

Uranium(IV) and Thorium(IV) Tetrakis-(dialkoxyphosphato) and Tetrakis-(alkoxy alkylphosphonato) Polynuclear Complexes*

N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski, and M. M. Labes

Received March 20, 1970

Reaction of UCl_4 and $ThCl_4$ with neutral phosphate and phosphonate esters at elevated temperatures leads to the precipitation of tetrakis-(dialkoxyphosphato) and tetrakis-(alkoxy alkylphosphonato) M^{IV} complexes. Characterization of these complexes by means of spectral, magnetic and X-ray studies led to the assignment of polymeric configurations involving octacoordinated metal ions, to these compounds. Solubility characteristics and magnetic moments, which are low for octacoordinated U^{IV} compounds, are in favor of polynuclear structures. Significant differences in the positions of the ν_{M-O} bands of the complexes of various phosphato and phosphonato ligands are suggestive of formation of two types of polymers. The ethyl ethylphosphonato, dimethylphosphato and di-n-butylphosphato complexes were tentatively assigned a cross-linked double-bridged configuration, and the methyl methylphosphonato and isopropyl methylphosphonato analogs a structure involving four-membered chelate rings and single phosphonato bridges. The n-butyl n-butyl-phosphonato complexes appear to be mixtures of these two types of polymers.

Introduction

Sn^{IV} , Zr^{IV} and Te^{IV} chlorides react at elevated temperatures with diisopropyl methylphosphonate (DIMP) to form cross-linked bis-(methylphosphonato)- M^{IV} polymers ($M(MP)_2$).^{1,2} Trivalent metal halides yield under the same conditions tris-(isopropoxy methylphosphonato)- M^{III} complexes ($M(IMP)_3$; $M = Al, Ga, In, Sc, Y, Ln, Ti, V, Cr, Fe$).^{1,3-5} These reactions involve evolution of isopropyl chloride and a mixture of HCl and propene, formed by catalytic dehydrochlorination of isopropyl chloride in the presence of the reacting complex metal halide.¹ Initially, monomeric adducts of the types $MCl_4 \cdot 2DIMP$ and $MCl_3 \cdot 3DIMP$ are formed, which decompose at high tem-

peratures yielding the above mentioned polymeric products.^{1,3-5} This is supported by the facts that $Sn(MP)_2$ can be obtained either by thermal decomposition of $SnCl_4 \cdot 2DIMP$ or by reaction of $SnCl_4$ with excess DIMP, and that an intermediate of this reaction of the type $[Sn(DIMP)(IMP)Cl_3]_x$ is tetrameric.² Polymerization thus occurs by intermolecular interactions in the decomposing metal halide-DIMP adducts, by a mechanism analogous to that proposed by Gutmann and Beer for the formation of tris-(dialkoxyphosphato)- M^{III} complexes.⁶

Direct reaction of di-n-butyl phosphate (DBP) with M^{III} and M^{IV} nitrates ($M = Al^{III}, Y^{III}, Ln^{III}, Fe^{III}, Ce^{IV}, Th^{IV}$) leads to formation of $M(DBP)_3$ and $M(DBP)_4$ complexes.^{7,8} It was of interest to us to explore the possibility of preparation of $M(DBP)_4$ and analogous compounds by reaction of metal tetrachlorides with tri-n-butylphosphate and other neutral organophosphoryl esters at elevated temperatures. Since the stoichiometry of the MCl_4 adducts with neutral organophosphoryl compounds is apparently influencing the nature of the final product of the decomposition reaction,² UCl_4 and $ThCl_4$ were selected for our studies. In fact, while $SnCl_4$ and $ZrCl_4$ form 1:2 adducts with phosphoryl compounds,⁹ UCl_4 and $ThCl_4$ form adducts with these ligands in molar ratios ranging between 1:1 and 1:4.^{10,11} Reaction of these tetrachlorides with neutral phosphate and phosphonate esters led indeed to the formation of ML_4 complexes ($M = U, Th$; $L =$ dialkoxyphosphato, alkoxy alkylphosphonato group). The present paper deals with the synthesis and characterization of these complexes.

Experimental Section

Chemicals. Trimethyl phosphate (TMP), TBP (Aldrich), DIMP (Edgewood Arsenal, Maryland), dimethyl methylphosphonate (DMMP), diethyl ethylphosphonate (DEEP) and di-n-butyl n-butylphospho-

(* The support of U. S. Army Edgewood Arsenal, Maryland, under contract No. DAAA 15-67-C-0644 is gratefully acknowledged.

(1) C. M. Mikulski, N. M. Karayannis, J. V. Minkiewicz, L. L. Pytlewski, and M. M. Labes, *Inorg. Chim. Acta*, **3**, 523 (1969).

(2) C. Owens, L. L. Pytlewski, N. M. Karayannis, J. Wysocznki, and M. M. Labes, *Polymer Lett.*, **8**, 81 (1970).

(3) N. M. Karayannis, C. M. Mikulski, J. V. Minkiewicz, L. L. Pytlewski, and M. M. Labes, *J. Less-Common Metals*, **20**, 29 (1970).

(4) J. J. Kokalas, D. N. Kramer, F. Block, and R. Levin, *Spectry Lett.*, **2**, 273 (1969); J. J. Kokalas, D. N. Kramer, A. A. Temperley, and R. Levin, *ibid.*, 283.

(5) C. M. Mikulski, N. M. Karayannis, M. J. Strocko, L. L. Pytlewski, and M. M. Labes, *Inorg. Chem.*, in press.

(6) V. Gutmann and G. Beer, *Inorg. Chim. Acta*, **3**, 87 (1969).

(7) T. D. Smith, *J. Inorg. Nucl. Chem.*, **9**, 150 (1959).

(8) W. H. Baldwin and C. E. Higgins, *ibid.*, **17**, 334 (1961).

(9) I. Lindqvist, « Inorganic Adduct Molecules of Oxo-Compounds », Springer-Verlag, Berlin 1963, and references therein.

(10) R. E. Panzer and J. F. Suttle, *J. Inorg. Nucl. Chem.*, **15**, 67 (1960).

(11) D. F. Peppard and J. R. Ferrario, *ibid.*, **10**, 275 (1959); D. F. Peppard, G. W. Mason and S. McCarty, *ibid.*, **13**, 138 (1960).

Table I. Analyses, Temperatures of Precipitation and Magnetic Moments (at 297°K) of Phosphato and Phosphonato U^{IV} and Th^{IV} Complexes ^a

Complex	Temp. of Precipitation, °C	$\chi_M^{corr} \times 10^6$	$\mu_{eff, BM}$	C%		H%		P%		Metal%	
				Calc	Found	Calc	Found	Calc	Found	Calc	Found
U(MMP) ₄	115	3141	2.74	14.25	13.97	3.59	3.26	18.38	18.01	35.31	35.37
U(EEP) ₄	170	2988	2.68	24.44	24.69	5.13	4.82	15.75	15.94	30.27	29.86
U(IMP) ₄	193	3250	2.79	24.44	23.97	5.13	4.99	15.75	15.23	30.27	30.52
U(BBP) ₄	205	3588	2.93	38.02	37.65	7.18	7.05	12.26	11.97	23.55	23.88
U(DMP) ₄	130	2960	2.67	13.02	13.36	3.28	3.32	16.78	16.32	32.24	32.90
U(DBP) ₄	180	3691	2.97	35.76	35.97	6.73	6.79	11.53	11.21	22.15	22.64
Th(MMP) ₄	90	Diamagnetic		14.38	14.39	3.62	3.70	18.54	18.12	34.73	34.48
Th(EEP) ₄	149	Diamagnetic		24.62	24.37	5.14	4.93	15.87	16.14	29.73	30.06
Th(IMP) ₄	192	Diamagnetic		24.62	24.85	5.14	4.99	15.87	15.44	29.73	30.14
Th(BBP) ₄	189	Diamagnetic		38.25	38.53	7.22	6.84	12.33	11.88	23.09	23.84
Th(DMP) ₄	80	Diamagnetic		13.12	13.49	3.30	3.50	16.92	17.07	31.69	31.20
Th(DBP) ₄	168	Diamagnetic		35.96	35.42	6.79	7.02	11.59	11.08	21.71	21.44

^a Analyses established that the new complexes are chlorine-free. The Th^{IV} complexes are white and the U^{IV} complexes light olive green to blue-green.

Table II. ν_{POO} , ν_{M-O} and far IR Ligand Bands in Phosphato and Phosphonato Complexes.

Complex	ν_{POO}	ν_{M-O}	ν Ligand (600-300 cm ⁻¹)
U(MMP) ₄	1680 m, 1140 vs, 1065 vs,sh	498 vs, 447 vs, 335 vs,b	570 m,sh, 550 sh, 400 sh, 350 sh, 310 m
U(EEP) ₄	1750 m, 1128 vs, 1060 vs,sh	539 m-s, 471 vs, 382 vs	565 m,sh, 520 s, 410 sh, 397 sh, 355 sh, 305 w
U(IMP) ₄	1720 m, 1132 vs, 1060 vs	496 vs, 430 vs, 342 s, 329 s	565 m, 540 sh, 510 s, 469 s, 395 sh
U(BBP) ₄	1675 w, 1122 vs,b, 1080 vs,sh	542 vs, 445 vs, 375 s, 332 s	582 m, 555 sh, 530 vs, 515 sh, 489 vs,b, 410 s, 340 sh
U(DMP) ₄	1660 m, 1175 vs, 1099 vs	512 s, 482 vs, 470 sh, ^a 390 vs	590 sh, 581 m, 574 sh, 537 sh, 520 sh, 302 m,sh
U(DBP) ₄	1760 m,b, 1154 vs, 1099 vs	520 vs, 464 vs, 386 s	580 m-s, 438 m,sh, 398 sh, 375 ssh, 355 sh, 325 m,sh, 315 m
Th(MMP) ₄	1678 m, 1150 vs, 1076 vs	496 vs, 447 vs, 338 s,sh, 334 s	570 m,sh, 550 sh, 539 m, 405 sh, 302 m
Th(EEP) ₄	1750 m, 1140 vs, 1070 vs	538 s, 471 vs, 380 vs	570 m,sh, 560 m, 521 s, 397 sh, 352 sh, 307 w
Th(IMP) ₄	1719 m, 1145 vs, 1064 vs	492 vs, 428 vs, 339 s, 328 s	560 m, 508 s, 462 s, 390 sh
Th(BBP) ₄	1690 w, 1130vs,b 1060 vs,b	538 vs, 443 vs, 365 s, 332 s, 328 s	582 m, 555 sh, 510 m, 489 vs, 410 s
Th(DMP) ₄	1655 m, 1192 vs, 1090 vs	511 s, 482 vs, 473 sh, ^a 390 vs	581 m, 575 sh, 539 sh, 520 sh, 305 w
Th(DBP) ₄	1760 m,b 1168 vs, 1102 vs	520 vs, 467 vs, 388 s	580 m-s, 435 m,sh, 398 m,sh, 328 m,sh, 315 m

s: strong, m: medium, w: weak, v: very, b: broad, sh: shoulder. ^a Bands overlapping with ligand absorptions.

Table III. Solid State (Nujol Mull) Electronic Spectra of U^{IV} Phosphato and Phosphonato Complexes in the 24-6 kK Region.

Complex	ν_{max} , kK
U(MMP) ₄	23.9, 23.1, 22.8, 20.6, 18.7, 18.3, 17.2 b, 16.3 vb, 15.6 b, 14.9, 13.1, 10.4, 9.4, 9.0, 8.7, 8.4, 7.9, 6.5 vb
U(EEP) ₄	23.9, 23.1, 22.7, 20.7, 18.7, 18.4, 17.4 b, 16.2, 15.9, 15.5, 15.3, 14.9, 13.1, 12.2 sh, 11.1 sh, 10.4, 9.3, 9.0, 8.6, 8.4, 7.9, 6.6, 6.4, 6.3
U(IMP) ₄	23.8, 22.7, 20.5, 18.6, 18.3, 17.3 b, 16.2, 15.9, 15.5, 15.3, 14.9, 13.1 b, 10.4, 9.5, 9.0, 8.4, 7.9, 6.7 v b
U(BBP) ₄	23.1 vb, 20.4, 18.8, 18.3, 17.6 b, 15.9 b, 15.5, 15.0, 13.1, 10.4, 9.4, 9.0, 8.8, 8.5, 7.9, 6.7 v b
U(DMP) ₄	23.7, 22.9, 22.2, 20.5, 18.6, 18.3, 17.7, 16.3, 16.0, 15.5, 15.3, 14.9 b, 13.1, 10.4, 9.4, 9.0, 8.7, 8.4, 7.9, 6.7 vb
U(DBP) ₄	23.2 v b, 20.4, 18.6 v b, 17.5 v b, 15.7 v b, 14.9 b, 13.1 b, 10.4, 9.4, 9.0, 8.8, 8.5, 7.9, 6.7 v b

b, broad; v, very; sh, shoulder.

nate (DBBP) (Mobil Chemical Co.) were utilized as received.¹ The purest commercially available hydrated metal tetrachlorides were used.

Synthesis. The new complexes were prepared by methods previously described.^{1,3-5} Precipitation was accompanied by evolution of methyl chloride (dimethoxyphosphato (DMP) and methoxy methylphosphonato (MMP) complexes) or a mixture of alkyl chloride, HCl and alkene (ethoxy ethylphosphonato (EEP), IMP, n-butoxy n-butylphosphonato (BBP) and DBP complexes). As is the case with analogous inorganic polymers,^{1,3-5} the new complexes do not melt or decompose at temperatures up to 300°C and are in-

soluble in all common organic solvents, water and neutral phosphate and phosphonate esters. Analyses (Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.), colors, magnetic moments (for the U^{IV} complexes) and temperatures of precipitation of the new compounds are given in Table I.

Spectral Magnetic and X-ray Powder Diffraction Studies. Magnetic moments (Table I), IR (Table II) and electronic (Table III) spectra and X-ray powder diffraction patterns were obtained as described elsewhere.^{1,3,12}

(12) N. M. Karayannis, L. L. Pytlewski, and M. M. Labes, *Inorg. Chim. Acta*, 3, 415 (1969).

Results and Discussion

Infrared Spectra and X-ray Patterns. The U^{IV} and Th^{IV} complexes with any of the ligands studied exhibit identical X-ray powder diffraction patterns and are, therefore, isomorphous. The IR spectra of the new complexes (Table II), which do not exhibit water bands, are characterized by two strong bands at 1200-1050 cm^{-1} , assigned as the asymmetric and symmetric ν_{POO} modes¹³ and a medium to weak band at 1750-1655 cm^{-1} , which has been attributed to a combination of vibrational modes of the POO group.¹⁴ These bands occur invariably in the analogous phosphonato and phosphato complexes with trivalent metal ions.^{1,3,5} The absence of significant absorption due to phosphorus-oxygen bonds in the 1250-1200 cm^{-1} region excludes the possibility of presence of uncoordinated P=O groups,¹⁴⁻¹⁶ which would lead to a coordination number lower than 8. Further, no bands attributable to M=O bonds are observed in the IR spectra of the new uranium complexes. The U^{IV} and Th^{IV} complexes of a given ligand exhibit very similar IR and far IR spectra, and the electronic spectra of the uranium complexes are typical of U^{IV} compounds (*vide infra*). The formulation of the new complexes as UL_4 and ThL_4 is, thus, justified on the basis of the above discussion.

Tentative assignments of ν_{M-O} bands in the far IR spectra of the new complexes (Table II) were effected by their comparison to the spectra of the Ti^{III} , V^{III} and Cr^{III} complexes, reported elsewhere.⁵ The spec-

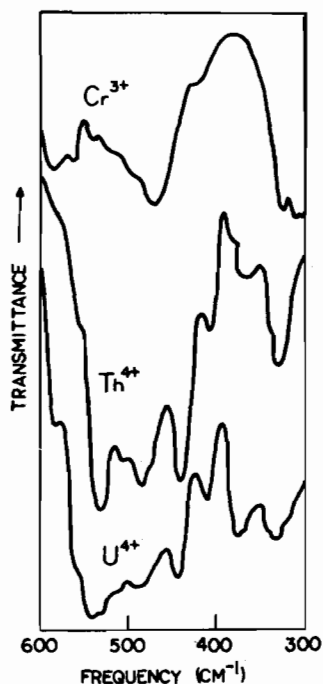


Figure 1. Far infrared spectra of $Cr(BBP)_3$, $Th(BBP)_4$, and $U(BBP)_4$.

- (13) J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **24**, 475 (1962).
 (14) L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, **20**, 467, 489 (1964); **21**, 1905 (1965).
 (15) E. Gryszkiewicz-Trochimowski, J. Quinchon, and M. Bousquet, *Bull. Soc. Chim. France*, 1645 (1962); H. Christol, M. Levy, and C. Marty, *J. Organometal. Chem.*, **12**, 459 (1968).
 (16) J. J. Pitts, M. A. Robinson, and S. I. Trotz, *J. Inorg. Nucl. Chem.*, **30**, 1299 (1968); **31**, 3685 (1969).

tra of $U(BBP)_4$, $Th(BBP)_4$ and $Cr(BBP)_3$ are illustrated in Figure 1. In the case of IMP complexes additional comparisons were made to the spectra of Al^{III} , Ga^{III} , In^{III} , Sc^{III} , Y^{III} and Ln^{III} -IMP complexes.^{1,3} Primarily ν_{U-O} and ν_{Th-O} bands occur at 540-320 cm^{-1} (Table II).³ ν_{U-O} bands in the same region have been reported for a number of U^{IV} hydroxo complexes.¹⁷ It is noteworthy that the ν_{M-O} bands of the MMP and IMP complexes occur at lower frequencies than in the other complexes. In particular, the lower frequency ν_{M-O} is observed at 342-328 cm^{-1} in the former compounds at 390-380 cm^{-1} in the EEP, DMP and DBP complexes, while in the BBP complexes two bands occur at 375-365 and 332-328 cm^{-1} (Table II, Figure 1). No anomalies of this type were observed in the IR spectra of the corresponding series of ML_3 complexes ($M = Ti, V, Cr$).⁵ The far IR spectral data reported here and the broad character of the ν_{POO} bands in the $M(BBP)_4$ complexes (Table II) may be interpreted in terms of existence of two structurally different types of compounds involving M-O bonds of different strength. The BBP complexes are, presumably, mixtures of complexes of these two types. Attempts at the correlation of $\Sigma\sigma$ substituent constants¹⁸ and ν_{M-O} frequencies⁵ led to V-shaped plots. Trends of this type in 3d metal complexes have been attributed to the influence of inductive effects on the extent of $d_{\pi}-p_{\pi}$ metal to ligand backbonding.¹⁹ ML_3 ($M = Ti, V, Cr$) phosphonato and phosphato complexes give V-shaped $\Sigma\sigma$ vs. ν_{M-O} plots.⁵ Nevertheless, in the complexes reported here the plots obtained cannot be attributed to π -bonding between ligand and metal. In fact, although $f_{\pi}-p_{\pi}$ back-donation is possible in the case of U^{IV} ,²⁰ Th^{IV} , with a noble gas electronic core, would certainly not be involved in bonding of this type.²¹ This discussion is in support of the existence of two types of compounds proposed above. $\Sigma\sigma$ vs. ν_{POO} (asymmetric) plots (Figure 2) indicate a trend of increase of the frequency

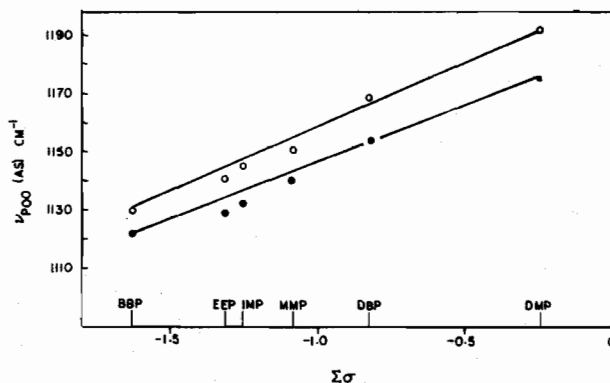


Figure 2. ν_{POO} (asymmetric) vs. $\Sigma\sigma$ ¹⁸ plots for U^{IV} and Th^{IV} tetrakis(dialkoxyphosphato) and (alkoxy alkylphosphonato) complexes.

- (17) J. Selbin and M. Schöber, *ibid.*, **28**, 817 (1966).
 (18) M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, **110**, 393 (1956); M. I. Kabachnik, G. A. Balueva, T. Ya. Medved, E. N. Tsvetkov and C. Chung-Yu, *Kinetika i Kataliz*, **6**, 212 (1965), and references therein.
 (19) L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta*, **3**, 473 (1969).
 (20) C. Wiedenheft, *Inorg. Chem.*, **8**, 1174 (1969).
 (21) F. E. Dickson, E. W. Gowling, and F. F. Bentley, *ibid.*, **6**, 1099 (1967); F. E. Dickson, E. W. Baker, and F. F. Bentley, *J. Inorg. Nucl. Chem.*, **31**, 559 (1969).

of this vibrational mode with decreasing electron releasing properties of the substituents, as expected.⁵ The two strong ν_{POO} bands occur at lower frequencies in the U^{IV} complexes. This demonstrates that the U–O bonds are stronger than the Th–O bonds,²² which is also confirmed by the occurrence of the $\nu_{\text{U-O}}$ at slightly higher frequencies than the $\nu_{\text{Th-O}}$ modes (Table II).

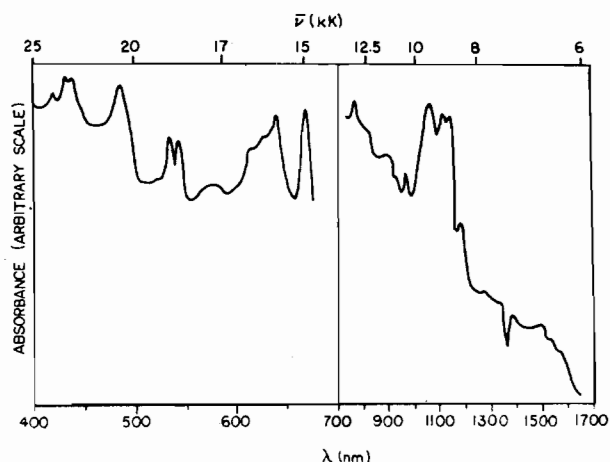


Figure 3. Solid state electronic spectrum (Nujol mull) of $\text{U}(\text{EEP})_4$.

Electronic Spectra and Magnetic Moments. The solid state electronic spectra of the uranium compounds (Table III) are typical of U^{IV} . The spectrum of $\text{U}(\text{EEP})_4$ is illustrated in Figure 3. All the new U^{IV} complexes exhibit similar spectra, but in some cases (e.g. $\text{U}(\text{DBP})_4$) resolution was not very satisfactory. These spectra show similarities to the spectra of both octa-²³ and hexa-^{24,25} coordinated U^{IV} compounds. In certain regions of the spectrum (i.e. 24.5–20.5, 10–6 kK), however, the patterns of the spectra of the new complexes show a greater resemblance to those reported for octa-coordinated U^{IV} complexes.²³ Thus, the electronic spectral evidence justifies the formulation of these compounds as UL_4 and, consequently, ThL_4 . Assignments of the spectral bands of UL_4 to specific (f–f) transitions, is not possible at this point, as no energy level calculations for the $5f^2$ configuration in square antiprismatic or dodecahedral ligand-fields have been reported. A distorted square antiprismatic symmetry is tentatively assigned to the new complexes.²³

The magnetic moments of the U^{IV} complexes (Table I) are in the «cubic» region for this metal ion.^{26,27} In fact, octahedral U^{IV} compounds exhibit magnetic moments close to the spin-only value of 2.84 BM,^{26–28}

while octacoordinated compounds of this metal ion show moments in the region of 3.4–3.8 BM.²⁶ Nevertheless, magnetic moments lower than the spin-only values have been reported for polymeric phosphato and phosphonato complexes of d¹–d⁵ metal ions (Ti^{III} , V^{III} , Cr^{III} , Fe^{III})^{1,5,29} and interpreted in terms of demagnetization by a super-exchange mechanism operating via the –O–P–O– bridges, while magnetic exchange to a small extent between adjacent polymeric molecules was also considered as possible.⁵ In addition, it was established that $[\text{Fe}(\text{O}_2\text{PCL}_2)_3]_n$ exhibits low magnetic moments over a wide temperature range and the Curie-Weiss law is obeyed for $\theta = -10^\circ$.²⁹ Effects of this type were not observed in the corresponding trivalent lanthanide complexes.³ 5f electrons are less well shielded than 4f electrons,²⁰ and may participate in magnetic exchange. Thus, the room temperature magnetic properties of the U^{IV} complexes are in favor of polynuclear configurations. A definitive assignment of polymeric structures to these compounds on the basis of the magnetic evidence should be substantiated by studies of the temperature dependence of χ_M , however.

Nature of the Phosphato and Phosphonato Complexes. The solubility characteristics, texture and low magnetic moments of the new complexes are similar to those observed in crystalline polymers of the types ML_3 (M=Al, Ga, In, Sc, Y, Ln, Ti, V, Cr; L=alkoxy alkylphosphonato or dialkoxyphosphato group) and $\text{M}(\text{MP})_2$ (M=Sn, Zr, Te) complexes.^{1–3,5} Monomeric thiophosphinato metal complexes¹⁶ and phosphonato oligomers (such as $[\text{Sn}(\text{DIMP})(\text{IMP})\text{Cl}_3]_4$)² are soluble in many organic solvents. The properties of the new complexes are, therefore, in favor of polynuclear structures. Polymeric complexes of 3d metal ions or Sn^{IV} with R_2POO are usually characterized by the exclusive presence of bridging –O–P–O– groups.³⁰ However, in the case of larger cations, such as U^{IV} and Th^{IV} , structures involving both chelating and bridging – PO_2 ligands are plausible.¹⁶

Although a rigorous treatment would require knowledge concerning the «purity» of ν_{POO} and $\nu_{\text{M-O}}$, as well as the corresponding stretching force constants, tentative structural assignments may be made from the IR data available. In fact, the lower frequency $\nu_{\text{M-O}}$ bands are split or broad in the MMP and IMP complexes, while the corresponding bands in the EEP, DMP, and DBP complexes are very sharp. In addition, the ν_{POO} bands at 1200–1050 cm^{-1} are sharper in the latter than in the former groups of compounds. These characteristics suggest that in the EEP, DMP and DBP complexes all the –O–P–O– groups are equivalent.^{22,31} Thus, these compounds may be formulated as cross-linked double-bridged polymers,^{5,16,32} involving exclusively eight-membered phosphato or

(22) L. S. Mayants and E. I. Matrosov, *Izv. Akad. Nauk SSSR, Neorg. Mat.*, 1, 546 (1965).

(23) J. Selbin and J. D. Ortego, *J. Inorg. Nucl. Chem.*, 29, 1449 (1967); 30, 313 (1968).

(24) R. Pappalardo and C. K. Jørgensen, *Helv. Phys. Acta*, 37, 79 (1964); R. A. Satten, C. L. Schreiber and E. Y. Wong, *J. Chem. Phys.*, 42, 162 (1965).

(25) B. C. Lane and L. M. Venanzi, *Inorg. Chim. Acta*, 3, 239 (1969).

(26) B. Jezowska-Trzebiatowska, and K. Bukietynska in «Theory and Structure of Complex Compounds», Macmillan, New York 1964, pp. 311–314.

(27) G. A. Candela, C. A. Hutchison, and W. B. Lewis, *J. Chem. Phys.*, 30, 246 (1959).

(28) B. Jezowska-Trzebiatowska, and J. Drozdzyński, *J. Inorg. Nucl. Chem.*, 31, 727 (1969).

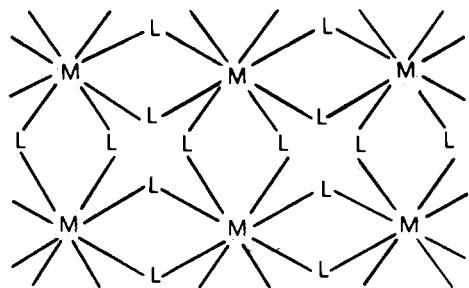
(29) H. Müller and K. Dehnicke, *Z. anorg. allgem. Chem.*, 350, 231 (1967).

(30) J. Danielsen and S. E. Rasmussen, *Acta Chem. Scand.*, 17, 1971 (1963); C. E. Wilkes and R. A. Jacobson, *Inorg. Chem.*, 4, 99 (1965); F. Giordano, L. Randaccio, and A. Ripamonti, *Chem. Commun.*, 19, 1239 (1967); D. Moras, A. Mitschler, and R. Weiss, *Acta Cryst.*, B25, 1720 (1969).

(31) G. H. Dahl and B. P. Block, *Inorg. Chem.*, 6, 1439 (1967).

(32) E. E. Flagg and D. L. Schmidt, *J. Amer. Chem. Soc.*, 90, 4173 (1968).

phosphonato bridges and octacoordinated metal ions ($L = -O-P(R_2)-O-$; R = alkoxy or alkyl group):

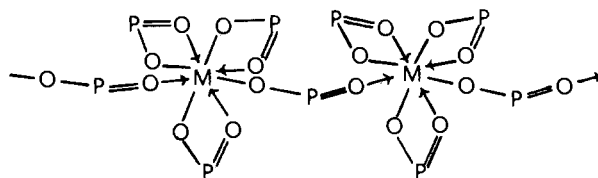


On the other hand, the splittings in the ν_{M-O} bands and the broader character of the ν_{POO} absorptions points to the presence of two sets of inequivalent phosphonato groups in the MMP and IMP complexes. The fact that ν_{M-O} bands occur at lower frequencies in these complexes can be attributed to the presence of four-membered phosphonato chelate rings. Structures involving four-membered chelate rings of this type are favored in the case of large metal ions.¹⁶ No crystallographic data are available for compounds containing chelating $-O-P-O-$ groups, but the

M—O—P angles are certainly smaller in compounds than in complexes involving eight-membered phosphonato bridges.⁹

This is corroborated by the fact that M—O bonds are significantly longer in complexes containing chelating acetato groups³³ than in bridged acetato compounds of the same metal ion (Zn^{II}).³⁴ A structure involving eight-membered phosphonato bridges is rather improbable, since the ν_{M-O} frequencies are considerably lower than those of the polymers discussed above. Single phospho-

nato bridges³⁵ between metal ions coordinated to three chelate rings may account for the occurrence of ν_{M-O} bands at approximately the same frequencies as those of the chelate rings:



These M—O bonds would be weaker than in double-bridged polymers, owing to steric hindrance caused by the coordination of three chelate rings to each metal ion.

The BBP complexes are undoubtedly mixtures of the two types of polymers discussed above. The Th^{IV} compound contains a substantially greater amount of the «chelate-single bridged» polymer, while the U^{IV} analog is an approximately 1:1 mixture of the two polymers (Figure 1).

In conclusion, reaction of neutral phosphate and phosphonate esters with UCl_4 and $ThCl_4$ at elevated temperatures leads to elimination of one alkoxy alkyl per ester molecule and formation of tetrakis-(dialkoxophosphato) or (alkoxy alkylphosphonato) M^{IV} complexes. The reaction most probably proceeds via formation of $MCl_4 \cdot 4L$ ($L =$ neutral phosphate or phosphonate ester) adducts.^{10,11} Although these products are generally of the type ML_4 ($M = Th, U$), their IR spectra indicate that they belong to two different structural types. The EEP, DMP, and DBP complexes have been tentatively assigned a cross-linked double-bridged polymeric structure, and the MMP and IMP complexes a polymeric structure involving four-membered chelate rings and single phosphonato bridges. Finally, the BBP complexes appear to be mixtures of two polymers of the types mentioned above. Further studies aiming at the determination of the conditions favoring the precipitation of polymers of the one or the other type are currently in progress.

(33) J. N. van Niekerk, F. R. L. Schoening, and J. H. Talbot, *Acta Cryst.*, **6**, 720 (1953).

(34) H. Koyama and Y. Sato, *Bull. Chem. Soc., Japan*, **27**, 112 (1954).

(35) V. Giacomini, F. Giordano, L. Randaccio, and A. Ripamonti, *I. Chem. Soc. (A)*, 757 (1968); F. Gemiti, V. Giacomini, and A. Ripamonti, *ibid.*, 763, and references therein.