information is given on any current masthead page.

Fujian Institute of Research on the Structure of
Matter and Fuzhou Laboratory of Structural
Chemistry
Chinese Academy of Sciences
Fuzhou, Fujian, China

B. S. Kang*[14]
L. H. Weng
D. X. Wu
F. Wang
Z. Guo
L. R. Huang
Z. Y. Huang
H. Q. Liu

Received October 7, 1987

Synthesis, Structure, and Reactivity of Tricoordinate Cerium(III) Aryloxides. The First Structurally Characterized Monomeric $Ln(OR)_3$ Complexes

Sir:

Compounds of the type $Ln(OR)_3$ (Ln = lanthanide metal, R = alkyl or aryl) generally exist as oligomers, both in solution and in the solid state[1]—a natural consequence of the preference for high coordination numbers by the lanthanide metal ions. The only previously reported monomeric complexes belonging to the above group are $Ln[2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O]_3$.[2] While the monomeric nature of these compounds in solution was established by cryoscopic measurements, their solid-state structures remained unknown. Interestingly, the corresponding Sc analogue[2] exhibits a near-planar MO_3 skeleton in sharp contrast to the pyramidal MN_3 skeletons for $Ln[N(SiMe_3)_2]_3$ compounds[3]—the only previously reported, structurally characterized, tricoordinate complexes of the lanthanide metals. Herein, we report the synthesis, structural elucidation, and reactivity of a series of Ce(III) aryloxides, $Ce[2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}XC_6H_2O]_3$ (X = H (**1a**), Me (**1b**), *t*-Bu (**1c**)). The noteworthy features of these complexes are as follows. (a) The crystal structure of **1a** constitutes the first structural characterization of a *monomeric* $Ln(OR)_3$ complex. Such well-defined aryloxide compounds are potentially useful as precursors to the corresponding oxides through the low-temperature sol-gel process.[4] (b) The above complexes are only the second general class of tricoordinate lanthanide metal compounds (vide supra). (c) **1a** exhibits a pyramidal structure *unlike* the near-planar Sc analogue and *like* the $Ln[N(SiMe_3)_2]_3$ compounds. (d) The ability of Ce(III) to adopt an apical position makes it accessible to a variety of incoming ligands, including the "soft" *t*-BuNC and tetrahydrothiophene, leading to the formation of $LCe(OR)_3$ species. (e) With slender ligands, 2:1 adducts, $L_2Ce(OR)_3$, were also formed. A crystal structure of the $(t\text{-}BuNC)_2Ce(OR)_3$ complex revealed a novel distorted trigonal bipyramid geometry with a cis disposition of the *t*-BuNC ligands.

The aryloxides **1a–e** were synthesized by the reaction of $Ce[N(SiMe_3)_2]_3$[5] with the appropriate phenol in pentane. The compounds were characterized by NMR, IR, and elemental analysis (C, H, N). All were volatile (sublimed at 180–190 °C, 10^{-5} Torr), yellow-green crystalline solids and were soluble in hydrocarbon solvents.

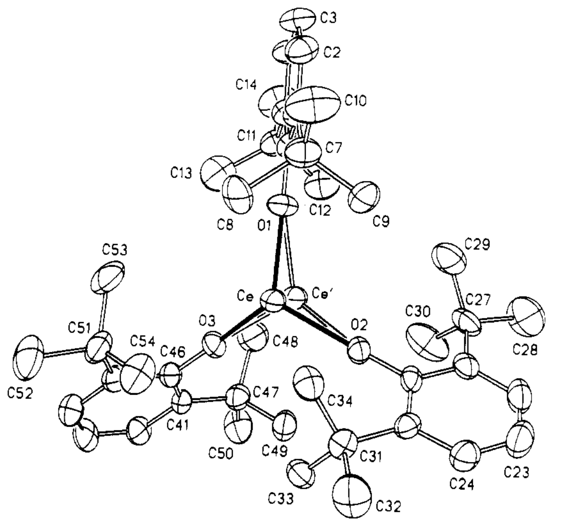

Figure 1. Thermal ellipsoid (40% probability) diagram for **1a**.[6] Important bond distances (Å) and angles (deg): Ce⋯Ce′, 1.075 (2); Ce–O(1), 2.140 (5); Ce–O(2), 2.174 (4); Ce–O(3), 2.135 (5); Ce′–O(1), 2.180 (5); Ce′–O(2), 2.112 (4); Ce′–O(3), 2.127 (5); O(1)–Ce–O(2), 114.9 (2); O(1)–Ce–O(3), 115.5 (2); O(2)–Ce–O(3), 110.2 (2); O(1)–Ce′–O(2), 115.9 (2); O(1)–Ce′–O(3), 114.2 (2); O(2)–Ce′–O(3), 114.2 (2); Ce–O(1)–C(6), 165.7 (4); Ce–O(2)–C(26), 161.7 (4); Ce–O(3)–C(46), 165.0 (5); Ce′–O(1)–C(6), 163.2 (5); Ce′–O(2)–C(26), 166.8 (4); Ce′–O(3)–C(46), 165.5 (5).

The structure of **1a** was determined by single-crystal X-ray diffraction and is shown in Figure 1.[6] The compound is monomeric with the oxygens arranged in a trigonal pyramid about Ce, which is disordered between two such sites. The oxygens and ipso carbons are coplanar to within 0.026 Å.[7] **1a** is significantly more pyramidal than any other known tricoordinate lanthanide complex, as measured by the distance of the metal from the plane of the ligating atoms (0.54 Å average for **1a** versus 0.44, 0.34, and 0.42 Å, respectively, for $M[N(SiMe_3)_2]_3$ (M = Sc,[8] Nd,[3b] Eu[8]) and 0.13 Å for $Sc[2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O]_3$[2]). The pyramidal structure may, however, be the result of crystal-packing forces since it has been reported that $Eu[N(SiMe_3)_2]_3$, which is also pyramidal in the solid state, has a solution dipole moment of zero.[8] This suggests that the metal can move freely perpendicular to the ligand plane and that its position is a function of the ligand environment—a property that may be responsible for what little coordination chemistry has been reported for other tricoordinate lanthanide metal complexes.[2,9]

The tendency of **1a** to form adducts with Lewis bases was probed by NMR spectral titrations. For example, the addition of tetrahydrofuran (THF) to a C_6D_6 solution of **1a** resulted in

---

(1) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic: New York, 1978.

(2) Hitchcock, P. B.; Lappert, M. F.; Singh, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1499.

(3) (a) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1. (b) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317.

(4) Hench, L. L., Ulrich, D. R., Eds. *Science of Ceramic Chemical Processing*; Wiley: New York, 1986.

(5) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

(6) Crystal data for $C_{42}H_{63}O_3Ce$: monoclinic, $P2_1/c$, $a = 11.345$ (2) Å, $b = 31.918$ (6) Å, $c = 11.808$ (2) Å, $\beta = 104.92$ (1)°, $V = 4131$ (1) Å^3, $Z = 4$, D(calcd) = 1.216 g cm^{-3}, μ(Mo Kα) = 11.4 cm^{-1}, $T = 295$ K. A capillary-mounted yellow-green crystal (0.35 × 0.35 × 0.40 mm) was obtained by slow evaporation of a heptane solution. Of 5865 reflections collected (maximum $2\theta = 45°$, no data beyond) and corrected for adsorption, 2743 independent, observed ($3\sigma F_o$) reflections were used to solve (heavy atom) and refine the structure. Two Ce atom locations exist along a psuedothreefold rotational axis; their refined occupancies are Ce (0.58) and Ce′ (0.42). At convergence (all non-hydogen atoms anisotropic, all hydrogen atoms idealized such that $d_{C-H} = 0.960$ Å and $U_H = 1.2U$ for attached carbon) $R(F) = 6.33\%$, $R(wF) = 6.57\%$, GOF = 1.23, $\Delta/\sigma = 0.07$, $\Delta(\rho) = 0.42$ e Å^{-3}, and $N_o/N_v = 7.7$. All computations used the SHELXTL (version 5.1) library (Nicolet Corp., Madison, WI).

(7) Deviations from the least-squares plane formed by the six atoms were as follows (Å): O1, 0.021; O2, −0.026; O3, −0.001; C6, −0.012; C26, 0.017; C46, 0.002.

(8) Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669.

(9) (a) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507. (b) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1166.

0020-1669/88/1327-1130$01.50/0

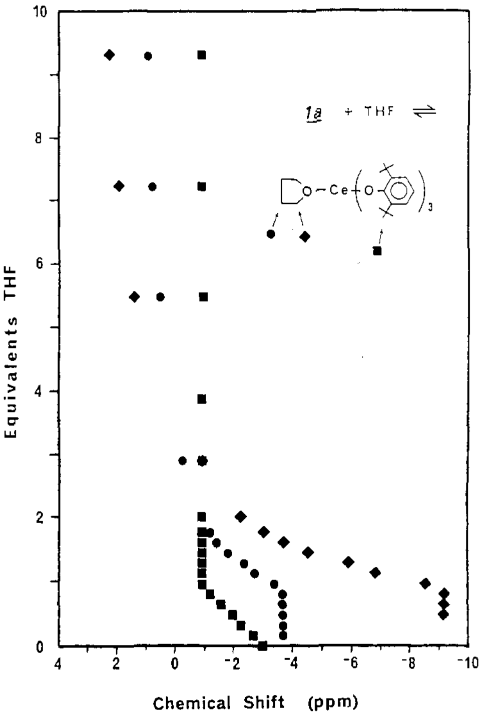

Figure 2. ^{1}H NMR spectral titration plot showing equivalents of THF added versus the chemical shifts of **1a** and THF in benzene-d_6.

changes in the NMR spectrum consistent with the formation of a 1:1 adduct in accordance with eq 1 (Figure 2). At THF:**1a**

$$\mathrm{Ce[2,6\text{-}\mathit{t}\text{-}Bu_2C_6H_3O]_3 + L \rightleftharpoons LCe[2,6\text{-}\mathit{t}\text{-}Bu_2C_6H_3O]_3} \quad (1)$$

$$\mathrm{L = THF, Ph_2CO, Et_3PO, \mathit{n}\text{-}BuNH_2, Et_2NH, MeCN,}$$
$$\mathrm{\mathit{t}\text{-}BuNC, \overline{CH_2CH_2CH_2CH_2S}}$$

ratios of less than 1, the NMR resonances of THF corresponded to those for coordinated THF and the chemical shifts for the protons of **1a** were the weighted averages of the values corresponding to $\mathrm{Ce(OR)_3}$ and $\mathrm{(THF)Ce(OR)_3}$. At THF:**1a** ratios of greater than 1, the chemical shifts of the phenoxide protons remained constant (corresponding to $\mathrm{(THF)Ce(OR)_3}$) and those of THF were the weighted averages of the values corresponding to free and coordinated THF. These results are consistent with eq 1 being fast on the NMR time scale.

Analysis of titration curves for the various added ligands allowed the estimation of the equilibrium constants corresponding to eq 1 for these ligands. Theoretical titration curves were computed for various values of K and compared to the experimental curves. The difference between the curves for $K = 10^4$ and 10^5 $\mathrm{M^{-1}}$ was so small that a lower limit of 10^4 $\mathrm{M^{-1}}$ was used for those ligands (THF, $\mathrm{Ph_2CO}$, $\mathrm{Et_3PO}$, n-$\mathrm{BuNH_2}$, MeCN, t-BuNC) displaying a sharp break at 1.0 equiv (cf. Figure 2). As the binding affinity of the ligands decreased, so did the sharpness of the break.

An investigation of the coordinating ability of a wide range of bases showed that the binding was sensitive to the size of the added ligand. Thus, n-$\mathrm{BuNH_2}$ bound more strongly to **1a** than $\mathrm{Et_2NH}$ ($K \geq 10^4$ $\mathrm{M^{-1}}$ versus $\sim 10^3$ $\mathrm{M^{-1}}$), and $\mathrm{Et_3N}$ did not bind. The "hardness" of the ligating atom was less of a factor. For example, the "hard" Ce(III) center formed 1:1 adducts not only with oxygen and nitrogen donors but with the relatively "soft" t-BuNC as well ($K \geq 10^4$ $\mathrm{M^{-1}}$). However, tetrahydrothiophene, which should be sterically similar to THF ($K \geq 10^4$ $\mathrm{M^{-1}}$) exhibited only a modest coordinating ability ($K \approx 10$ $\mathrm{M^{-1}}$).

With slender, sterically unencumbered, ligands (n-$\mathrm{BuNH_2}$, MeCN, t-BuNC) there was some evidence from the NMR titration curves for the formation of an additional, weak 2:1 adduct with **1a**. Moreover, a t-BuNC adduct, **2**, that analyzed as $\mathrm{L_2Ce(OR)_3}$ by both NMR spectroscopy and elemental analysis (C, H, N), was isolated from a solution containing excess ligand. The structure of **2** as determined by single-crystal X-ray diffraction is shown in Figure 3.[10] The compound adopts a distorted trigonal-bipyramidal structure in which one t-BuNC occupies an axial position and the other an equatorial one. This surprising structure may be viewed as a $\mathrm{Ce(OR)_3}$ molecule with *both* added t-BuNC ligands attached to the Ce atom on the same side of the $\mathrm{O_3}$ plane. Interestingly, the Ce atom in **2** is no further away from the $\mathrm{O_3}$ plane (0.54 Å) than it is in **1a**.

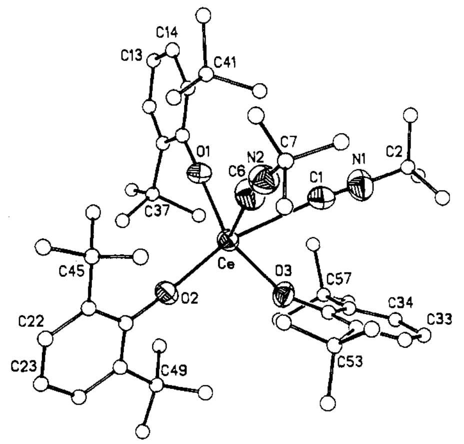

Figure 3. Thermal ellipsoid (50% probability) diagram for **2**.[10] The phenyl and *tert*-butyl carbons appear as spheres of arbitrary radius for clarity. Important bond distances (Å) and angles (deg): Ce–O(1), 2.239 (5); Ce–O(2), 2.225 (7); Ce–O(3), 2.231 (7); Ce–C(1), 2.831 (13); Ce–C(6), 2.786 (12); O(1)–Ce–O(2), 108.9 (2); O(1)–Ce–O(3), 134.0 (3); O(2)–Ce–O(3), 98.4 (3); O(1)–Ce–C(1), 89.0 (3); O(1)–Ce–C(6), 94.0 (4); O(2)–Ce–C(1), 161.9 (3); O(2)–Ce–C(6), 106.6 (3); O(3)–Ce–C(1), 69.4 (3); O(3)–Ce–C(6), 113.2 (3); C(1)–Ce–C(6), 68.4 (4); Ce–O(1)–C(16), 176.1 (7); Ce–O(2)–Ce(26), 174.5 (5); Ce–O(3)–C(36), 153.3 (6).

Finally, **1a** served as an excellent shift reagent for the added ligands. For example, for the 1:1 adduct with n-$\mathrm{BuNH_2}$, the NMR shifts (at 200 MHz) of the $\mathrm{NH_2}$, α-, β-, and γ-$\mathrm{CH_2}$, and the $\mathrm{CH_3}$ groups were at −33.1, −14.4, −6.1, −3.6, and −1.8 ppm, respectively (free ligand: 1.6, 2.6, 1.2–1.6, and 0.9 ppm, respectively).

Acknowledgment. A.S. acknowledges the support of this research by the National Science Foundation (Grant No. CHE-8312380) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The X-ray diffractometer at the University of Delaware was partially funded by the NSF.

Registry No. **1a**, 113034-77-8; **1b**, 113034-78-9; **1c**, 113034-79-0; **2**, 113034-80-3; (t-BUNC)Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-81-4; $(\overline{\mathrm{CH_2CH_2CH_2CH_2S}})\mathrm{Ce[2,6\text{-}\mathit{t}\text{-}Bu_2C_6H_3O]_3}$, 113034-82-5; $\mathrm{Ce[N(SiMe_3)_2]_3}$, 41836-21-9; (THF)Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-83-6; ($\mathrm{Ph_2CO}$)Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-84-7; ($\mathrm{Et_3PO}$)Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-85-8; (n-$\mathrm{BuNH_2}$)Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-86-9; ($\mathrm{Et_2NH}$)Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-87-0; (MeCN)Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-88-1; (n-$\mathrm{BuNH_2)_2}$Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-89-2; $\mathrm{(MeCN)_2}$Ce[2,6-t-$\mathrm{Bu_2C_6H_3O]_3}$, 113034-90-5.

Supplementary Material Available: Atomic coordinates (Tables S1 and S6), bond lengths (Tables S2 and S7), bond angles (Tables S3 and S8), anisotropic thermal parameters (Tables S4 and S9), and H atom coordinates (Tables S5 and S10) for **1a** and **2** and a table of ^{1}H NMR data for **1** and **2** (13 pages); tables of observed and calculated structure

---

(10) Crystal data for $\mathrm{C_{52}H_{81}N_2O_3Ce}$: monoclinic, $P2_1$, $a = 11.507$ (3) Å, $b = 18.865$ (6) Å, $c = 12.381$ (4) Å, $\beta = 103.34$ (3)°, $V = 2615$ (1) Å^3, $Z = 2$, D(calcd) = 1.171 g cm^{-3}, μ(Mo Kα) = 9.1 cm^{-1}, $T = 295$ K. With a capillary-mounted yellow crystal (0.31 × 0.35 × 0.38 mm), 3730 data were collected (maximum $2\theta = 48°$) and 3200 independent, observed ($3\sigma F_o$) reflections were used to solve (heavy atom) and refine the structure. Only the noncentrosymmetric space group $P2_1$ was compatible with the structure, which cannot accommodate mirror-plane symmetry. At convergence (all non-hydrogen atoms anisotropic, all hydrogen atoms idealized such that $d_{\mathrm{C-H}} = 0.960$ Å and $U_{\mathrm{H}} = 1.2U$ for attached carbon) $R(F) = 4.39\%$, $R(wF) = 5.66\%$, GOF = 1.30, $\Delta/\sigma = 0.06$, $\Delta(\rho) = 0.46$ e Å^{-3}, and $N_o/N_v = 6.6$. Refinement of a multiplicative factor for $\Delta f''$ determined the correctness of the enantiomorph reported. Software was as in ref 6.

(11) Alfred P. Sloan Research Fellow, 1984–1988.

factors for **1a** and **2** (51 pages). Ordering information is given on any current masthead page.

Chandlee Laboratory
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Hilmar A. Stecher
Ayusman Sen*[11]

Department of Chemistry
University of Delaware
Newark, Delaware 19716

Arnold L. Rheingold*

Received October 7, 1987

Occurrence of a Chemically Reactive Intermediate Formed via a Doublet-State Pathway in the Photoaquation of the *cis*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) Ion

Sir:

The photosubstitutional mechanisms of octahedral chromium(III) complex ions containing ammonia and saturated organic amine ligands continue to elicit considerable debate on several key issues: the relative chemical importance of the lowest electronically excited states (spin-forbidden doublet and spin-allowed quartet states), the role of thermally activated back intersystem crossing (bisc) from the lowest doublet to a low-lying quartet state(s), and recently the suggested involvement of chemically reactive intermediates.[1-6] The results reported herein on the photoaquation of *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$, where cyclam is the macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane, now provide direct evidence for the occurrence of a chemically reactive intermediate. Because this system represents one of the few examples where prompt chemical reaction is not observed following laser excitation of the ligand field quartet bands, its photobehavior affords a propitious opportunity to address more directly the aforementioned issues.

An earlier study of *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ has reported on its synthesis, its phosphorescence emission centered around 680 nm in aqueous solutions, and the chemical quantum yield of 0.2 (steady-state photolysis, 365 nm) for photoaquation (eq 1).[7] In acidic media, protonation of free ammonia is very rapid and will lead to a change in conductivity.[8] In the present study, ac and dc conductivity techniques with microsecond and submicrosecond time resolutions, respectively, have been used to follow such changes and to correlate them with emission from the doublet state.[9] To generate this state, the first and second quartet absorption bands were irradiated by using laser lines at 530 and 347 nm, respectively, under the following conditions: deaerated solutions of 0.6–3.0 mM complex; pH 2.65–5.4; 22–27 °C.

$$cis\text{-}[Cr(cyclam)(NH_3)_2]^{3+} + H_2O \xrightarrow{h\nu} cis\text{-}[Cr(cyclam)(H_2O)(NH_3)]^{3+} + NH_3 \quad (1)$$

$$NH_3 + H^+ \rightarrow NH_4^+ \quad (2)$$

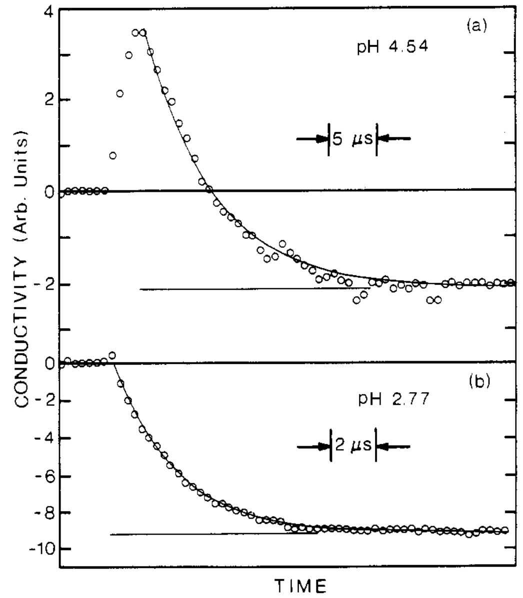

Figure 1. Conductivity changes occurring on irradiation of deaerated solutions of 2.0 mM *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ for 347-nm excitation: (a) pH 4.54; (b) pH 2.77. Solid curves represent first-order kinetic fits.

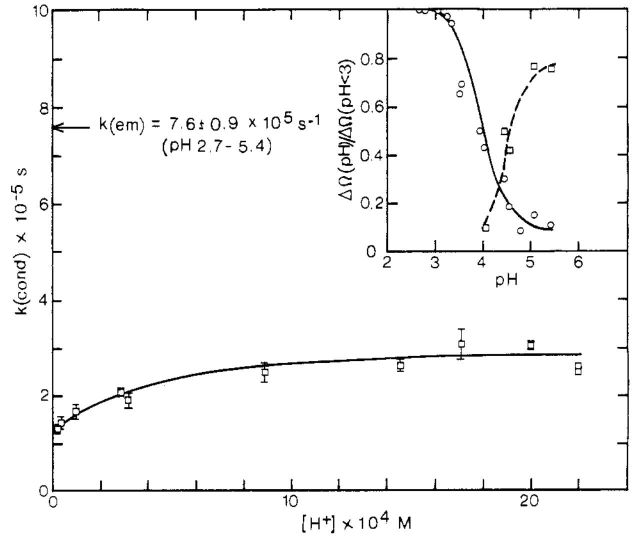

Figure 2. Plot of the observed first-order rate constant for the long-term decrease in conductivity versus the concentration of proton. The insert shows the fractional changes in conductivity relative to the net decrease in conductivity for pHs <3 ($\Delta\Omega$(pH <3)) versus solution pH: (○) $\Delta\Omega$(pH) represents the long-term net decrease in conductivity; (□) $\Delta\Omega$(pH) represents the maximum net initial increase in conductivity.

For these conditions, the emission lifetime remains constant at 1.3 ± 0.2 μs whereas the nature of the conductivity changes depends upon the pH as exemplified in Figure 1. Between pH 4.0 and 5.4 (and concomitant with the decay of emission), a net increase in conductivity occurs relative to that of the unirradiated solution. Its subsequent decay gives rise to an overall net decrease in conductivity. At pHs below 4, only this latter change is observed (Figure 1b), and in general, no further alteration occurs over our longest period of observation (1 s).

The development of this net decrease in conductivity obeys a first-order rate law over the entire range of pHs used, but as shown in Figure 2, the value of the rate constant initially increases with increasing acid concentration until a plateau region is reached at pH ≃3; this position also corresponds to the maximum extent of the decrease in the conductivity level. The plot of the fractional change in conductivity versus pH (insert of Figure 2; open circles) indicates that the final product exhibits an acid–base process with a pK_a of 4.0. This value is typical of those found for a water

---

(1) Endicott, J. F.; Ramasami, T.; Tamilarasan, R.; Lessard, R. B.; Ryu, C. K. *Coord. Chem. Rev.* **1987**, *77*, 1-87.
(2) Endicott, J. F.; Lessard, R. B.; Lei, Y.; Ryu, C. K.; Tsamilarasan, R. *ACS Symp. Ser.* **1986**, *No. 307*, 85-103.
(3) Hollebone, B. R.; Langford, C. H.; Serpone, N. *Coord. Chem. Rev.* **1981**, *39*, 181-224.
(4) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301-393.
(5) Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225-263.
(6) Vanquickenborne, L. G.; Ceulemans, A. *Coord. Chem. Rev.* **1983**, *48*, 157-202.
(7) Kane-Maguire, N. A. P.; Wallace, K. C.; Miller, D. B. *Inorg. Chem.* **1985**, *24*, 597-605.
(8) Eigen, M. *Angew. Chem.* **1963**, *75*, 489-588.
(9) Waltz, W. L.; Lilie, J.; Lee, S. H. *Inorg. Chem.* **1984**, *23*, 1768-1775.