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SYNTHESIS AND CHARACTERIZATION OF MONONUCLEAR AND DINUCLEAR ADDUCTS OF CARBAMYLMETHYLENEPHOSPHONATE WITH URANYL BIS(β-DIKETONATES)

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Abstract—The carbamylmethylenephosphonate adducts of uranyl bis(β-diketonates) of the type $[UO_2(\overline{OO})_2 \cdot CMP]$ and $[\{UO_2(\overline{OO})_2\}_2 \cdot CMP]$ (where $\overline{OO}$ = TTA or DBM; CMP = DBDECMP or DHDECMP) were prepared and characterized by elemental analysis, IR and multinuclear NMR techniques. The spectral studies show that CMP acts as a monodentate ligand in $[UO_2(\overline{OO})_2 \cdot CMP]$ complexes and coordinates through the phosphoryl oxygen atom, whereas it acts as a bridging bidentate ligand in $[\{UO_2(\overline{OO})_2\}_2 \cdot CMP]$ complexes and coordinates through both the carbonyl and phosphoryl oxygen atoms.

The bifunctional carbamylmethylenephosphonates (CMP) and carbamylmethylenephosphine oxides (CMPO) are known to be effective liquid–liquid extractants for the lanthanide and actinide ions from acid media[1–6] and the fundamental coordination chemistry of these ligands with lanthanide and actinide ions are well known.[7–14] It is reported that these ligands act as bidentate chelates in all these complexes. An enhancement in the extraction is noticed when a mixture of β-diketone and CMP or CMPO are used.[15–17] However, there is a paucity of literature on the isolation and characterization of the species responsible for the synergism. Since the coordination number of most of the uranyl bis(β-diketonates) and neutral ligand adducts is invariably seven, it is expected that the CMP or CMPO ligand can form either mononuclear (coordinating through either P=O or C=O) or dinuclear complexes (coordinating through both P=O and C=O). As part of our work on the coordination complexes of actinides, the dinuclear complexes of the uranyl ion in which the CMP acts as a bridging bidentate ligand are presented here.

EXPERIMENTAL

The chemicals uranyl nitrate hexahydrate $[UO_2(NO_3)_2] \cdot 6H_2O$ (BDH, U.K.), thenoyltrifluoroacetone (HTTA, E. Merck), dibenzoylmethane (HDBM, Fluka), di-n-butyl(N,N-diethylcarbamyl)-methylenephosphonate (DBDECMP) and di-n-hexyl(N,N-diethylcarbamyl)methylenephosphonate (DHDECMP, Columbia Organic Chemical Co. Inc., Camden, U.S.A.) were obtained from commercial sources. The CMP ligands were purified according to the reported method prior to use.[18] The complexes $[UO_2(\overline{OO})_2] \cdot 2H_2O$ were prepared from $[UO_2(NO_3)_2] \cdot 6H_2O$ by the reported method.[19] The carbon and hydrogen analyses were performed by the Analytical Chemistry Division of this centre. The IR spectra were recorded on a Philips (PU9510) instrument using KBr discs (4000–400 cm^{-1}) and the samples were mounted as Nujol mulls. The ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Varian VXR-300S machine

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Abbreviations: TTA = thenoyltrifluoroacetonate ion $[C_4H_3SCOCHCOCF_3]^-$; DBM = dibenzoylmethanate ion $[C_6H_5COCHCOC_6H_5]^-$; DBDECMP = di-n-butyl(N,N - diethylcarbamyl)methylenephosphonate $[(C_4H_9O)_2P(O)CH_2C(O)N(C_2H_5)_2]$; DHDECMP = di-n - hexyl(N,N - diethylcarbamyl)methylenephosphonate $[(C_6H_{13}O)_2P(O)CH_2C(O)N(C_2H_5)_2]$.

operating at 300, 75.4, 282 and 121 MHz, respectively. The chemical shifts were relative to internal TMS (^{1}H and ^{13}C), external $CFCl_3$ (^{19}F) and external 85% H_3PO_4 (^{31}P) peaks.

Preparation of $[UO_2(TTA)_2]\cdot CMP$

DBDECMP (123 mg, 0.40 mmol) was added to a hot chloroform solution (40 cm^3) of $[UO_2(TTA)_2]\cdot 2H_2O$ (300 mg, 0.40 mmol) and refluxed for 30 min. The solvent was evaporated *in vacuo*, and the residue was extracted with chloroform and filtered. To the filtrate was added hexane (3 cm^3) and set aside for crystallization. The solid obtained was filtered, washed with a little hexane and dried. The complex $[UO_2(DMB)_2]\cdot$DBDECMP was obtained as a paste.

Preparation of $[\{UO_2(DBM)_2\}_2]\cdot$DBDECMP

DBDECMP (62 mg, 0.20 mmol) was added to a hot chloroform solution of $[UO_2(DBM)_2]\cdot 2H_2O$ (302 mg, 0.4 mmol), and refluxed for 30 min. The solvent was removed *in vacuo*, and the residue was extracted with chloroform and filtered. To the filtrate was added hexane (5 cm^3) and set aside for crystallization. The orange-coloured crystals obtained were removed by filtration and washed with hexane and dried.

The other complexes were prepared similarly and the pertinent data are given in Table 1.

RESULTS AND DISCUSSION

The reaction of carbamylmethylenephosphonates (CMP) with one or two equivalents of uranyl bis(β-diketonates) $[UO_2(\overline{OO})_2]\cdot 2H_2O$ in chloroform gave the products uranyl bis(β-diketonato)carbamylmethylenephosphonate $[UO_2(\overline{OO})_2]\cdot$CMP and di-{uranyl bis($\beta$-diketonato)} carbamylmethylenephosphonate $[\{UO_2(\overline{OO})_2\}_2]\cdot$CMP. The IR spectra of 1 : 1 complexes (Table 2) show that the CMP ligand is coordinating only through the phosphoryl oxygen atom (P=O) to the metal ion, whereas in the 1 : 2 complexes it is coordinating through both the phosphoryl (P=O) and carbonyl oxygen (C=O) atoms to the metal ion. The observed frequency differences $\Delta\nu_{co}$ and $\Delta\nu_{po}$ ($\Delta\nu = \nu_{\text{free ligand}} - \nu_{\text{complex}}$) agree well with the structurally characterized complexes[7–14] in which the CMP ligand is coordinating through both P=O and C=O groups (ν_{co}, ν_{po} for the free ligands are 1645 and 1250 cm^{-1}, respectively). This is further supported by the ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectral studies. The ^{31}P{^{1}H} NMR of the complexes (both 1 : 1 and 1 : 2) show that the phosphorus atom of the phosphoryl group is deshielded relative to the free ligands (Table 2) (δ_{po} for free ligand DBDECMP is 22.06 ppm and DHDECMP is 22.08 ppm), indicating that the ligand is coordinating through the P=O groups to the metal in all the complexes. The ^{13}C{^{1}H} NMR of the 1 : 1 complexes show that there is no change in the carbonyl carbon's frequency compared with that of the free ligands (δ_{co} for free ligand DBDECMP is 163.7 ppm), indicating that the carbonyl oxygen is not coordinated to the metal ion. The spectra of the 1 : 2 complexes show that the carbonyl carbon is deshielded about 6.6 ppm relative to the free ligand, indicating that the C=O group is coordinated to the metal ion.

The coordination of both the P=O and C=O

Table 1. Analytical data for the complexes $[UO_2(\overline{OO})_2]\cdot$CMP and $[\{UO_2(\overline{OO})_2\}_2]\cdot$CMP

Complexes	Solvents of crystallization	M. pt (°C)	Analysis (%) Found/(Calc.) C	H
$[UO_2(TTA)_2]\cdot$DBDECMP	$CHCl_3$/hexane	120	35.1 (35.3)	3.6 (3.7)
$[UO_2(DBM)_2]\cdot$DBDECMP	(Paste)	—	52.0 (51.6)	5.4 (5.1)
$[\{UO_2(TTA)_2\}_2]\cdot$DBDECMP	$CHCl_3$/dodecane	165	31.6 (31.9)	3.7 (2.7)
$[\{UO_2(DBM)_2\}_2]\cdot$DBDECMP	$CHCl_3$/dodecane	95	50.9 (51.1)	4.2 (4.3)
$[\{UO_2(TTA)_2\}_2]\cdot$DHDECMP	$CHCl_3$/hexane	140	33.8 (33.6)	2.9 (3.0)
$[\{UO_2(DBM)_2\}_2]\cdot$DHDECMP	$CHCl_3$/hexane	145	52.4 (52.2)	4.7 (4.6)

Table 2. The IR and NMR spectral data for the complexes $[UO_2(\overline{OO})_2]\cdot CMP$ and $[\{UO_2(\overline{OO})_2\}_2]\cdot CMP$

Complexes	IR (ν in cm^{-1})	^{31}P NMR (δ in ppm)	^{19}F NMR (δ in ppm)	^1H NMR (δ in ppm)	^{13}C NMR (δ in ppm)
$[UO_2(TTA)_2]\cdot DBDECMP$	1650–1580 [CO{CMP}, CO··M{TTA}]; 1190 [PO]; 930 [O=U=O]	28.12	−74.77	8.2 (b), 7.29 (t), 4 Hz), 7.8–7.84 (m) [C_4H_3S]; 6.81 [CCH_2C]; 4.47–4.10 (b) [NCH_2, $POCH_2$]; 3.3–3.7 (b) [PCH_2]; 1.1–1.67 (m) [CH_2{Bu}, NCH_3]; 0.87 (t, 7.2 Hz) [CH_3{Bu}]	12.57 [CH_3 {Bu}]; 13.37, 13.79 [N—CH_3]; 18.42 [$OCCC^a$]; 32.1[OCC^a]; 32.2[PCH_2, $^1J\{PC\}$ = 140 Hz]: 43.5, 41.2[NCH_2]; 68.6[POC, $^2J\{PC\}$ = 7.5 Hz]; 95.9[OCC^aCO]; 120.6 [CF_3, q, $^1J\{CF\}$ = 286 Hz]; 128.7, 132.9, 134.7 143.7 [C_4H_3S]; 163.7 [CO, CMP]: 174.3 [OC^a CF_3, $^2J\{CF\}$ = 41 Hz]; 185 [C_4H_3S—C^aO]
$[\{UO_2(TTA)_2\}_2]\cdot DBDECMP$	1610 [CO{CMP}]; 1590 [CO··M{TTA}]; 1190 [PO]; 930 [O=U=O]	27.12	−74.81	8.28 (d, 4 Hz), 7.8 (t, 5 Hz), 7.3 (m) [C_4H_3S]; 6.83, 6.80 [CCH_2C]; 4.45 (dt $^3J\{HH\}$ = 7 Hz, $^3J\{PH\}$ = 30 Hz) [$POCH_2$]; 4.1, 4.05 [NCH_2]; 3.77 ($^2J\{PH\}$ = 30 Hz) [PCH_2]; 0.9–1, 1.15–1.35, 1.5–1.64 (m) [CH_2{Bu}, NCH_3}]; 0.73 (t, 7 Hz) [CH_3 {Bu}]	12.4 [CH_3{Bu}]; 13.3 [N—CH_3]; 18.23 [$OCCC^a$]; 31.9 [d, $^3J\{PC\}$ = 6 Hz, OCC^a]; 32.3 [d, $^1J\{PC\}$ = 137 Hz, PCH_2]; 44.7, 42.8 [NCH_2]; 69.4 [d, $^2J\{PC\}$ = 7.5 Hz, POC]; 96.1 [OC—C^a—CO]; 120.6 [q, $^1J\{CF\}$ = 284 Hz, CF_3]; 128.7, 133.1, 134.8, 143.7 [C_4H_3S]; 170.3 [CO, CMP]; 172.7 [q, $^2J\{CF\}$ = 32 Hz, OC^a CF_3]; 186.1 [C_4H_3S —C^aO]
$[UO_2(DBM)_2]\cdot DBDECMP$	1645 [CO{CMP}]; 1590 [CO··M{DBM}]; 1190 [PO]; 915 [O=U=O]	27.2	—	7.4–7.7 (m) [C_6H_5]; 7.2 [CCH_2C]; 4.5 −4.2 (b) [NCH_2, $POCH_2$]; 3.31 (d, $^2J\{PH\}$ = 40 Hz) [PCH_2]; 1.22–176 (m) [NCH_3, CH_2 {Bu}]; 1.04 (t, 7.3 Hz) [NCH_3]; 0.80 (t, 7.3 Hz) [CH_3{Bu}]	12.6 [CH_3, {Bu}]; 13.37, 13.79 [NCH_3], 18.4 [$OCCC^a$]; 32.1 [d, $^3J\{PC\}$ = 7 Hz, $POCC^a$]; 32.3 [d, $^1J\{PC\}$ = 137 Hz, PCH_2]; 41.0, 43.6 [NCH_2]; 68.0 [d, $^2J\{PC\}$ = 7.5 Hz, POC]; 97.6 [OC—C^a—CO]; 128.1, 128.3, 131.1, 140.1 [C_6H_5]; 163.7 [CO, CMP]; 188.0 [CO, DBM]

Table 2. (*Continued*)

Complexes	IR (ν in cm^{-1})	^{31}P NMR (δ in ppm)	^{19}F NMR (δ in ppm)	^{1}H NMR (δ in ppm)	^{13}C NMR (δ in ppm)
$[\{UO_2(DBM)_2\}_2]\cdot$DBDECMP	1610 [CO{CMP}]; 1590 [CO··M{DBM}]; 1180 [PO]; 910 [O=U=O]	27.8	—	8.4 (b), 7.4–7.9 (b) [C_6H_5]; 7.20 [CCH_2C]; 4.33 (dt, $^3J\{HH\} = 6.5$ Hz, $^3J\{PH\} = 21$ Hz) [$POCH_2$]; 4.1, 4.05 [NCH_2]; 3.47 (d, $^2J\{PH\} = 79$ Hz) [PCH_2]; 1.25–1.46 (m) [$CH_2\{Bu\}$, NCH_3]; 1.06 (t, $^3J\{HH\} = 7.3$ Hz) [NCH_3]; 0.65 (t, $^3J\{HH\} = 7.6$ Hz) [$CH_3\{Bu\}$]	12.5 [N—CH_3]; 13.4 [$CH_3\{Bu\}$]; 18.3 [OCCC^a]; 31.9 (d, $^3J\{PC\} = 6.5$ Hz, POCC^a); 32.4 [d, $^1J\{PC\} = 140$ Hz]; 42.1, 44.1 [NCH_2]; 68.8 (d, $^2J\{PC\} = 7.5$ Hz, POC); 96.0 [OC—C^a—CO]; 128.1, 128.4, 131.6, 140.1 [C_6H_5]; 169 [CO, CMP]; 188.0 [CO, DBM]
$[\{UO_2(TTA)_2\}_2]\cdot$DHDECMP	1610 [CO{CMP}]; 1590 [CO··M{TTA}]; 1190 [PO]; 930 [O=U=O]	26.93	−74.80	8.27 (d, 4 Hz), 7.7 (m), 7.3 (d, 4 Hz) [C_4H_3S]; 6.83, 6.80 [CCH_2C]; 4.5–4.2 (m) [NCH_2, $POCH_2$]; 3.79 (d, $^2J\{PH\} = 36$ Hz) [PCH_2]; 1.1–1.8 (m) [$CH_2\{Bu\}$, NCH_3]; 0.85 (t, $^3J\{HH\} = 6$ Hz) [NCH_3]; 0.74 (t, $^3J\{HH\} = 7.3$ Hz) [$CH_3\{Hexyl\}$]	—
$[\{UO_2(DBM)_2\}_2]\cdot$DHDECMP	1610 [CO{CMP}]; 1590 [CO··M{DBM}]; 1192 [PO]; 910 [O=U=O]	27.72	—	8.4–8.0, 7.4–7.9 (m) [C_6H_5]; 7.20 [CCH_2C]; 4.34 (dt, $^3J\{HH\} = 6$ Hz, $^3J\{PH\} = 25$ Hz) [$POCH_2$]; 4.04, 4.13 [NCH_2]; 3.47 (d, $^2J\{PH\} = 75$ Hz) [PCH_2]; 0.8–1.8 (m) [NCH_3, $CH_2\{hexyl\}$]; 0.72 (t, $^3J\{HH\} = 7$ Hz [$CH_3\{hexyl\}$]	

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[a] Resonance for that particular carbon atom.

groups to the same metal ion is completely ruled out, since the coordination number of most of the uranyl bis(β-diketonates) and neutral ligand (phosphine oxide, sulphoxide, ketones, THF, etc)[20–22] adducts is normally seven. If such coordination were possible then it should have been shown in the 1 : 1 complexes. These studies suggest clearly that the P=O and C=O groups are coordinated to two different metal ions in the 1 : 2 complexes. The dimeric nature of the 1 : 2 complexes was confirmed by the Osmometric molecular-weight determination (molecular weight calc.: for $[\{UO_2(TTA)_2\}_2] \cdot$ DBDECMP and $[\{UO_2(DBM)_2\}_2] \cdot$ DBDECMP are 1731 and 1739, respectively; Found: 1678 and 1802, respectively).

The ^1H NMR of all the complexes gave the expected peaks and multiplicity. The CMP ligand protons —CH_2—, $POCH_2$ and NCH_2 were deshielded in the complexes (Table 2) relative to those of the free ligands {for the free ligand δ 3.02 [^2J(PH) = 25 Hz] for P—CH_2—; δ 3.42 [^3J(PH) = 21, ^3J(HH) = 6 Hz] for —CH_2O—P; δ 4.1 [^3J(HH) = 6 Hz] for NCH_2}, indicating that there is an electron-density transfer from ligand to metal on complexation. The methylene proton of the β-diketonate ligand gave only one peak for both 1 : 1 and 1 : 2 complexes when $\overline{OO}$ = DBM, whereas it gave one signal for the 1 : 1 complex and two signals for the 1 : 2 complexes when the $\overline{OO}$ = TTA. This shows that the 1 : 1 complexes exclusively exist in only one isomeric form. The presence of two peaks for the methylene proton for the 1 : 2 complex show the presence of either two possible isomers or two different β-diketonate rings. The first option is ruled out because if there are two possible isomers then it should have been seen in the 1 : 1 complex.

The $^{19}F\{^1H\}$ NMR of the complex $[UO_2(TTA)_2] \cdot$ DBDECMP showed only one peak at δ -74.77 ppm, supporting the view that the 1 : 1 complex exclusively exists in only one isomeric form. The 1 : 2 complexes $[\{UO_2(TTA)_2\}] \cdot$ DBDECMP and $[\{UO_2(TTA)_2\}_2] \cdot$ DBDECMP showed only one broad peak at δ -74.81 and -74.80 ppm, respectively, instead of two peaks as observed in the ^1H NMR spectra. This may be due to the line broadening and hence the two uranyl TTA parts attached to the P=O and C=O group could not be resolved.

CONCLUSION

The 1 : 1 reaction of CMP ligands with uranyl bis(β-diketonates) gives the mononuclear complex in which the ligand acts as a monodentate ligand and coordinates through the phosphoryl oxygen atom. The 1 : 2 reaction gives the dinuclear complex in which there is a bridging bidentate ligand and coordinates through both the carbonyl and phosphoryl oxygen atoms.

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REFERENCES

1. W. W. Schulz and L. D. McIsaac, *Transplutonium Elements* (Edited by W. Muller and R. Lindner), p. 433. North-Holland, Amsterdam (1976).
2. W. W. Schulz and J. D. Navaratil, *Recent Developments in Separation Science* (Edited by N. N. Li), Vol. 7, p. 31. CRC Press, Boca Raton, Florida (1982).
3. E. P. Horwitz, H. Diamond and D. G. Kalina, *Plutonium Chemistry*, ACS. Symp. ser. vol. 216, p. 433 (1983).
4. E. P. Horwitz and D. G. Kalina, *Solv. Ext. Ion Exch.* 1984, **2**, 179.
5. (a) H. Petrzilova, J. Binka and L. Kuca, *J. Radioanal. Chem.* 1979, **51**, 107; (b) J. N. Mathur, M. S. Murali and P. R. Natarajan, *J. Radioanal. Nucl. Chem. Lett.* 1991, **155**, 195.
6. (a) E. P. Horwitz, D. G. Kalina, H. Diamond, G. F. Vandegrift and W. W. Shulz, *Solv. Extr. Ion Exch.* 1985, **3**, 75; (b) J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka and A. Banerji, *Talanta* 1992, **39**, 493.
7. S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem.* 1982, **21**, 261.
8. S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta* 1982, **61**, 155.
9. S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chem.* 1983, **22**, 286.
10. S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta* 1984, **84**, 221.
11. L. J. Caudle, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta* 1985, **110**, 91.
12. D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chem.* 1985, **24**, 4626.
13. L. J. Caudle, E. N. Duelser and R. T. Paine, *Inorg. Chem.* 1985, **24**, 4441.
14. S. Karthikeyan, R. T. Paine and R. R. Rayan, *Inorg. Chim. Acta* 1988, **144**, 135.
15. D. J. Pruett, M. C. Clark and D. D. Ensor, *Sep. Sci. Technol.* 1990, **25**, 1777.
16. S. Umetani and H. Freiser, *Inorg. Chem.* 1987, **26**, 3179.
17. V. B. Sagar and K. V. Chetty, *Radio. Chim. Acta* 1995, **68**, 69.
18. W. W. Schulz and L. D. McIssac, Report ARH-SA-263 (1977).

19. K. M. Abubacker and N. S. K. Prasad, *J. Inorg. Nucl. Chem.* 1961, **16**, 296.
20. (a) J. C. Taylor and A. B. Waugh, *J. Chem. Soc., Dalton. Trans.* 1977, 1636; (b) T. H. Lu, T. J. Lee, T. Y. Lee and C. Wong, *Inorg. Nucl. Chem. Lett.* 1977, **13**, 363.
21. G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. J. Jacobson and J. C. Scanlon, *Inorg. Chem.* 1980, **19**, 1340.
22. S. Kannan, M. R. A. Pillai, D. D. Sood, P. A. Droage and C. L. Barnes, *Polyhedron* 1995, to be published.