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Spectroscopic and crystal structure data of the alkali-, thallium (I) and onic-salts of dimethyl-*N*-trichloracetylamidophosphate

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Abstract

Alkali-, thallium (I) and onic-salts of dimethyl-*N*-trichloracetylamidophosphate [HL] were synthesized from non-aqueous solutions and characterized by means of X-ray diffraction, IR and ^{1}H NMR spectroscopy. An ionic type of metal–ligand interaction was determined in Na[L] (**1**), Rb[L] (**2**) and Tl[L] (**3**). Several compounds containing the tetraphenylphosphonium cation, such as PPh_4[L] (**4**), $(PPh_4)_2[L]Br \cdot H_2O$ (**5**) and $(PPh_4)_2[Na_4L_6]$ (**6**), were obtained by an exchange reaction between PPh_4Br and (**1**) in different molar ratios. Compound **6** may be considered as the first example of an anionic complex of an alkali element in the coordination chemistry of carbacylamidophosphates. Synthesis and investigation of $[SbPh_4L]$ (**7**) allowed the determination of the preferable donor center of the L^- ligand (the oxygen atom of the phosphoryl group).

Keywords: Carbacylamidophosphates; Phosphorylic ligands; X-ray diffraction

1. Introduction

Recently, the coordination chemistry of polyfunctional phosphorus compounds has been expanded. The research interest concerning urea phosphine derivates of the type $[Ar_2PNHC(E)NHPAr_2]$ (E = O, S, Se) has studied them as potential chelates to a range of late transition metals through both phosphorous and chalcogen donor atoms [1–3]. On the other hand, carbacylamidophosphates containing the oxidized structural frame [P(O)NHC(E)] (E = O) of the above compounds have been known for some considerable time [4]. There has recently been a resurgence of interest in their coordination chemistry as a consequence of the steric control that this ligand system may impart compared to, for example, β-diketonates. The especially interesting feature of carbacylamidophosphate ligands was the bidentate or μ^2-bidentate chelate character of coordination to the central atom [5]. However, in our previous studies [6,7], it was determined that the protonated form of the ligand has never taken part in coordination. In this contribution, we report the molecular structure of some alkali-metal, thallium (I), onic-salts and a tetraphenylstibonium complex formed with dimethyl-*N*-trichloracetylamidophosphate [HL].

2. Experimental

2.1. Synthesis

All the chemicals were commercial products of reagent grade, used without further purification. The ligand HL and its deuterium analogue D[L-d_6] were

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prepared by reacting phosphorus pentachloride with trichloroacetamide, followed by addition of methanol in accordance with the literature method [8].

Metal salts Na[L] (**1**), Rb[L] (**2**), Tl[L] (**3**) were synthesized in aqueous-alcoholic media.

2.1.1. *Na[L] (**1**)*

Sodium carbonate (0.106 g, 1 mmol) was added in several portions to a solution of H[L] (0.541 g, 2 mmol) in 10 ml of aqueous 2-propanol (1:3). The solution was stirred with heating until total dissolution of Na_2CO_3 was observed. The solvent was removed in vacuo and the colorless product recrystallized from isopropanol. Yield: 0.573 g, 98%. *Anal.* Calc. for $C_4H_6Cl_3NNaO_4P$: C, 16.43; H, 2.07; N, 4.79. Found: C, 16.47; H, 2.1; N, 4.67%. ^{1}H NMR (D_2O): 3.55 d [6H, $^3J_{PH}$ 11.2 Hz, $PO(OCH_3)_2$]; ^{31}P NMR (D_2O): 16.09 h [$^3J_{PH}$ 11.3 Hz, $PO(OCH_3)_2$]. Na[L-d_6] (**1a**). The compound was obtained as **1**. $NaHCO_3$ and D[L-d_6] were used as starting materials. Yield: 0.585 g, 98%.

2.1.2. *Rb[L] (**2**)*

Rubidium carbonate (0.231 g, 1 mmol) was added in parts to 10 ml of an aqueous-alcoholic (1:3) solution of [HL] (0.541 g, 2 mmol). A solution of the product was allowed to stand at room temperature in a vacuum desiccator over $CaCl_2$ for 20 days, after which the colorless well-faceted crystals that were deposited were filtered out, washed with few drops of isopropanol and dried over $CaCl_2$. Yield: 0.653 g, 92%. *Anal.* Calc. for $C_4H_6Cl_3NRbO_4P$: C, 13.54; H, 1.70; N, 3.95. Found: C, 13.2; H, 1.76; N, 3.64%. ^{1}H NMR (D_2O): 3.57 d [6H, $^3J_{PH}$ 11.2 Hz, $PO(OCH_3)_2$]; ^{31}P NMR: (D_2O) 16.11 h $^3J_{PH}$ 11.3 Hz, $PO(OCH_3)_2$].

The thallium compound Tl[L] (**3**) was synthesized in a similar fashion by reacting HL (0.584 g, 2 mmol) and Tl_2CO_3 (0.4688 g, 1 mmol) in aqueous 2-propanol. Yield: 0.824 g, 87%. *Anal.* Calc. for $C_4H_6Cl_3NTlO_4P$: C, 10.14; H, 1.28; N, 2.96. Found: C, 10.14; H, 1.42; N, 2.93%. ^{1}H NMR (D_2O): 3.57 d [6H, $^3J_{PH}$ 11.2 Hz, $PO(OCH_3)_2$]; ^{31}P NMR: (D_2O) 16.09 h $^3J_{PH}$ 11.3 Hz, $PO(OCH_3)_2$].

2.1.3. *PPh_4[L] (**4**)*

To a solution of **1** (0.584 g, 2 mmol) in 10 ml acetonitrile, a solution of 0.838 g PPh_4Br (2 mmol) in 15 ml CH_3CN was added under stirring. Then, the reaction mixture was cooled to room temperature. The white precipitate of NaBr was filtered off, and the solvent was removed in vacuo and the yellow product was recrystallized from isopropanol and hexane. Yield: 1.132 g, 93%. *Anal.* Calc. for $C_{28}H2_6Cl_3NO_4P_2$: C, 55.24; H, 4.30; N, 2.3. Found: C, 55.0; H, 4.15; N, 2.16%. ^{1}H NMR (D_2O): 7.74 m [8H $(PPh_4)^+$ – *ortho*, 7.56 m [12H $(PPh_4)^+$ – *meta* + *para*], 3.55 d [6H, $^3J_{PH}$ = 11.2 Hz, L$^-$]; ^{31}P NMR: (D_2O) 23.48 m $(PPh_4)^+$, 16.03 [$^3J_{PH}$ 11.3 Hz, $PO(OCH_3)_2$].

2.1.4. *$(PPh_4)_2[L]Br \cdot H_2O$ (**5**)*

To a solution of Na[L], that was prepared as above, PPh_4Br (0.838 g, 2 mmol in 15 ml CH_3CN) was added in the ratio 1:2. The white precipitate of NaBr was filtered off, the solvent was removed in vacuo and the off-white product was recrystallized from an isopropanol–hexane mixture. Yield: 0.941 g, 90%. *Anal.* Calc. for $C_{52}H_{48}BrCl_3NO_5P_3$: C, 59.7; H, 4.63; N, 1.34. Found: C, 60.0; H, 4.63; N, 1.30%. ^{1}H NMR $(CD_3)_2CO$: 7.93 m [20H, $(PPh_4)^+$], 3.25 d [3H, $^3J_{PH}$ = 11.2 Hz, L$^-$]; ^{31}P NMR: ($(CD_3)_2CO$) 24.05 m $(PPh_4)^+$, 13.05 [$^3J_{PH}$ 11.3 Hz, $PO(OCH_3)_2$].

2.1.5. *$(PPh_4)_2[Na_4L_6]$ (**6**)*

To a solution of 0.8772 g (3 mmol) Na[L], 0.419 g PPh_4Br (1 mmol in 10 ml CH_3CN) was added. The white precipitate of NaBr was filtered off, the solvent was removed in vacuum and the colourless product was recrystallized from isopropanol and hexane. Yield: 1.015 g, 85%. *Anal.* Calc. for $C_{72}H_{76}Cl_{18}N_6Na_4O_{24}P_8$: C, 36.22; H, 3.21; N, 3.52. Found: C, 36.54; H, 3.32; N, 3.41%. ^{1}H NMR ($(CD_3)_2CO$): 7.9 m [10H, $(PPh_4)^+$], 3.53 d [9H, $^3J_{PH}$ 11.2 Hz, $PO(OCH_3)_2$]; ^{31}P NMR ($(CD_3)_2CO$): 22.35 m $(PPh_4)^+$, 12.64 h ($^3J_{PH}$ = 11.2 Hz, $PO(OCH_3)_2$).

All the compounds are soluble in water, DMFA, DMSO, acetone, sparingly soluble in isopropanol, 1,4-dioxane and insoluble in non-polar aprotic solvents.

2.1.6. *[$SbPh_4L$] (**7**)*

To a solution of Na[L] (0.293 g 1 mmol) in 10 ml acetonitrile was added $SbPh_4Br$ (0.511 g, 1 mmol) in 15 ml acetonitrile. After 15 min, a white precipitate of NaBr was filtered off and the solution was allowed to stand in a vacuum desiccator over $CaCl_2$. After a while colorless crystals of **7** precipitated from the solution, that were recrystallized from isopropanol. The compound is soluble in polar protic solvents, insoluble in water, ethers, benzene and alkanes. Yield: 0.569 g, 85%. *Anal.* Calc. for $C_4H_6Cl_3NTlO_4P$: C, 47.73; H, 4.43; N, 1.99. Found: C, 47.70; H, 4.65; N, 1.74%. ^{1}H NMR ($(CD_3)_2CO$): 7.88 dd [8H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.6 Hz, $(SbPh_4)^+$ – *ortho*], 7.61 m [12H, $(SbPh_4)^+$ – *meta* + *para*], 3.25 d [6H, $^3J_{PH}$ = 11.2 Hz, L$^-$]; ^{31}P NMR ($(CD_3)_2CO$): 12.08 h ($^3J_{PH}$ = 11.2 Hz, L$^-$).

2.2. *Methods*

2.2.1. *NMR, IR-spectroscopy*

IR spectra of the compounds were recorded on an UR-10 spectrometer in the range 400–4000 cm^{-1} (samples as KBr pellets or nujol mulls). ^{1}H and ^{31}P NMR spectra were recorded on a Varian AMX 400 spec-