Supporting Information

"A Glimpse of The Inner Workings of The Templated site"

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Cobalt Acetate IR Analysis

Salts of anhydrous $Co(CH_3COO)_2$ and the tetra hydrate were analysed using a Varian UMA FT-IR spectrometer in ATR mode.

Characterisation of cobalt(II) complexes of acetate, pyridine and water have been presented in the literature and examples include the use of FR-IR and crystallography[i]. In order to shed some light of the effect of ligand exchange in the proposed cobalt(II) acetate-pyridine-DBM complexes, dried samples of $Co(II)Ac_2$ (Table 1) were analysed. Attempted analyses of complexes in solution were also performed but unfortunately the sensitivity was not sufficient for our purposes. The IR spectra of the hydrate (**II**) was in agreement with previous studies1a and the main differences from the anhydrous salt (**I**) were the bands related to H_2O; 3500cm^{-1} (OH asymmetric stretching) and different adsorption bands between 670 to 870cm^{-1}. Moreover the adsorption ~1510cm^{-1} (CO_2 asymmetric stretching) in **II** is shifted to ~1550cm^{-1} in **I**, Figure 1.

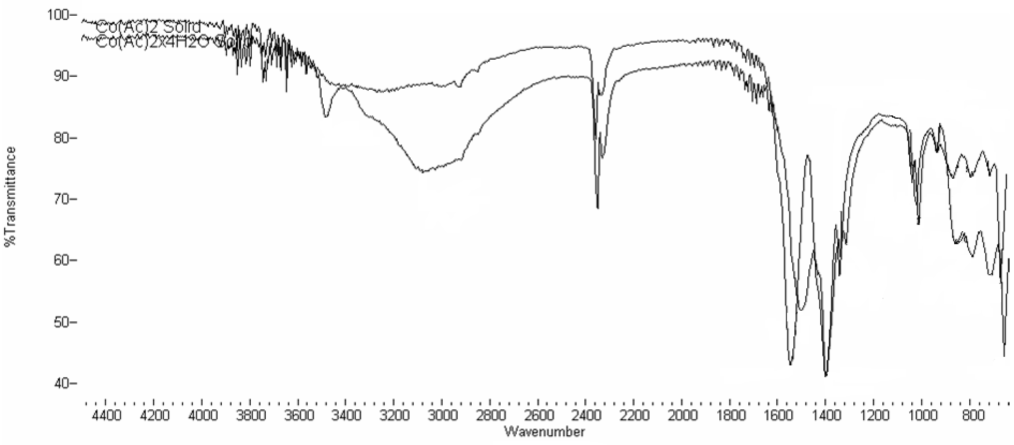

Figure 1: FT-IR spectra of: $Co(Ac)_2$ (**I**) (above) and $Co(Ac)_2$ x $4H_2O$ (**II**) (below).

The spectra (Figure 2) of salts **III** and **IV** indicates that MeOH displaces water as a ligand, this is supported by the observation that the adsorption bands in the 700-1000cm^{-1} range for **IV** resembles that of **I**. Interestingly the CO_2 band at 1510cm^{-1} in **IV** has shifted ~30cm^{-1}, almost to the same position as that observed in **I**. The addition of pyridine appears to result, to some extent, in the displacement of acetate. This becomes evident as some of the bands assigned to the acetate group are much reduced or absent. Especially for **VI** where the following "acetate" bands are missing completely; ~1330 (CH_3 symmetric bending), 1050 (CH_3 rocking), and 950cm^{-1} (C-C stretching), assignment based on Nickolov et al.[1a]

Table 1: Cobalt solids

Compound	No
$CoAc_2$	I
$CoAc_2$ x $4H_2O$	II
$CoAc_2$ (MeOH)	III
$CoAc_2$ x $4H_2O$ (MeOH)	IV
$CoAc_2$ (Pyr)	V
$CoAc_2$ x $4H_2O$ (Pyr)	VI
$CoAc_2$ + DBM (MeOH)	VII
$CoAc_2$ x $4H_2O$ + DBM (MeOH)	VIII
$CoAc_2$ + DBM (Pyr)	IX
$CoAc_2$ x $4H_2O$ + DBM (Pyr)	X
DBM	XI
MeOH	XII
Pyridine	XIII

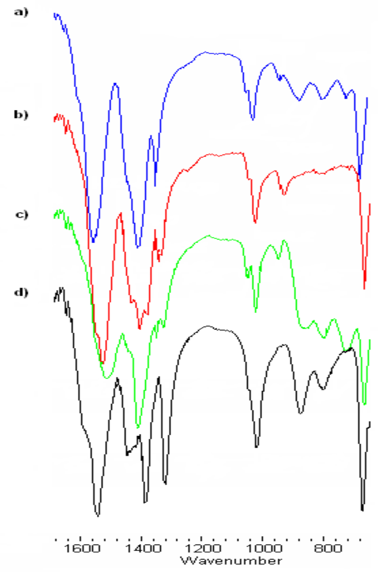

Figure 2: FT-IR Spectra of a) $CoAc_2$ (**I**), b) $CoAc_2$ dried from MeOH (**III**), c) $CoAc_2$ x $4H_2O$ (**II**), and d) $CoAc_2$ x 4H2O dried from MeOH (**IV**)

The dried salts with DBM (**VII-X**) were quite difficult to analyse due to overlap of signals (Figure 3). However it appears that competition between the acetate and DBM only occurs if water is present in the cobalt complex, i.e. salts **VIII** and **X**, (Figure 3).

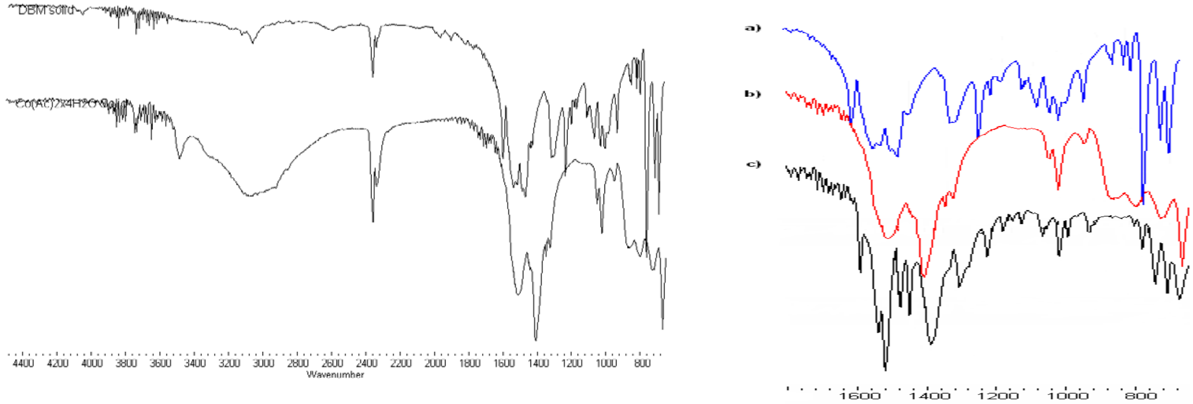

Figure 3: Left; FT-IR spectra of: DBM (above) and **II** (below), and Right, a) DBM, b) **II**, and **VIII**.

In addition to these IR data, VIS spectra were recorded on a Perkin Elmer Lambda 5 UV/VIS spectrometer. Solutions of Cobalt acetate (anhydrous and tetra hydrate) containing combinations of different ratios of Pyridine and DBM as well as pure samples were analysed. Pyridine increased the cobalt acetate absorbance maximum (λmax:520nm) but not a shift in wavelength. Addition of DBM shifted the absorbance maximum to around 420nm. Subsequent addition of pyridine to this complex shifted the maximum further. The spectroscopic data presented here support the theory of replacement of the water and acetate ligands in favour for DBM and Pyridine.

Experimental Section

Polymer synthesis

The polymers were synthesised as described by Matsui et al.[2] After polymerization the samples were ground and sieved to yield particles in the range of 25-52µm. Extensive washing was performed using three consecutive MeOH:AcOH (7:3) incubations with stirring of at least 16h each. Finally the polymers were washed with acetone and dried.

Impregnation experiments

The MIP and NIP polymers (500mg) were placed in 10ml glass vials. Methanol (2.5ml), DBM (5mg), and cobalt acetate (5mg) were added and the slurry stirred for 16h. The same experiment was repeated without cobalt acetate. The solutions were filtered and the polymers dried.

Data acquisition and analysis

X-ray absorption spectroscopy was carried out using dipole radiation on beamline 7.1 at the CCRL Daresbury Laboratory. X-ray absorption spectra were measured in fluorescence mode by a multi-element, energy-sensitive Canberra solid-state detector. The EXAFS results were analyzed using standard procedures. The statistical significance of each shell of neighbours reported has been confirmed by the standard test.[3] Energy minimization calculations were performed with Chem3D Ultra (version 9) using MM2 force fields. Solid samples of cobalt salts were analysed using a Varian FTIR in ATR mode.

References

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