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Structural (EXAFS) and Solution Equilibrium Studies on the Oxotechnetium(V) Complexes $TcOX_4^-$ and $TcOX_5^{2-}$ (X = Cl, Br)

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The equilibrium between the technetium(V) complexes $TcOCl_4^-$ and $TcOCl_5^{2-}$ has been investigated in 12 M HCl and in CH_2Cl_2 solutions by Raman spectroscopy. In both media the five-coordinate complex is the predominant species, but in the aqueous medium water competes for the sixth coordination site and causes formation of the six-coordinate $TcOCl_5^{2-}$ anion to be even less favorable ($K_{eq} = 0.6 \pm 0.3\ M^{-1}$ in CH_2Cl_2; $K_{eq} = 0.0015 \pm 0.0010\ M^{-1}$ in 12 M HCl). Procedures are described for generating good yields of either $TcOX_4^-$ or $TcOX_5^{2-}$ (X = Cl, Br) salts from the same reaction mixture. The complexes $TcOCl_4^-$, $TcOCl_5^{2-}$, $TcOBr_4^-$, $TcOBr_5^{2-}$, and TcI_6^{2-} have been structurally characterized by EXAFS techniques. Observed Tc═O and Tc—X bond lengths are consistent with the known dependence of bond length on coordination number, the established structural trans effect induced by the Tc═O linkage, and existing crystallographic data on $TcOCl_4^-$ and related molybdenum(V) complexes.

Introduction

A large number of recent reports on the coordination chemistry of technetium have focused on complexes containing oxotechnetium(V) cores.[3-6] This situation stems largely from the advent of a convenient synthesis of both $TcOCl_4^-$[7] and $TcOBr_4^-$.[8] These anions have proven to be especially effective starting materials for the preparation of a variety of oxotechnetium(V) complexes via simple ligand-substitution reactions.[3-6]

The $TcOX_4^-$ anions (X = Cl, Br) are readily prepared by reduction of pertechnetate ($Tc^{VII}O_4^-$) with concentrated HX in aqueous media.[7,8] However, in these media, as well as in other media used for ligand-substitution reactions, the chemistry of the oxotechnetium(V) core is complicated by the equilibrium

$$TcOX_4^- + X^- = TcOX_5^{2-} \qquad (1)$$

A lack of appreciation of the importance of this equilibrium has led to confusing and contradictory reports in some of the older literature dealing with the chemistry of technetium.[3,9,10] Especially relevant in this context are observations that $TcOX_5^{2-}$ species are important intermediates in the reduction of Tc(V) to Tc(IV); anation of the initial $Tc(OH_2)X_5^-$ products yields the classic Tc(IV) complexes TcX_6^{2-}.[11,12] Reduction of the $TcOX_4^-/TcOX_5^{2-}$ complexes to the Tc(IV) oxidation state is thermodynamically favored in HX media and thus constitutes a serious barrier to investigation of the chemistry of these Tc(V) systems. For instance, while it is possible to obtain single crystals of salts of $TcOCl_4^-$,[13] we have not been able to grow crystals of $TcOBr_4^-$ presumably due to the greater reducing power of bromide. Likewise, in our hands all attempts to grown single crystals of $TcOX_5^{2-}$ have led to TcX_6^{2-}, presumably because of the relative ease of reduction of the $TcOX_5^{2-}$ anions and the high concentration of X^- necessary to maintain the oxotechnetium(V) core in this six-coordinate form.

In this paper we report on the structural chemistry of the $TcOX_4^-$ and $TcOX_5^{2-}$ (X = Cl, Br) complexes, assessed by using EXAFS techniques that do not require single crystals.[14] Observations on the $TcOX_4^-/TcOX_5^{2-}$ equilibria, estimates of the equilibrium quotient when X = Cl, and convenient procedures for selectively isolating salts of $TcOX_4^-$ and $TcOX_5^{2-}$ from equilibrium mixtures are also reported.

Experimental Section

General Data. All common laboratory chemicals were of reagent grade. The $NH_4{}^{99}TcO_4$ was of >99% radiochemical purity and was obtained from Oak Ridge National Laboratories, Oak Ridge, TN. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Micro. Anal. Co., Tucson, AZ. UV-visible spectra were recorded on a Cary 210 spectrophotometer in dimethyl sulfoxide. IR spectra were recorded on a Perkin-Elmer 599 in Nujol mulls with CsI plates. The Raman spectra were recorded on a SPEX Ramalog Raman spectrophotometer. Excitation at 514.5 nm was accomplished by a Coherent Innova 90 argon ion laser. The solid-state spectra of pure solids were measured in sealed glass capillary tubes. The solution spectra were measured in cylindrical 1.0-cm quartz cells.

Syntheses. The tetrabutylammonium and potassium hexahalotechnate(IV) complexes were prepared from the ammonium salts[15] by simple metathesis. Tetrabutylammonium oxotetrachlorotechnetate(V), $(n\text{-}Bu_4N)[TcOCl_4]$, and tetrabutylammonium oxotetrabromotechnetate(V), $(n\text{-}Bu_4N)[TcOBr_4]$, were synthesized as previously described.[7,8] The dicesium oxopentahalotechnate salts, $Cs_2[TcOX_5]$ (X = Cl, Br), were generated by methods similar to those previously reported.[12,16] Specific synthetic procedures used in this work are reported below.

Dicesium Oxopentachlorotechnetate(V), $Cs_2[TcOCl_5]$. To 40.2 mg of NH_4TcO_4 in a 10-mL beaker was added 4 mL of concentrated HCl (12 M) at ambient temperature. The resulting solution was stirred for 10 min, and then the magnetic stir bar was removed and rinsed with 0.5 mL of 12 M HCl. The reaction solution was cooled to 0 °C in an ice bath, and then 0.075 mL of 1.67 M CsCl in water was added to yield a light olive green precipitate. The product was removed by filtration, washed with two 5-mL aliquots of absolute ethanol, and dried for 4 h at 25 °C (ca. 0.1 torr); yield 0.116 g (95%). Anal. Calcd for $Cs_2[TcOCl_5]$: Cs, 47.64; Cl, 31.77. Found: Cs, 50.74; Cl, 32.81.

Bis(tetraethylammonium) Oxopentachlorotechnetate(V), $[(CH_3CH_2)_4N]_2[TcOCl_5]$. Initially 81.8 mg of $(n\text{-}Bu_4N)[TcOCl_4]$ was dissolved in 3 mL of CH_2Cl_2 at ambient temperature. Then, 3 mL of 0.40 M $(CH_3CH_2)_4NCl$ in CH_2Cl_2 was slowly added to this solution with stirring to yield a light yellow-tan precipitate. The reaction mixture was stirred for an additional 20 min; the solid product was removed by filtration, washed with three 5-mL aliquots of CH_2Cl_2 followed by three 10-mL aliquots of anhydrous diethyl ether, and dried for 2 h at 25 °C (ca. 0.1 torr); yield 0.066 g (78%). Anal. Calcd for $[(CH_3CH_2)_4N]_2TcOCl_5$: C, 34.79; H, 7.30; N, 5.07; Cl, 32.09. Found: C, 34.60; H, 7.00; N, 4.99; Cl, 32.30.

Dicesium Oxopentabromotechnetate(V), $Cs_2[TcOBr_5]$. Initially 48.0 mg of NH_4TcO_4 in a 10-mL beaker was cooled to −8 °C in a NaCl ice bath. Then, 4 mL of 48% HBr (at −8 °C) was added to the solid NH_4TcO with stirring. After 10 min of stirring 0.75 mL of 2.05 M CsBr

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Table I. IR and Raman Spectroscopic Data for $TcOX_4^-$ and $TcOX_5^{2-}$ (X = Cl, Br), plus $MoOCl_4^-$ and $MoOCl_5^-$, Complexes

complex	IR ν, cm^{-1}	IR intens	Raman ν, cm^{-1}	Raman intens	assignt
$(n\text{-}Bu_4N)[TcOCl_4]$,[a] solid	1020	vs	1027	vs	Tc=O str
	375	vs	358	vs	Tc–Cl str
trans-$[TcOCl_4(OH)]^-$ in H_2O			1011	vs	Tc=O str
$TcOCl_4^-$ in CH_2Cl_2			1026	vs	Tc=O str
$(n\text{-}Bu_4N)[TcOBr_4]$,[a] solid	1011	vs	1015	m[b]	Tc=O str
	306	vs		[b]	Tc–Br str
$Cs_2[TcOCl_5]$, solid	954	vs[c]	955	vs	Tc=O str
	330	vs[c]	323	vs	Tc–Cl str
$TcOCl_5^{2-}$ in H_2O			965	vs	Tc=O str
$TcOCl_5^{2-}$ in CH_2Cl_2			958	vs	Tc=O str
$Cs_2[TcOBr_5]$, solid	952	vs	950	vs	Tc=O str
	248	m-s[d]	245	w	Tc–Br str
$(Ph_4As)[MoOCl_4]$,[e] solid	1015				Mo=O str
$Cs_2[MoOCl_5]$,[f] solid	950	vs			Mo=O str
	324	s			Mo–Cl str

[a] Data from ref 8. [b] Spectrum degraded by thermal decomposition of sample. [c] Data from this work and ref 24. [d] Intensity assignment uncertain since this absorption is near the lower limit of the IR spectrometer. [e] Reference 25. [f] Brown, D. *J. Chem. Soc.* 1964, 4944.

(at −8 °C) was slowly added to the reaction mixture to yield an orange-red precipitate. After 10 min the precipitate was removed by filtration, washed with two 3-mL aliquots of 48% HBr (at −8 °C) followed by seven 3-mL aliquots of absolute ethanol, and dried for 8 h at 25 °C (ca. 0.1 torr); yield 0.125 g (60%). Anal. Calcd for $Cs_2[TcOBr_5]$: Cs, 34.07; Br, 51.21. Found: Cs, 36.91; Br, 53.99.

General Synthesis of $TcOX_4^-$ and $TcOX_5^{2-}$ (X = Cl, Br) from the Same Reaction Mixture. The $TcOCl_4^-/TcOCl_5^{2-}$ solution was generated by the method of Davison.[7] To one aliquot of this solution was added a 75% w/w solution of tetrabutylammonium chloride in water to yield gray $(n\text{-}Bu_4N)[TcOCl_4]$ in 95% yield. To a second aliquot of the original reaction solution was added a 1.65 M solution of CsCl in water to yield olive green $Cs_2[TcOCl_5]$ in 91% yield. The bromo congeners were generated from a $TcOBr_4^-/TcOBr_5^{2-}$ solution prepared by the method of Thomas.[8] To one aliquot of this solution was added a 0.38 M solution of tetrabutylammonium bromide in water to yield light green $(n\text{-}Bu_4N)[TcOBr_4]$ in 68% yield. To a second aliquot was added a 2.06 M CsBr solution in water to yield orange-red $Cs_2[TcOBr_5]$ in 58% yield. The identities of all four products were confirmed by IR spectrophotometry (vide infra).

Equilibrium Measurements. Raman spectra of strong acid solutions containing equilibrium mixtures of $TcOCl_4^-$ and $TcOCl_5^{2-}$ were obtained with saturated solutions prepared by dissolving NH_4TcO_4 in concentrated HCl (12 M) until the formation of solid $(NH_4)_2[TcOCl_5]$ was first observed. The supernatant was then transferred to a 1-cm quartz cell, and spectra were recorded within 1 h to minimize the formation of any Tc(IV) species.[12,15] Solutions containing equilibrium mixtures of $TcOCl_4^-$ and $TcOCl_5^{2-}$ in CH_2Cl_2 were prepared with CH_2Cl_2 dried over $MgSO_4$, $(n\text{-}Bu_4N)[TcOCl_4]$ recrystallized from CH_2Cl_2/pentane, and $n\text{-}Bu_4NCl$. Ionic strength was maintained at 0.7 M with $n\text{-}Bu_4NPF_6$ that had been recrystallized three times and dried over P_2O_5 in vacuo. Spectra were again recorded within 1 h of solution preparation.

The relative concentrations of the $TcOCl_4^-$ and $TcOCl_5^{2-}$ anions were inferred from the relative areas of the appropriate Tc=O peaks in the Raman spectra of the equilibrium mixtures. Peak areas were measured by triangulation. Correction for the overlap of the $n\text{-}Bu_4NCl$ absorption at 1035 cm^{-1} with the Tc=O absorption at 1025 cm^{-1} was accomplished by using the ratio of areas of the $n\text{-}Bu_4NCl$ peaks at 1061 and 1035 cm^{-1} (independently determined on a 1.67 M solution of $n\text{-}Bu_4NCl$ in CH_2Cl_2). The relative scattering coefficients of $TcOCl_4^-$ and $TcOCl_5^{2-}$ were measured in the solid state on an equimolar mixture of $(n\text{-}Bu_4N)[TcOCl_4]$ and $[(CH_3CH_2)_4N]_4[TcOCl_5]$.

EXAFS Measurements. X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) with synchrotron radiation from the SPEAR ring. The monochromator (Si crystals cut to [2, 2, 0]) and transmission mode ionization chambers are available at the facility and have been previously described.[17] Transmission measurements were made by passing the monochromated radiation (slit size 1.0 mm) through the incident beam ionization chamber (to measure I_0) and then through the sample chamber filled with He gas and finally into a second ionization chamber (to measure the transmitted I). The transmission ionization chambers were filled with N_2 gas.

Fluorescence measurements were concurrently collected with a fluorescent ionization chamber detector (filled with Ar gas) purchased from F. Lytle (EXAFS Co., Seattle, WA).[18] Typically, 340 steps were recorded beyond the edge with a variable integration time of 1–8 s/step, the longer time being used for regions most removed from the edge. A usual range for data collection was 20.6–22.1 keV, which encompasses the K-absorption edge of Tc. EXAFS spectra were recorded at room temperature on finely ground solid samples diluted with dextrose or Li_2CO_3 to maintain the absorption, μt, less than 1.0 (t = 0.75 or 1.00 mm).

The extraction of EXAFS from the absorption or fluorescence spectrum followed the technique of Hodgson.[14,19] Programs used were local modifications of programs originated by Hodgson and co-workers.[20,21] The modifications include a new optimization program utilizing the theoretical amplitude and phase (TAP) functions of Teo and Lee.[22] Fourier filtering techniques were used for all the spectra with a square window function over the ranges indicated in Table II. A weighting factor of k^3 was used in all fits.

Results

The cesium salts of $TcOX_5^{2-}$ (X = Cl, Br) are insoluble in most organic solvents, are slightly soluble in aqueous solutions of their corresponding hydrohalic acids, and are fairly soluble in dimethyl sulfoxide. The tetraethylammonium salt of $TcOCl_5^{2-}$ is slightly soluble in CH_2Cl_2 and dissolves readily in methanol or absolute ethanol with decomposition to yield $[(CH_3CH_2)_4N][TcOCl_4]$ and $(CH_3CH_2)_4NCl$. All complexes are sensitive to the presence of water, which ultimately causes hydrolysis and disproportionation to $TcO_2{\cdot}xH_2O$ and TcO_4^-.

The visible–UV spectrum of $Cs_2[TcOBr_5]$ in dimethyl sulfoxide exhibits maxima at 520 (sh), 451, 393, and 333 nm (sh). IR and Raman spectral parameters for $TcOX_4^-$ and $TcOX_5^{2-}$ (X = Cl, Br) are summarized in Table I.

The equilibrium constant governing eq 1 in concentrated HCl is $(1.5 \pm 1.0) \times 10^{-3}$ M^{-1} at ambient temperature. The equilibrium constant for this reaction in CH_2Cl_2 is 0.6 ± 0.3 M^{-1} at μ = 0.7 M and ambient temperature. The relative Raman scattering coefficients of the Tc=O stretches for $[(CH_3CH_2)_4N]_2[TcOCl_5]/(n\text{-}Bu_4N)[TcOCl_4]$ is 2 in the solid state.

The structural parameters N (number of scatterers) and r (interatomic distance) are obtained by fitting observed data to the usual EXAFS equation

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} F_j(k)\, e^{-2\sigma_j^2 k^2} \sin\left(2kr_j + \phi_j(k)\right) \qquad (2)$$

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Table II. Results of EXAFS Analysis on TcX_6^{2-}, $TcOX_4^-$, and $TcOX_5^{2-}$ Complexes

Tc complex	retransform range, Å	fitting range, Å		EXAFS anal.[a,b]		crystallogr. anal.	
				r, Å	*N*	*r*, Å	*N*
$TcCl_6^{2-}$	1.36-2.30	4-14.5	TcCl[c]	2.37	6.1	2.35[d]	6
$TcBr_6^{2-}$	1.79-2.50	4-14.5	Tc-Br[c]	2.52	6.8	2.52[e]	6
TcI_6^{2-}	1.87-2.74	6-14.5	Tc-I[c]	2.72	6.0		
$TcOCl_4^-$	1.09-2.17	4-12	Tc-O	1.65	1.3	1.61[f]	1
			Tc-Cl	2.30	3.0	2.31	4
$TcOCl_5^{2-}$	1.09-2.24	4-12	Tc-O	1.65	1.2		
			$Tc-Cl_{cis}$[g]	2.36	3.6		
			$Tc-Cl_{trans}$[g]	2.50	0.8		
$TcOBr_4^-$	1.16-2.46	4-12	Tc-O	1.66	1.4		
			Tc-Br	2.48	5.4		
$TcOBr_5^{2-}$	1.16-2.46	4-12	Tc-O	1.66	1.0		
			$Tc-Br_{cis}$[g]	2.54	5.4		
			$Tc-Br_{trans}$[g]	2.74	1.6		

[a] EXAFS fits accomplished by k^3 weighting. Empirical methods were used unless otherwise noted. [b] Errors (estimated in this laboratory by comparing the EXAFS parameters with known crystallographic parameters for 29 Tc complexes) are for single-shell fits: 1 esd in *r* is 0.01 Å and the average percent discrepancy in N is 8%. For multishell fits these parameters are 0.022 Å and 31%. [c] TAP was used in these fits, which yielded the following refined values: for $TcCl_6^{2-}$, $\sigma = 0.05$ and $\Delta E_0 = -24.09$ eV; for $TcBr_6^{2-}$, $\sigma = 0.06$ and $\Delta E_0 = -22.90$ eV; for TcI_6^{2-}, $\sigma = 0.06$ and $\Delta E_0 = -39.58$ eV. [d] Elder, M.; Fergusson, J. E.; Gainsford, G. J.; Hickford, J. H.; Penfold, B. R. *J. Chem. Soc. A* 1967, 1423. [e] Elder, R. C.; Estes, G., unpublished data. [f] Reference 13. [g] EXAFS data do not allow an unambiguous assignment of cis and trans sites.

Table III. Equilibrium Data for the Reaction of $MOCl_4^-$ (M = Mo, Tc) with Cl^- in CH_2Cl_2

reaction A + B = C	μ, M	[B]:[A]	$[M_{tot}]$, M	$[C]:[A]_{obsd}$	K_{eq}, M^{-1}
$(n\text{-}Bu_4N)[TcOCl_4] + n\text{-}Bu_4NCl = (n\text{-}Bu_4N)[TcOCl_5]$	0.15	128	0.00118	0.08	0.53
	0.30	255	0.00118	0.20	0.67
	0.61	517	0.00118	0.38	0.62
	0.70[a]	128	0.00118	1.12	0.79
	0.70[a]	255	0.00118	0.20	0.66
	0.70[a]	517	0.00118	0.26	0.43
$[Ph_4As][MoOCl_4] + Ph_4AsCl = [Ph_4As]_2[MoOCl_5]$[b]	0.0090[c]	2.0	0.0030	0.07	12[c]
	0.0092[c]	5.0	0.00153	0.11	14[c]
	0.034[c]	15.0	0.00153	0.31	14[c]

[a] Ionic strength maintained by $n\text{-}Bu_4NPF_6$. [b] Data taken from ref 25. [c] Calculated from data in ref 25.

where the sum is over each scattering shell, k is the photoelectron wave vector, and σ is the Debye–Waller parameter. The amplitude and phase functions ($F(k)$ and $\phi(k)$, respectively) can be calculated by comparison to the spectra of known model complexes (empirical methods) or by reference to ab initio calculations[22] (theoretical amplitudes and phases). The parameter σ either can be treated as a variable (in conjunction with TAP's) or can be assumed to be that found for a model compound (empirical fitting procedure). TAP's were used in the analysis of the spectra of $TcCl_6^{2-}$, $TcBr_6^{2-}$, $TcBr_6^{2-}$, and TcI_6^{2-}. In these analyses four parameters were varied: N, r, σ, and E_0, the energy at which $k = 0$.

Because empirical methods are generally easier to apply in multishell complexes, empirically determined amplitudes and phases were used in the analyses of $TcOCl_4^-$, $TcOCl_5^{2-}$, $TcOBr_4^-$, and $TcOBr_5^{2-}$. The model spectra, which provided transferable amplitude and phase information for Tc═O, Tc—Cl, and Tc—Br scattering, were from $KTcO_4$, $(n\text{-}Bu_4N)_2[TcCl_6]$, and $(n\text{-}Bu_4N)_2[TcBr_6]$. In empirical analyses, two parameters per shell are varied in the fit, yielding values for N and r. Table II shows the results of EXAFS fits on halide and oxo halide complexes of technetium. For comparison, crystallographically determined bond lengths are noted where available. Figure 1 illustrates the agreement between the observed EXAFS data and the calculated fits summarized in Table II.

Discussion

When TcO_4^- is reduced by concentrated solutions of HX (X = Cl, Br), the resulting reaction solution can be made to yield salts of either $TcOX_4^-$ or $TcOX_5^{2-}$ by the judicious choice of counterion.[23] Addition of K^+, Cs^+, NH_4^+, or $N(CH_2CH_3)_4^+$ generates salts of $TcOX_5^{2-}$,[12,16,24] while addition of $(C_6H_5)_4As^+$ or $n\text{-}Bu_4N^+$ yields salts of $TcOX_4^-$.[7,8] This qualitative observation demonstrates that in concentrated HX solutions the two species $TcOX_4^-$ and $TcOX_5^{2-}$ are rapidly interconvertible and thus are presumably in equilibrium with each other via eq 1. Analysis of the Raman spectrum of a 12 M HCl solution containing a $TcOCl_4^-/TcOCl_5^{2-}$ equilibrium mixture (Figure 2) leads to an estimated equilibrium constant of $(1.5 \pm 1.0) \times 10^{-3}$ M^{-1}. Thus, it is apparent that in aqueous media $TcOCl_5^{2-}$ is not the favored species and even in 12 M HCl the $TcOCl_4^-$ anion is predominant by about a factor of 60. It should be noted here that although $TcOCl_4^-$ is known to be five-coordinate in the solid state,[13] in aqueous solution this species almost undoubtedly contains a loosely bonded water molecule trans to the Tc═O linkage; thus, eq 1 is better represented as

$$trans\text{-}TcO(OH_2)Cl_4^- + Cl^- = TcOCl_5^{2-} + H_2O \quad (3)$$

In aqueous media the equilibrium constant governing eq 3 is too small to permit quantitative investigation of the equilibrium by varying chloride ion concentration (even in 12 M HCl the amount of $TcOCl_5^{2-}$ formed is barely detectable by Raman spectroscopy—see Figure 2). However, in the noncoordinating solvent CH_2Cl_2, the equilibrium constant is sufficiently large ($K_{eq} = 0.6 \pm 0.3$ M^{-1}) to allow variation in the chloride concentration (Figure 3; Table III). Analysis of the resulting variations in $TcOCl_4^-$ and $TcOCl_5^{2-}$ concentrations shows that they are adequately described within eq 1, thus providing quantitative evidence for the existence of this equilibrium. The fact that the equilibrium constant in CH_2Cl_2 is ca. 400 times larger than that in aqueous media presumably results from the fact that in this noncoordinating solvent the coordination site trans to the Tc═O linkage in $TcOCl_4^-$ is vacant, and thus the actual equilibrium process is best expressed as

$$TcOCl_4^- + Cl^- = TcOCl_5^{2-} \quad (4)$$

rather than as eq 3. In aqueous media the incoming chloride ligand

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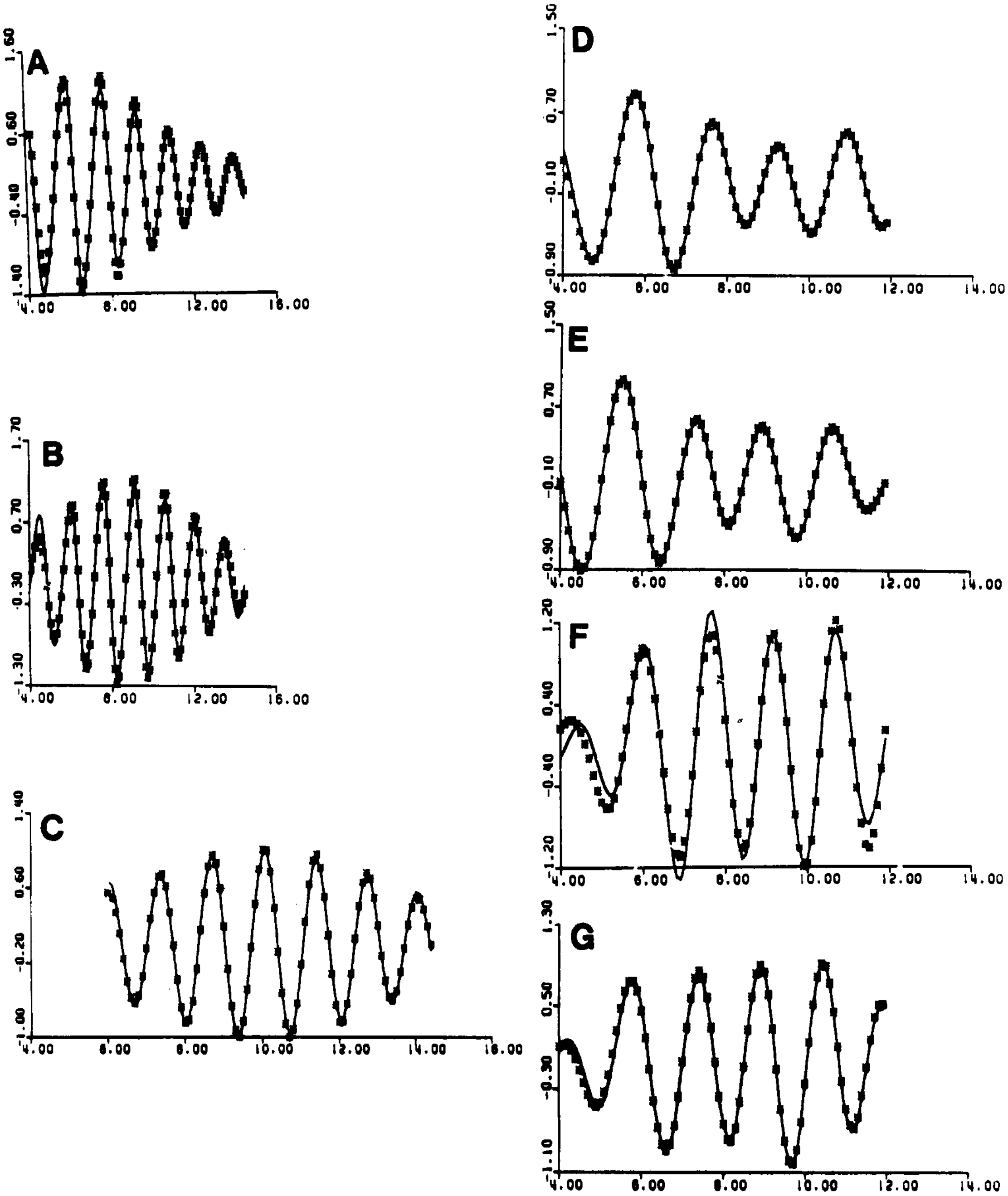

Figure 1. Plots of observed (points) and calculated (lines) Fourier-filtered EXAFS data over the indicated k range vs. $(\chi)(k)^2$ for halide complexes of technetium. A–C are for TcX_6^{2-}, X = Cl, Br, and I, respectively; note the progression of the envelope maximum to higher k with increasing atomic number of the back-scattering atom. D–G are for $TcOCl_4^-$, $TcOCl_5^{2-}$, $TcOBr_4^-$, and $TcOBr_5^{2-}$, respectively; note the beat patterns in the EXAFS due to dissimilar distances within the set of back-scattering atoms.

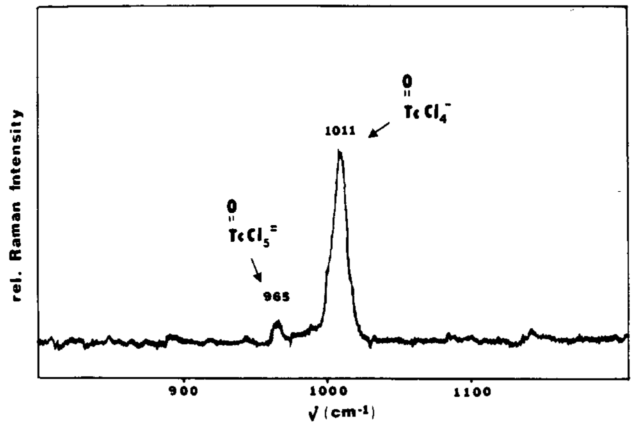

Figure 2. Raman spectrum of a $TcOCl_4^-/TcOCl_5^{2-}$ equilibrium mixture generated by the reduction of NH_4TcO_4 in 12 M HCl.

competes with H_2O for the sixth coordination site, whereas in CH_2Cl_2 the incoming chloride either directly occupies a vacant site or, at most, competes with a loosely bonded CH_2Cl_2 molecule.

Mabbs and co-workers[25] have studied the analogous equilibrium process for Mo(V) in CH_2Cl_2 media:

$$MoOCl_4^- + Cl^- = MoOCl_5^{2-} \qquad (5)$$

They find that K_{eq} for this process is 20 ± 8 M^{-1}, apparently larger than the 0.6 ± 0.3 M^{-1} found for the Tc(V) equilibrium (eq 4). Despite the fact that the large uncertainties associated with each determination cause the ratio of equilibrium constants to be indistinguishable from 1 ($K_{Mo}/K_{Tc} = 33 \pm 21$), examination of the detailed experimental data makes it clear that the constant measured by Mabbs and co-workers is indeed larger than the constant measured in this work. This may reflect a legitimate

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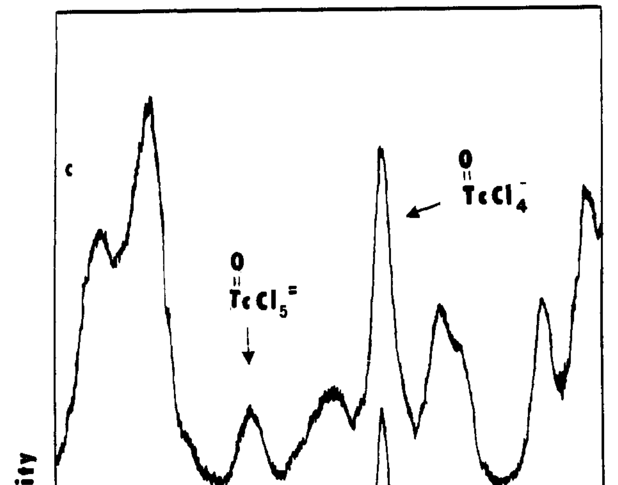

Figure 3. Raman spectra of a $TcOCl_4^-/TcOCl_5^{2-}$ equilibrium mixture in CH_2Cl_2 with n-Bu_4NCl as the source of chloride ion: (A) 0.0018 M (n-Bu_4N)[$TcOCl_4$] in CH_2Cl_2; (B) 0.0018 M (n-Bu_4N)[$TcOCl_4$] and 0.125 M n-Bu_4NCl; (C) 0.0018 M (n-Bu_4N)[$TcOCl_4$] and 0.250 M n-Bu_4NCl.

chemical difference between Mo(V) and Tc(V) or may merely reflect ion pairing, or medium, effects engendered by the use of different counterions (($(C_6H_5)_4As^+$ vs. n-Bu_4N^+) and/or different ionic strengths in the two studies. However, recent studies by Kim and Murmann[26] in aqueous media support the conclusion that $MoOCl_4^-$ has a significantly higher affinity for Cl^- than does $TcOCl_4^-$. Thus, in 12 M HCl $MoOCl_5^{2-}$ is favored over $MoOCl_4^-$ whereas in this medium $TcOCl_4^-$ is favored over $TcOCl_5^{2-}$ (vide supra). It appears that in both aqueous media and in CH_2Cl_2 the Mo(V) center has a higher affinity for chloride than does the Tc(V) center. This may reflect a greater thermodynamic trans effect induced by the Tc=O linkage (relative to the Mo=O linkage).

The IR and Raman data of Table I clearly show that the M=O stretching frequencies of the $TcOCl_4^-$, $TcOBr_4^-$, and $MoOCl_4^-$ complexes shift to lower energies upon coordination of a halide ligand trans to the M=O linkage. For the three five-coordinate complexes the IR stretch is in the range 1010–1020 cm^{-1}, while for the three six-coordinate complexes the IR stretch is in the range 950–955 cm^{-1}. This shift implies, as expected, a weakening of the M=O bond upon coordination of a halide ligand in the trans position. However, this weakening is a relatively minor effect that is not manifested in M=O bond lengths. Thus, both $MoOCl_4^-$ and $MoOCl_5^{2-}$ have a Mo=O bond length of 1.61 (1) Å,[27,28] while all four bond lengths determined by EXAFS for $TcOCl_4^-$, $TcOCl_5^{2-}$, $TcOBr_4^-$, and $TcOBr_5^{2-}$ are identical within experimental error (1.65–1.66 Å).

Using structural parameters derived from the crystallographically characterized Tc(IV) complexes $TcCl_6^{2-}$ and $TcBr_6^{2-}$, EXAFS measurements and analyses have led to structural parameters for four complexes that are inherently difficult to crystallize, i.e. TcI_6^{2-}, $TcOCl_5^{2-}$, $TcOBr_4^-$, and $TcOBr_5^{2-}$. As a check on the accuracy of these EXAFS procedures, structural parameters were also derived for $TcOCl_4^-$, a complex that had been previously characterized by single-crystal techniques.[13] The resulting agreement (Table II) is both typical and satisfying: bond lengths derived from EXAFS agree well with those determined crystallographically (for Tc=O, 1.65 Å by EXAFS vs. 1.61 (1) Å by crystallography; for Tc—Cl, 2.30 Å by EXAFS vs. 2.31 (1) Å by crystallography). However, the number of coordinating atoms is relatively poorly defined by the EXAFS technique (for Tc=O, 1.3 by EXAFS vs. exactly 1 by crystallography; for Tc—Cl, 3.0 by EXAFS vs. exactly 4 by crystallography). Thus, considerable confidence can be placed in the values of the bond lengths determined by EXAFS, but definitive knowledge about the composition of the coordination sphere must come from other techniques.

The Tc–I bond length of 2.72 Å determined by EXAFS for TcI_6^{2-} is the only measure of this parameter known to us and certainty is reasonable in light of the comparable Tc–Br and Tc–Cl distances in $TcBr_6^{2-}$ and $TcCl_6^{2-}$ (Table II). Likewise, EXAFS-derived bond length data for $TcOBr_4^-$ are exactly as expected; the Tc=O bond length is the same as that observed in $TcOCl_4^-$, and the Tc–Br bond length is slightly shorter than that observed in $TcBr_6^{2-}$ (2.48 vs. 2.52 Å) due to the greater crowding in the six-coordinate complex. This increase in Tc–X bond length on going from a five- to a six-coordinate complex has been noted several times and has been documented in detail.[4] The effect is also seen in comparing $TcOCl_4^-$ and $TcOCl_5^{2-}$ structures (*cis*-Tc–Cl lengths of 2.30 and 2.36 Å) as well as in the $TcOBr_4^-$ and $TcOBr_5^{2-}$ structures (*cis*-Tc–Br lengths of 2.48 and 2.54 Å). Correspondingly, the pairs of six-coordinate structures TcX_6^{2-} and $TcOX_5^{2-}$ have approximately equal Tc–X bond lengths (2.37 and 2.36 Å for Tc–Cl, 2.52 and 2.54 Å for Tc–Br, considering only *cis*-Tc–X bonds for $TcOX_5^{2-}$).

Despite the uncertainties in numbers of coordinating atoms, EXAFS analysis of the $TcOX_5^{2-}$ species clearly shows two different types of Tc–X bonds, with the halogen associated with the shorter Tc–X length having a considerably higher site occupancy. These two types of Tc–X linkages are thus readily assigned as the *cis*- and *trans*-Tc–X bonds since the oxo group is known to exert a strong structural trans effect (STE) that lengthens the trans situated bond.[3,4,29–31] From the EXAFS analyses, the STE for $TcOX_5^{2-}$ is calculated to be 0.14 (3) Å for X = Cl and 0.20 (3) Å for X = Br.[32]

Further support for the accuracy of the EXAFS results presented in Table II can be obtained by comparing EXAFS derived data for Tc(V) complexes to crystallogrphically derived data for

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analogous Mo(V) complexes. The Mo=O distance in $MoOCl_4^-$ and $MoOCl_5^{2-}$ is 1.61 Å[27,28] and that in the *trans*-$MoOX_4(OH_2)^-$ complexes (X = Cl, Br, I) is 1.64 (2) Å, independent of X.[33] These values compare well with the EXAFS-derived Tc=O bond lengths in Table III. Even more importantly, the *cis*- and *trans*-MoCl lengths in $MoOCl_6^{2-}$ (2.39 and 2.59 Å, respectively)[28] are in good agreement with the *cis*- and *trans*-Tc-Cl lengths derived for $TcOCl_5^{2-}$ (2.36 and 2.50 Å). Similarly, the *cis*-Mo–Cl and *cis*-Mo–Br lengths in *trans*-$MoOX_4(H_2O)^-$ (2.364 (5) and 2.53 (2) Å, respectively)[33] are in good agreement with the *cis*-Tc–Cl and *cis*-Tc–Br lengths derived for $TcOX_5^{2-}$ (2.36 and 2.54 Å, respectively).

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Preparation and Characterization of Heterobimetallic Halogen-Bridged Palladium–Platinum Complexes. Crystal and Molecular Structure of $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$

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Attempts to prepare and characterize unambiguously heterobimetallic complexes of the type $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ (R = Et, *n*-Pr, Bu, Ph; $PR_3 = PMe_2Ph$) using infrared, ^{31}P and ^{195}Pt NMR, and mass spectroscopies are described. It is established that, in solution, an equilibrium exists between $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$, $[(PR_3)_2Pd_2Cl_4]$, and $[(PR_3)_2Pt_2Cl_4]$, the latter two species always being in 1:1 molar ratio; this equilibrium is temperature independent but is influenced by excess of either one of the dimers $[(PR_3)_2M_2Cl_4]$ (M = Pt, Pd). The reactions of the heterobimetallic products with $SnCl_2 \cdot 2H_2O$ have been investigated, as well as the bridge-cleavage reactions with various donor ligands, in order to elucidate the chemical behavior of the heterobimetallic dichloro bridge; neutral ligands appear to be distributed equally between Pd and Pt. Crystals of the reaction product, with a composition corresponding to $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ are monoclinic, space group $P2_1/n$, with $a = 7.590$ (2) Å, $b = 12.216$ (1) Å, $c = 12.119$ (1) Å, and $\beta = 101.87$ (1)°. With $Z = 2$ the molecules must lie about inversion centers, and the Pd and Pt atoms are mutually disordered. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters; $R = 0.030$ and $R_w = 0.033$ for 2451 observed reflections. The unique metal atom has slightly distorted square planar geometry with M–P = 2.214 (1), M–Cl (terminal) = 2.275 (1), M–Cl (bridging trans to P) = 2.437 (1), and M–Cl (bridging trans to Cl) = 2.314 (1) Å. The data do not unambiguously identify the solid product but, in combination with the NMR and mass spectroscopic data, do establish conclusively the existence of these heterobimetallic complexes.

Introduction

Halogen-bridged palladium and platinum complexes of the type $[MCl_2(ER_3)]_2$ (M = Pd, Pt; E = P, As, Sb; R = alkyl, aryl) are well-known[1–6] and, from X-ray structural analyses[7,8] usually have symmetrical trans structures. Analogous heterobimetallic complexes containing both palladium and platinum have not been isolated although their existence in solution has been proposed by Masters et al.[9,10] Recently, several heterobimetallic complexes of palladium and platinum containing chelating ligands have been isolated in the solid state.[11–14]

Simple heterobimetallic complexes of the type $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ are of interest to us in terms of (i) their stereochemistry and bonding, (ii) their behavior in bridge-cleavage reactions with donor ligands, and (iii) their behavior as catalysts or catalyst precursors. We now describe our attempts to prepare the complexes $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ and to characterize them unambiguously through the determination of the crystal and molecular structure of $[(PEt_3)ClPd(\mu\text{-}Cl)_2PtCl(PEt_3)]$ and through NMR spectroscopic and mass spectroscopic studies.

Results and Discussion

Halogen-bridged heterobimetallic complexes containing both palladium and platinum, of the type $[(PR_3)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ with R = Et, Pr, *n*-Bu, or Ph or $PR_3 = PMe_2Ph$, can apparently be easily prepared by the reactions of *trans*-$(PR_3)_2PtCl_2$ with palladium(II) chloride, or $(PR_3)_2\,PdCl_2$ with platinum(II) chloride, in refluxing xylene in an inert atmosphere. The resulting products are orange, crystalline solids readily soluble in dichloromethane, chloroform, benzene, toluene, and xylene (except the triphenylphosphine complex, which is sparingly soluble in these solvents). Analytical and physical data are given in Table I.

This synthesis might obviously be extended to systems such as *trans*-$[(PtHCl(PEt_3)_2]$ with $PdCl_2$, in which, if the analogous reaction occurred, a heterobimetallic species containing both hydrido and chlorobridging might be obtained. Unfortunately,

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