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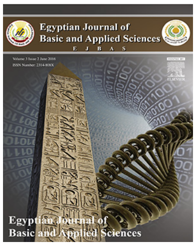

Full Length Article

# Facile synthesis and vapochromic studies of Co(II) complexes bearing NO and OO donor ligands

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ABSTRACT

Two Co(II) complexes containing malonic and isonicotinic acids have been prepared by manual grinding of stoichiometric amounts of the starting materials. Elemental analysis (CHN), IR, UV-vis spectroscopic techniques, TGA-DTG investigation and X-ray powder diffraction analysis were used to characterize the two compounds. Isonicotinic acid coordinated to the metal via the pyridine ring nitrogen and one oxygen atom of the carboxylic group while malonic acid coordinated via both oxygen atoms of the carboxylate groups indicating bidentate coordination mode in the two compounds. The compounds were exposed to some volatile organic compounds (VOCs) containing nitrogen or oxygen donor atoms in the solid state and their vapochromic behaviours studied using colour changes, FT-IR and solid state UV-vis spectroscopies. Heating the samples exposed to the VOCs for a few minutes at 100 °C regenerates the original material without degradation, even after several heating cycles.

## 1. Introduction

Vapochromic materials that display colour or luminescence changes upon exposure to vapours have been a subject of continued research in recent years due to their potential applications in chemical vapour detection in food and chemical industries, electronic noses and safety in toxic ambient conditions [1–4]. Although a variety of chemical sensors have been successfully commercialized, there still exists the need for improvement on their performance and several investigations are ongoing in this regard. Applications of coordination complexes as sensors for VOCs detection have been reported [2–4]. Coordination complexes have several advantages such as structural diversity, possibility for post-synthetic modification and a wide range of chemical and physical properties over other sensor types [5,6]. Coordination complexes also compare well to zeolites in terms of large internal surface areas, extensive

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porosity, and high degree of crystallinity, consequently they have been utilized for many of the same applications including gas storage and separations [7,8].

Complexes are thermally robust with decomposition temperatures above 300 °C, in few cases they can be stable up to 500 °C and are also capable of overcoming the challenge of selectivity that plague other sensor materials [9]. Because complexes contain metal ions in addition to their organic components, they have characteristics similar to discrete coordination complexes, and changes in the coordination sphere of these metal centres can play a role in complex sensing. The polymeric Prussian Blue complex $Co^{2+}/[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) produced dramatic changes in the visible spectrum when exposed to specific VOCs; the colour changes were linked to the sensed solvent impacting the geometry and hydration around the Co(II) centres with a change in coordination environment from the octahedral to tetrahedral geometry [10]. Several metal organic framework materials and coordination polymers based on Au(I), Pd(II) and Pt(II) have been extensively investigated for vapochromic responses [11,12].

One of the major goals of green chemistry is to limit the extensive use of solvents or even better to carry out the synthetic reaction in the absence of them. Solvent-free synthesis has therefore been applied over the years both in academic and industrial laboratories [13,14]. Solvent-free reactions are thought to occur in the solid phase, hence the problem of releasing toxic volatile organic compounds; low yield and slow reaction time associated with solution synthesis are avoided. Co(II) complexes are well-known for dramatic colour changes associated with inter-conversion between octahedral and tetrahedral coordination geometries [10]. As a continuation of our work on the use of solvent-free techniques to prepare functional materials [15–18], we hereby report mechanochemical solvent-free synthesis of Co(II) compounds of isonicotinic and malonic acids. Their vapochromic responses to a series of analytes such as methanol, ethanol, benzene, dimethylformamide and dichloromethane were also investigated.

## 2. Experimental

All reagents were purchased from Sigma-Aldrich and were used without further purification. The melting points were determined in capillary tubes using a Gallen-Kamp melting point apparatus. FT-IR spectra were recorded in KBr pellets within the range of 4000–400 cm$^{-1}$ on a SHIMADZU scientific model 500 FITR spectrophotometer. Electronic spectra of the complexes in solution were recorded on SHIMADZU UV-1650pc UV-vis spectrophotometer. Elemental analyses were carried out in a 2400 Series II Perkin-Elmer CHN Analyzer. Powder XRD analyses were performed on a Syntag PADS diffractometer at 294 K using Cu Kα radiation (λ = 1.54059 Å). Each sample was analyzed between 4.0 and 40.01 2θ with a total scan time of 5.0 min. The thermal analysis (TGA/DTG) was carried under nitrogen atmosphere with a heating rate of 10 °C/min using Shimadzu TGA Q500 V6.7 Build 203 thermal analyzer. Solid-state electronic spectra were measured on polycrystalline samples on *Analtikjena Specord 210-plus UV-Vis* spectrophotometer over the range 350–900 nm at scanning rate of 5 nm s$^{-1}$.

$$Co(CH_3COO)_2.4H_2O + H_2L \xrightarrow[\text{No solvent}]{\text{Grinding, RT, 15 min}} [Co(L)(H_2O)_2]_n + 2CH_3COOH$$

($H_2L$ = malonic acid, isonicotinic acid)

**Scheme 1 – Equation of reaction for solvent-free mechanochemical synthesis of 1 and 2.**

### 2.1. *Synthetic methods*

The two complexes were prepared by modification of a literature procedure [19].

#### 2.1.1. *$[Co(Mal)].2H_2O]_n$ (1)*

Malonic acid (0.208 g, 2 mmol) and cobalt acetate tetrahydrate (0.332 g, 1 mmol) were weighed into a clean agate mortar and ground together continuously for 15 minutes. The orange powder obtained was washed with methanol to remove any unreacted starting material, dried at room temperature and then stored in a desiccator over $CaCl_2$. The general chemical equation of the reaction is as shown in Scheme 1. Yield: 92%, M. wt. = 196.93 g/mol, m.pt. = 230 °C, Anal. Calcd for $C_3H_6O_6Co$ (%): C, 18.28; H, 3.05. Found: C, 18.28; H 3.07. IR (KBr, cm$^{-1}$): 3288b ν(O-H band of $H_2O$), 1573 $\nu_{asym}(COO^-)$, 1460 $\nu_{sym}(COO^-)$, 542 ν(M–N), 457 ν(M–O); UV-vis (DMSO) nm: 260, 295, 532, 682, 930.

#### 2.1.2. *$[Co(Ina)_2].2H_2O]_n$ (2)*

Isonicotinic acid (0.246 g, 2 mmol) and cobalt acetate tetrahydrate (0.332 g, 1 mmol) were weighed into an agate mortar and ground together continuously for 15 minutes. The light pink powder obtained was washed with methanol to remove any starting material, dried at room temperature and then stored in a desiccator over $CaCl_2$. Yield: 93%, m.wt. = 341 g/mol, m.pt. = decomposed > 300 °C; Anal. Calcd for $C_{12}H_{12}N_2O_6Co$: C, 42.48; H, 3.54 N, 8.26. Found: C, 42.23, H, 3.52, N, 8.21; IR (KBr, cm$^{-1}$): 3244 ν(O-H band of $H_2O$), 548 ν(M–N), 457 ν(M–O); UV-vis (DMSO) nm: 264, 302, 476, 516, 1078.

### 2.2. *Vapochromic studies*

The vapochromic studies of compounds **1** and **2** were carried out following a literature procedure [20]. The compounds were activated by heating at 180 °C for 20 minutes and placed in small open vials. The vials containing the compounds were then placed in a larger vial containing each of the volatile oxygen or nitrogen donor solvent (methanol, ethanol, dimethylformamide, dichloromethane, benzene and $NH_4OH$). The larger vials were then tightly closed for 24 hours. Changes in colour were observed and vapochromic properties were monitored by running IR and solid-state UV-Vis spectra of the samples before and after exposure.

## 3. Results and discussion

The composition of the complexes was determined by elemental analyses, FT-IR and PXRD. The experimentally determined elemental analysis data were in agreement with the calculated values. The two compounds were obtained with good yields exceeding 90% for both compounds; they are crystalline