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A synthetic and crystal structure study of a collection of coordination polymers based on alkaline aroylhydrazonates

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ABSTRACT

The reactions of two aroylhydrazone ligands $H_2\mathbf{L}^{S}$ and $H_2\mathbf{L}^{Ac}$ with alkaline Li(I), Na(I), K(I) and Ba(II) metal ions afforded nine new coordination polymers with different dimensionalities. These illustrate the ionic radii, the ligand substitution and the solvent influence on the formation of the final product. Interestingly, one of them shows porous structure with a 40% unoccupied volume.

1. Introduction

The synthesis of new coordination polymers (CPs) or metal organic frameworks (MOFs) has captured researchers' interest owing to the variety of compositions and topologies of the produced compounds [1–9] together with their interesting functional properties and applications [10–20]. The properties of such systems are controlled by their chemical composition and structure, which are easily monitored by simply varying the reactants and reaction conditions. Considerable attention has been given toward developing the ability to control the reactions so that the products can be engineered towards desired properties [21,22].

Aroylhydrazones is a class of excellent multidentate organic ligands that has been extensively studied for the chemistry of transition metals (3d), what has resulted in polynuclear coordination clusters [23,24], also with interesting biological properties, e.g. antiamoebic activity [25], DNA synthesis inhibition or antiproliferative behaviour [26–28], anticonvulsant, analgesic, antiinflammatory, antiplatelet, antitubercular and antitumoral activities [29]. Interestingly, a recent study from Matoga et al. showed that this class of organic moieties can be used along with Cu(II) metal ions to produce water soluble CPs [30]. We also reported the synthesis and properties of a CP with an aroylhydrazone based ligand coordinating to a Mn centre [31].

A comprehensive survey shows that a systematic study of the influence of the alkali metal ions and the solvent on the construction of alkali aroylhydrazonates based CPs has not been reported so far. We have thus embarked on a program of synthesizing new aroylhydrazone ligands, so far with a sulfonate functional group (SO_3), aiming towards producing new water soluble CPs which could also be suitable for attachment to a variety of surfaces including biological molecules.

Having all these in mind, we synthesized the two new organic ligands $H_2\mathbf{L}^{S}$ and $H_2\mathbf{L}^{Ac}$ (see Scheme 1) and studied their coordination abilities to alkali metal ions, i.e. Li(I), Na(I), K(I) and Ba(II) cations. We report herein the syntheses, structure determination, and topological evaluation of ten new compounds (including both ligands in Scheme 1), i.e. [**pyr**][$H\mathbf{L}^{Ac}$] (pyr = 3,5,5-trimethyl-4,5-dihydro-1H-pyrazolium), $K_2(\mathbf{L}^{S})(DMF)_2$, $Li_2(\mathbf{L}^{S})(H_2O)_5{\cdot}H_2O$ (**C1**), $Na_4(\mathbf{L}^{S})(H_2O)_{22}{\cdot}2H_2O$ (**C2**), $K2(\mathbf{L}^{S})(H_2O)_2$ (**C3**), $Ba(\mathbf{L}^{S})(H_2O)_4$ (**C4**), $[Li(\mathbf{L}^{Ac})(H_2O)_2][Li(H_2O)_4]{\cdot}H_2O{\cdot}OC_3H_6$ (**C5**), $Na2(\mathbf{L}^{Ac})(H_2O)_2$ (**C6**), $K_2(\mathbf{L}^{Ac})(H_2O)$ (**C7**) and $Ba(\mathbf{L}^{Ac})(H_2O)_4{\cdot}H_2O$ (**C8**), which were

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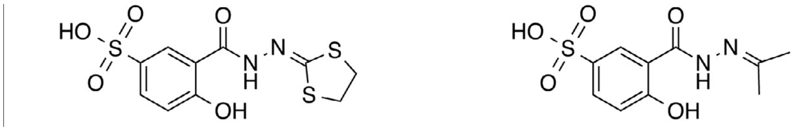


5-sulfosalicyloylhydrazono-1,3-dithiolane 5-sulfosalicyloylhydrazono-2-propane

$H_2\mathbf{L}^{S}$ $H_2\mathbf{L}^{Ac}$

Scheme 1. The protonated form of the two new aroylhydrazone ligands described in this study.

prepared from 5-sulfosalicyloylhydrazono-1,3-dithiolane potassium salt $K_2\mathbf{L}^{S}$ or from the hydrazinium salt of the 5-sulfosalycilic hydrazide, respectively (see Schemes 2 and 3).

2. Experimental

2.1. Materials and instrumentation

Reactions were carried out under aerobic conditions using standard Schlenk techniques with chemicals and solvents obtained from commercial sources and used as received without further purification. Anhydrous solvents were either obtained from commercial sources and used as received without further purification or purified using a solvent purification system (MBraun SPS). TLC was performed with silica gel plates (Merck, 60F-254). Flash chromatography was performed with 40–63 μm SiO_2. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at ambient temperature at 300, 400, 500 or 600 MHz with tetramethylsilane (TMS) as an internal standard (Bruker AVANCE). Chemical shifts (δ) of samples in $CDCl_3$, CH_3OD, $[D_6]$acetone, $[D_6]$DMSO or D_2O are in parts per million (ppm). The splitting patterns are designated as: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants (*J*) between two nuclei separated by n chemical bonds are denoted in Hertz (Hz). FTIR spectra were measured in the range 4000–400 cm^{-1} with a Nicolet 67000 FT-IR (ATR mode, ZnSe). Elemental analyses were obtained at the analytical facility of the IUT Robert Schuman, University of Strasbourg.

Single crystals of complexes $K_2(\mathbf{L}^{S})(DMF)_2$, $Li_2(\mathbf{L}^{S})(H_2O)_5{\cdot}H_2O$ (**C1**), $Na_4(\mathbf{L}^{S})(H_2O)_{22}{\cdot}2H_2O$ (**C2**), $K2(\mathbf{L}^{S})(H_2O)_2$ (**C3**) and $Ba(\mathbf{L}^{S})(H_2O)_4$ (**C4**) were prepared from 5-sulfosalicyloylhydrazono-1,3-dithiolane potassium salt $K_2\mathbf{L}^{S}$, whilst single crystals of complexes $[Li(\mathbf{L}^{Ac})(H_2O)_2][Li(H_2O)_4]{\cdot}H_2O{\cdot}OC_3H_6$ (**C5**), $Na2(\mathbf{L}^{Ac})(H_2O)_2$ (**C6**), $K_2(\mathbf{L}^{Ac})(H_2O)$ (**C7**) and $Ba(\mathbf{L}^{Ac})(H_2O)_4{\cdot}H_2O$ (**C8**) were prepared from the hydrazinium salt of the 5-sulfosalycilic hydrazide. Crystal structure of pyrazolium salt derivative of the ligand $H_2\mathbf{L}^{Ac}$ was also determined and is discussed in the present study as well. All 10 compounds were characterized by structural resolution using single crystal X-ray diffraction using the following procedure: diffraction measurements were performed at 173 K by using a Nonius Kappa-CCD or a Bruker APEX-II DUO Kappa-CCD diffractometer with Mo K radiation (Mo Kα = 0.71073 Å). The crystal structures were solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of organic ligands were introduced using the riding model (SHELXL-97). Crystal data and refinement details are given in Tables X1, X2 and X3 in Supplementary materials.

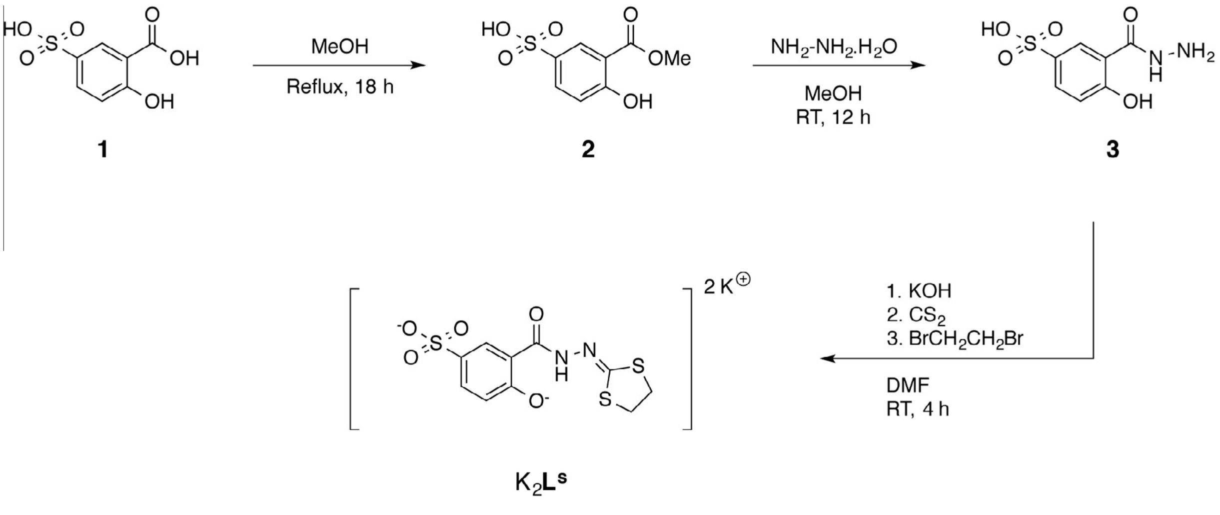
2.2. Synthesis of the compounds

2.2.1. Synthesis of 5-sulfosalicyloylhydrazono-1,3-dithiolane ($H_2\mathbf{L}^{S}$)

The ligand $H_2\mathbf{L}^{S}$ was obtained in 4 steps following the procedure described hereafter.

*2.2.1.1. 5-Sulfosalycilic methyl ester (**2**).* 5-Sulfosalycilic acid (4 g, 18.3 mmol) was refluxed in MeOH (50 mL) for 18 h. After evaporation of the solvent, title ester was isolated as a white powder (quant.). ^{1}H NMR (DMSO-d_6): δ = 8.03 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 8.6 Hz, *J* = 2.2 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 4.68 (brs), 3.90 (s, 3H) ppm.

*2.2.1.2. 5-Sulfosalycilic hydrazide (**3**).* Ester **2** (4.04 g, 17.4 mmol) and hydrazine monohydrate (1.1 mL, 20.9 mmol, 1.2 eq) were



Scheme 2. Synthetic route to $K_2\mathbf{L}^{S}$.