental log $K_1(NH_3)$ values for the Ln^{III} ions shown in Figure 8 are known, and, indeed, because of hydrolysis problems, it is probably impossible to obtain log $K_1(NH_3)$ values for Ln^{III} ions in aqueous solution. The log $K_1(NH_3)$ values for La^{III}, Gd^{III}, and Lu^{III} used to draw Figure 8 were predicted[12,13] by DFT calculation, and Figure 8 goes some way toward validating the results of those DFT calculations.

Terpy forms complexes that are in most cases considerably more stable than those formed by bipy, as seen for some metal ions in Table 4. One sees that phen forms complexes that are more stable than those of bipy because of the preorganization imparted by the backbone of the phen ligand. DPP has four pyridyl-type N donors, as well as a reinforced backbone, and so forms complexes of considerable stability, even with hard metal ions such as Ca^{II} or La^{III}. Quaterpy, which is being studied by us at present, forms complexes with large metal ions of greater stability than does terpy but of lower stability than the more preorganized DPP. Extending the ligand design logic in deriving DPP from quaterpy, we are currently studying the complexes of

Table 4. Formation Constants of the Polypyridyl Ligands terpy, bipy, phen, and DPP, together with Ionic Radii (r^+) of the Metal Ions Studied in This Paper, plus Am^{III}

	metal ion									
	Mg^{II}	Ca^{II}	Sr^{II}	Ba^{II}	La^{III}	Gd^{III}	Am^{III}	Zn^{II}	Cd^{II}	Pb^{II}
r^+ (Å)[a]	0.74	1.00	1.18	1.36	1.03 (1.22)	0.94 (1.11)	0.85 (1.09)	0.74	0.96	1.19
log K_1(terpy)[b]	0.74	0.85	−0.5	−0.6	2.08	2.60	(3.4)[c]	7.6	6.33	6.0
log K_1(bipy)[d]	0.36	−0.05	−0.21	−0.31	0.8[e]	0.8[e]		5.12	4.24	3.1
log K_1(phen)[d]	1.48	1.00	0.7	0.4	2.8[f]		(4.4)[g]	6.38	5.66	4.62
log K_1(DPP)[h]		2.9			5.1	6.2		8.7	12.2	7.8

[a] For six-coordination.[19] Values are given in parentheses for nine-coordinate Ln^{III} ions and eight-coordinate Am^{III}. [b] This work. [c] 75% methanol.[40] [d] Reference 15. [e] Reference 38. [f] Literature value[15] for Nd^{III} in 5 M NaCl.39 A preliminary value of log K_1(phen) ~ 2.3 in 0.1 M $NaClO_4$ for La^{III} has been obtained: Carolan, A. N.; Hancock, R. D., to be published. [g] The value of log K_1(phen) = 2.6 for Am^{III} reported in ref 11 was not selected for the critical compilation of Martell and Smith[15] and appears to be too low because the same authors report log K_1 values for Ln^{III} ions with phen of about 1.0, which are too low in comparison with the preferred values[15] of log K_1 ~ 2.8. The value of log K_1(phen) given for Am^{III} is thus an estimate that preserves the difference in log K_1(phen) of 1.6 log units[11] between Am^{III} and Ln^{III} ions but brings the latter in line with the best value[14] for Nd^{III} given here. [h] Reference 26.

metal ions with the ligand diphen, which has two reinforcing bridges in its backbone, compared to the single reinforcing bridge of DPP. There is currently not much information on the affinity of Am^{III} for polypyridyl ligands. Table 4 suggests, however, that Am^{III} has a higher affinity[11] for phen than do Ln^{III} ions, which observation supports the idea that polypyridyl-type ligands should be useful in the design of selective extractants for Am^{III}. Table 4 suggests that tetradentate ligands such as DPP complex metal ions much more strongly than do tridentate ligands such as terpy and that a useful direction in the development of ligands for selective complexation of Am^{III} might lie in ligands such as BTPH (Figure 1), a tetradentate analogue of BTP, currently a promising basis of Am^{III} selective solvent extractants.[3]

The log K_1(terpy) values for Cd^{II} and Zn^{II} measured here are (Table 3) considerably higher than those reported previously.[17] The latter authors measured the forward and reverse rates of formation and breakup of the terpy complexes of Zn^{II} and Cd^{II} by stopped-flow techniques, and it is difficult to assess what problems there might be with such an approach to obtaining log K_1 values. The log K_1(terpy) values for Zn^{II} and Cd^{II} reported here are based on well-tried techniques,[25] and statistical analysis indicates a very good fit to the absorbance/pH data obtained, so one feels confident that the higher log K_1(terpy) values for the ions reported here are to be preferred.

Structure of 1. The structure of the complex cation $[Ni(terpy)_2]^{2+}$ from **1** is shown in Figure 2, and bond lengths and angles of interest for the structure are given in Table 2. The complex cation $[Ni(terpy)_2]^{2+}$ in **1** is structurally quite similar to where it occurs in other reports of structures containing this cation.[1] The Ni^{II} in $[Ni(terpy)_2]^{2+}$ is six-coordinate with average Ni−N lengths of 1.990(2) Å for bonds involving the central N donors of terpy (Ni−N2 and Ni−N5) and of 2.107(10) Å for the Ni−N bonds involving the peripheral N donors (Ni−N1, Ni−N3, Ni−N4, and Ni−N6) of terpy. At an average difference of 0.12 Å in Ni−N bond lengths between the central and peripheral Ni−N bonds with terpy, this is quite significant. Examination of the 873 reported structures[14] of complexes with terpy in the CSD shows that this is quite common but that the extent of the difference in the M−N length is dependent on the size of the metal ion. This type of effect can be conveniently analyzed using data extracted from the CSD,[14] where the *Conquest* program[14] creates an *EXCEL* file containing the selected structural data. Such an analysis for the central and peripheral M−N bond lengths of terpy complexes is seen in Figure 9. The linear relationship between the peripheral and central M−N lengths for terpy complexes can be expressed as a linear equation with a correlation coefficient (R^2) of 0.978:

$$\text{M}-\text{N(central)} = 1.1591\text{M}-\text{N(peripheral)} - 0.4203 \quad (2)$$

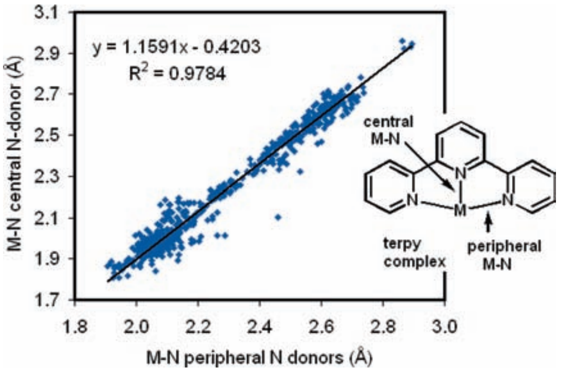


Figure 9. Relationship between the M−N bond lengths in terpy complexes for the central M−N bonds versus the peripheral M−N bonds. Bond length data from ref 1 representing 873 structures. The equation on the diagram is for the least-squares best-fit line, with the correlation coefficient (R^2) for the equation also given. Plot made with *EXCEL*.[25].

Such relationships, more usually involving L−M−L (L = ligand) bond angles and M−L bond lengths, are commonly found[36] for structures of a particular ligand with a series of metal ions that differ in size and offer insights not only into the structural features of the complexes but also into the metal-ion-size-based selectivity observed in aqueous solution. What eq 2 suggests is that, for a metal ion with a M−N bond length of 2.642 Å, all three M−N lengths in the terpy complex will be equal, while for short M−N lengths in the vicinity of 1.90 Å, the central M−N length will be shorter by about 0.1 Å. What this relationship illustrates is the greater rigidity of aromatic ligands such as terpy, which is much more able to control the metal-ion geometry than saturated ligands such as dien. This is particularly true for ligands such as DPA or Q-phen. As will be reported in a future paper, the high levels of preorganization[37] of ligands such as DPA and Q-phen lead to extremely high complex stability and, in the case of Q-phen, acute selectivity for small metal ions based on the formation of a rigid six-membered chelate ring.[18]

CONCLUSIONS

The ligand terpy is rather water-insoluble, in agreement with other observations,[40] and is prone to the formation of precipitates in the presence of electrolytes added to control the ionic strength. Satisfactory studies of terpy complexation in aqueous solution may be carried out with 2×10^{-5} M terpy in the absence of added electrolytes and avoidance of materials on which terpy might adsorb. This work has shown the reasonable affinity of pyridyl-based ligands such as terpy for "hard" metal ions such as the alkali-earth metal ions and the Ln^{III} ions. The $\pi-\pi^*$ transitions of terpy provide an excellent tool for studying complex formation in aqueous solution, in the marked sharpening of these bands that may be attributed to rigidification of the ligand upon complex formation, which alters vibrations that are coupled to the $\pi-\pi^*$ transitions. The log $K_1(NH_3)$ values of metal ions, both experimental and predicted,[12,13,15] are important parameters in understanding the affinity that metal ions have for N-donor ligands in solution. A study of the stability of complexes of Am^{III} with polypyridyl ligands in aqueous solution would be most informative.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hancockr@uncw.edu.

ACKNOWLEDGMENT

The authors thank the University of North Carolina at Wilmington and the Department of Energy (Grant DE-FG07-07ID14896) for generous support for this work.

REFERENCES

(1) Nash, L. L.; Madic, C.; Mathur, J. N.; Lacquement, J. *The chemistry of the actinide and transactinide elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., eds.; Springer: Amsterdam, The Netherlands, 2006, Vol. 4, p 2622.

(2) Musikas, C. *Inorg. Chim. Acta* **1987**, *140*, 197.

(3) Petit, L.; Adamo, C.; Maldivi, P. *Inorg. Chem.* **2006**, *45*, 8517.

(4) Morss, L. R.; Rogers, R. D. *Inorg. Chim. Acta* **1997**, *255*, 193.

(5) Ensor, D. D.; Jarvinen, G. D.; Smith, B. F. *Solvent Extr. Ion Exch.* **1988**, *6*, 439.

(6) Madic, C.; Hudson, M. J. Report EUR 18038 EN, 1998.

(7) Hudson, M. J.; Boucher, C. E.; Braekers, D.; Desreux, J. F.; Drew, M. G. B.; Foreman, M. R.; Harwood, L. M.; Mark, R. St. J; Hill, C.; Madic, C.; Marken, F. *New J. Chem.* **2006**, *30*, 1171.

(8) Foreman, M. R. S.; Hudson, M. J.; Drew, M. G. B.; Hill, C.; Madic, C. *Dalton Trans.* **2006**, 1645.

(9) Drew, M. G. B.; Iveson, P. B.; Hudson, M. J.; Liljenzin, J. O.; Spjuth, L.; Cordier, P.-Y.; Enarsson, A.; Hill, C.; Madic, C. *Dalton Trans.* **2000**, 821.

(10) Diamond, R. M.; Street, K.; Seaborg, G. T. *J. Am. Chem. Soc.* **1954**, *76*, 1461.

(11) Musikas, C.; Le Marois, G.; Fitoussi, R.; Cuillerdier, C. In *Actinide Separations*; Navratil, J. D., Schulz, W. W., Eds.; ACS Symposium Series 117; American Chemical Society: Washington, DC, 1980; p 131.

(12) Hancock, R. D.; Bartolotti, L. J. *J. Chem. Soc., Chem. Commun.* **2004**, 534.

(13) Hancock, R. D.; Bartolotti, L. J. *Inorg. Chem.* **2005**, *44*, 7175.

(14) Cambridge Structural Database, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

(15) Martell, A. E.; Smith, R. M. Critical Stability Constant Database No. 46; National Institute of Science and Technology (NIST): Gaithersburg, MD, 2003.

(16) Pearson, R. G. *Chemical Hardness*; Wiley-VCH: Weinheim, Germany, 1997.

(17) Holyer, R. H.; Hubbard, C. D.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1966**, *5*, 622.

(18) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.

(19) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(20) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(21) Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420.

(22) Gephart, R. T., III; Williams, N. J.; Reibenspies, J. H.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 8201.

(23) ORTEP-3 for Windows, version 1.08: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(24) Billo, E. J. *EXCEL for Chemists*; Wiley-VCH: New York, 2001.

(25) Martell, A. E.; Motekaitis, R, J. *The Determination and Use of Stability Constants*; VCH Publishers: New York, 1989.

(26) Cockrell, G. M.; Zhang, G.; Van Derveer, D. G.; Thummel, R. P.; Hancock, R. D. *J. Am. Chem. Soc.* **2008**, *130*, 1420.

(27) Melton, D. L.; VanDerveer, D. G.; Hancock, R. D. *Inorg. Chem.* **2006**, *45*, 9306.

(28) Dean, N. E.; Hancock, R. D.; Cahill, C. L.; Frisch, M. *Inorg. Chem.* **2008**, *47*, 2000.

(29) Williams, N. J.; Dean, N. E.; Van Derveer, D. G.; Luckay, R. C.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 7853.

(30) Merrill, D.; Hancock, R. D. *Radiochim. Acta* **2011**in press.

(31) Buist, D.; Williams, N. J.; Reibenspies, J. H.; Hancock, R. D. *Inorg. Chem.* **2010**, *49*, 5033.

(32) Robertson, K. N.; Bakshi, P. K.; Lantos, S. D.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1988**, *76*, 583.

(33) Liantonio, R.; Logothetis, T. A.; Messina, M. T.; Metrangolo, P.; De Santis, A.; Pilati, T.; Resnati, G. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1373.

(34) Bessel, C. A.; See, R. F.; Jameson, D. L.; Churchill, M. R.; Takeuchi, K. J. *J. Chem. Soc., Dalton Trans.* **1992**, 3223.

(35) Hergold-Brundic, A.; Popovic, Z.; Matkovic-Calogovic, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 3154.

(36) Hancock, R. D.; Melton, D. L.; Harrington, J. M.; McDonald, F. C.; Gephart, R. T.; Boone, L. L.; Jones, S. B.; Dean, N. E.; Whitehead, J. R.; Cockrell, G. M. *Coord. Chem. Rev.* **2007**, *251*, 1678.

(37) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Brown, S. B.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 3645.

(38) Hancock, R. D.; Jackson, G.; Evers, A. *J. Chem. Soc., Dalton Trans.* **1979**, 1384.

(39) Xia, Y. X.; Chen, J. F.; Choppin, G. R. *Talanta* **1996**, *43*, 2073.

(40) Miguirditchian, M.; Guillaneuz, D.; Francois, N.; Airvault, S.; Ducros, S.; Thauvin, D.; Madic, D.; Illemassène, M.; Lagarde, G.; Krupa, J.-C. *Nucl. Sci. Eng.* **2006**, *153*, 223.