Inorganica Chimica Acta 469 (2018) 217–226

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Transition metal complexes of tris(aminomethyl)phosphine oxide (**tampo**) – Thermodynamic and X-ray diffraction studies

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ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form 8 September 2017
Accepted 12 September 2017
Available online 15 September 2017

Keywords:
Tripodal ligands
Crystal structures
Stability constants
Potentiometry

ABSTRACT

The coordination behaviour of tris(aminomethyl)phosphine oxide (**tampo**) to selected transition metal ions was studied. In the case of Co(III), Ni(II) and Cu(II) complexes with metal-to-ligand 1:2 stoichiometry, bis(tripodal) **tampo** coordinations forming octahedral coordination spheres (in the case of Cu(II) complex with significant Jahn-Teller distortion) were found by X-ray diffraction analysis. Based on the potentiometric study, the tripodal coordination of the title ligand is also expected in solution. The stability of the metal complexes follows the Irving-Williams trend. Compared with the structurally "parent" 1,1,1-tris(aminomethyl)ethane (**tame**) ligand, the complexation of **tampo** occurs at a lower pH as the consequence of low ligand basicity [$\log K_1 = 6.72(1)$, $\log K_2 = 5.34(1)$ and $\log K_3 = 3.82(1)$], although the values of the stability constants of the metal complexes are relatively low.

1. Introduction

Organophosphorus compounds – phosphines and phosphine oxides as well as (di)alkylphosphinic, alkylphosphonic and phosphorus acids and their derivatives – have found a variety of applications [1]. Examples include the use of ligands in catalytic systems (typically phosphines and phosphine oxides) [2], water technologies (polyphosphate derivatives) [3], biologically active compounds (phosphinate and phosphonate functions mimic the transition state of a peptide bond hydrolysis and, therefore, behave as enzymatic inhibitors) used as medicinal drugs [4–6] or pesticides (with glyphos as the most known example) [7,8], bis(phosphate) analogues used for the treatment of bone diseases [9], ligands for (radio)metals used in diagnostic or therapeutic methods [10], and extractants used in metal separation technologies (*e.g.* widely used tributyl-phosphate) [11,12].

Aminoalkylphosphorus acid derivatives in particular are of high interest due to their related biological activity (given by structural similarity to amino acids) and their coordination chemistry. However, in relation to the above-mentioned applications, it is surprising that the chemistry of aminoalkylphosphines and phosphine oxides has not been explored to such an extent as the behaviour of other classes of derivatives, although they have proved their significance in various applications. As examples, ligands *P*-(*N*,*N*-dimethylaminomethyl)-*P*,*P*-diphenylphosphine oxide (**dmpo**) and *P*-(*N*,*N*-dimethylaminoethyl)-*P*,*P*-diphenylphosphine oxide (**depo**) used in metal extractions can be mentioned [13,14]. In the field of platinum-based anti-cancer agents, dimethyl(aminomethyl) phosphine oxide (**dmao**), methyl-bis(aminomethyl)phosphine oxide (**mbpo**) and bis(dimethylphosphorylmethyl)amine (**bdmpa**) were studied as supporting ligands and their therapeutic relevance and potential have been revealed [15–19]. From the family of aminoalkylphosphines, adamantan-like water soluble 1,3,5-triaza-7-phosphadamantane (**pta**) and its derivatives have received high interest in recent years due to their suitable properties [20,21]. The complexes with Rh(I), Ru(II) and Pd(II) ions have been used in aqueous phase or biphasic homogenous catalysis [22], the Ru(II) or Pt(II) complexes have been utilized as potential antitumor agents in medicinal chemistry [23], and the Au(I) complexes were suggested for photoluminescence applications [24–26]. The coordination chemistry of 1,3,5-triaza-7-phosphadamantane-7-oxide (**ptao**) was also extensively studied [27], showing for example high potential as building blocks for new metal-organic frameworks (MOFs) or polymers [28]. However, these adamantan-related structures are sterically rigid and the ligands **pta** and **ptao** themselves cannot serve as poly(dentate) ligands in mononuclear complexes, but only after appropriate substitution by a suitable pending arm [29] or after opening of the skeleton [30].

Tris(aminoalkyl)phosphine oxides structurally resemble well-known tripodal ligands, like tris(2-aminoethyl)amine (**tren**) or

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https://doi.org/10.1016/j.ica.2017.09.034
0020-1693/

structurally closely related 1,1,1-tris(aminomethyl)ethane (**tame**). The latter in particular has been extensively studied as a template precursor in synthesis of cage molecules [31–35]. Indeed, the phosphorus atom can serve as a cap of the sepulchrate-like structures [36], but the phosphorus-containing part has been introduced in the very last synthetic step on the basis of Mannich-type reaction of the open template complex with formaldehyde and *in situ* generated PH_3 [37]. Therefore, it opens a question of study of coordinating behaviour of the phosphine-based tripodal structures, which surprisingly only rarely occur in the literature.

Tripodal κ-N_3-coordination of tris(aminomethyl)phosphine oxide fragment has been reported only rarely in the literature, and structurally characterized only in such cases where the phosphine oxides are substituted with three heteroatomic penta-fold aromatic rings. In the case of tris(2-isopropyl-1H-imidazol-4-yl) phosphine oxide, its facial κ-N_3-coordination was observed in octahedral Re(I) and Co(II) complexes [38,39], and in square-pyramidal Cu(II) complex [39]. However, in the cases of Co(II) and Zn(II) complexes with this ligand, only bidentate κ-N_2-coordination mode was found, and in the case of Ni(II) complex, κ-*O*,*N*-coordination was observed [40]. Tripodal κ-N_3-coordination of related ligand, tris(1-phenyl-1H-1,2,3-triazol-4-yl)phosphine oxide, was structurally characterized in its octahedral *fac* Rh(III) [41] and Pt (IV) [42] complexes and in dimeric bis[Cu(I)] complex with tetrahedral sphere [43]. In the case of aliphatic tris(alkylamino) phosphine oxides, complexes of tris(2-aminoethyl)phosphine oxide (**teapo**) [44], tris(*N*,*N*-dimethylaminomethyl)phosphine oxide (**tmpo**) [45] and tris(piperidin-*N*-ylmethyl)phosphine oxide (**tppo**) [46] can be mentioned whose coordination behaviour with Co(II), Cu(II), Zn(II) and Cd(II) ions has been studied in detail. However, in the metal complexes of these ligands, only κ-*O*,*N*-coordination mode was found in the solid state, with no evidence of tripodal binding.

Surprisingly, no study has been reported of the coordination behaviour of the simplest prototype, tris(aminomethyl)phosphine oxide (**tampo**), although the compound has been known for nearly 40 years [47,48], and only protonation constants were determined using NMR spectroscopy [49]. To fill this gap, here we report on the coordination behaviour of **tampo** ligand towards selected transition metal ions. The complexes were characterized by X-ray diffraction, and their stability was determined by means of potentiometry and spectroscopic methods.

2. Experimental section

2.1. General

Commercially available chemicals had a synthetic purity and were used as received. NMR spectra were recorded on a Varian VNMRS300 using 5 mm sample tubes. UV-Vis spectra were recorded on a Specord 50 Plus Analytik Jena in 10 mm quartz cuvettes. Mass spectra were recorded using a Bruker ESQUIRE 3000 spectrometer equipped with electrospray ion source and ion-trap detection.

2.2. Synthesis

2.2.1. Synthesis of tris(aminomethyl)phosphine oxide trihydrochloride

Tris(aminomethyl)phosphine oxide (**tampo**) was synthesized according to the literature method [47]. The free base was dissolved in diluted hydrochloric acid, precipitated by addition of ethanol and isolated and stored as a trihydrochloride salt. Elem. anal.: found (calcd. for (H_3**tampo**)Cl_3, $C_3H_{15}Cl_3N_3OP$, $M_r = 246.50$): C 14.81 (14.62), H 6.07 (6.13), N 16.68 (17.05).

2.2.2. Synthesis of bis{tris(aminomethyl)phosphine oxide}cobalt(III) chloride

The complex was prepared by the procedure analogous to synthesis of [Co(**tame**)$_2$]Cl_3 [31]. Cobalt(II) chloride hexahydrate (1.30 g, 5.47 mmol) was dissolved in water (10 ml), then hydrochloric acid (0.5 ml, 36%) and active charcoal (0.20 g) were added. To this solution, **tampo** (1.50 g, 11.0 mmol, 2.0 equiv.) was added and air was slowly bubbled through the resulting solution for 4 h. During this time the mixture turned dark red. The mixture was filtered through filter paper and the filtrate was mixed with 1 M HCl (5 ml). The solution was concentrated under reduced pressure at 60 °C and cooled in an ice bath to deposit bright red crystals. The product was collected by filtration, washed with ethanol and dried in air. The crystals obviously lost some solvate molecules as evidenced by their disintegration in air. Yield 0.802 g (31%). Elem. anal.: found (calcd. for [Co(**tampo**)$_2$]$Cl_3\cdot 2H_2O$, $C_6H_{28}Cl_3CoN_6O_4P_2$, $M_r = 475.56$): C 15.63 (15.15), H 6.26 (5.93), N 17.82 (17.67), Cl 22.52 (22.36). UV–Vis: λ_{max} (ε): 348 nm ($^1T_2 \leftarrow {}^1A_1$, 93 $dm^3\cdot mol^{-1}\cdot cm^{-1}$); 492 nm ($^1T_1 \leftarrow {}^1A_1$, 94 $dm^3\cdot mol^{-1}\cdot cm^{-1}$).

2.2.3. Preparation of single crystals

Single crystals of (H_3**tampo**)Cl_3 were prepared by diffusion of ethanol vapour into an acidified (drop of HCl) solution of (H_3**tampo**)Cl_3 in water. Single crystals of [Co(**tampo**)$_2$]$Cl_3\cdot 2.75H_2O$ were prepared by recrystallization of the isolated complex from hot water. Single crystals of $[LiCl(H_2O)]_2$[M(**tampo**)$_2$]$Cl_2\cdot 2H_2O$ (M = Ni, Cu) were prepared in the following way: metal(II) chloride hydrate (66 mg of $CuCl_2\cdot 2H_2O$ or 93 mg of $NiCl_2\cdot 6H_2O$, 0.39 mmol) was dissolved in water (2 ml) and the solution was mixed with the solution of **tampo**·3HCl (0.20 g, 0.81 mmol, 2.1 equiv.) in 2 ml. The reaction mixture was neutralized to pH ~7 by aq. LiOH. The solution was concentrated under reduced pressure and LiCl (30 mg) was added. The single crystals were formed on diffusion of ethanol vapours. A few single crystals of $Li_{1.375}Na_{0.125}$[Cu(**tampo**)Cl_2]$Cl_{1.5}\cdot 1.5H_2O$ were isolated from the mother liquor after crystallization of $[LiCl(H_2O)]_2$[Cu(**tampo**)$_2$]$Cl_2\cdot 2H_2O$.

2.3. Potentiometry

Methodology for the potentiometric titrations and processing of the experimental data were analogous to those previously reported [50–52]. The stock solution of the ligand was prepared by dissolution of exactly weighted material in a calibrated volumetric flask. The ligand concentration and hydrochloride content were also determined by calculation of their concentration together with the ligand protonation constants, giving virtually the same results as when concentration calculated from the weight of the material was used (refined formula of the solid material was **tampo**·2.996HCl). The stock solutions of the metal nitrates (recrystallized from deionized water) were standardized by titration with Na_2H_2edta according to the recommended procedure [53,54]. The stock solution of nitric acid (~0.03 M) was prepared from recrystallized KNO_3 on cation-exchange resin (Dowex 50). Carbonate-free KOH stock solution (~0.2 M) was standardized against potassium hydrogen phthalate and the HNO_3 solution against the KOH solution. The titrations were carried out in a vessel thermostated at 25 ± 0.1 °C at ionic strength $I = 0.1$ M KNO_3 with addition of an excess of HNO_3 to the starting mixture. The starting volumes of the titrated solutions were ~5 cm^3. Stock solution of KOH was gradually added using 2-ml ABU 900 automatic piston burette, and the sample solutions were equilibrated for 20–60 s before reading electrode potential (GK 2401B combined electrode) using a PHM 240 pH-meter (all Radiometer). Before and after each titration, electrode calibration titrations (titration of standard HNO_3 with standard KOH solutions) were performed to determine