

The Acidity and Coordination Properties of Carbamylmethylenephosphonate Ligands: Synthesis and Molecular Structure of Dialkyl N,N-Diethylcarbamylmethylenephosphonate Mercury(II) Nitrate Complexes

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The acidity and coordination properties of carbamylmethylenephosphonate ligands $(RO)_2P(O)CH_2C(O)N(C_2H_5)_2$, $R = C_2H_5$, $i-C_3H_7$, $n-C_4H_9$ and $n-C_6H_{13}$, have been investigated. The reactions of the ligands with Na or NaH in benzene, hexane or THF result in the formation of the anionic bases $(RO)_2P(O)CHC(O)N(C_2H_5)_2^-$ which have been characterized by spectroscopic methods. Dialkyl N,N-diethylcarbamylmethylenephosphonate mercury(II) nitrate complexes, $Hg[(RO)_2P(O)CHC(O)N(C_2H_5)_2]_2(NO_3)_2$, have been prepared from the combination of acidic aqueous $Hg(NO_3)_2$ and the respective neutral phosphonate ligands in hexane or benzene and characterized by infrared and 1H , $^{13}C\{^1H\}$ and ^{31}P NMR spectroscopy. The crystal and molecular structure of diethyl N,N-diethylcarbamylmethylenephosphonate mercury(II) nitrate, $[Hg(DEDECMP-H)NO_3]_2 \cdot C_{10}H_{21}N_2O_7 \cdot PHg$, was determined at $-40^\circ C$ from 5914 independent reflections obtained with a computer automated diffractometer. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.631(3)$ Å, $b = 9.656(3)$ Å, $c = 9.866(3)$ Å, $\alpha = 67.31(3)^\circ$, $\beta = 77.22(3)^\circ$, $\gamma = 77.24(3)^\circ$, $Z = 2$, $V = 816.2(5)$ Å³ and $\rho_{calc} = 2.09$ g cm⁻³. The structure was solved by standard heavy atom methods and blocked least squares refinement of the structure converged with $R_F = 7.6\%$, $R_{wF} = 7.4\%$. The crystals contain dimeric $[Hg(DEDECMP-H)NO_3]_2$ units with each Hg atom σ bonded to the central methine carbon atom of one anionic phosphonate ligand, to two oxygen atoms of one nitrate group and to the carbonyl and phosphoryl oxygen atoms of the phosphonate ligand which is carbon bonded to the second mercury atom. Several important bond distances include the mercury atom–methine carbon atom distance $Hg(1)–C(1)$ 2.110(10) Å, the mercury atom–nitrate oxygen atom distances $Hg(1)–O(5)$ 2.134(11) Å and $Hg(1)–O(6)$ 2.797(12) Å, the phosphoryl dis-

tance $P(1)–O(1)$ 1.460(7) Å and the carbonyl distance $C(2)–O(4)$ 1.269(10) Å. The Hg atom interaction distances with the second (DEDECMP-H) ligand are $Hg(1)–O(1')$ 2.483(6) Å and $Hg(1)–O(4')$ 2.504(6) Å.

Introduction

Carbamylmethylenephosphonate (CMP) ligands, $(RO)_2P(O)CH_2C(O)NR_2$, are used for the extraction of tripositive actinide ions from acidic radioactive waste solutions [1–5]; however, little is known about the general chemistry or the nature of the interaction of the ligands with actinide, lanthanide or transition metal ions. Siddall and coworkers [6–8] first studied the extraction properties and mechanism for CMP ligands and, based upon infrared and distribution coefficient data, it was concluded that tris complexes, ML_3^{3+} , are formed with trivalent lanthanide and actinide ions in acidic aqueous solutions. It was proposed that the metal ion bonded to the CMP ligands with a bidentate coordination mode through the P=O and C=O oxygen atoms. Additional distribution coefficient studies have supported these early conclusions [9, 10]; however, confirmatory evidence for the formation of bidentate chelate complexes has not been obtained.

In the course of developing methods for the purification of dihexyl N,N-diethylcarbamylmethylenephosphonate (DHDECMP), McIsaac and coworkers first noted the formation of an interesting mercury(II) complex $Hg(DHDECMP-H)NO_3^*$ [11]. Sub-

*The notation (CMP-H) or (DRⁿDECMP-H) will be used here to indicate the formation of the anionic, deprotonated ligand species $[(RO)_2P(O)CHC(O)NEt_2]^-$.

sequently, we have studied the acidic character of CMP ligands and the formation of a variety of transition metal complexes of the anionic (CMP-H) species. We report here the synthesis and characterization of the anionic $(\text{RO})_2\text{P}(\text{O})\text{CHC}(\text{O})\text{NEt}_2^-$ ligand and complexes $[\text{Hg}\{(\text{RO})_2\text{P}(\text{O})\text{CHC}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2\}\text{NO}_3]_2$ with $\text{R} = \text{C}_2\text{H}_5$, $i\text{-C}_3\text{H}_7$, C_4H_9 and C_6H_{13} . In addition, the crystal and molecular structure of $[\text{Hg}\{(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CHC}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2\}\text{NO}_3]_2$ is described.

Experimental

General Information

The carbamylmethylenephosphonate ligands were prepared [6] and purified [5] by standard methods. Infrared spectra were recorded on a Perkin Elmer Model 621 infrared spectrometer. The samples were investigated as KBr pellets, and the spectra were calibrated with standard absorptions from a polystyrene film. The NMR spectra were recorded on Varian XL-100 and FT-80 NMR spectrometers using pulse-Fourier transform techniques. For the XL-100, samples were contained in 5 mm tubes rigidly placed in a 12 mm tube containing a deuterated lock sample. For the FT-80, samples were contained in 5 mm tubes with an internal deuterium lock sample. Spectral standards were $(\text{CH}_3)_4\text{Si}$ (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P).

Synthesis of Anionic, Na(CMP-H) Ligands

Typically, 15 mmol of CMP ligand were added under nitrogen to a 100 ml Schlenk flask, the flask was frozen and evacuated, and 30 ml of dry THF were condensed onto the ligand. After allowing the contents to warm to 25 °C the solution was added to a previously evacuated 100 ml Schlenk flask containing an excess of NaH in THF. The resulting mixture was stirred for several hours and the contents were then frozen at -196 °C. The evolved hydrogen was quantitatively recovered with a Toepler pump. The solvent was then removed by vacuum evaporation leaving a white solid which was found to be soluble in benzene, hexane, and THF. When quantitative determination of evolved hydrogen was unnecessary the reaction was performed under a dry nitrogen atmosphere. Benzene, hexane, or THF was condensed onto the CMP ligand in a 100 ml Schlenk flask and excess Na or NaH was added directly to the frozen solution under a brisk nitrogen flow. The flask was connected to a mercury bubbler and the slurry stirred overnight. The excess Na or NaH was then filtered or decanted from the yellow solution and the resulting salt, Na(CMP-H), was recovered by vacuum evaporation of the filtrate.

Synthesis of $[\text{Hg}(\text{CMP-H})\text{NO}_3]_2$ Complexes

Typically, a solution 1 M in $\text{Hg}(\text{NO}_3)_2$ and 1 M in HNO_3 was contacted with a solution of one of the CMP ligands 20% in n-hexane or benzene. The amounts of the solutions were chosen so that there was a 2:1 Hg(II)/CMP ratio. The mixtures were contained in polyethylene bottles, and they were agitated over 24 hr on a mechanical shaker. The resulting white precipitates were collected by filtration and washed with hexane and water. The products are soluble in CH_2Cl_2 , CHCl_3 , and CH_3CN and slightly soluble in $\text{C}_2\text{H}_5\text{OH}$.

Crystal Structure Determination

A single crystal of $[\text{Hg}\{(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CHC}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2\}\text{NO}_3]_2$ **1** was obtained by slow recrystallization from $\text{C}_2\text{H}_5\text{OH}$. A crystal, 0.1 mm \times 0.2 mm \times 0.4 mm was glued to the end of a glass fiber which was attached to a brass pin with clay. The crystal was slowly cooled to -40 °C and centered on a Syntex P3/F automated diffractometer. The determinations of the crystal class, orientation matrix and accurate unit cell parameters were performed in a standard manner [12]. The data were collected at -40 °C by the θ -2 θ technique using Mo- $\text{K}\alpha$ radiation, a scintillation counter and pulse height analyzer. Details of the data collection are presented in Table I. Inspection of the collected data indicated a triclinic space group $\text{P}\bar{1}$. The redundant and equivalent reflection data were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects. Absorption corrections were made empirically based upon ψ scans.

Solution and Refinement of the Structure

All calculations were performed on a Syntex R3/SHELXTL 79 structure determination package [12]. Anomalous dispersion terms were included for all atoms where $Z > 2$. Least squares refinement in this package uses a blocked cascaded algorithm with full matrix blocks of 103 parameters [13]. The function minimized during the least squares refinement* was $\sum w(|F_o| - |F_c|)^2$.

The solution and refinement of the structure of **1** were based on 5914 reflections with $F \geq 2\sigma(F)$. The mercury atom was located using Patterson methods in space group $\text{P}\bar{1}$ and subsequent difference Fourier syntheses revealed the locations of all remaining non-hydrogen atoms. The methylene carbon C(9) was located in a position where the O(3)-C(9) distance was 1.44(5) Å and the C(9)-C(10) distance was 1.29(6) Å. A difference map without C(9) showed three possible sites [C(9), C(9'), C(9'')].

*Discrepancy indices used in the text are defined as follows: $R_F(\%) = [\sum ||F_o| - |F_c||] / \sum |F_o| \times 100$, $R_wF(\%) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \times 100$.

TABLE I. Experimental Data for the X-Ray Diffraction Study of $[\text{Hg}[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CHC}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2][\text{NO}_3]_2$.

Crystal system	triclinic	Z	2
Space group	$\text{P}\bar{1}$	F(000)	492
a , Å	9.631(3)	ρ_{calcd} g cm ⁻³	2.09
b , Å	9.656(3)	μ , cm ⁻¹	97.5
c , Å	9.866(3)	mol. formula:	$\text{C}_{10}\text{H}_{21}\text{N}_2\text{O}_7\text{PHg}$
α , deg	67.31(3)	mol. wt.:	512.9
β , deg	77.22(3)		
γ , deg	77.24(3)		
V , Å ³	816.2		
Diffractometer	Syntex P3/F		
Radiation	MoK α ($\lambda = 0.71069$ Å)		
Temperature	-40 °C (± 2 °C)		
Monochromator	highly oriented graphite crystal		
Reflections measured	$\pm h, \pm k, +l$		
2θ range	1–70°		
Scan type	$\theta' - 2\theta$		
Scan speed	5.86–29.3°/min		
Scan range	from $[2\theta(\text{K}\alpha_1) - 1.0]^\circ$ to $[2\theta(\text{K}\alpha_2) + 1.0]^\circ$		
Reflections observed	7241, 5914 with $F > 2\sigma(F)$		

TABLE II. Fraction Coordinates and Thermal Parameters for $[(\text{DEDECMP-H})\text{HgNO}_3]_2$.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	0.49420(3)	0.01616(4)	1.20288(4)	0.0322(1)	0.0416(2)	0.0255(2)	-0.0135(1)	-0.0046(1)	-0.0078(1)
P	0.4401(2)	-0.2791(3)	1.1613(3)	0.0330(9)	0.0310(10)	0.0416(11)	-0.0090(9)	-0.0011(8)	-0.0024(8)
O(1)	0.5306(7)	-0.2539(8)	1.0166(8)	0.047(3)	0.036(3)	0.047(4)	-0.015(3)	0.003(3)	-0.005(3)
O(2)	0.3132(7)	-0.3698(8)	1.1881(9)	0.048(4)	0.043(4)	0.074(5)	-0.034(4)	-0.009(3)	-0.014(3)
O(3)	0.5232(8)	-0.3729(9)	1.2954(9)	0.052(4)	0.048(4)	0.058(4)	-0.005(4)	-0.017(3)	0.007(3)
O(4)	0.2747(6)	0.0214(8)	0.9636(7)	0.031(3)	0.050(4)	0.034(3)	-0.013(3)	-0.005(2)	-0.004(2)
O(5)	0.6047(9)	0.1553(10)	1.2527(8)	0.063(4)	0.078(6)	0.044(4)	-0.018(4)	-0.010(3)	-0.033(4)
O(6)	0.6460(10)	-0.0531(13)	1.4378(12)	0.056(4)	0.080(7)	0.087(7)	-0.014(6)	-0.026(5)	-0.006(5)
O(7)	0.7100(9)	-0.1581(12)	1.4245(10)	0.067(5)	0.103(7)	0.068(5)	-0.046(5)	-0.024(4)	-0.016(5)
N(1)	0.1089(7)	0.0334(8)	1.1625(8)	0.028(3)	0.033(3)	0.046(4)	-0.016(3)	-0.009(3)	0.004(2)
N(2)	0.6515(10)	-0.0882(13)	1.3782(11)	0.051(5)	0.077(7)	0.050(5)	-0.020(5)	-0.012(4)	-0.014(5)
C(1)	0.3462(8)	-0.1168(10)	1.2052(9)	0.026(3)	0.039(4)	0.036(4)	-0.014(3)	-0.000(2)	-0.005(3)
C(2)	0.2414(7)	-0.0173(9)	1.1037(9)	0.025(3)	0.030(3)	0.037(4)	-0.018(3)	-0.003(2)	-0.002(2)
C(3)	0.0077(10)	0.1416(12)	1.0627(13)	0.039(4)	0.048(5)	0.072(7)	-0.030(5)	-0.019(4)	0.002(4)
C(4)	-0.0029(16)	0.3010(14)	1.0556(19)	0.079(8)	0.048(7)	0.119(12)	-0.042(8)	-0.042(8)	0.014(6)
C(5)	0.0542(10)	-0.0159(13)	1.3226(11)	0.038(4)	0.067(7)	0.046(5)	-0.024(5)	-0.002(4)	0.005(4)
C(6)	-0.0006(13)	-0.1669(17)	1.3752(14)	0.051(6)	0.086(9)	0.061(7)	-0.027(7)	0.020(5)	-0.018(6)
C(7)	0.3403(12)	-0.5092(13)	1.1544(16)	0.054(6)	0.043(5)	0.087(8)	-0.037(6)	0.005(5)	-0.007(4)
C(8)	0.2402(13)	-0.6131(13)	1.2588(15)	0.068(7)	0.040(5)	0.073(8)	-0.014(5)	-0.006(6)	-0.019(5)
C(10)	0.7564(19)	-0.4830(27)	1.3767(24)	0.068(9)	0.134(17)	0.113(14)	-0.003(13)	-0.036(10)	-0.009(10)
Atom	x/a	y/b	z/c	U_{iso}					
C(9)	0.6726(34)	-0.3557(38)	1.3070(37)	0.0659(71)					
C(9')	0.6807(38)	-0.4330(44)	1.2435(42)	0.0598(75)					
C(9'')	0.6418(58)	-0.4863(66)	1.3135(65)	0.0541(111)					
HC(1)	0.2972(78)	-0.1493(88)	1.3093(85)	0.0145(168)					
HC(31)	0.0404	0.1385	0.9645	0.059*					

(continued overleaf)

TABLE II. (continued)

Atom	x/a	y/b	z/c	U _{iso}
HC(32)	-0.0861	0.1113	1.0983	0.059
HC(41)	-0.0694	0.3668	0.9897	0.093
HC(42)	-0.0902	0.3329	1.0195	0.093
HC(43)	-0.0364	0.3057	1.1531	0.093
HC(51)	0.1305	-0.0268	1.3759	0.062
HC(52)	-0.0232	0.0593	1.3416	0.062
HC(61)	-0.0356	-0.1973	1.4798	0.083
HC(62)	0.0765	-0.2424	1.3565	0.083
HC(63)	-0.0772	-0.1563	1.3225	0.083
HC(71)	0.3254	-0.4854	1.0543	0.072
HC(72)	0.4377	-0.5574	1.1653	0.072
HC(81)	0.2566	-0.7046	1.2371	0.075
HC(82)	0.1428	-0.5642	1.2485	0.075
HC(83)	0.2558	-0.6374	1.3488	0.075
HC(91)	0.6646	-0.2852	1.3563	0.080
HC(92)	0.7244	-0.3149	1.2053	0.080
HC(9'1)	0.7263	-0.3521	1.1692	0.075
HC(9'2)	0.6870	-0.5171	1.2183	0.075
HC(9''1)	0.6869	-0.4845	1.2101	0.064
HC(9''2)	0.6102	-0.5830	1.3667	0.064

*The hydrogen atomic parameters, except for HC(1), were not varied in the least squares refinements. Their positions were fixed at idealized coordinates and their U_{iso} were fixed at 1.2 × U_{iso} of their parent carbon atom. The thermal parameters are in the forms $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2(U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*))]$, anisotropic and $\exp[-8\pi^2U_{iso}(\sin^2\theta/\lambda^2)]$, isotropic.

These were each given 1/3 occupancy and the U_{iso} varied with the positional parameters. After 10 cycles of least squares, an average U_{iso} was found and used as a fixed parameter for C(9), C(9'), and C(9''), and the occupancy allowed to vary. Another 10 cycles of least squares resulted in the occupancies: C(9) 0.456, C(9') 0.387, C(9'') 0.237, $\Sigma = 1.075$. The occupancies were normalized to 0.424, 0.360, and 0.216 to give a total occupancy of 1.000 and these were used in the final least squares refinements** [14]. Because of the diffuse thermal parameters associated with C(10) and the disorder of C(9), attempts were made to find other sites for C(10); however, no other discrete electron density could be found.

Refinement of the positional and individual isotropic thermal parameters for the non-hydrogen atoms by means of a least-squares procedure gave convergence at R_F = 7.8%. Individual anisotropic

thermal parameters were then applied to all non-hydrogen atoms (except C(9) as noted above). Refinement by a least-squares procedure using the weighting scheme $w = [\sigma^2(F_o) + gF^2]^{-1}$, where $g = 0.001$, and an isotropic extinction parameter, $x = -0.0010(2)$ ***, gave convergence at R_F = 7.6%. Hydrogen positions were calculated about all carbon atoms except C(10) and idealized with appropriate bond angles and lengths. A final least squares refinement gave discrepancy indices R_F = 7.6% and R_{wF} = 7.4%. A final difference Fourier synthesis revealed the highest peaks (1.7–0.6 e Å⁻³) to be ≤ 1.73 Å away from Hg. The remaining peaks were no greater than 0.5 e Å⁻³. A table of observed and calculated structure factor amplitudes is available [15]. Positional and thermal parameters are collected in Table II.

Results and Discussion

The CMP ligands qualitatively resemble acetylacetone [16] and it might be predicted that the central CH₂ group hydrogen atoms should be acidic. In this study, the acidic character was noted in reac-

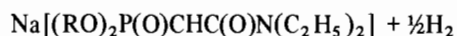
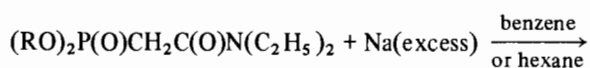
**The standard deviations on the C(9) positions for the disordered model are larger than for the ordered C(9) model; although the anisotropic values for C(9) ordered are quite unreasonable for a single C(9) site. The resultant averaged bond lengths and angles from the disordered C(9) model seem much more in line with the second O(2)–C(7)–C(8) geometry.

*** $F = F_o (1 - (xF_o^2 \times 10^{-4})/\sin \theta)$.

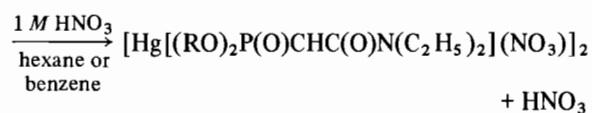
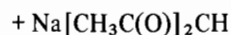
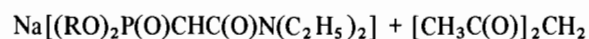
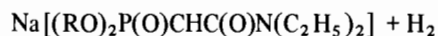
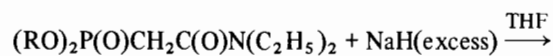
TABLE III. Selected Infrared Frequencies for CMP Ligands and Complexes.

Compound	Frequencies (cm ⁻¹)		
	$\nu(\text{P}=\text{O})$	$\nu(\text{P}=\text{O})$	$\nu(\text{POC})$
(C ₂ H ₅ O) ₂ P(O)CH ₂ C(O)N(C ₂ H ₅) ₂	1651	1264	969
(i-C ₃ H ₇ O) ₂ P(O)CH ₂ C(O)N(C ₂ H ₅) ₂	1639	1247	988
(n-C ₄ H ₉ O) ₂ P(O)CH ₂ C(O)N(C ₂ H ₅) ₂	1648	1262	980
(n-C ₆ H ₁₃ O) ₂ P(O)CH ₂ C(O)N(C ₂ H ₅) ₂	1641	1262	999
Na[(C ₂ H ₅ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂]	1644	1230	1052
Na[(i-C ₃ H ₇ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂]	1638	1228	985
Na[(C ₄ H ₉ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂]	1590	1223	1025
Na[(C ₆ H ₁₃ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂]	1634	1244	1035
Hg[(C ₂ H ₅ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂](NO ₃)	1591	1204	986
Hg[(i-C ₃ H ₇ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂](NO ₃)	1588	1198	986
Hg[(n-C ₄ H ₉ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂](NO ₃)	1610	1221	1020
Hg[(n-C ₆ H ₁₃ O) ₂ P(O)CHC(O)N(C ₂ H ₅) ₂](NO ₃)	1602	1203	993

tions of the CMP ligands with NaH, Na, acetylacetone and Hg(NO₃)₂. The results of these reactions are summarized by the following equations.



R = Et, i-Pr, Bu, Hx



In the first two reactions, the Na(CMP-H) salts were isolated in high yield as sticky, colorless or slightly yellow solids, and in the second reaction the evolved hydrogen was quantitatively recovered. The salts are soluble in THF, hexane and benzene and the anionic ligands are rapidly protonated in water. NMR analysis of the third reaction showed that it lies far to the right, and the reverse reaction does not occur

to a measurable extent. This is consistent with the CMP ligands acting as poorer protic acids than acetylacetone.

The combinations of an aqueous solution 1 M in Hg(NO₃)₂ and 1 M in HNO₃ with benzene or hexane solutions of CMP ligands released acid to the aqueous phase and produced white precipitates at the solvent interface. The solids are soluble in CH₂-Cl₂, CHCl₃ and CH₃CN and slightly soluble in C₆H₆ and C₂H₅OH. Elemental analyses were found to be consistent with the formulations [Hg(CMP-H)NO₃]*; however, molecular weight determinations in benzene solution, M.W._{obs} = 1051, M.W._{calc} for [Hg-(DBDECMP-H)NO₃] = 569, for [Hg(DBDECMP-H)-NO₃]₂ = 1138, suggested that the molecules might be dimeric.

The CMP ligands, the (CMP-H) anions and the mercury complexes, subsequently shown to be [Hg(DEDECMP-H)(NO₃)]₂ 1, [Hg(DiPDECMP-H)(NO₃)]₂ 2, [Hg(DBDECMP-H)(NO₃)]₂ 3 and [Hg(DHDECMP-H)(NO₃)]₂ 4, have been characterized by infrared and ¹H, ¹³C and ³¹P NMR spectroscopy, and these data are summarized in Tables III and IV. Stewart and Siddall [8] have previously used infrared spectra in an attempt to assign structures for lanthanide-CMP complexes. It was proposed that down frequency shifts, $\Delta\nu_{\text{CO}} \sim 30 \text{ cm}^{-1}$ and $\Delta\nu_{\text{PO}} \sim 50 \text{ cm}^{-1}$, indicated the bidentate coordination of the neutral CMP ligand with a lanthanide ion. Similarly, Cotton and Schunn [17] used large infrared ν_{CO} and ν_{PO} shifts to indicate bidentate coordination of [(EtO)₂P(O)]₂CH⁻ and [(EtO)₂-P(O)CHC(O)CH₃]⁻ with Na(I), Zn(II), Co(II) and

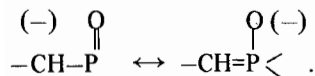
*See footnote on p. 53.

TABLE IV. Selected NMR Spectroscopic Data for CMP Ligands and Complexes.

Compound	δ $^{31}\text{P}^a$	δ $^{13}\text{C}\{^1\text{H}\}$ P(O)CH _x -	δ $^{13}\text{C}\{^1\text{H}\}$ C(O)	δ ^1H P(O)CH _x
DEDECMP	23.7	34.1 $^1J_{\text{PC}} = 132.3$	164.3 $^2J_{\text{PC}} = 5.3$	2.89 $^2J_{\text{PH}} = 21.9$
DiPDECMP	22.0	34.8 $^1J_{\text{PC}} = 133.6$	163.8 $^2J_{\text{PC}} = 5.4$	2.86 $^2J_{\text{PH}} = 22.0$
DBDECMP	24.0	34.0 $^1J_{\text{PC}} = 131.6$	164.4 $^2J_{\text{PC}} = 5.3$	2.83 $^2J_{\text{PH}} = 22.0$
DHDECMP	23.6	34.3 $^1J_{\text{PC}} = 133.9$	163.9 $^2J_{\text{PC}} = 5.4$	2.93 $^2J_{\text{PH}} = 22.0$
Na(DEDECMP-H)	45.3	38.4 $^1J_{\text{PC}} = 222.9$	173.3 $^2J_{\text{PC}} = 10.9$	2.44 $^2J_{\text{PH}} = 13.8$
Na(DiPDECMP-H)	43.6	38.7 $^1J_{\text{PC}} = 222.0$	172.7 $^2J_{\text{PC}} = 15.5$	2.78 $^2J_{\text{PH}} = 14.5$
Na(DBDECMP-H)	43.7	39.01 $^2J_{\text{PC}} = 214.4$	173.5 $^2J_{\text{PC}} = 15.6$	2.28 $^2J_{\text{PH}} = 13.9$
Na(DHDECMP-H)	46.0	38.4 $^2J_{\text{PC}} = 222.9$	173.3 $^2J_{\text{PC}} = 16.1$	2.44 $^2J_{\text{PH}} = 13.2$
Hg(DEDECMP-H) 1	31.0 $^2J_{\text{PHg}} = 444.5$	—	167.2 $^2J_{\text{PC}} = 2.0$	3.66 $^2J_{\text{PH}} = 16.7$
Hg(DiPDECMP-H) 2	27.0 $^2J_{\text{PHg}} = 447.5$	35.0 $^1J_{\text{PC}} = 150.6$	169.5	3.48 $^2J_{\text{PH}} = 16.7$
Hg(DBDECMP-H) 3	31.0 $^2J_{\text{PHg}} = 446.7$	34.8 $^1J_{\text{PC}} = 148.7$	170.4	3.57 $^2J_{\text{PH}} = 15.5$
Hg(DHDECMP-H) 4	31.0 $^2J_{\text{PHg}} = 442.1$	34.5 $^1J_{\text{PC}} = 153.6$	170.5	3.43 $^2J_{\text{PH}} = 16.6$

^a δ ^{31}P standard H_3PO_4 , δ ^{13}C , ^1H standard $(\text{CH}_3)_4\text{Si}$.

Cr(III). In the present study, with the exception of (DBDECMP-H), the shifts in ν_{CO} from the neutral ligands to the anionic forms are relatively small ($\sim 10 \text{ cm}^{-1}$) while the shifts in ν_{PO} are somewhat larger ($20\text{--}40 \text{ cm}^{-1}$). If it is assumed that deprotonation occurs from the central methylene carbon atom, $\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})^-$, the frequency shifts are in agreement with an electron density delocalization toward the phosphoryl oxygen atom as represented by the resonance pair



The formation of the Hg(II) complexes gives rise to larger down frequency shifts from the neutral ligand for both ν_{CO} and ν_{PO} . Similar shifts have been observed in the spectra of solid $\text{Th}(\text{CMP})_2(\text{NO}_3)_4$ [18] and solid $\text{Ln}(\text{CMP})_2(\text{NO}_3)_3$ [8] complexes; therefore, these shifts may be interpreted in favor of a strong bidentate interaction of the carbonyl and phosphoryl oxygen atoms with the Hg(II) atom.

Some of the NMR spectra for the ligands and complexes warrant brief discussion. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the neutral CMP ligands show a singlet in the expected region 22–24 ppm [17, 19]. Related ligands display a resonance in the same region: δ 18.8–23 ppm [17, 20, 21] $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$, δ 20.1 ppm [21] $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{C}_2\text{H}_5$, δ 19.7 ppm [20] $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{N}(\text{CH}_3)_2$, δ 19.5 ppm [21] $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OC}_2\text{H}_5$, δ 19–25 ppm [17, 22] $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$, δ 18 ppm [23] $(\text{EtO})_2\text{P}(\text{O})\text{C}(\text{H})\text{N}(\text{CH}_3)_2\text{P}(\text{O})(\text{OEt})_2$. Upon formation of the Na(CMP-H) salts the singlet is shifted downfield to δ 43–46 ppm. Similar downfield shifts from a neutral ligand counterpart have been reported for $[(\text{EtO})_2\text{P}(\text{O})\text{CHC}(\text{O})\text{CH}_3]$ δ 38 ppm, $[(\text{EtO})_2\text{P}(\text{O})\text{CHP}(\text{O})(\text{OEt})_2^-]$ δ 41.5 ppm and $[(\text{EtO})_2\text{P}(\text{O})\text{C}(\text{NMe}_2)\text{P}(\text{O})(\text{OEt})_2^-]$ δ 33 ppm. The downfield shift is qualitatively consistent with electron delocalization onto the phosphoryl oxygen atom upon deprotonation of the methylene group and the formation of a planar $[\text{P}(\text{O})\text{CHC}(\text{O})^-]$ backbone. The formation of the

Hg(II) complexes, 1–4, results in resonances centered in the region 27–31 ppm. These resonances are intermediate between the neutral ligand and anionic ligand consistent with ligand electron transfer to the Hg ion. These shifts compare favorably with those found for Th(DEDECMP)₂(NO₃)₄ δ 27.7 ppm [18] and La-(DiPDECMP)₂(NO₃)₃ [24] δ 22.4 ppm. The doublet satellite structure for 1–4, $J = 442$ – 448 Hz, results from two bond phosphorus–mercury coupling, and this provides further evidence for the formation of molecular complexes.

The ¹³C{¹H} spectra have been fully assigned; however, only those resonances corresponding to the central methylene or methine carbon atom and the carbonyl group are informative. The carbonyl resonance, δ 162–165 ppm, in the neutral ligands is a doublet resulting from ²J_{CP}, and it appears in the region expected for carbonyl amides [25]. This resonance is shifted downfield to 172–174 ppm upon formation of the sodium salts. This shift is larger than that found in a study of salts of acetylacetone $\Delta\delta$ 1 to 3 ppm [25]. The formation of the Hg(II) complexes, 1–4, results in an intermediate carbonyl shift, 167–171 ppm. The J_{CHg} coupling is not resolved in these spectra. The ¹³C{¹H} spectra for the central methylene carbon atom in the neutral ligands, ¹P(O)CH₂–C(O)–, and the spectra for the resulting methine carbon atom in the anions provide unambiguous evidence for deprotonation at this site. In the neutral ligands, the methylene resonance is a doublet with $J_{\text{PC}} = 131$ – 134 Hz at δ 34–35 ppm. A similar resonance position, δ 42.5 ppm ($J_{\text{PC}} = 127$ Hz), was reported for (EtO)₂P(O)CH₂C(O)CH₃ [26] while a lower field resonance, δ 99.8 ppm was reported for acetylacetone [25, 27]. Upon deprotonation, the doublet shifts to lower field, δ 38–39 ppm, and the coupling is dramatically enlarged, $J_{\text{PC}} = 214$ – 223 Hz. The large coupling constant change is consistent with an sp³ to sp² carbon atom rehybridization [27]. In the Hg(II) complexes the chemical shifts and coupling constants return to values similar to the free ligand, δ 34–35 ppm, $J_{\text{PC}} = 148$ – 154 Hz. For the Th(DiPDECMP)₂(NO₃)₄ complex, the methylene bridge appears at higher field, δ 30.5 ppm.

The ¹H resonance for the central CH₂ group in the neutral ligands appears at 2.8–2.9 ppm. This compares favorably with resonances in (EtO)₂P(O)CH₂–C(O)CH₃ [20] δ 3.1 ppm (²J_{PH} = 22.0 Hz), (EtO)₂–P(O)CH₂C(O)Et [21] δ 3.12 ppm (²J_{PH} = 22.5 Hz), (EtO)₂P(O)CH₂C(O)CH₂NEt₂ [20] δ 3.22 ppm (²J_{PH} = 22.3 Hz), (EtO)₂P(O)CH₂C(O)OH [28] δ 3.0 ppm (²J_{PH} = 21.7 Hz) and [(EtO)₂P(O)]₂–CH₂ [17] δ 2.3 ppm (²J_{PH} = 20.3 Hz). The related resonance in acetylacetone appears at δ 5.1 ppm [27]. Upon formation of the (CMP-H) anions, the methine resonance is shifted upfield to 2.3–2.8 ppm. This shift is similar to shifts found in related anionic

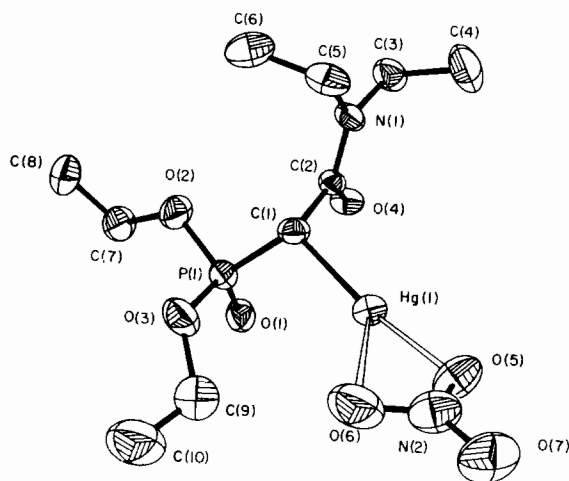


Fig. 1. A view of one-half of the dimeric unit.

ligands except for (EtO)₂P(O)CH₂C(O)CH₃ which displays a downfield shift upon deprotonation [17]. The Hg(II) complexes show sizeable downfield shifts, δ 3.4–3.7 ppm from the free ligand which suggests deshielding of the remaining hydrogen at the bridge position. In the Th(DEDECMP)₂(NO₃)₄ complex, δ 2.54 ppm (²J_{PH} = 19.9 Hz), the methylene hydrogens become slightly shielded relative to the free ligand.

The spectroscopic data clearly indicate that deprotonation of the neutral CMP ligands occurs by loss of a proton from the methylene bridge spanning the carbonyl and phosphoryl groups. In addition, the data are consistent with the formation of Hg(II) complexes in which the Hg atom may bond to the anionic ligand through a Hg–C σ bond at the bridging methine carbon atom and Hg–O bonds at the carbonyl and phosphoryl groups. However, in order to unambiguously assign the solid state structure of these complexes, a single crystal X-ray diffraction analysis of 1 was undertaken.

The results of the X-ray study indicate a dimeric composition: [Hg[(C₂H₅O)₂P(O)CHC(O)N(C₂H₅)₂](NO₃)₂]₂. A view of one-half of the dimeric unit is shown in Fig. 1 and a view of the dimeric unit with the nitrate groups omitted is shown in Fig. 2. The packing of the molecule is illustrated in Fig. 3. Selected interatomic distances and angles are summarized in Table V.

The dimeric molecule possesses C_i– $\bar{1}$ symmetry and the coordination number about each mercury is five made up by the carbon atom of one (DEDECMP-H) ligand, the carbonyl and phosphoryl oxygen atoms of the second (DEDECMP-H) ligand and two oxygen atoms of a coordinated nitrate group. The mercury atom is bonded directly to the central methine carbon atom of the deprotonated (DEDECMP-H) ligand with a Hg–C(1) distance,

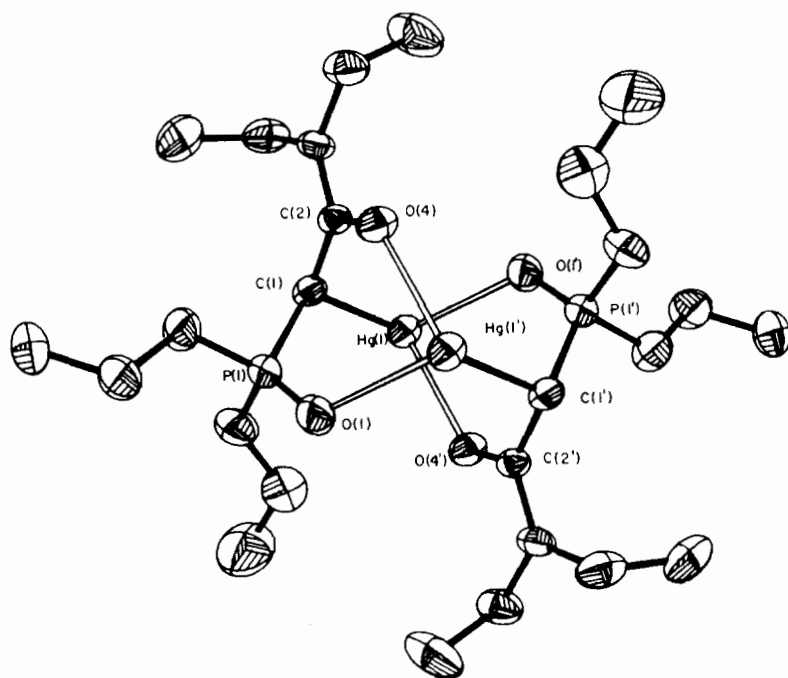


Fig. 2. A view of the dimeric unit.

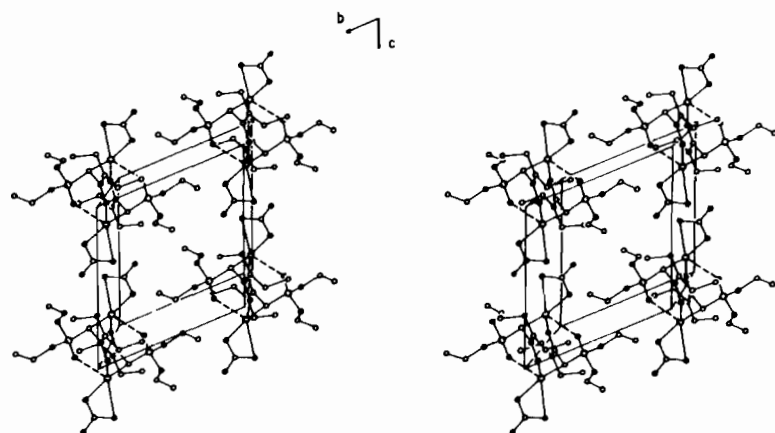


Fig. 3. The packing of the molecule.

2.110(10) Å, which is comparable in magnitude with Hg–C σ bond distances, 1.96–2.30 Å in other organomercury compounds [29–34]. The coordination of the methine carbon atom provides a tetrahedral configuration about C(1). This coordination mode is not entirely unexpected since Hg(II), Pt(II), Au(I), Mn(I) and Rh(I) form methine carbon–metal bonds with acetylacetonate [16].

A comparison of the (DEDECMP-H) ligand structural parameters with parameters obtained for the related diethoxyphosphonylacetylmethane anion (DEPAM) in $\text{Co}_3[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CHC}(\text{O})\text{CH}_3]_6$ [35] is informative. In $\text{Co}_3(\text{DEPAM})_6$, the

DEPAM ligands act both as bidentate chelates, by bonding a cobalt atom with the oxygen atoms of the phosphoryl and carbonyl groups, and as bridging ligands. A complex trimeric array of fused octahedra is formed in which the methine carbon atoms of the six ligands apparently are not involved in the bonding to the Co atoms. Using bond distance comparisons, Cotton and coworkers [17, 35] attempted to analyze the degree of π delocalization in the $\text{O}=\text{P}-\text{C}-\text{C}=\text{O}^-$ chelate fragment. It was suggested that three canonical resonance forms may play a role in bidentate chelate ring formation [35]:

TABLE V. Selected Interatomic Distances (Å) and Angles (Deg) for [(DEDECMP-H)HgNO₃]₂.

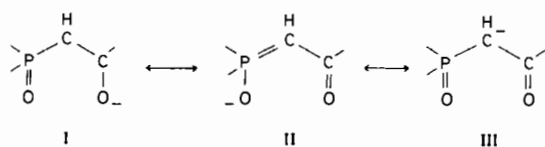
<i>Contact Distances</i>			
Hg(1)–O(5)	2.134(11)	O(2)–C(7)	1.464(17)
Hg(1)–O(6)	2.797(12)	O(3)–C(9)*	1.48(4)
Hg(1)–C(1)	2.110(10)	C(9)–C(10)*	1.39(5)
Hg(1)–O(1')	2.483(6)	C(7)–C(8)	1.479(16)
Hg(1)–O(4')	2.504(6)	N(1)–C(3)	1.481(12)
P(1)–O(1)	1.460(7)	N(1)–C(5)	1.470(12)
P(1)–O(2)	1.575(9)	C(3)–C(4)	1.495(10)
P(1)–O(3)	1.560(8)	C(5)–C(6)	1.517(20)
P(1)–C(1)	1.785(10)	N(2)–O(5)	1.286(13)
C(1)–C(2)	1.490(10)	N(2)–O(7)	1.226(19)
C(1)–H(1)	0.99(7)	N(2)–O(6)	1.267(16)
C(2)–O(4)	1.269(10)		
C(2)–N(1)	1.349(9)		
<i>Non-bonded Distances</i>			
Hg(1)–Hg(1')	4.109(1)	O(1)–O(4)	3.165(10)
Hg(1)–P(1)	3.197(3)	Hg(1)–O(1)	3.648(7)
Hg(1)–O(7)	4.070(10)	Hg(1)–O(4)	3.480(6)
<i>Bond Angles</i>			
O(5)–Hg(1)–C(1)	164.4(3)	C(1)–C(2)–O(4)	121.4(6)
O(5)–Hg(1)–O(6)	49.8(3)	C(1)–C(2)–N(1)	119.1(7)
O(1')–Hg(1)–C(1)	107.0(3)	O(4)–C(2)–N(1)	119.5(7)
O(4')–Hg(1)–C(1)	111.3(3)	C(2)–N(1)–C(5)	124.0(7)
P(1)–C(1)–Hg(1)	110.0(3)	C(2)–N(1)–C(3)	119.6(7)
P(1)–C(1)–C(2)	114.5(7)	C(3)–N(1)–C(5)	116.4(7)
C(2)–C(1)–Hg(1)	108.2(6)	N(1)–C(5)–C(6)	110.7(11)
O(3)–P(1)–O(2)	104.1(4)	N(1)–C(3)–C(4)	112.5(12)
O(3)–P(1)–O(1)	113.8(4)	Hg(1)–O(5)–N(2)	112.6(8)
O(1)–P(1)–O(2)	114.3(5)	O(6)–N(2)–O(5)	115.7(13)
O(1)–P(1)–C(1)	118.0(4)	O(7)–N(2)–O(6)	124.5(11)
O(2)–P(1)–C(1)	101.4(4)	O(7)–N(2)–O(5)	119.4(11)
O(3)–P(1)–C(1)	103.5(5)		
P(1)–O(2)–C(7)	120.3(6)		
O(2)–C(7)–C(8)	109.1(10)		
O3–C(9)–C(10)	116.3(36)*		

*This represents the averaged value.

TABLE VI. Comparison of Estimated and Observed Chelate Ring Dimensions for DEPAM[−] and DEDECMP[−].

Bond	Localized ^a	Delocalized ^a	Co ₃ (DEPAM) ₄	<i>l</i>
PO	1.38–1.56	1.55–1.65	1.464(5)	1.460(7)
PC	1.81	1.72–1.75	1.73(1)	1.785(10)
CC	1.34	1.40	1.36(1)	1.490(10)
CO	1.31	1.29	1.30(1)	1.270(10)
P–OR	1.56–1.64	1.56–1.64	1.56–1.59	1.560(8)–1.575(9)

^aBond lengths estimated from data compiled in several sources: Corbridge, D.E.C., *Topics in Phosphorus Chem.*, 3, 57 (1966); Corbridge, D.E.C., 'The Structural Chemistry of Phosphorus', Elsevier, Amsterdam, 1974.



It would be expected that structure I would most closely represent an electron localized DEPAM^- ion while a delocalized ligand would be described by contributions from each of the three resonance forms. Table VI summarizes estimated bond distances for the idealized electron localized and delocalized structures [30], as well as, measured bond distances for $\text{Co}_3(\text{DEPAM})_6$ [35] and *I*. For $\text{Co}_3(\text{DEPAM})_6$, bond distance comparisons have not permitted an unambiguous assignment of localized or delocalized ligand structure. However, in *I*, it appears that the major contribution to the CMP ligand structure is best represented by an ion similar to III. Both $\text{P}(1)\text{--O}(1)$ and $\text{C}(2)\text{--O}(4)$ bond distances are short indicating significant double bond character in the phosphoryl and carbonyl groups, and both $\text{P}(1)\text{--C}(1)$ and $\text{C}(2)\text{--C}(1)$ bond distances are long indicating little double bond character in these bonds.

The interaction of the Hg atom in one $\text{Hg}(\text{II})$ (DEDECMP-H) unit with the second (DEDECMP-H) anion occurs through Hg–phosphoryl, $\text{Hg}(1)\text{--O}(4')$ 2.504(6) Å, and Hg–carbonyl, $\text{Hg}(1)\text{--O}(1')$ 2.483(6) Å, bonds. The $\text{Hg}(1)\text{--Hg}(1')$ separation in the dimer is 4.109(1) Å and the nonbonded separations, $\text{Hg}(1)\text{--O}(1)$ 3.648(7) Å and $\text{Hg}(1)\text{--O}(4)$ 3.480(6) Å, are well outside the sum of the van der Waals radii, 2.9 Å.

Each Hg atom is also bonded to a nitrate ion in an asymmetric fashion with $\text{Hg}(1)\text{--O}(5)$ 2.134(11) Å, $\text{Hg}(1)\text{--O}(6)$ 2.797(12) Å, $\text{O}(6)\text{--Hg}(1)\text{--O}(5)$ 49.8(3)° and $\text{O}(6)\text{--N}(2)\text{--O}(5)$ 115.7(13)°. The asymmetric bidentate chelation displayed by the NO_3^- ligand is similar to the NO_3^- chelation observed in $[\text{Hg}(\text{PCy}_3)(\text{NO}_3)_2]_2$ in which the Hg–O distances are 2.15(1) Å and 2.73(1) Å [36]. In each case, the long Hg–O distance is well within the range found in other asymmetric bidentate nitrate–metal complexes [37] and it is shorter than the sum of the van der Waals radii, 2.9 Å. The $\text{Hg}(1)\text{--O}(7)$ separation, 4.070(10) Å, is too long to be considered a bonding distance.

Although Hg–C σ bonded coordination is now established for *I*, it is not expected that the trivalent actinides and lanthanides present in radioactive process wastes will be coordinated by CMP ligands in this fashion. It is instead expected that the classically predicted bidentate coordination mode will be found. Indeed structure determinations for $\text{Th}(\text{DEDECMP})_2(\text{NO}_3)_4$ [18] and $\text{Sm}(\text{DiPDECMP})_2(\text{NO}_3)_3$ show only bidentate metal–oxygen binding with the neutral CMP ligands. The present result is important, however, since bimetallic coextraction may be found in solutions which contain $\text{Hg}(\text{II})$ or related soft cations

and harder trivalent metal cations. Work is proceeding which will define such coordination chemistry in mixed metal systems.

Acknowledgements

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Supplementary Material Available

Tables of observed and final calculated structure factors (43 pages) are available.

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