tances are found in the molecules with the substituents F (sulfur hexafluoride itself[26]), F_2N, and FO and longer ones in molecules with the substituents Cl, Br, and C≡CH. The shortest distance is found for the substituent FO, which has the highest group electronegativity. The more electronegative substituents lead to the highest positive charge densities on the sulfur atom and thus to larger Coulombic attractions between it and the ligands. When a fluorine atom is replaced by a less electronegative atom or group, such as Cl, Br, O, CF_3, HN, and C≡CH, the charge density on sulfur lessens and the bonds to the fluorines correspondingly increase in length. (The group F_2N appears to be an exception; it leads to a decrease in average S—F bond length.) The above discussion concerns inductive effects, and a question may be asked about evidence for possible electron delocalization from the C≡CH group. The C≡C distance in our molecule, for which we estimate $r_a^0 \simeq r_e$, is very nearly the same as in acetylene[23] ($r_e =$ 1.2031 (5) Å), and the average S—F distance is similar to those in other molecules in which electron delocalization would not be expected. There is a great deal of variability in the lengths of S—C bonds in S^{VI} compounds. At 1.727 (5) Å in our molecule it is very much shorter than the 1.887 (8) Å found in F_5SCF_3,[9] and somewhat shorter than the 1.771 (4) Å found in $O_2S(CH_3)_2$.[27] Since sp hybridization at carbon leads to bonds about 0.07 Å shorter than the sum of tetrahedral covalent single-bond radii, and since the Pauling tetrahedral radii for sulfur and carbon sum to 1.81 Å, we regard our S—C distance as normal. All in all, these distance comparisons indicate that there is very little electron delocalization in $F_5SC≡CH$.

The angle values in $F_5SC≡CH$ also have a simple interpretation. The widely successful VSEPR theory[28] calls for greater repulsion between the S—F_e bonds and the bond to groups less electronegative than the fluorine atom than between the S—F_a and S—F_e bonds. The consequence is ∠F_a–S–F_e < 90°. A similar angle deformation is to be expected from a balancing of steric interaction between the small axial and equatorial fluorine atoms, on the one hand, with that between the equatorial fluorines and the bulkier substituents on the other.

The important question of the relative lengths of the two types of S–F bonds in $F_5SC≡CH$ is unfortunately not resolved. Our preferred model A shows their lengths to be the same to within the uncertainty of the measurement. Moreover, as is seen from the results for model B in Table II, this result is independent of the exclusion of the high-angle data from our short-camera experiments. Model C provides a test. When the equatorial S—F bond is set and held at a value 0.010 Å longer than the axial one, the quality of fit is virtually identical with that obtained with model A and, as tests showed, is as good as when this bond is made the shorter one by the same amount. We conclude that the relative lengths of the two kinds of S—F bonds cannot be determined from electron diffraction data alone, even though, as ours do, they extend to much larger than the usual scattering angles. A similar situation was encountered in the case of F_5SCl[3,4] and was eventually resolved by an analysis[4] that incorporated rotational constants for several isotopic species. It seemed less likely that rotational constant data would be of help in the case of our symmetric-top molecule because there are several more structural parameters to which the rotational constant is very sensitive. We checked the matter as follows. First, the rotational constant B_z for our preferred model A was calculated. Its value was then successively changed by ±5 and ±10 MHz and the structure refined with these four B_z's used as constraints. The only parameter that obtained values beyond the range of uncertainty listed for it in model A was r(C—S); even so, its values lay in the narrow range 1.720 (5) ≤ r(C—S)/Å ≤ 1.734 (4). Corresponding results for the S—F bond length difference were −0.003 (6) ≤ Δr(S—F)/Å ≤ 0.005 (6). We conclude it is not possible to determine which of the two types of S—F bonds is longer to within the uncertainty given for it in model A.

(25) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111–145.
(26) Kelly, H. M.; Fink, M. *J. Chem. Phys.* **1982**, *77*, 1813.
(27) Hargittai, M.; Hargittai, I. *J. Mol. Struct.* **1974**, *20*, 283.
(28) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 389. Gillespie, R. J. *Molecular Geometry*; Van Nostrand-Reinhold: New York, 1972.

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Thermodynamic Study of Lanthanide Complexes of 1,4,7-Triazacyclononane-N,N',N''-triacetic Acid and 1,4,7,10-Tetraazacyclododecane-N,N',N'',N'''-tetraacetic Acid

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Current interest in the complexation properties of lanthanide selective reagents has led to the synthesis of many new macrocycles derived from cyclic polyaza and cyclic polyaza polyoxa ligands with a wide variety of ionizable functional groups.[1-5] The thermodynamics of lanthanide complexation with these ligands should depend upon internal cavity size,[6] rigidity, and nature of the donating atoms.

Although there has been much interest in design of new lanthanide selective ligands, there have been few studies of the thermodynamic stability of such complexes.[7-10] We have been interested in using lanthanide complexes of macrocyclic polyaza polyacetate ligands as aqueous NMR shift reagents and MRI contrast agents.[11,12] As some of these ligands form complexes too slowly with the lanthanides for thermodynamic measurements to be made by the usual potentiometric methods, we have developed a spectrophotometric technique that allows the determination of stability constants over a wide range of values. The thermodynamic stability constants for the lanthanide complexes of 1,4,7-triazacyclononane-N,N',N''-triacetic acid (NOTA) and 1,4,7,10-tetraazacyclododecane-N,N',N'',N'''-tetraacetic acid (DOTA) are reported in this work.

Experimental Section

Reagents. The ligands NOTA and DOTA were synthesized by methods reported previously.[11,13] Arsenazo III (99.99%), purchased from Aldrich Chemical Co., was used without further purification. Solutions of the lanthanides were prepared from the trichloride salts and were standardized by titration with EDTA with xylenol orange used as the indicator.

Spectrophotometric Titrations. The lanthanide and Arsenazo III solutions were buffered at pH 3.89 with 0.01 M acetate buffer at an ionic strength of 0.1 (NaCl). Conditional stability constants for the 1:1 and 1:2 complexes[14] of the lanthanides with Arsenazo III were determined by titrating a standard lanthanide solution directly in a 1.00-cm cuvette with a standard Arsenazo III solution while the absorbance was monitored at 660 nm. Free Arsenazo III absorbs only slightly at this wavelength and pH (ϵ = 650 L/(mol cm)) while the 1:1 and 1:2 lanthanide complexes of Arsenazo III have extinction coefficients of 35 000 and 50 000 l/(mol cm), respectively. Titrant was added to the cuvette so that the lanthanide:Arsenazo III ratio varied between 3:1 and 1:1.7.

The conditional stability constants of the lanthanides with NOTA and DOTA were measured by titrating a solution of the lanthanide–Arsenazo III mixture, containing a mixture of 1:1 and 1:2 complexes, with the desired ligand. As it took several days for the macrocycle–lanthanide–Arsenazo III mixtures to reach equilibrium at the low concentrations used in this work, it became expedient to maintain the solutions at 60 °C in a sealed cuvette for 12–18 h followed by an additional 6–10-h room-

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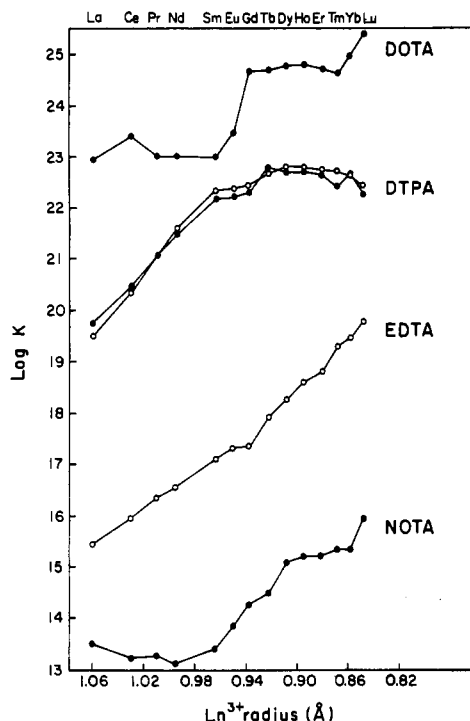* To whom correspondence should be addressed.

Figure 1. Variation of stability constant with ionic radii of the lanthanides. Literature values for EDTA and DTPA (open circles) are shown for comparison with measured values (closed circles).
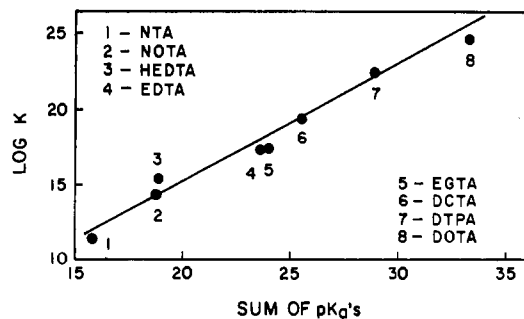

Figure 2. Plot of Gd^{3+} stability constants vs. $\sum pK_a$ for a variety of polyamino polycarboxylate ligands. The regression line shown was calculated without the values obtained for Gd(NOTA) and Gd(DOTA)⁻.

temperature equilibration. Spectrophotometric measurements showed that longer periods of equilibration were unnecessary for the system to reach equilibrium. The conditional stability constants obtained for the lanthanides with NOTA and DOTA were converted to thermodynamic constants by using pK_a values previously determined for these chelates at 0.1 M ionic strength.[15,16] All spectrophotometric measurements were made on a HP-8450A linear diode-array spectrometer.

Computational Methods

All stability constant calculations were performed by a computer program written to evaluate the absorbance data. The program consisted of a simplex[17] nonlinear regression algorithm for refinement of the equilibrium constants along with a Newton–Raphson[18] algorithm for calculation of the equilibrium concentrations of all solution species.

The accuracy of this technique was verified by measuring the thermodynamic stability constant for the lanthanides with diethylenetriaminepentaacetic acid (DTPA). The resulting stability constants measured with our spectrophotometric method are compared with potentiometrically determined values[19] for the Ln(DTPA) complexes in Figure

1. The agreement between our results and the literature values was excellent, with an average deviation in log K of 0.13. This is quite acceptable since literature values for these constants are usually reported within ±0.2 log K precision.

Results and Discussion

The thermodynamic stability constants for the Ln(NOTA) and Ln(DOTA)⁻ complexes with 14 lanthanide cations are reported in Figure 1. Also shown are the Ln(DTPA)²⁻ results and literature values[19] for the Ln(EDTA)⁻ complexes for comparison. The progressive increase in Ln(EDTA)⁻ stability constants along the Ln^{3+} cation series is characteristic of chelates that are flexible and show increasing stability with charge density on the cation. DTPA forms stronger complexes with the lanthanides than does EDTA primarily because it is octadentate vs. hexadentate. However, it is thought that the Ln(DTPA)²⁻ stability constants reach a maximum at the Tb^{3+}–Ho^{3+} triad because DTPA is less flexible than EDTA and cannot wrap around the smaller lanthanides successfully. This leads to a drop in stability for the last four cations in the series.

NOTA is a hexadentate chelate like EDTA but with three nitrogen and three oxygen donor atoms. The resulting Ln(NOTA) complexes are all less stable than the corresponding Ln(EDTA)⁻ complexes by a factor of 100 (La^{3+} complexes) to a factor of 5620 (Lu^{3+} complexes). The overall trend in the stability of the Ln(NOTA) complexes is probably a result of the restricted size of the triazacyclononane ring in NOTA. The stability constants for the Ln(NOTA) complexes are nearly constant for the first five ions in the series and then increase progressively with a further decrease in cation size, showing a slope similar to that of the Ln(EDTA)⁻ complexes. Previous NMR and fluorescence results[11,20] have shown that the larger lanthanide cations form mixed complexes with NOTA, including both hexadentate and pentadentate structures. This would be consistent with the thermodynamic results presented here. The larger cations, i.e. La^{3+}, may be too large for the combined steric requirements of the triaza ring and the acetate groups. Near the center of the lanthanide series, the chelate may accommodate the cations into a position well above the plane defined by the three nitrogen atoms, with the acetate arms in equatorial positions relative to the cation. Once this critical size requirement is met, the stability constants increase with increasing charge density similar to the Ln(EDTA)⁻ constants.

The lower stability of the Ln(NOTA) complexes, as compared to those for EDTA, reflect the ionic nature of these complexes. The entropy and enthalpy changes resulting from complexation of the lanthanide cations are predominately hydration effects and tend to cancel so that the free energy of complexation is a good measure of the lanthanide–chelate interaction.[21] Thus the stability of a Ln–chelate complex should correlate with the basicity of the ligand. Figure 2 shows a plot of Gd^{3+} log K values versus $\sum pK_a$ for several amino carboxylate ligands. All the ligands shown in Figure 2 form 5-membered O–Ln–N rings so that additional entropy effects in log K due to steric strain in the chelate are

(1) Alberts, A. H.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3545.
(2) Weitl, F. L; Raymond, K. N.; Smith, W. L.; Howard, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 1170.
(3) Takagi, M.; Takaki, M.; Ueno, K. *Chem. Lett.* **1978**, 1179.
(4) Desreux, J. F.; Merciny, E.; Loncin, M. F. *Inorg. Chem.* **1981**, *20*, 987.
(5) Delgado, R.; Frausto da Silva, J. J. R. *Talanta* **1982**, *29*, 815.
(6) Lehn. J. N; Sauvage, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6700.
(7) Massaux, J.; Desreux, J. F.; Delchambre, C.; Duyckaerts, G. *Inorg. Chem.* **1980**, *19*, 1893.
(8) Chang, C. A.; Rowland, M. E. *Inorg. Chem.* **1983**, *22*, 3866.
(9) Chang, C. A.; Ochaya, V. O.; Sekhar, V. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1724.
(10) Chang, C. A.; Ochaya, V. O. *Inorg. Chem.* **1986**, *25*, 355.
(11) Sherry, A. D.; Singh, M.; Geraldes, C. F. G. C. *J. Magn. Reson.* **1986**, *66*, 511.
(12) Geraldes, C. F. G. C.; Sherry, A. D.; Brown, R. D., III; Koenig, S. H. *Magn. Reson. Med.* **1986**, *3*, 242.
(13) Desreux, J. F. *Inorg. Chem.* **1980**, *19*, 1319.
(14) Budesinsky, B. *Talanta* **1968**, *15*, 1063.
(15) Geraldes, C. F. G. C.; Alpoim, M. C.; Marques, M. P. M.; Sherry, A. D.; Singh, M. *Inorg. Chem.* **1985**, *24*, 3876.
(16) Micheloni, M.; Sabatini, A.; Paoletti, P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 828.
(17) Cacei, M. S.; Cacheris, W. P. *Byte* **1984**, *5*, 340.
(18) Margenau, H.; Murphy, R. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 476.
(19) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1974; Vol. 1.

(20) Bryden, C. C.; Reilley, C. N. *Anal. Chem.* **1982**, *54*, 610.
(21) Choppin, G. R. *J. Less-Common Met.* **1985**, *112*, 193.

absent. The linear nature of this relationship predicts that Gd-(NOTA) should be less stable than Gd(EDTA)⁻.

DOTA is a octadentate chelate like DTPA. Although DOTA has one less oxygen donor atom than DTPA, the Ln(DOTA)⁻ complexes are all more stable than the corresponding Ln(DTPA)²⁻ complexes. This is precisely what one would predict from the $\sum pK_a$ values for the two chelates. The log K value predicted for Gd(DOTA)⁻ from the correlation shown in Figure 2 is within 5% of our measured value. Loncin et al.[22] have recently reported log K values for Eu(DOTA)⁻ and Tb(DOTA)⁻ (28.2 and 28.6, respectively) as determined by a gravimetric technique. Our measurements indicate that these values are about 3 orders of magnitude too high.

The solid-state structure of Eu(DOTA)⁻ indicates that the chelate is strained, resulting in variable Eu–N bond lengths.[23] This suggests that the Eu³⁺ cation is too large to fit into the lowest energy [3333] square conformation of the tetraazadodecane ring, and hence the complex is slightly distorted. A NMR study[13] has shown that La(DOTA)⁻, Pr(DOTA)⁻, and Eu(DOTA)⁻ have similar free energies of activation for ethylenediamine proton interconversion between two staggered conformations. Our results indicate that these three ions are too large to satisfy the stereochemical requirements of the tetraazadodecane ring and, although these complexes are quite rigid on the NMR time scale at room temperature, they are considerably more flexible than the complexes formed by the heavier cations,[13] i.e., Yb(DOTA)⁻ and Lu(DOTA)⁻. The sharp increase in log K we observe between Eu(DOTA)⁻ and Gd(DOTA)⁻ may reflect a more precise cation size requirement of the chelate. The nearly constant log K values found for Gd³⁺–Tm³⁺ complexes with DOTA indicate that ion size is not a critical determinant of stability once a cation of favorable size, i.e., Gd³⁺, has been presented to the chelate. It is not until the charge denstiy on the cation greatly increases does the stability of the complex begin to increase again, as in the case of Yb(DOTA)⁻ and Lu(DOTA)⁻.

Registry No. NOTA, 56491-86-2; DOTA, 60239-18-1; La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm, 7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3.

(22) Loncin, M. F.; Desreux, J. F.; Merciny, E. *Inorg. Chem.* **1986,** *25,* 2646.
(23) Spirlet, M. R.; Rebizant, J.; Desreux, J. F.; Loncin, M. F. *Inorg. Chem.* **1984,** *23,* 359.

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Luminescence from and Absorption by the ³T₁g Level of the Hexacyanocobaltate(III) Ion

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The properties of the ³T₁g level of the hexacyanocobaltate(III) ion and its importance in the photochemistry of the ion have been extensively investigated.[1] All photochemical activity of Co(CN)₆³⁻ is believed to originate from this level.

(1) Zinato, E. In *Concepts of Inorganic Photochemistry*; Adamson, A., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 4.
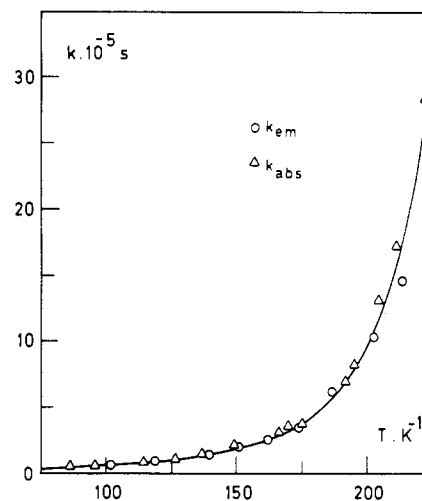

Figure 1. First-order decay rate constants as a function of temperature: solvent, EPA; k_{abs}: absorption data; k_{em}, emission data.

The emission from the triplet state has been observed in solids,[2–4] but its intensity is strongly temperature dependent. Luminescence of Co(CN)₆³⁻ in solution is extremely weak at room temperature: only by using a sampling technique and by deconvoluting the data, in order to separate the signal from the laser pulse, were Conti et al.[5] able to calculate a lifetime of 2.6 ns.

Although the triplet is usually populated via intersystem crossing from the ¹T₁g level, direct singlet–triplet absorption from the ¹A₁g ground level has been observed around 396 nm.[6,7]

We reported on the spectral features of a transient species, formed upon laser flash photolysis of the Co(CN)₆³⁻ ion at 94 K, which we assumed to be the ³T₁g triplet state.[8] We present now experimental evidence that the luminescence, observed earlier,[2–4] and the transient spectrum measured by us related indeed to the same species. The kinetic behavior as a function of temperature is indeed the same for the absorbing and the emitting entity.

Experimental Section

The experimental set up for transient absorption measurements was identical with the one used earlier.[8] Samples of (TBA)₃Co(CN)₆ were either dissolved in EPA (ethanol–isopentane–ethyl ether) or in ethylene glycol–water mixtures (60/40 vol. %). The spectrophotometric cell was suspended in an all-quartz Dewar and cooled by means of a thermostated stream of cold nitrogen gas. For the observation of the luminescence an additional Jobin Yvon H20-IR monochromator was mounted at 90° relative to the exciting beam. In order to minimize the interference of the laser pulse, special precautions were required: the fundamental component of the ruby laser light (694 nm) was removed by means of a CuSO₄ solution with a path length of 10 cm. The 347-nm component was prevented from entering the monochromator by means of a suitable glass filter.

The emission spectra were corrected for the variations in sensitivity of the detection system by using the emission data of a tungsten lamp with known spectral distribution.

A second correction factor is required in order to take into account the variation of the absorption at the wavelength of the laser, when the samples are cooled. When the sample is cooled from 293 to 110 K the absorbance at 347 nm of [(n-C₄H₉)₄N]₃Co(CN)₆ decreases by a factor of 5! Presumably the important decrease is due to a combination of the band being vibronic and the laser exciting into the low-energy edge.

Photosolvation quantum yields at low temperature were measured by using the same Dewar setup. The irradiation was performed with the 313-nm line of a high-pressure mercury arc, whose light output was monitored with a chemical actinometer. The amount of light incident

(2) Mingardi, M.; Porter, G. B. *J. Chem. Phys.* **1966,** *44,* 4354.
(3) Kirk, D.; Ludi, A.; Schläfer, H. *Ber. Bunsen-Ges Phys. Chem.* **1969,** *73,* 669–683.
(4) Kataoka, H. *Bull. Chem. Soc. Jpn.* **1973,** *46,* 2078–2086.
(5) Conti, C.; Castelli, F.; Forster, L. S. *J. Phys. Chem.* **1979,** *83,* 2371–2376.
(6) Fujita, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1963,** *36,* 1281–1285.
(7) Loeb, B.; Zuloaga, F. *J. Phys. Chem.* **1977,** *81,* 59–63.
(8) Viaene, L.; D'Olieslager, J.; Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1979,** *101,* 1405–1409.