Inorganica Chimica Acta 362 (2009) 2977–2981

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Na(I) binding by tartaric acid derivatives

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ARTICLE INFO

Article history:
Received 25 June 2008
Received in revised form 16 January 2009
Accepted 22 January 2009
Available online 31 January 2009

Keywords:
Tartrates
Binding studies
Sodium
Crown ethers
Crystal structures

ABSTRACT

A study of the binding of Na^+ by two readily available tartaric acid derivatives, dimethyl tartrate and dipyrrolidine tartramide, has been carried out. These binding studies reveal binding stoichiometries of 1:1 for the dimethyl tartrate and 2:1 for the dipyrrolidine tartramide, and binding affinities (association constants) of 6.61 M^{-1} for the dimethyl tartrate and 70.4 M^{-2} for the dipyrrolidine tartramide indicating weak binding of Na^+ in both cases. An X-ray crystal structure of a NaI complex of dipyrrolidine tartramide has also been determined. The binding stoichiometry is 1:1 in the solid state as opposed to the 2:1 binding stoichiometry that is observed in solution. The 1:1 binding in the solid state results in a coordination polymer in which half of the carbonyl oxygens and half of the hydroxy oxygens of the dipyrrolidine tartramide ligand bridge between adjacent Na^+ cations. This allows each Na^+ cation to achieve an octahedral coordination geometry. The iodides are ordered in a linear fashion, and each column of iodides is separated from the other columns by the coordination polymer and by linear columns of water molecules.

1. Introduction

Recently we reported that the addition of hard metal cations to styrene hydroformylation reactions catalyzed by Rh(I) complexes of the bis(phosphite) ligands caused a significant increase in the regioselectivity (an approximately three fold increase in the *iso*/*n* ratio was observed with a 32:1 ratio of $LiBPh_4$ to Rh when the bis(phosphite) ligand was (*R*,*R*)-Chiraphite® [1]. This increase was attributed to cation binding to phosphite ligands during the regioselectivity determining step.

Our catalytic results suggest that the incorporation of groups that are capable of binding hard metal cations may have interesting effects on the regioselectivities of hydroformylation catalysts. Because a number of bis(phosphorus-donor) ligands used in hydroformylation catalysts are derived from tartaric acid [2–6], cation binding by tartaric acid derivatives is of interest. Unfortunately, there are no studies of the alkali metal binding by tartrate esters or tartramides so it is impossible to predict, *a priori*, if hard metal cation binding to these tartaric acid derivatives will occur.

To remedy this deficiency, we have studied the ability of dimethyltartrate and dipyrrolidine tartramide (**1**) to bind sodium cations. The binding stoichiometries were determined using Job plots and binding affinities were determined by fitting NMR titration data to the appropriate model. An X-ray crystal structure of a NaI complex of dipyrrolidine tartramide has also been determined, and the insights that it provides into the binding of NaI by these molecules are discussed.

2. Experimental

2.1. General considerations

NMR spectra were recorded on a Bruker DRX400 spectrometer. Chemical shifts for ^1H and ^{13}C data are reported in ppm downfield from internal tetramethylsilane (TMS) using residual protons (or carbons) in the acetonitrile-d_3 (1.94 ppm for ^1H and 118.69 ppm and 1.39 ppm for ^{13}C). Acetonitrile-d_3 was obtained from Cambridge Isotope Laboratories and used as received. THF was obtained from Aldrich and distilled from Na/benzophenone prior to use. Dimethyl tartrate and NaI were purchased from Aldrich and used without further purification. The dipyrrolidine tartramide (**1**) was synthesized using a known literature procedure [7].

2.2. Synthesis of dipyrrolidine tartramide-NaI complex (**2**)

A solution of 1.0 g (4.0 mmol) of dipyrrolidine tartramide (**1**) in 8.0 mL of THF and was stirred as 0.6 g (4 mmol) of NaI was added. Then the reaction mixture was stirred overnight during which time a white solid precipitated from the solution. The precipitate collected by filtration and dried *in vacuo*. Recrystallization from acetone/ethyl acetate yielded 0.9 g (90%) of **1** · NaI · H_2O as colorless prisms. ^1H NMR (CD_3CN): δ 4.56 (d, 2H, $|^3J(HH)|$ 7.5 Hz, CH), 4.34 (d, 2H, $|^3J(HH)|$ 8.4 Hz, OH), 3.61 (m, 2H, CH_2N), 3.46 (m, 6H, CH_2N), 2.21 (s, 2H, H_2O), 1.92 (m, 8H, CH_2C). ^{13}C NMR (CD_3CN): δ 170.31 (s, C=O), 69.97 (s, CH), 47.65 (s, CH_2N), 47.27 (s, CH_2N), 26.85 (s, CH_2C), 24.46 (s, CH_2C). *Anal. Calc.* for $C_{12}H_{21}O_5N_2NaI$: C, 33.98; H, 5.23. Found: C, 34.22; H, 5.23%.

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doi:10.1016/j.ica.2009.01.019

Table 1
Crystal data and structure refinement data for Na complex of **2**.

CCDC#	692427
Empirical formula	$C_{12}H_{18}IN_2NaO_5$
Formula weight	420.17
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	7.307(5)
b (Å)	13.416(5)
c (Å)	16.515(5)
α (°)	90.000(5)
β (°)	90.000(5)
γ (°)	90.000(5)
V (Å^3)	1619.0(14)
Z	4
Density (calculated) (mg/m^3)	1.724
Absorption coefficient (mm^{-1})	2.025
F(000)	832
Crystal size (mm^3)	0.5 × 0.58 × 1.0
Theta range for data collection (°)	2.47–22.50
Index ranges	$-7 \leqslant h \leqslant 1$, $-14 \leqslant k \leqslant 14$, $0 \leqslant l \leqslant 17$
Reflections collected	2795
Independent reflections [$R_{(int)}$]	2116 [0.0364]
Completeness to theta = 22.50° (%)	99.9
Absorption correction	empirical
Maximum and minimum transmission	0.2804 and 0.2123
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2116/0/191
Goodness-of-fit (GOF) on F^2	1.141
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0334$, $wR_2 = 0.0836$
R indices (all data)	$R_1 = 0.0343$, $wR_2 = 0.0845$
Absolute structure parameter	−0.01(3)
Extinction coefficient	0.061(3)
Largest difference peak and hole (e Å^{-3})	0.807 and −0.846

2.3. Procedure for the determination of binding stoichiometry using a Job plot

A 0.50 M stock solution of NaI in acetonitrile-d_3 (0.150 g of NaI in 2.0 mL) and a 0.50 M stock solution of either dimethyl tartrate in acetonitrile-d_3 (0.178 g of dimethyl tartrate in 2.0 mL) or the dipyrrolidine tartramide in acetonitrile-d_3 (0.256 g of tartramide in 2.0 mL) were prepared. These stock solutions were then used to prepare ten solutions in NMR tubes with varying ratios of the tartrate derivative to the NaI. In each case, the total concentration of the sample remained constant. A ^{13}C NMR spectrum of each solution was then taken, and the chemical shifts of the methyne carbons (^{13}C δ: 70.30 ppm for tartrate and 70.75 ppm for tartramide), which were sensitive to cation binding, were measured. The resulting data was then plotted as the change in chemical shift ($\Delta\delta$) times the concentration of tartrate or tartramide versus the mole fraction (χ) of NaI. The binding stoichiometry was determined by the point at which the curve reached a maximum.

2.4. Procedure for the determination of binding constants by NMR titrations of dimethyl tartrate or dipyrrolidine tartramide with NaI

For each titration, a 0.50 M stock solutions of NaI in acetonitrile-d_3 (0.150 g in 2.0 mL) and a 0.050 M stock solution of the tartaric acid derivative in acetonitrile-d_3 (0.0045 g of dimethyl tartrate in 0.50 mL or 0.0064 g dipyrrolidine tartramide in 0.5 mL) were prepared. Both stock solutions were completely clear. The solution of tartaric acid derivative was placed in an NMR tube and then portions of the NaI solution were added using a 5 μL Hamilton syringe. A ^{13}C NMR spectrum was run after each aliquot was added. The addition was continued until almost no change ^{13}C in the ^{13}C NMR chemical shift of the methyne carbons (^{13}C δ: 70.30 ppm for dimethyl tartrate and 70.75 ppm for dipyrrolidine tartramide) was observed. The data was then plotted as the change in chemical shift ($\Delta\delta$) versus the NaI concentration. The binding constants were determined by fitting the plots to either a 1:1 or 2:1 literature binding models [8,9] that were modified for our experiments (see Supplementary material).

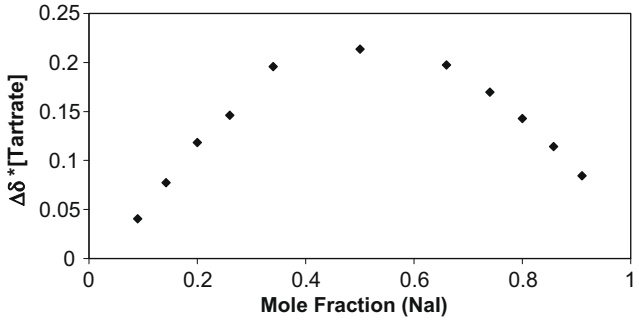

Fig. 1. Job plot showing 1:1 binding of dimethyl tartrate (**1**) with NaI.

2.5. X-ray data collection and solution

A suitable single crystal of the compound was glued on a glass fiber with epoxy and aligned upon an Enraf Nonius CAD4 single crystal diffractometer under aerobic conditions. Standard peak search and automatic indexing routines followed by least-squares fits of 25 accurately centered reflections resulted in accurate unit cell parameters for each. The space group of the crystal was assigned on the basis of systematic absences and intensity statistics. The data collection was carried out using the CAD4-PC software [10], and details of the data collection are given in Table 1. The analytical scattering factors of the complex were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. The data was corrected for the effects of absorption and for Lorentz and polarization effects.

All crystallographic calculations were performed with the Siemens SHELXTL-PC program package [11]. All heavy atom positions were located using Direct Methods. Full matrix refinement of the positional and anisotropic thermal parameters for all these atoms versus F^2 was carried out. All hydrogen atoms were placed in calculated positions with the appropriate molecular geometry and with a d(C–H) of 0.97 Å for methylenes and of 0.98 Å for methynes. The isotropic thermal parameter associated with each hydrogen atom was fixed equal to 1.2 times the U_{eq} of the atom to which it was bound. Crystallographic data for the complex has been deposited with the Cambridge Crystallographic Database (**Na Complex w/1**: 692427).

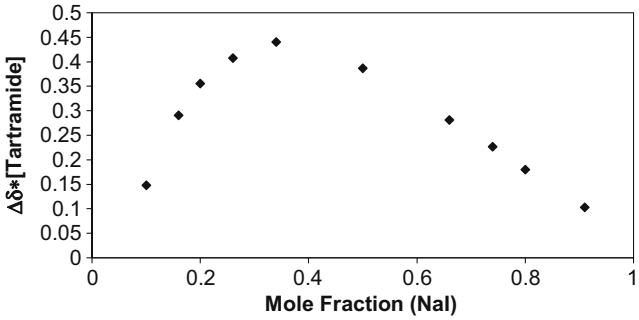

Fig. 2. Job plot showing 2:1 binding of dipyrrolidine tartramide (**2**) with NaI.