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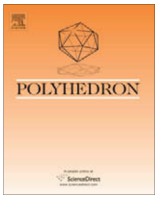

Linear $\mathrm{Mn}^{\mathrm{II}}_3$ and cubane $\mathrm{Mn}^{\mathrm{II}}_4$ carboxylate clusters derived from di-2-pyridyl ketone: Synthesis, characterization and magnetic properties

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ABSTRACT

The employment of di-2-pyridyl ketone, $(\mathrm{py})_2\mathrm{CO}$, in manganese(II) benzoate chemistry is reported. The syntheses, crystal structures and spectroscopic (IR, EPR) characterization are described for $[\mathrm{Mn}^{\mathrm{II}}_3(\mathrm{O_2CPh})_6\{(\mathrm{py})_2\mathrm{CO}\}_2]$ (**1**), $[\mathrm{Mn}^{\mathrm{II}}_3(\mathrm{O_2CPh})_6\{(\mathrm{py})_2\mathrm{CO}\}_2]\cdot 2\mathrm{MeCN}$ (**2** · 2MeCN) and $[\mathrm{Mn}^{\mathrm{II}}_4(\mathrm{O_2CPh})_4\{(\mathrm{py})_2\mathrm{C(OH)O}\}_4]$ (**3**), where $(\mathrm{py})_2\mathrm{C(OH)O}^-$ is the monoanion of the *gem*-diol form of $(\mathrm{py})_2\mathrm{CO}$. Variable-temperature, magnetic susceptibility studies on **3** have also been performed. Complexes **1** and **2** · 2MeCN are linkage isomers. The trinuclear molecules of both complexes have a linear structure, with one $\eta^1{:}\eta^2{:}\mu_2$ and two *syn, syn*- $\eta^1{:}\eta^1{:}\mu_2$ $\mathrm{PhCO_2^-}$ groups spanning each pair of $\mathrm{Mn^{II}}$ atoms. The terminal $\mathrm{Mn^{II}}$ atoms are each capped by one $\kappa^2 N,N'$ $(\mathrm{py})_2\mathrm{CO}$ ligand in orange **1** and one $\kappa^2 N,O$ $(\mathrm{py})_2\mathrm{CO}$ molecule in the yellow isomer **2** · 2MeCN. The molecule of **3** has a cubane topology with the $\mathrm{Mn^{II}}$ centers and the deprotonated oxygen atoms from the $\eta^1{:}\eta^3{:}\eta^1{:}\mu_3$ ligands occupying alternate vertices of the cube. A terminal monodentate $\mathrm{PhCO_2^-}$ group completes a distorted octahedral coordination at each $\mathrm{Mn^{II}}$ atom. The IR data are discussed in terms of the coordination modes of the ligands that are present in the complexes. The X-band EPR spectra of powdered **1** and **2** at 4 K indicate that the populated spin states exhibit a zero-field splitting, while the spectrum of **3** at 18 K is consistent with the presence of magnetically interacting $\mathrm{Mn^{II}}$ atoms in the solid state. The magnetic properties of **3** in the 300–5 K range have been modelled with two J values, which reveal weak antiferromagnetic interactions within the molecule. Some suggestions have been made concerning the great stability of complex **3**.

1. Introduction

Molecular Mn carboxylate cluster chemistry continues to attract intense attention from many research groups around the world. The reasons for this are many, but the two most important ones are the relevance of the chemistry of Mn to bioinorganic chemistry [1] and to the ongoing efforts to develop new routes to high-spin molecules [2] and single-molecule magnets (SMMs) [3]. SMMs are molecules that retain their magnetization below a blocking temperature (T_{B}) in the absence of an applied field, thus representing a molecular, "bottom up" approach to nanoscale magnets.

In this study, we have sought to extend our previous work where we had employed di-2-pyridyl ketone ($(\mathrm{py})_2\mathrm{CO}$, Scheme 1) in Mn acetate reactions, and had obtained structurally interesting new complexes [4]. Due to its highly activated carbonyl group, $(\mathrm{py})_2\mathrm{CO}$ is a unique ligand [5]. Water, among other nucleophiles [5,6], has been shown to add to the carbonyl group *upon coordination of the 2-pyridyl rings and/or the carbonyl oxygen* forming the ligand $\{(\mathrm{py})_2\mathrm{C(OH)}_2\}$ [the *gem*-diol form of $(\mathrm{py})_2\mathrm{CO}$]. Upon deprotonation, the latter can function either as mono- or dianionic ligand depending on the reaction conditions. Herein, we report the synthetic investigation of the $\mathrm{Mn^{II}}/\mathrm{PhCO_2^-}/(\mathrm{py})_2\mathrm{CO}$ reaction system that resulted in the isolation of three manganese(II) benzoate clusters. Portions of this work have been communicated [7].

2. Experimental

2.1. General information and techniques

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received.

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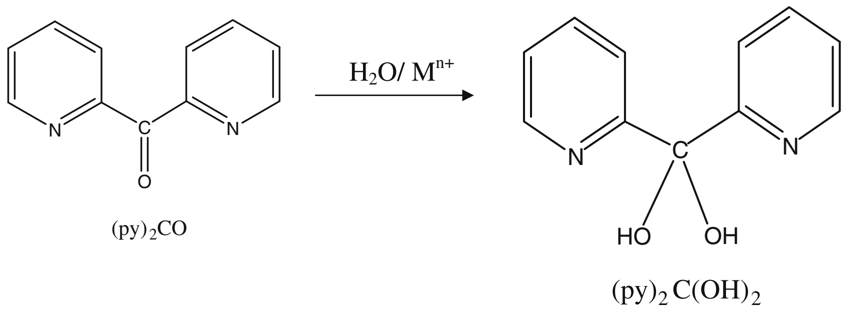

Scheme 1. Ligands discussed in the text. Note that (py)$_2$C(OH)$_2$ and its anions do not exist as free species but exist only in their respective metal complexes. M^{n+} = metal ion; n = 2, 3.

$Mn(O_2CPh)_2 \cdot 2H_2O$ was prepared as described elsewhere [8]. Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA Carlo Erba analyzer.

IR spectra (4000–400 cm^{-1}) were recorded on a Perkin–Elmer 16 PC FT-IR spectrometer with samples prepared as KBr pellets. FT-Raman spectra were recorded on a Bruker IFS 66v interferometer with a FT-Raman FRA 106 module. The compounds were excited by the 1064 nm line of a Nd:YAG laser operating at 200 mW. For each spectrum, 1000 scans were recorded and averaged. Solid state EPR spectra in the 4.2–300 K range were recorded on a Bruker ER 200D-SRC X-band spectrometer equipped with an Oxford ESR 9 cryostat. Dc magnetic measurements were carried out on a polycrystalline sample of the cubane complex (vide infra) using a Quantum Design MPMS SQUID magnetometer operating at a constant magnetic field of 0.1 T between 5.0 and 300 K. The experimental molar susceptibility was corrected for the diamagnetic contribution from the sample holder and the diamagnetic response from the sample, which was evaluated from Pascal's constants.

2.2. Compound preparation

2.2.1. [$Mn_3(O_2CPh)_6\{(py)_2CO\text{-}\kappa^2N,N'\}_2$] (**1**), [$Mn_3(O_2CPh)_6\{(py)_2CO\text{-}\kappa^2N,O\}_2$]·2MeCN (**2**·2MeCN) and [$Mn_4(O_2CPh)_4\{(py)_2C(OH)O\}_4$] (**3**) in a mixture

A colourless solution of $Mn(O_2CPh)_2{\cdot}2H_2O$ (300 mg, 0.9 mmol) in freshly distilled MeCN (20 ml) was treated with solid (py)$_2$CO (110 mg, 0.6 mmol) under mild stirring. The solid soon dissolved and the colour of the solution turned to bright yellow. Stirring was maintained for 20 min, and the solution flask was sealed and left undisturbed overnight. After several hours the solution began to afford a mixture of orange crystals of **1** and yellow crystals of **2**·2MeCN, while the colour of the solution faded to orange. One crystal from each compound was removed from the mixture and its identity was crystallographically established. The orange crystals proved to be complex **1,** while the unstable yellow crystals corresponded to complex **2**·2MeCN. After 3 days, the precipitation was judged to be complete producing more orange crystals and no yellow ones. The ratio of orange to yellow crystals was estimated to be approximately 4:1; the combined yield of the precipitated materials was about 55%. After 1 week a quantity of colourless polyhedral crystals, crystallographically identified as [$Mn_4(O_2CPh)_4\{(py)_2C(OH)O\}_4$] (**3**), was precipitated in 30% yield, while the supernatant mother solution was colourless. The reaction mixture was then left to slowly evaporate in the air and upon atmospheric oxidation the (py)$_2$CO-free known compound [$Mn_6O_2(O_2CPh)_{10}(MeCN)_4$] formed as brown rectangular plates in ~10% yield (all yields are based on the total Mn content of the reaction mixture).

2.2.2. [$Mn_3(O_2CPh)_6\{(py)_2CO\text{-}\kappa^2N,N'\}_2$] (**1**)

A colourless solution of $Mn(O_2CPh)_2{\cdot}2H_2O$ (300 mg, 0.9 mmol) in freshly distilled MeCN (20 ml) was treated with solid (py)$_2$CO (110 mg, 0.6 mmol) under mild stirring. The solid ligand soon dissolved and the colour of the solution instantly turned to bright yellow. Then a reflux condenser was attached to the reaction flask and the solution maintained under reflux for 24 hours under vigorous stirring. The colour of the solution gradually turned to orange. The reaction flask was cooled to room temperature and left undisturbed to produce orange crystals of pure **1** over a period of 3 days. The crystals were filtered, washed with Et$_2$O (2 × 3 ml) and dried in the air. 60% yield.

IR (KBr pellet, cm^{-1}): ν = 3062m, 2828w, 1710s, 1602s, 1560s, 1474m, 1446sh, 1432m, 1386sb, 1296m, 1258w, 1222m, 1016m, 950m, 802m, 776m, 750w, 724s, 678s, 636m. *Anal.* Calc. for $C_{64}H_{46}O_{14}N_4Mn_3$ (1259.9): C, 61.01; H, 3.69; N, 4.45. Found: C, 60.67; H, 3.55; N, 4.52%.

2.2.3. [$Mn_3(O_2CPh)_6\{(py)_2CO\text{-}\kappa^2 N,O\}_2$] · 2MeCN (**2** · 2MeCN)

A colourless solution of $Mn(O_2CPh)_2{\cdot}2H_2O$ (600 mg, 1.8 mmol) in freshly distilled MeCN (20 ml) was treated with solid (py)$_2$CO (220 mg, 1.2 mmol) in small portions under gentle stirring. The solid ligand soon dissolved and the bright yellow solution obtained was left undisturbed to produce a yellow microcrystalline powder. The powder was collected after 6 h, since after that time orange crystals of **1** began to form. The yellow material was collected by filtration, washed with Et$_2$O (2 × 3 ml) and dried in the air. The yield was 30%. (KBr pellet, cm^{-1}): ν = 3064m, 2830w, 1640s, 1596s, 1546br, 1470m, 1430sh, 1408s, 1384sh, 1296w, 1268w, 1028m, 1016m, 978w, 772m, 724s, 678m, 640w, 615sh. The solid analyzed as solvent-free. *Anal.* Calc. for $C_{64}H_{46}O_{14}N_4Mn_3$ (1259.9): C, 61.01; H, 3.69; N, 4.45. Found: C, 60.87; H, 3.73; N, 4.40%.

2.2.4. [$Mn_4(O_2CPh)_4\{(py)_2C(OH)O\}_4$] (**3**)

To a colourless solution of $Mn(O_2CPh)_2{\cdot}2H_2O$ (167 mg, 0.5 mmol) in "wet" CH$_2$Cl$_2$ (25 ml) was added solid (py)$_2$CO (92 mg, 0.5 mmol). The solid soon dissolved to yield a pale yellow solution. The solution became colourless after 30 min of stirring. The solution was layered with *n*-hexane (50 ml). Slow mixing gave large, polyhedral crystals of the product after 3 days in 90% yield. The crystals were collected by filtration, washed with Et$_2$O (2 × 3 ml) and dried in the air. IR (KBr pellet, cm^{-1}): ν = 3416br, 1596s, 1558s, 1434m, 1390s, 1292w, 1258w, 1222m, 1016m, 950m, 774m, 726s, 680m, 662w, 636m. *Anal.* Calc. for $C_{72}H_{56}O_{16}N_8Mn_4$ (1509.0): C, 57.30; H, 3.75; N, 7.43. Found: C, 57.42; H, 3.96; N, 7.33%.

2.3. Single-crystal X-ray crystallography

A crystal of **1** was mounted in air, while crystals of **2**·2MeCN and **3** were mounted in capillary. Diffraction measurements were made