

Full Paper

Synthesis and Structural Characterization of the Sodium Salt of a New Sulfonate-containing Water Soluble N-Donor Ligand — Self-assembly in the Solid State by π – π Stacking Interactions

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Abstract: The synthesis, spectroscopic characterization, and X-ray crystal structure of the sodium salt of a new sulfonated water-soluble ligand, sodium 2-(2-pyridin-2-yl-ethylamino)-benzenesulfonate (**L**) are described. Compound **L** crystallizes in the centrosymmetric space group Pbcn, orthorhombic, $a=31.930(13)$ Å, $b=7.153(3)$ Å, $c=14.193(6)$ Å, $\alpha=90.00$, $\beta=90.00$, $\gamma=90.00$, $V=3220(2)$ Å³, $Z=9$. π – π stacking contacts involving interactions between the π -donor benzene and the π -acceptor pyridine systems reinforce and direct the self-assembly of the structural motifs in the solid state.

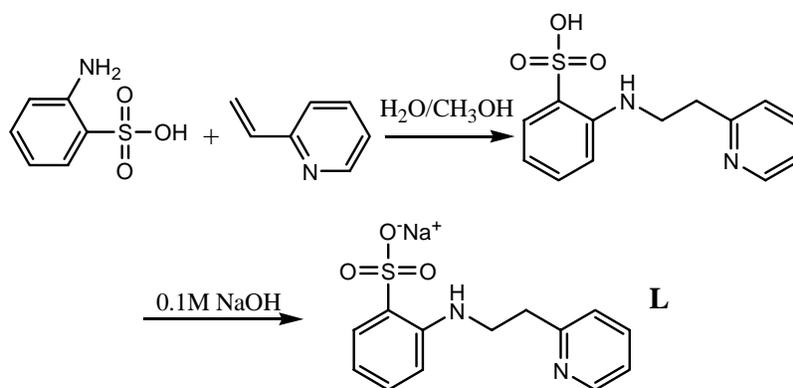
Keywords: Sulfonate, Water-soluble Ligand, π – π Stacking, Michael-type Addition.

Introduction

Water-soluble ligands and the corresponding derived catalysts are of great interest for aqueous catalysis. Typically there are many more phosphine P-donor ligands than amine N-donor ligands specifically modified by incorporation of hydrophilic groups such as hydroxyl, carboxylate or sulfonate moieties to increase their water-solubility [1, 2]. We are interested in preparing water-soluble N-donor ligands containing sulfonate groups for synthesizing metal complexes that can catalyze the

hydrolysis of organic molecules such as esters, phosphate esters and amides in water. Recently, we reported the synthesis of such sulfonate-containing *N*-donor ligands by a new route which involves the Michael-type addition reaction of primary or secondary amines with sodium vinylsulfonate in water [3]. Herein, we report on the sodium salt of a new, sulfonate-containing *N*-donor ligand, sodium 2-(2-pyridin-2-yl-ethylamino)benzenesulfonate (**L**), prepared via a similar synthetic pathway (Scheme 1). Compound **L** has been characterized by ^1H - and ^{13}C -NMR and IR spectroscopies, mass spectrometry and X-ray crystallography. Although the solid state superstructure of compound **L** is not a primary focus for our research on water-soluble ligands and complexes, an interesting π - π stacking effect, typically used for the generation of a wide variety of superstructures [4-8], was also observed in **L** in the solid state (*vide infra*).

Scheme 1



Results and Discussion

Compound **L** was synthesized via a Michael-type addition reaction between 2-vinylpyridine and aniline-2-sulfonic acid in refluxing water and methanol similar to related reactions reported in the literature [9]. Compared with other potential synthetic routes to **L**, such as unselective alkylation using alkyl halides [10], the selective conjugate addition reaction that was employed greatly decreased the amount of undesired side-products formed. As shown in Scheme 1, an aqueous solution of aniline-2-sulfonic acid was mixed with 1.2 equivalents of 2-vinylpyridine, leading to the formation of **L** in 73% yield after 15 days. Only very little tertiary amine side-product was isolated in the reaction, probably due to the relatively slow kinetics and higher steric effect of the formation of tertiary amines compared to secondary amines in the reaction. Furthermore, no quaternary ammonium side-products resulted from the reaction, as might have been the case with an alkylation reaction using an alkyl halide [10].

White crystals suitable for X-ray crystallography were obtained by recrystallization of **L** from 50% aqueous methanol solution. The structure of **L** is shown in Figure 1, with 30% thermal ellipsoids probability. A more elaborate structural construction is showed in the 2D polymeric structure depicted in Figure 2. As can be seen in this figure, the organic portions of **L** are bridged by sodium ions ($\text{Na}(1)\text{-O}(1)$, 2.3269(16) Å), and π - π stacking involving interactions between the π -donor benzene and the π -acceptor pyridine systems (ring \cdots ring separation 3.847 Å) reinforce and direct the self-assembly of the structural motifs, which form a three-layer sandwich structure with an octahedrally-

coordinated sodium cation in the middle and two ligand molecules on the sides. On the basis of the repeating pattern in the solid state, we can propose that π -stacking occurs preferentially over the suitable spatial arrangement. Transition metal complexes of **L** and the catalytic activities of the corresponding complexes are currently being investigated and will be reported soon.

Figure 1. The molecular structure of **L** with atomic labeling and thermal ellipsoids shown at the 30% probability level. Solvent molecules are omitted for clarity.

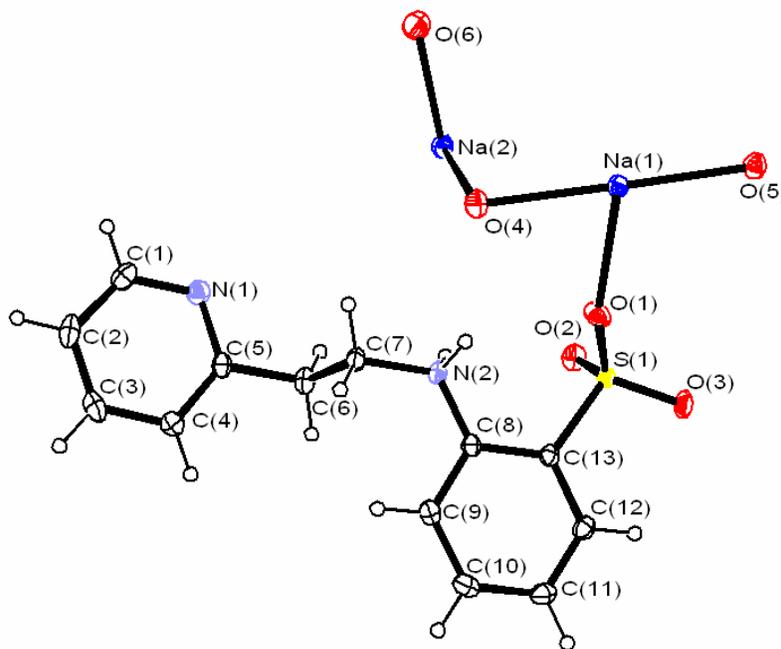
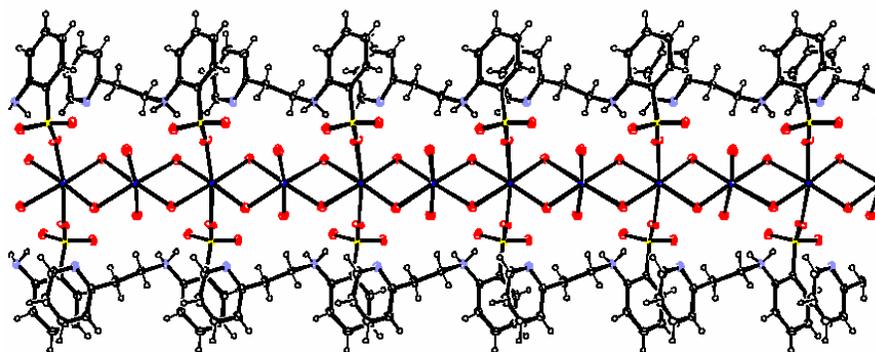


Figure 2. 2D Polymeric structure of **L**.



Conclusions

A new, water-soluble *N*-donor ligand was synthesized in good yield and without major side-products. The result of X-ray crystallographic studies on the sodium salt of the ligand showed that π - π stacking effects play an important role in the self-assembly of the compound in the solid state.

Acknowledgments

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Experimental

General

All chemicals used for synthesis were purchased from Aldrich and were used in this study as received without further purification. $^1\text{H-NMR}$ spectra were recorded on a Varian Inova 500 or Varian Gemini 200 spectrometers. $^{13}\text{C-NMR}$ spectra were recorded on Varian Inova 500 spectrometer. Chemical shifts were reported as parts per million (ppm) downfield from 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid. IR spectra were obtained on KBr disks using an FT-IR spectrophotometer (Perkin-Elmer 1600 series). A ThermoFinnigan LCQ was used for ESI-MS analysis. The sample was run using direct infusion from a Cole Parmer 74900 series syringe pump at $10\ \mu\text{L}\ \text{min}^{-1}$ in the positive-ion mode.

Synthesis of **L**

An aqueous solution (50.0 mL) of aniline-2-sulfonic acid (10.0 g, 56.1 mmol) was mixed with 2-vinylpyridine (7.0 g, 1.2 equiv) dissolved in methanol (5 mL). The mixture was refluxed for 15 days until tlc of the reaction mixture showed no further increase in the formation of the desired product **L**. The resulting solution was loaded onto silica gel (250.0 g) and eluted with methanol. The appropriate fractions were combined, concentrated via rotary evaporation, and dried under reduced pressure to give a white solid product, which was treated with 1 equiv. of sodium hydroxide to give the final product (12.3 g, 40.9 mmol, 73.0%). $^1\text{H-NMR}$ (200 MHz, D_2O): δ 8.46 (d, py-6-*H*), 7.76 (t, py-4-*H*), 7.66 (d, ph-3-*H*), 7.39 (t, py-3-*H*), 7.33 (t, py-5-*H*), 7.30 (d, ph-5-*H*), 6.90 (d, ph-6-*H*), 6.78 (d, ph-4-*H*), 3.59 (t, py- $\text{CH}_2\text{CH}_2\text{N}$), 3.12 (t, py- $\text{CH}_2\text{CH}_2\text{N}$); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.7 MHz, D_2O): δ 161.4 (py-2), 151.2 (py-6), 147.6 (ph-1), 141.0 (py-4), 135.7 (ph-5), 130.3 (ph-3), 129.0 (ph-2), 127.3 (py-3), 125.1 (py-5), 119.3 (ph-4), 115.7 (ph-6), 45.9 (py- $\text{CH}_2\text{CH}_2\text{N}$), 39.2 (py- $\text{CH}_2\text{CH}_2\text{N}$); FT-IR (NaCl pellet, cm^{-1}): 3069 ($\nu_{\text{C-H}}$, str), 1598, 1570, 1518, 1438 (pyridine ring), 1216 ($\nu_{\text{S=O}}$, asym str), 1178 ($\nu_{\text{S=O}}$, sym str); MS (ESI) m/z 279.1([**L**+ H] $^+$).

X-ray Crystal Structural Determination [11].

A white crystal was mounted onto a glass fiber. The data collection was performed on a CAD4 X-ray diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda=0.71073\ \text{\AA}$) using the $\omega/2\theta$ scan mode at 293 K in the 1.28 to 27.79 range. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS. The structure was solved by direct methods using SHELXS-97. All non-hydrogen atoms were refined anisotropically. Full-matrix least-squares methods were used to refine an overall scale factor and positional and thermal parameters. The refinement data is summarized in Table 1.

Table 1: Summary of Crystallographic Data and Parameters for **L**.

Parameter	L
Empirical formula	C ₁₃ H ₁₃ N ₂ O ₃ SNa
fw	300.30
temp (K)	273 (2)
radiation (Å)	0.71073
cryst syst	Orthorhombic
space group	Pbcn.
cell constants	
<i>a</i> (Å)	31.930(13)
<i>b</i> (Å)	7.105(3)
<i>c</i> (Å)	14.193(6)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
<i>V</i> (Å ³)	3220(2)
δ _{calcd} (g/cm ³)	1.394
<i>Z</i>	9
abs coeff (mm ⁻¹)	0.9371
<i>F</i> (000)	1404
cryst size (mm ³)	0.21×0.14×0.15
θ range (deg)	1.28–27.79
<i>h, k, l</i> ranges collected	–40 ≤ <i>h</i> ≤ 40 –9 ≤ <i>k</i> ≤ 9 –18 ≤ <i>l</i> ≤ 18
no. reflns collected	3762
no. unique reflns	3134
Completeness	98.7%
abs correction	Empirical
Refinement method	Full-matrix least-squares on <i>F</i> ²
No. of params	209
Data/param ratio	18.00
GOF _w ^c	1.104
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 ^a = 0.0452 <i>wR</i> 2 ^b = 0.1363
<i>R</i> indices(all data)	<i>R</i> 1 = 0.0552 <i>wR</i> 2 = 0.1486
^a <i>R</i> 1 = Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o . ^b <i>wR</i> 2 = [Σ <i>F</i> _o ² - <i>F</i> _c ²]/Σ <i>w</i> (<i>F</i> _o) ² ^{1/2} . ^c <i>w</i> = 1/[(<i>F</i> _o ²) ² + (0.1276 <i>P</i>) ² + 2.6903 <i>P</i>], where <i>P</i> = (<i>F</i> _o ² + <i>F</i> _c ²)/3.	

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11. CCDC-282737 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the URL <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Sample Availability: Available from the authors.