Table V. ^1H NMR Data for $PcM(tBuNC)_2$ (M = Fe, Ru, Os)[a]

	Pc		
M	H^1	H^2	CH_3
Fe[29]	9.31	7.96	−0.51
Ru[29]	9.25	7.94	−0.49
Os	9.11	7.87	−0.44

[a] Shifts are given in δ (ppm) vs $CHCl_3$. Data for free tBuNC: CH_3, 1.44 ppm (1:1:1).[34]

Table VI. ^{13}C NMR (100.6 MHz) Data for the C Atoms of the Axially Coordinated tBuNC in $PcM(tBuNC)_2$ (M = Fe, Ru, Os)[a]

M	C≡N	$C(CH_3)_3$	CH_3
Fe[29]	143.0	55.0	28.7
Ru[29]	133.9	54.5	28.7
Os	116.8	54.5	28.8

[a] Shifts are given in δ (ppm) vs $CDCl_3$. Data for free tBuNC (ppm):[35] C≡N (153.2), $C(CH_3)_3$ (54.1), CH_3 (30.2).

washing the mixture with methanol at the end of the reaction. Both pyrazine and *tert*-butyl isocyanide do not react with crude $PcOsL_x$; i.e., they are not able to substitute the coordinated impurity in $PcOsL_x$.

As observed for the pyridine complexes, infrared spectra of $PcOs(dmso)_2$·dmso, $PcOs(pyz)_2$, and $PcOs(tBuNC)_2$ are almost indistinguishable from those of their corresponding ruthenium compounds.[16,20,21,29] The infrared spectrum of $PcOs(pyz)_2$ shows an intense band at 1578 cm^{-1}, which is assigned to the centrosymmetric vibrational mode of the axially coordinated pyrazine ligand.

Depending on the corresponding σ-donor and π-acceptor contribution, coordination to an isocyanide can either raise or lower the value of the NC frequency.[31-33] When isocyanides are coordinated to divalent metals, as is the case for most metal phthalocyanines, generally the σ-donor contribution dominates. The NC valence frequency is then shifted to higher wavenumbers. With increasing π-donor ability of the metal, however, this shift decreases. The pronounced π-back-bonding ability of the osmium ion even lowers the NC valence frequency compared to that of the free isocyanide (Table IV).

The electronic influence of the central metal ion on the macrocycle can also be seen in the UV–vis spectra. When $PcOs(dmso)_2$·dmso, $PcOs(pyz)_2$, and $PcOs(tBuNC)_2$ are compared with the corresponding ruthenium compounds, the Q band and the Soret band are found shifted to shorter wavelengths.[16,20,29]

The ^1H NMR spectrum of $PcOs(dmso)_2$·dmso confirms the stoichiometry of the compound. $PcOs(pyz)_2$ is also sufficiently soluble in $CDCl_3$ to allow the measurement of a ^1H NMR spectrum (Table II). The singlet of the free pyrazine (8.57 ppm) is split into an AA′XX′ pattern (H^a, 2.99 ppm; H^b, 6.46 ppm) by coordination to the (phthalocyaninato)osmium system. $PcOs(pyz)_2$ is thermally more stable than the corresponding ruthenium compound. The separation of the axial ligand in $PcOs(pyz)_2$ starts at about 260 °C with an endothermic maximum at 310 °C. Tables V and VI show some ^1H and ^{13}C NMR data of $PcM(tBuNC)_2$ for M = Fe, Ru, and Os.

Experimental Section

(Phthalocyaninato)osmium(II) (PcOs). A mixture of $OsCl_3$ (1 g, 3.4 mmol), *o*-cyanobenzamide (15 g, 0.1 mol), and naphthalene (10 g, 78 mmol) was heated under nitrogen at 290 °C for 1 h and then allowed to cool. The melt was crushed with a pestle and a mortar, washed with ethanol, and extracted with glacial acetic acid for 3–4 days. The residue was dried in vacuo at 120 °C and chromatographed on an aluminum oxide column (neutral, I) by eluting with $CHCl_3$: yield 400 mg of crude $PcOsL_x$; purple powder; analytically impure.

The product was heated slowly to 400 °C under an inert-gas stream (2 K/min), and this temperature was maintained for 1 h: yield 270 mg (11%); blue-black powder; pure PcOs. Anal. Calcd for $C_{32}H_{16}N_8Os$ (M_r = 702.7): C, 54.69; H, 2.29; N, 15.95. Found: C, 54.35; H, 2.49; N, 15.65.

Acknowledgment. We thank H. Schultz for her help with the manuscript. P.V. thanks the Evangelischen Studienwerk Villigst for a grant.

Registry No. $PcOs^{II}$, 47823-18-7; $PcOs(py)_2$, 123775-08-6; $PcOs(dmso)_2$, 123775-09-7; $PcOs(pyz)_2$, 123775-10-0; $PcOs(t\text{-}BuNC)_2$, 123775-11-1; *o*-cyanobenzamide, 17174-98-0.

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Mixed-Ligand Complexes of Tetravalent Metal Ions with Amine-*N*-polycarboxylates and Fluoride

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Received June 7, 1989

Formation of the mixed-ligand complexes of metal ions with amine-*N*-polycarboxylates and fluoride has recently been studied to examine the affinities of highly hydrolizable metal ions to fluoride and to estimate the solution structures of the parent and the mixed-ligand complexes.[1,2] Such equilibrium data are also of analytical importance, since the extent of formation of the mixed-ligand complexes defines the efficiency of masking reagents for metal ions in the determination of fluoride with ion-selective electrodes.[3] In this paper, we have made a systematic study on the formation of the mixed-ligand complexes of tetravalent metal ions (M = Ge, Sn, Ti, Zr, Hf, Th) with amine-*N*-polycarboxylates (L)[4] and fluoride and have found in the Th–EGTA–F^- system an exceptionally large stability constant, which is ascribed to a mode of formation of mixed-ligand complexes different from that of the others.

The tetravalent metal complexes with EDTA were isolated as described in literature.[5] Thorium complexes with other ligands were prepared in solution without isolation. All these complexes hydrolyze even in an acidic medium, and the resultant mixed-ligand complexes with a hydroxo or oxo group generally have much lower affinities to fluoride.[2] The $-\log [H^+]$ ranges for existence of ML were estimated as shown in Table I from the equilibrium data in literature.[6-9] Several solutions containing a metal complex

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Table I. Stability Constants for the Mixed-Ligand Complexes of M(IV) with Amine-*N*-polycarboxylates and Fluoride at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

parent complex	$-\log[H^+]$[a]	log const[b,c]	
		$K_{MLF}{}^{F}$	$K_{MLF_2}{}^{F}$
Ge-EDTA	<1		
Sn-EDTA	<1.5		
Ti-EDTA	<1.3		
Zr-EDTA	0-4	4.53 (-)	
Hf-EDTA	0-3	4.41 (-)	
Th-TTHA	1<		
Th-DTPA	1-7	3.52 (2-)	
Th-CDTA	2-5.5	4.18 (-)	3.47 (2-)
Th-EDTA	1-5	4.72 (-)	3.82 (2-)
Th-EGTA	<5	5.36 (-)	3.45 (2-)
Th-HEDTA	3	5.74 (0)	4.29 (-)

[a] $-\log[H^+]$ range for existence as ML. [b] Electric charge on the resultant mixed-ligand complex in parentheses. [c] Missing table entries represent negligibly small values.

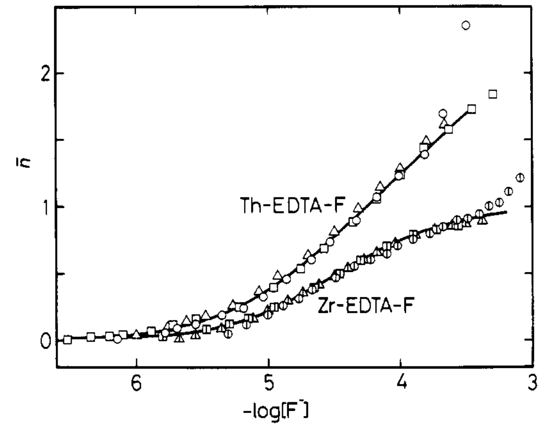

Figure 1. Plot of $\bar{n}$ vs $-\log[F^-]$ for Th-EDTA-F^- and Zr-EDTA-F^- systems (25 °C, 0.1 mol dm^{-3} KNO_3). $-\log[H^+]$: circle, 2.3; box 3.1; triangle, 5.0; circle with bar, 2.8; box with bar, 3.4; triangle with bar, 4.2. The solid curves were calculated with the constants in Table I.

at such $-\log[H^+]$ were potentiometrically titrated with a potassium fluoride solution. The average number of fluorides bound to the metal ion, $\bar{n}$, was calculated with $-\log[H^+]$ and $-\log[F^-]$, as described previously.[2]

Figure 1 shows $\bar{n}$ vs $-\log[F^-]$ diagrams for the Th- and Zr-EDTA-F^- systems. The change in $-\log[H^+]$ does not displace the formation curves, which have a limiting $\bar{n}$ value of 2 for Th and of 1 for Zr. Abrupt increase in $\bar{n}$ at lower $-\log[H^+]$ and $-\log[F^-]$ is due to formation of simple fluoro complexes MF_m accompanied by dissociation of EDTA from the parent complexes. The stability constants of the mixed-ligand complexes, $K_{MLF}{}^{F} = [MLF]/[ML][F^-]$ and $K_{MLF_2}{}^{F} = [MLF_2]/[MLF][F^-]$, were calculated by the conventional method (Table I).

The stability constants of the mixed-ligand complexes are much smaller than those of the corresponding tetravalent metal fluoro complexes.[10] The constants except for $K_{MLF}{}^{F}$ of Th-EGTA are classified into three groups depending only on the charge of the mixed-ligand complexes: $10^{3.5\pm0.3}$ for dianionic, $10^{4.4\pm0.3}$ for monoanionic, and $10^{5.7}$ for neutral complexes. The difference between $K_{MLF}{}^{F}$ and $K_{MLF_2}{}^{F}$ is $10^{1.4}$ for Th-HEDTA and $10^{0.7-0.9}$ for Th-EDTA and Th-CDTA. The latter value is similar to that ($10^{1.0}$) for Fe-NTA, showing the same change in the electric charge on the formation of the mixed-ligand complexes.[2]

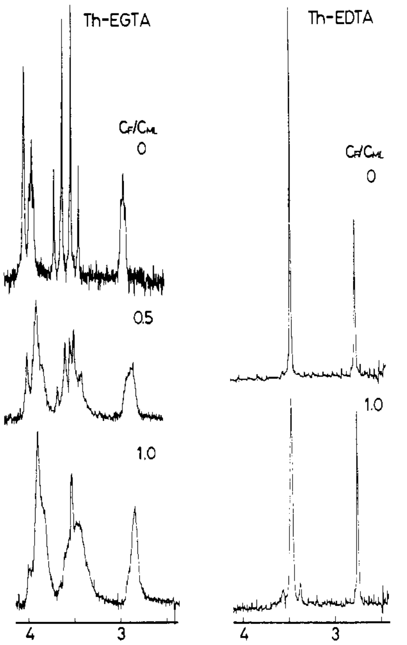

Figure 2. ^1H NMR spectra (200 MHz) of Th-EDTA and Th-EGTA in the absence and presence of fluoride at various molar ratios.

In the solid state, Ti-EDTA and Sn-EDTA have a coordinated water together with EDTA of hexadentate chelation and exhibit seven-coordination.[11,12] For these smaller metal ions including Ge, however, no mixed-ligand complexes with fluoride were found down to the $-\log[F^-]$ region where fluoride replaces EDTA. Eight-coordination having two coordinated water molecules is likewise established for Zr-EDTA in solid.[13] In solution, the same structure is proposed from the strong tendency to form mixed-ligand complexes with bidentate ligands.[7b] With fluoride, on the other hand, only MLF was identified for metal ions of moderate size, Zr and Hf. The EDTA complex of thorium, which has the largest ionic radius among the metal ions examined, is expected to have two or three water molecules, as those of rare-earth metals,[14] and forms a series of stable mixed-ligand complexes with bidentate ligands.[9b] With fluoride, both MLF and MLF_2 are found for the EDTA complex as well as Th-CDTA and Th-HEDTA. In the cases of hexadentate ligands, each ligand keeps its full ability of denticity, and coordinated water molecules are displaced with fluoride ions to such an extent that the electrostatic repulsion between fluoride and carboxylate oxygen or repulsion between fluoride ions does not preclude the incorporation of fluoride. Whether these mixed-ligand complexes still bear coordinated water molecules or not is uncertain.

The thorium complex with potentially octadentate DTPA forms a mixed-ligand complex with fluoride having appreciable stability, whereas the complex with potentially decadentate TTHA does not. Similarly, Th-DTPA forms a mixed-ligand complex with hydroxide of stability comparable to those of Th-CDTA and Th-EDTA ($K_{ML(OH)}{}^{OH} = 10^5$ for L = DTPA, 10^6 for CDTA, and 10^7 for EDTA),[9a] whereas no such species are found for Th-TTHA.[9d] Since Th-DTPA is expected to have a single coordinated water molecular together with DTPA of octadentate chelation, as those of rare-earth metals,[15,16] the reaction with fluoride

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or hydroxide is also ascribed to replacement of a coordinated water molecule.

In contrast to the above stabilities, K_{MLF}^{F} of Th-EGTA-F^- is exceptionally large. Recent X-ray crystal structural studies have shown that Ca-EGTA, Cd-EGTA, and Mn-EGTA have a distorted dodecahedral coordination sphere utilizing the ligand's octadentate chelating ability.[17] The bond distances of M-O(ether) are shorter than those of M-N for calcium, whereas for transition-metal ions the reverse trend is found. Since thorium has an ionic radius (Å) between those of the other metal ions (Th, 1.08; Ca, 1.12; Cd, 1.10; Mn, 0.96), Th-EGTA is expected to have a quite similar structure. Two weak Th-O(ether) bonds in the parent complex are easily broken by coordination of the first fluoride, and the resultant mixed-ligand complex has EGTA of hexadentate chelation together with fluoride and water molecules. The second stability constant ($10^{3.45}$) is comparable to that of Th-EDTA or -CDTA, and the reaction is assigned as the usual displacement of a water molecule with fluoride. In Th-EGTA, the ligand can coat the thorium ion to disturb the coordination of water molecules to the metal center, and this is the reason for the exceptionally high affinity of this complex to the first fluoride.

Formation of the mixed-ligand complexes was monitored also by ^{1}H NMR spectroscopy at 200 MHz (Figure 2). The parent Th-EDTA complex has a singlet pattern for both acetate and ethylene protons with reasonable chemical shifts compared to those of other EDTA complexes.[18] The reaction with fluoride does not cause change in the chemical shift, although slight splitting into an A-B quartet is observed for acetate protons. In contrast, the parent Th-EGTA has an A-B quartet for acetate protons, two triplets for ethylene protons between ether and amino groups, and a singlet for ethylene protons between ether groups. Increase in the chemical shift for the ethylene protons between ether groups (4.0 ppm) compared to that of the free ligand (3.7-3.8 ppm)[19] indicates the coordination of ether groups. The reaction with fluoride decreases the chemical shift ($\sim$3.9 ppm), although the spectrum is broadened and complicated. This change supports the uncoordination of ether oxygen atoms in the mixed-ligand complex as proposed above.

Acknowledgment. We wish to thank Miho Harada for her help in the potentiometric measurements. This investigation was supported by a Grant-in-Aid for Scientific Research (No. 61127007) from the Ministry of Education, Science and Culture (Japan).

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Pressure and Temperature Effects on the Coordination Equilibrium of a Cobalt(III) $[Co(N)_4Cl]$ System

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Received February 28, 1989

Paramagnetic cobalt(III) complexes are relatively rare. Complexes having a spin-triplet ground or close-lying excited state have been characterized, including square-planar,[1] five-coordinate trigonal-bipyramidal,[2] and five-coordinate square-pyramidal[3] complexes.

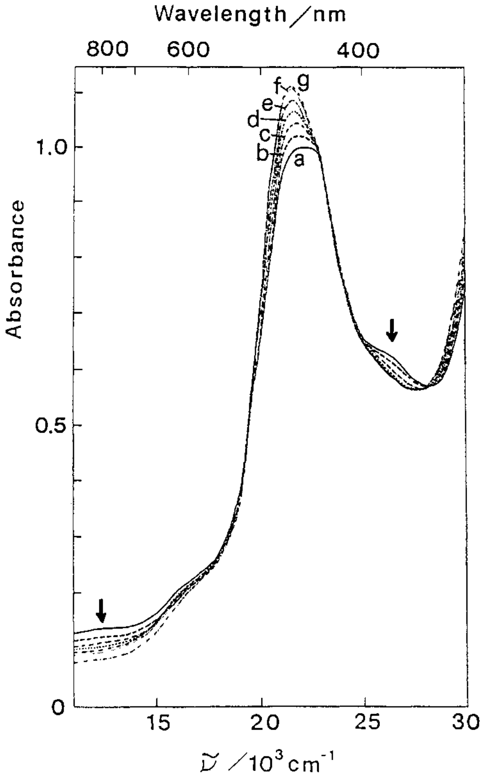
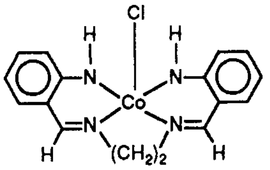


Figure 1. High-pressure spectra of 9.5×10^{-5} M [Co(aben)Cl] in pyridine at 19.3 °C (optical path length 16 mm): (a) 0.001 kbar; (b) 0.5 kbar; (c) 1.0 kbar; (d) 1.5 kbar; (e) 2.0 kbar; (f) 2.5 kbar; (g) 3.0 kbar.

The paramagnetic ($S = 1$) five-coordinate cobalt(III) compound [Co(aben)Cl] (I; aben = 1,2-bis(*o*-iminobenzylideneamino)ethane)



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has been reported[3b,c] to be in equilibrium with the diamagnetic ($S = 0$) six-coordinate complex in pyridine solution (eq 1). The

$$[Co(N)_4Cl] + py \rightleftharpoons [Co(N)_4Cl(py)] \qquad (1)$$

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