the corresponding difluoro, dichloro, and dibromo complexes, which are only slightly dissociated in solution and exist exclusively in the *cis* configuration.[2] Steric effects no doubt contribute to the stability of the *trans* isomer in the case of the diiodide. $Ti(acac)_2I_2$ also differs from the other dihalides in its ease of oxidation, which makes it considerably more difficult to handle.

Acknowledgments.—The support of this research by National Science Foundation Grant GP-7851 is gratefully acknowledged. We thank Drs. W. M. Gulick and Michael Eastman for running esr spectra and Professor G. H. Morrison for the emission spectrum. R. C. F. thanks Professor S. F. Mason for his generous hospitality during a period of sabbatical leave.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DREXEL UNIVERSITY, PHILADELPHIA, PENNSYLVANIA 19104

Characterization Studies of Tris(dialkoxyphosphato)- and Tris(alkoxyalkylphosphonato)titanium(III), -vanadium(III), and -chromium(III) Crystalline Polymers

BY C. M. MIKULSKI, N. M. KARAYANNIS, M. J. STROCKO, L. L. PYTLEWSKI, AND M. M. LABES

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Interaction of MCl_3 (M = Ti, V, Cr) with neutral phosphate and phosphonate esters at elevated temperatures leads to the formation of tris(dialkoxyphosphato)- and tris(alkoxyalkylphosphonato)metal(III). These crystalline complexes were characterized by means of spectral, magnetic, and X-ray studies. Solubility characteristics are strongly in favor of polymeric configurations. The polynuclear complexes most probably involve eight-membered phosphato or phosphonato bridges. Linear ν_{POO} *vs.* $\Sigma\sigma$ (Hammett–Kabachnik substituent constant) and V-shaped ν_{M-O} or Dq *vs.* $\Sigma\sigma$ plots were obtained. These trends are discussed in terms of the inductive effects of the alkyl and alkoxy substituents on phosphorus. Electronic spectra of the crystalline polymers demonstrate that each metal ion is under the influence of a distorted octahedral ligand field. Many of the new complexes exhibit subnormal magnetic moments. The possibilities of a superexchange mechanism operating *via* the –O–P–O– bridges and some intermolecular magnetic exchange are discussed.

Introduction

In a series of recent communications, we reported the reactions of diisopropyl methylphosphonate (DIMP) with tri- and tetravalent metal halides.[1-3] Trivalent metal chlorides react with DIMP at elevated temperatures, yielding tris-isopropoxymethylphosphonato complexes ($M(IMP)_3$; M = Al, Ga, In, Sc, Y, Ln, Ti, V, Cr,[1,2] and Fe[4]). Similar products were obtained during reaction of trimethyl phosphate (TMP) with trivalent 3d metal chlorides (*i.e.* tris-dimethoxyphosphato complexes, $M(DMP)_3$; M = Ti, V, Cr).[5] Comparison of the far-ir spectra of the IMP complexes of Sc(III), Y(III), Ln(III), Ga(III), and In(III) shows a general similarity in their patterns.[2] The far-ir spectrum of $Cr(IMP)_3$ is, however, distinctly different from those of the above complexes and has been attributed to π bonding between metal and ligand.[2] Metal to oxygen d_π–p_π back-bonding may occur in transition metal complexes of organophosphoryl compounds,[6] while for $Fe(IMP)_3$ and analogous phosphonatoiron(III) complexes the possibility of metal to phosphorus d_π–d_π back-bonding was discussed.[4] These observations, in combination with the recent interest in inorganic phosphinato polymers[7-9] and our general study of the influence of inductive and steric effects on the properties of metal complexes of organophosphorus compounds,[10] prompted us to undertake characterization studies of phosphato and phosphonato complexes of Ti(III), V(III), and Cr(III), which are herein reported.

Experimental Section

Chemicals.—TMP and tri-*n*-butyl phosphate (TBP) (Aldrich), dimethyl methylphosphonate (DMMP), diethyl ethylphosphonate (DEEP), di-*n*-butyl *n*-butylphosphonate (DBBP) (Mobil Chemical Co.), and DIMP (Edgewood Arsenal, Md.) were utilized as received. No precautions for the removal of traces of water were necessary, as it was found that the same final products are obtained with either anhydrous or hydrated metal chlorides.[1] The purest commercially available salts and solvents were used.

Synthetic Procedure.—The complexes were prepared by methods previously described.[1,5] The syntheses of the Ti(III) complexes were performed in a nitrogen atmosphere, while those of the V(III) and Cr(III) compounds were done in the presence of air.[1] The anhydrous metal chlorides were used as starting materials for the preparation of all the Ti(III) and V(III) com-

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TABLE I

ANALYSES, COLORS, AND TEMPERATURES OF PRECIPITATION OF THE NEW TRIS(DIALKOXYPHOSPHATO)- AND TRIS(ALKOXYALKYLPHOSPHONATO)METAL(III) COMPLEXES[a]

			Analyses, %							
			C		H		P		Metal	
Complex	Color	Temp of ppn, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Ti(MMP)_3$	Purple	100	19.22	19.00	4.84	4.79	24.78	24.13	12.77	12.40
$Ti(EEP)_3$	Light blue	130	31.39	30.96	6.58	6.36	20.23	19.89	10.43	10.83
$Ti(BBP)_3$	Lavender	150	45.94	45.69	8.67	8.63	14.81	14.48	7.63	7.33
$Ti(DBP)_3$	Lavender	144	42.67	42.46	8.06	8.05	13.76	13.56	7.09	7.07
$V(MMP)_3$	Light green	90	19.06	19.20	4.80	4.91	24.58	24.22	13.47	13.57
$V(EEP)_3$	Light yellow-green	145	31.17	31.33	6.54	6.72	20.10	20.33	11.02	10.97
$V(BBP)_3$	Pale green	150	45.72	45.26	8.63	8.49	14.74	15.15	8.08	8.41
$V(DBP)_3$	Pale green	168	42.48	43.03	8.02	8.47	13.69	13.52	7.51	7.66
$Cr(MMP)_3$	Green	165	19.01	18.62	4.79	4.56	24.51	24.47	13.71	13.33
$Cr(EEP)_3$	Light green	125	31.11	30.53	6.53	6.85	20.06	19.72	11.22	10.88
$Cr(BBP)_3$	Light green	175	45.64	45.26	8.62	8.47	14.71	15.08	8.23	8.81
$Cr(DBP)_3$	Light green	170	42.42	41.94	8.01	8.41	13.67	13.84	7.65	8.08

[a] Analyses established that the new complexes are chlorine free.

TABLE II

ν_{POO}, ν_{M-O}, AND FAR-IR LIGAND BANDS IN PHOSPHATO AND PHOSPHONATO COMPLEXES (CM^{-1})[a]

Complex	ν_{POO}	ν_{M-O}	ν_{ligand} (600–300 cm^{-1})
$Ti(MMP)_3$	1700 m, b, 1158 vs, b, 1067 vs	585 m, b, 542 vs, b, 448 vs, 328 vs, 311 vs	499 m, b, 395 sh, 386 s
$Ti(EEP)_3$	1650 m, b, 1144 vs, 1075 vs	564 s, 458 vs, 302 vs, b	510 vs, 485 vs, 420 sh, 412 s, 348 m, b
$Ti(IMP)_3$	1735 m, 1154 s, 1063 vs	545 vs, 435 vs, 290 vs	512 m, 460 m, 410 m, sh, 390 m, sh, 320 m, sh
$Ti(BBP)_3$	1659 w, b, 1132 vs, 1080 vs, sh	573 vs, 447 vs, 325 vs, sh, 296 vs	544 s, sh, 530 sh, 420 vs, 395 sh
$Ti(DMP)_3$	1660 m, 1194 vs, 1090 vs, sh	597 s, 485 vs, 330 vs, 320 sh	570 sh, 512 vs, sh, 435 vs, b, 379 m
$Ti(DBP)_3$	1750 w, b, 1175 vs, 1105 vs	590 s, sh, 465 vs, 325 vs, sh, 300 vs, b	562 s, 540 s, sh, 511 s, 440 vs, b
$V(MMP)_3$	1685 m, 1153 vs, b, 1069 vs	588 s, 552 vs, 455 vs, 330 vs, 314 vs, sh	493 s, 390 s, 300 sh
$V(EEP)_3$	1660 m, b, 1144 vs, 1075 vs	572 vs, 461 vs, 308 vs, b	540 sh, 512 s, 480 sh, 420 s, 349 sh
$V(IMP)_3$	1734 m, 1148 s, 1060 s	555 vs, 440 vs, 299 vs	509 s, 469 s, 415 s, 390 m, sh, 320 m, sh
$V(BBP)_3$	1670 w, b, 1128 vs, 1084 vs, sh	580 vs, 458 vs, 329 vs, sh, 305 vs	557 sh, 539 sh, 430 sh, 395 sh
$V(DMP)_3$	1650 m, b, 1191 vs, 1096 vs	602 vs, 480 vs, 330 vs, 313 vs	565 sh, 528 vs, 439 s, 376 m
$V(DBP)_3$	1750 w, b, 1167 vs, b, 1110 vs	597 s, 470 vs, 328 vs, sh, 311 vs	562 vs, 540 vs, sh, 511 vs, 445 vs, b
$Cr(MMP)_3$	1685 w, b, 1146 vs, sh, 1072 vs	597 s, 562 vs, 468 vs, 318 vs, sh, 308 vs, b	493 s, sh, 402 m, 346 sh
$Cr(EEP)_3$	1660 m, b, 1132 vs, sh, 1060 s	577 vs, 478 vs, 313 vs	512 s, 430 sh, 372 sh, 348 sh, 320 sh
$Cr(IMP)_3$	1732 m, 1135 s, 1073 s	564 vs, 467 vs, b,[b] 306 s, b	505 s, 410 s, 320 sh
$Cr(BBP)_3$	1660 w, b, 1116 vs, 1082 vs, sh	590 vs, 473 vs, 329 vs, sh, 310 vs	565 s, 541 sh, 515 sh, 430 sh, 400 sh
$Cr(DMP)_3$	1650 m, 1185 vs, b, 1095 vs	610 vs, 490 vs, 331 vs, 312 vs	568 m, 502 s, 445 s, 365 s
$Cr(DBP)_3$	1750 w, b, 1159 vs, b, 1100 vs	605 s, 474 vs, 329 vs, 311 vs	560 vs, sh, 539 vs, 515 vs, b, 360 b, sh

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. [b] Overlaps with ligand absorptions.

plexes. Anhydrous $CrCl_3$, however, dissolves only in DIMP and DBBP at elevated temperatures, yielding the corresponding phosphonato complexes. For the preparation of the other phosphonato- and phosphatochromium(III) complexes, hydrated $CrCl_3$ was used as the starting material. Precipitation of the complexes was accompanied by evolution of methyl chloride (DMP, MMP (methoxymethylphosphonato))[5] or a mixture of alkyl chloride, hydrogen chloride, and alkene (EEP (ethoxyethylphosphonato), IMP, BBP (*n*-butoxy-*n*-butylphosphonato), DBP (di-*n*-butoxyphosphato)).[1-3] The formation of HCl and alkene has been attributed to dehydrochlorination of the alkyl chloride in the presence of the complex metal halide residue.[1-3] All the complexes prepared are insoluble in all common organic solvents and water and do not melt or decompose at temperatures up to 300°.[1,2] The DMP[5] and IMP[1] complexes have been reported. Analyses (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.), properties, and temperatures of precipitation for the new complexes reported (*i.e.*, MMP, EEP, BBP, and DBP) are given in Table I.

Spectral, Magnetic, and X-Ray Powder Diffraction Studies.—Ir (Table II) and electronic (Table III) spectra, magnetic moments (Table III), and X-ray powder diffraction patterns (Table IV) of the complexes reported were obtained as described elsewhere.[1,2,11]

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Results and Discussion

Infrared Studies. Nature of the Complexes.—As is the case with the IMP complexes,[1,2] the ir spectra of the phosphonato and phosphato complexes reported are characterized by two strong to very strong bands and one medium to weak band in the 1800–1050-cm^{-1} region (Table II), which are associated with vibrational modes of the POO group.[12,13] Medium-intensity bands at *ca.* 1700 cm^{-1} have been attributed to a combination of vibrational POO modes in acidic organophosphoryl compounds,[12] while two strong bands in the 1300–1050-cm^{-1} region in metal salts or complexes of these compounds were assigned as the asymmetric and symmetric ν_{POO} modes.[13] The latter two bands are well defined in the new complexes and only in the case of the ethyl and *n*-butyl ligands does the lower frequency bond (ν_{POO}, symmetric) overlap partially with the strong ligand absorption at 1100 or 1065 cm^{-1}, respectively.[12] The spectra of the complexes do not show any bands

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Table III
Solid-State Electronic Spectra (Nujol Mull) and Magnetic Moments at 297°K of Phosphato- and Phosphonatometal Complexes

Complex	λ_{max},[a] nm	$10^6\chi_M^{cor}$	μ_{eff}, BM
$Ti(MMP)_3$	<300 s, 540 s, sh, 640 sh	1027	1.57
$Ti(EEP)_3$	<300 vs, 598 sh, 685 sh	1002	1.56
$Ti(IMP)_3$	304 sh, 564 s, 652 sh	985	1.53
$Ti(BBP)_3$	<300 vs, 541 s, 690 sh	1390	1.82
$Ti(DMP)_3$	330 s, 538 s, 695 sh	288	0.83
$Ti(DBP)_3$	295 vs, 541 s, 647 sh	1273	1.75
$V(MMP)_3$	<300 vs, 416 s, sh, 676 m	2448	2.42
$V(EEP)_3$	292 vs, sh, 447 s, 700 m	2455	2.43
$V(IMP)_3$	311 vs, 452 s, 706 ms	2522	2.45
$V(BBP)_3$	<300 vs, 418 s, 688 m	2955	2.66
$V(DMP)_3$	<300 vs, 423 s, 685 m	2438	2.42
$V(DBP)_3$	291 vs, 423 s, 689 m	3294	2.81
$Cr(MMP)_3$	274 s, sh, 454 s, 469 sh, 635 s, 659 s, 688 s	5163	3.50
$Cr(EEP)_3$	<300 vs, 444 s, 471 sh, 631 s, 658 s, 682 sh	5601	3.66
$Cr(IMP)_3$	308 sh, 460 s, 638 s, 661 s, 690 sh	5303	3.56
$Cr(BBP)_3$	276 s, sh, 447 s, 479 sh, 611 s, 640 s, 659 s, 687 s	6247	3.87
$Cr(DMP)_3$	307 s, 424 s, 456 s, 647 s, b, 685 sh	2747	2.56
$Cr(DBP)_3$	268 vs, sh, 455 s, 618 s, 647 s, 682 sh	6298	3.89

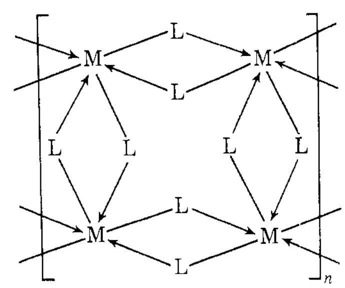
[a] The bands at 260–315 nm are due to ligand absorption.[1]

Table IV
Main Bands in the X-Ray Powder Diffraction Patterns of Phosphato- and Phosphonatometal Complexes (3–22 Å)

Complex	*d* spacings, Å (*I* in parentheses)
$Ti(MMP)_3$	10.16 (45), 9.21 (100), 6.32 (15), 5.24 (45), 4.77 (50), 4.35 (15), 3.70 (8)
$V(MMP)_3$	11.02 (20), 10.04 (100), 5.98 (17), 4.62 (24), 3.94 (38), 3.78 (11), 3.30 (8)
$Cr(MMP)_3$	13.80 (25), 8.84 (100), 5.98 (20), 4.67 (15), 3.97 (18), 3.64 (23), 3.40 (20)
$Ti(EEP)_3$	12.62 (28), 11.18 (100), 6.15 (5), 4.74 (8), 3.93 (14), 3.45 (8)
$V(EEP)_3$	12.62 (25), 11.33 (100), 6.23 (5), 4.72 (8), 3.95 (14), 3.45 (8)
$Cr(EEP)_3$	12.44 (28), 11.02 (100), 6.15 (6), 4.72 (10), 3.93 (12), 3.42 (9)
$Ti(IMP)_3$	11.33 (100), 5.71 (10), 4.44 (12), 3.98 (9), 3.56 (12)
$V(IMP)_3$	11.33 (100), 5.75 (10), 4.46 (13), 4.00 (10), 3.56 (13)
$Cr(IMP)_3$	11.33 (100), 5.75 (12), 4.46 (18), 3.94 (12), 3.56 (14)
$Ti(BBP)_3$	16.05 (36), 14.24 (100), 7.62 (8), 6.37 (4), 4.95 (12), 4.37 (10)
$V(BBP)_3$	16.05 (38), 14.48 (100), 7.55 (8), 6.37 (5), 4.95 (10), 4.37 (11)
$Cr(BBP)_3$	16.05 (35), 14.02 (100), 7.49 (10), 6.37 (9), 5.00 (13), 4.37 (13)
$Ti(DMP)_3$	15.23 (28), 12.80 (45), 10.77 (100), 9.30 (15), 5.15 (27), 4.53 (33), 3.54 (15)
$V(DMP)_3$	12.99 (22), 11.18 (41), 10.04 (100), 5.27 (35), 4.82 (38), 4.44 (26), 3.26 (12)
$Cr(DMP)_3$	16.66 (25), 9.60 (100), 5.68 (30), 4.92 (32), 4.48 (35), 3.32 (15)
$Ti(DBP)_3$	17.66 (35), 15.77 (100), 8.26 (5), 5.24 (8), 4.62 (12), 4.35 (12), 3.97 (8), 3.56 (7)
$V(DBP)_3$	17.66 (37), 15.77 (100), 8.26 (6), 5.24 (10), 4.62 (15), 4.33 (12), 3.97 (10), 3.54 (10)
$Cr(DBP)_3$	17.66 (40), 16.05 (100), 8.18 (5), 5.30 (8), 4.64 (15), 4.31 (13), 3.98 (8), 3.56 (8)

characteristic of –OH[14] or uncoordinated phosphoryl[9,14] groups. The fact that only two ν_{POO} bands are observed in the 1200–1050-cm^{-1} region suggests that the complexes are characterized by equivalent phosphorus–oxygen–metal bonds.[7,15] The presence of chelating phosphonato groups in these compounds is rather improbable. In fact, stereochemical considerations led to the conclusion that metal complexes of R_2POO (R = alkyl, alkoxy, aryl) are more likely to be polymeric, involving bridging –O–P–O– groups.[7–9,15] This prediction has been substantiated by a number of crystal structure determinations.[16,17] Polymers of this type are usually insoluble in most organic solvents,[7–9] while monomeric thiophosphinato or thiophosphato complexes (*e.g.*, $[(C_6H_5)_2P(S)S]_3Al$,[9] $[(C_2H_5O)_2P(S)S]_3V$[18]) and oligomeric phosphonato complexes (*e.g.*, $[Sn(DIMP)(IMP)Cl_3]_4$[3]) dissolve in many organic solvents.

The insolubility of the new complexes in all common organic solvents is, thus, strongly in favor of a polymeric structure for these compounds. On the basis of this property and the above discussion, it may be concluded that the Ti(III), V(III), and Cr(III) complexes contain exclusively phosphonato or phosphato bridges and have most probably a cross-linked double bridged polymeric structure (L = –O–P(R_2)–O–; R = alkyl or alkoxy group)[9]



The far-ir spectra of alkyl alkylphosphonates are generally characterized by two medium broad bands at 570–540 and 500–450 cm^{-1} and a weak absorption at 320–300 cm^{-1}.[19] Dialkyl phosphates exhibit very broad absorptions from 560 to 490 cm^{-1} and very weak bands from 450 to 300 cm^{-1}.[19] Bands at 575–560, 515–502, 472–460, 422–410, and 330–320 cm^{-1} are common in $M(IMP)_3$ complexes and were assigned to primarily ligand vibrations.[2] IMP complexes of nontransition (Ga, In) and rare earth (Sc, Y, Ln) metal ions exhibit three strong bands attributed to primarily ν_{M-O} modes at 538–502, 436–380, and 371–359 cm^{-1}.[2] The corresponding 3d metal complexes exhibit distinctly different far-ir spectra from those of the IMP complexes of the above metal ions. Comparisons of the spectra of some $M(IMP)_3$ complexes, which were

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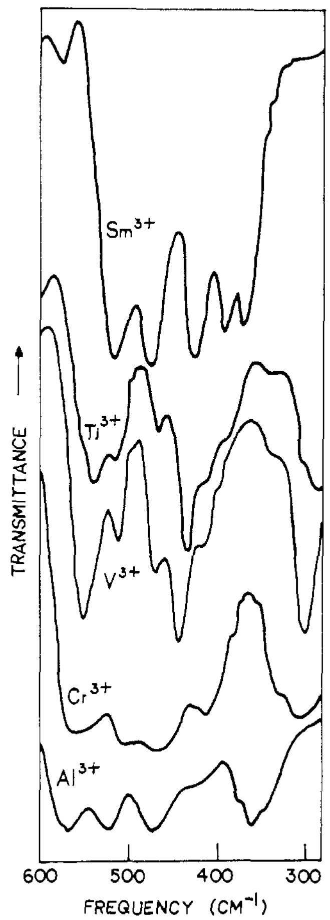

Figure 1.—Far-infrared spectra (600–280 cm^{-1}) of $Sm(IMP)_3$, $Ti(IMP)_3$, $V(IMP)_3$, $Cr(IMP)_3$, and $Al(IMP)_3$.

available,[1,2] are given in Figure 1 (see also ref 2). The metal-sensitive bands at 564–545, 468–448, and 306–290 cm^{-1} in the spectra of the 3d metal–IMP complexes are tentatively assigned as primarily ν_{M-O} modes (Table II, Figure 1). Aluminum-oxygen vibrations in $Al(IMP)_3$ occur at 570, 530, and 362 cm^{-1} (Figure 1). The above assignments of ν_{M-O} are supported by the fact that the frequencies of these bands increase along the series Ti < V < Cr < Al and In < Ga < Al,[2] which is the same order as that observed in oxalato and acetylacetonato complexes.[20] Further, metal-sensitive bands at 600–400 cm^{-1} have been assigned as ν_{M-O} in metal complexes involving -O-P-O- bridges,[15,21] while the data of the present work (Table II, Figure 1) establish the metal sensititivy of the lower frequency (371–290-cm^{-1}) band. Similar considerations led us to the tentative assignments of ν_{M-O} in the other complexes reported which are given in Table II. As shown in this table, splittings of the lower frequency ν_{M-O} band are observed in some cases, while the $M(MMP)_3$ complexes exhibit also splittings of the higher frequency ν_{M-O} absorption.

Successful correlations of the Hammett σ constants, as modified by Kabachnik for organophosphorus compounds,[22] to various properties of these compounds have been reported.[23] Although definitive conclusions would require knowledge concerning the "purity" of the ν_{POO} and ν_{M-O} modes, as well as the corresponding stretching force constants, it was felt that correlation of the above vibrations to the $\Sigma\sigma$ constants[23] would provide some information on the effects of substituents on the properties of the metal complexes. Figure 2 illustrates plots

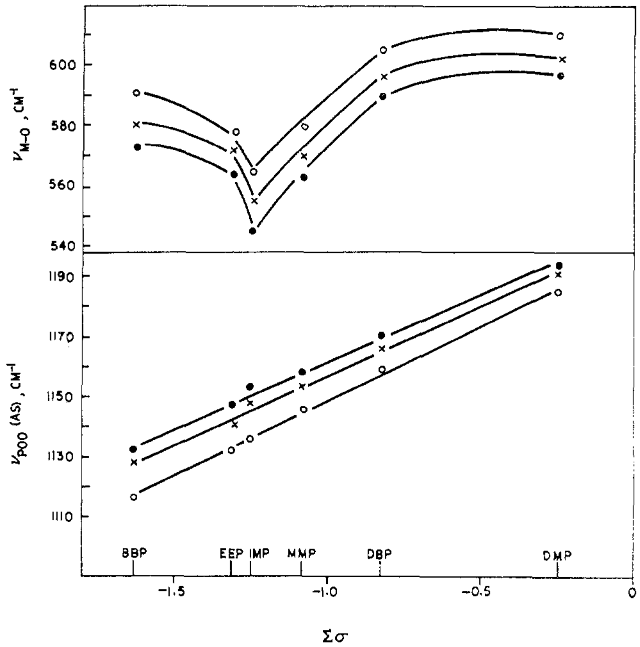

Figure 2.—Plots of $\Sigma\sigma$[22,23] *vs.* ν_{POO} (asymmetric) and the higher frequency ν_{M-O} (610–545 cm^{-1}) (ν_{M-O} values for MMP complexes are the average of the two bands observed in this region): ●, Ti^{3+}; ×, V^{3+}; O, Cr^{3+}.

of ν_{POO} (asymmetric) and the higher frequency ν_{M-O} band *vs.* $\Sigma\sigma$. A linear relationship is observed for the ν_{POO} *vs.* $\Sigma\sigma$ plots. ν_{POO} increases with increasing electron sink properties of the substituents on phosphorus,[24] owing to the increase of the P–O bond order. For a given ligand (*e.g.*, BBP) the ν_{POO} frequencies decrease along the series Ti > V > Cr, while the reverse order is observed for the ν_{M-O} bands. These trends are consistent with increasing M–O bond strength in the order Ti < V < Cr.[15,20] ν_{M-O} *vs.* $\Sigma\sigma$ plots are V shaped (Figure 2). Similar diagrams are obtained by plotting $\Sigma\sigma$ *vs.* the lower frequency ν_{M-O} bands, with the exception of MMP which shows higher ν_{M-O} values than BBP in this region. V-shaped ν_{M-O} *vs.* $\Sigma\sigma$ plots in 4-substituted quinoline N-oxide 3d metal complexes were interpreted in terms of increasing M–O bond order with increasing metal-to-oxygen π bonding for electron-withdrawing substituents and increasing basicity for electron-releasing substituents.[25] The ν_{M-O} *vs.* $\Sigma\sigma$ plots discussed here may merely be reflecting a ligand or metal ion dependent coupling of ν_{M-O} with other vibra-

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tions of the complex.[26] Nevertheless, similar trends are observed in Dq *vs.* $\Sigma\sigma$ plots (*vide infra*). Combination of the information obtained by correlation of $\Sigma\sigma$ to ν_{M-O} and Dq suggests that in the phosphonato complexes the M–O bond strength is influenced by the combined effect of the electron-releasing (alkyl group) and electron-sink (alkoxy group) properties of the two substituents (*i.e.*, basicity *vs.* metal-to-oxygen π-bonding effect, respectively).[25] In the case of the phosphato complexes the effect of π bonding must be predominant, since these ligands contain two alkoxy substituents. The polymeric structure proposed for the complexes reported, which exclusively involves –O–P–O– bridges, rules out the possibility of metal-to-phosphorus d_π–d_π back-bonding.[4] This is also supported by the fact that the ligand bands at 600–400 cm^{-1}, which were attributed to –C–P–O– and –O–P–O– vibrational modes,[15,21] occur at the same frequencies in transition and nontransition metal complexes.

Electronic Spectra, Magnetic Moments, and X-Ray Patterns.—X-Ray patterns (Table IV) of the Ti(III), V(III), and Cr(III) complexes of the same ligand are very similar in the cases of EEP, IMP, BBP, and DBP. Thus, the complexes of the three metal ions with any of these ligands are of about the same structure. In contrast, the three DMP or MMP complexes exhibit distinctly different X-ray patterns and have, obviously, different structures. The electronic spectra of the complexes reported (Table III, Figure 3) clearly indicate that the metal ions in these compounds are under the influence of a distorted octahedral ligand field.[1] In fact, the splittings of the d–d bands in the Cr(III) complexes (Table III, Figure 3) are indicative of the

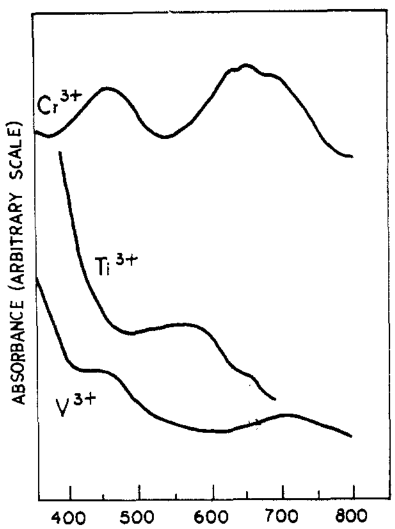

Figure 3.—Solid-state (Nujol mull) electronic spectra of Ti(IMP)$_3$, V(IMP)$_3$, and Cr(IMP)$_3$ (350–800 nm).

presence of lower symmetry components in the ligand field.[27] The shoulder in the d–d band of the Ti(III) complexes is also indicative of a distorted octahedral symmetry.[28] Although splittings[18] are not observed in the bands of the V(III) complexes (mull spectra), a distorted octahedral configuration is assigned to them, on the basis of the X-ray evidence. Approximate calculations of the spectrochemical parameters for a pure O_h ligand field, based on the assignments of the d–d bands as $^2E_g \leftarrow {}^2T_{2g}$ (Ti(III)) and $^3T_{2g}$ (F) $\leftarrow {}^3T_{1g}$ (F) and $^3T_{1g}$ (P) $\leftarrow {}^3T_{1g}$ (F) (V(III))[28] lead to the following results: Dq toward Ti(III), cm^{-1}: MMP, 1852; IMP, 1773; BBP, 1818; DMP, 1859; DBP, 1848 (the band in Ti(EEP)$_3$ appears as a shoulder of an intense charge-transfer band). Dq toward V(III), cm^{-1} (β in parentheses): MMP, 1613 (0.83); EEP, 1539 (0.72); IMP, 1523 (0.71); BBP, 1607 (0.84); DMP, 1589 (0.82); DBP, 1585 (0.82). As already mentioned, Dq *vs.* $\Sigma\sigma$ plots corroborate the trends observed in ν_{M-O} *vs.* $\Sigma\sigma$ plots. Dq values for MMP are higher than those calculated for BBP and in agreement to the plots of $\Sigma\sigma$ *vs.* the lower frequency ν_{M-O} (*vide supra*) rather than the plots of Figure 2. The Dq values of the complexes reported are generally lower than those of the corresponding hexaaquo ions.[1,5]

The magnetic moments (Table III) of the complexes of the methyl-, ethyl- and isopropyl-substituted ligands are generally lower than the spin-only values for d^1–d^3 metal ions. Ti(DMP)$_3$ and Cr(DMP)$_3$ exhibit quite low moments. These magnetic properties and the fact that polymeric tris(dichlorophosphato)iron(III) has a moment of 5.02 BM[29] indicate that subnormal magnetic moments are usual in transition metal polymers of the type $[M(R_2POO)_3]_n$. A general trend of increase of the magnetic moments with increasing bulkiness of the ligand is observed in the new complexes (Table III). Thus, the DBP and BBP complexes have moments close to the spin-only values. The magnetic properties of the complexes reported are the subject of detailed studies recently undertaken by this laboratory. Nevertheless, the available room-temperature data (Table III) and the fact that it was established that the Curie–Weiss law is obeyed ($\theta = -10°$) in the case of $[Fe(O_2PCl_2)_3]_n$[29] allow a preliminary discussion of the possible magnetic interactions.

Müller and Dehnicke rule out a direct intramolecular Fe to Fe magnetic interaction and suggest the possibility of demagnetization by a magnetic exchange mechanism.[29] Direct intramolecular spin–spin interaction may also be excluded in the new complexes.[30] In fact, the crystal structure determination of a Cr(III) double-bridged phosphinato polymer revealed that the Cr–Cr separation is 5.03 Å,[17a] while in triple-bridged Co(II) and Zn(II) analogs the metal–metal separation is 3.55 Å.[17b] In trimeric chromium(III) and iron(III) carboxylates of the type $M_3O(RCO_2)_6(H_2O)_3^+$ subnormal magnetic moments are due to magnetic exchange between the metal ions *via* the oxygen atom of the M_3O group.[30] Superexchange in the present case operating

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via the –O–P–O– bridges is plausible. In fact, an analogous case is that of copper(II) formate tetrahydrate, the subnormal moment of which has been primarily attributed to superexchange through a π pathway set up by using 3d orbitals of the Cu(II) ion and 2pπ orbitals of bridging $HCOO^-$ radicals.[31] Magnetic exchange to a small extent between adjacent polymeric molecules is also possible.[30] Such an interaction would account for the decreased demagnetization with increasing bulkiness of the ligand.

In conclusion a number of Ti(III), V(III), and Cr(III) crystalline complexes of monoacidic phosphates and phosphonates were prepared and characterized. The properties of these compounds are in favor of polymeric configurations, probably involving eight-membered phosphato or phosphonato bridges. The Ti(III), V(III), and Cr(III) complexes of EEP, IMP, BBP, or DBP are almost isostructural, but the MMP and DMP analogs exhibit different X-ray pattens. Apparently in the case of the bulkier ligand complexes the arrangement of the substituent groups in space is the factor determining the stereochemistry of the polymeric molecule as well as that of the ligand-field symmetry of each metal ion. However, in the complexes of the less bulky methyl-substituted ligands the central metal ion influences the degree of distortion from pure O_h symmetry and the overall structure of the crystalline polymers.

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CONTRIBUTION NO. 2520 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Electron-Transfer Reactions between Hexaaquochromium(II) Cation and Chlorodiaquotriamminechromium(III), Chlorotriaquodiamminechromium(III), and Chlorotetraaquoamminechromium(III) Cations[1]

BY THEODORE J. WILLIAMS AND CLIFFORD S. GARNER

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In an attempt to isolate factors contributing to the overall activation energy, particularly nonbridging ligand effects, for electron-transfer reactions between Cr_{aq}^{2+} and Cr(III) complexes of the type $Cr(NH_3)_n(OH_2)_{5-n}X^{2+}$, the kinetic parameters for electron exchange between Cr_{aq}^{2+} and three recently synthesized complexes were measured by spectrophotometrically observing their Cr_{aq}^{2+}-catalyzed ammine aquation in 1.5 *F* $HClO_4$ at 20–30°. These complexes, $Cr(NH_3)_3(OH_2)_2Cl^{2+}$, $Cr(NH_3)_2(OH_2)_3Cl^{2+}$, and $Cr(NH_3)(OH_2)_4Cl^{2+}$, are all thought to have the chloro and an aquo ligand in *trans* positions, and with *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ they give four examples where the only variable may be considered to be a change in ligand field strength in positions *cis* to the chloro ligand. These complexes were all shown to undergo electron transfer by an inner-sphere mechanism (*i.e.*, the chloro ligand is transferred *via* a Cl-bridged activated complex to the oxidized product, $Cr(OH_2)_5Cl^{2+}$). Kinetic parameters were also remeasured for $Cr(NH_3)_5Cl^{2+}$, *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. The activation energies for this series of six complexes are discussed as a function of changing ligand field strength in terms of a simple model for the activated complex. For $Cr(NH_3)_3(OH_2)_2Cl^{2+}$, $Cr(NH_3)_2(OH_2)_3Cl^{2+}$, and $Cr(NH_3)(OH_2)_4Cl^{2+}$, respectively, at 25° values of k from the rate law $R = k[Cr^{2+}][\text{complex}]$ are 2.19 ± 0.25, 6.94 ± 0.80, and 19.1 ± 1.9 M^{-1} sec^{-1}; E_a: 9.9 ± 0.4, 9.1 ± 0.4, 8.4 ± 0.3 kcal mol^{-1}; log PZ(M^{-1} sec^{-1}): 7.59 ± 0.29, 7.50 ± 0.29, 7.44 ± 0.22.

Introduction

The $Cr(OH_2)_6^{2+}$-catalyzed aquation of a number of Cr(III) complexes has been studied, and in every case where a hydroxo or halo ligand is present in the Cr(III) coordination sphere the rate of aquation appears to be controlled by the rate of the electron-transfer reaction between Cr(II) and Cr(III) *via* a bridged activated complex or transition state. Meaningful correlations of reaction rates for earlier data with changes in the nature of the Cr(III) complex are complicated by unknown acid dissociation constants in the case of hydroxo complexes and by the limited data for series of reactions where only one feature of the Cr(III) complex is systematically changed. With the determination of electron-transfer rates between Cr_{aq}^{2+} and $Cr(NH_3)_3(OH_2)_2Cl^{2+}$, $Cr(NH_3)_2(OH_2)_3Cl^{2+}$, and $Cr(NH_3)(OH_2)_4Cl^{2+}$, we have extended the data for complexes of the type $Cr(NH_3)_n(OH_2)_{5-n}Cl^{2+}$ to six examples having their geometry with respect to the chloro ligand known reasonably well. This permits a discussion of the effects of changing the nonbridging ligands in positions *cis* and *trans* to the bridge in the activated complex, as well as of overall effects. The available data have also been treated semiempirically, using the approach of Marcus (*i.e.*, the activation energy is given by the sum

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