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Note

Crystal structures, spectral and magnetic properties of cobalt(II) pyridinecarboxylates: A novel polymeric chain in $\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\text{-}\{2,6\text{-}(MeO)_2nic\}_2 \cdot 6H_2O\}_n$

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Abstract

Synthesis and characterization of two new cobalt(II) complexes, namely monomeric $[Co(2\text{-}MeSnic)_2(H_2O)_4] \cdot 4H_2O$ (2-MeSnic is 2-methylthionicotinate) and polymeric $\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\{2,6\text{-}(MeO)_2nic\}_2 \cdot 6H_2O\}_n$ (2,6-$(MeO)_2$nic is 2,6-dimethoxynicotinate), are reported. The characterizations were based on elemental analysis, infrared and electronic spectra as well as magnetic measurements. Crystal structures of both complexes have been determined. In both of them – ($[Co(2\text{-}MeSnic)_2(H_2O)_4] \cdot 4H_2O$ and $\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\{2,6\text{-}(MeO)_2nic\}_2 \cdot 6H_2O\}_n$) – the Co^{II} atom is six-coordinated. In the 2nd complex, there are two nonequivalent Co^{II} central atoms, involved in forming a linear polymeric chain with alternating cationic and neutral part. One of them is octahedrally coordinated by a carboxyl oxygen atom of 2,6-$(MeO)_2$nic, two water molecules and the corresponding centrosymmetrically located atoms. The second Co^{II} atom is also octahedrally coordinated by six water molecules. Both coordination polyhedra are bridged by a water molecule. The charge of the cationic part is compensated for by two independent anionic 2,6-$(MeO)_2$nic units. The structure is held together by a complicated system of hydrogen bonds.

Keywords: Crystal structure; Pyridinecarboxylate complexes; Cobalt(II) complexes; Polymeric complexes; Spectral and magnetic properties

1. Introduction

Copper(II) and cobalt(II) complexes of carboxylato ligands have been the subject of a large number of research studies as pyridinecarboxylic acids and their derivatives play a significant role in medicine and their copper(II) and cobalt(II) complexes are of interest both from chemical and biological point of view. A carboxylate ion, $RCOO^-$, can coordinate to metals in a number of ways, namely as a unidentate ligand, as a chelating ligand, as a bridging bidentate ligand in *syn–syn*, *syn–anti* or *anti–anti* configuration, or as a monoatomic bridging ligand, either alone, with additional bridging, or in arrangements involving chelation and bridging [1,2].

Preparation, spectral properties, magnetic properties and crystal structure of Cu^{II} and Co^{II} complexes $[MX_2(H_2O)_4]$ (X = nicotinate – nic or isonicotinate – isonic), $[Cu(2\text{-}MeSnic)_2(H_2O)]_2$ (2-MeSnic = 2-methylthionicotinate) and $[Cu\{2,6\text{-}(MeO)_2nic\}_2(H_2O)]_2$ (2,6-$(MeO)_2$nic = 2,6-dimethoxynicotinate) as well as of their adducts with chelating

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and N-heterocyclic ligands have been described in several previous papers [3–8].

In this paper, we describe the synthesis, spectral properties and crystal structures as well as magnetic measurements of mononuclear $[Co(2\text{-}MeSnic)_2(H_2O)_4]\cdot 4H_2O$ and polynuclear $\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\{2,6\text{-}(MeO)_2nic\}_2\cdot 6H_2O\}_n$.

2. Experimental

2.1. Chemical reagents, analysis and physical measurements

All the chemicals used were of reagent grade (Aldrich or Sigma) and used without further purification. All organic reagents were purchased from Aldrich; their purity was checked by IR spectra.

Cobalt was determined by electrolysis of water solutions obtained by the sample mineralisation (acid digestion) with a mixture of sulfuric acid and potassium peroxodisulfate; carbon, hydrogen, nitrogen and sulfur were determined by microanalytical methods (Thermo Electron Flash EA 1112).

Electronic spectra (9000–50 000 cm^{-1}) of the powdered samples in nujol mulls were recorded at room temperature (r.t.) on a Specord 200. IR spectra in the region of 400–4000 cm^{-1} were recorded on a Magna 750 spectrometer at r.t. Spectra of the solid samples were obtained in nujol mulls and KBr pellets (1 wt%).

Magnetic susceptibility measurements in the temperature range of 1.8–300 K were carried out on powdered samples of the complexes, at the magnetic field of 5 kG, using a Quantum Design SQUID Magnetometer (type MPMS-XL5). Corrections for diamagnetism of the constituting atoms were calculated using the Pascal constants [9], the value of 150×10^{-6} cm^3 mol^{-1} was used as the temperature-independent paramagnetism of cobalt(II) ion. The effective magnetic moments were calculated from the expression

$$\mu_{eff} = 2.83\sqrt{\chi_m^{corr}\cdot T}\ (BM).$$

2.2. Crystallography

Crystal data collection procedures, and refinement results for the complexes $[Co(2\text{-}MeSnic)_2(H_2O)_4]\cdot 4H_2O$ and $\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\{2,6\text{-}(MeO)_2nic\}_2\cdot 6H_2O\}_n$ are given in Table 1. Data collection and cell refinement were carried out using Nonius CAD-4 diffractometer. The diffraction intensities were corrected for Lorentz, polarization and absorption effects.

The structures of the complexes were solved with SHELXS-97 [10] using direct methods, while further refinement with full-matrix least-squares on F^2 was carried out with SHELXL-97 [11]. Geometrical analysis was performed using SHELXL-97 [11]. The structure of the complexes was drawn by ORTEP-3 [12] (Figs. 1 and 2). Selected bond distances and angles for $[Co(2\text{-}MeSnic)_2(H_2O)_4]\cdot 4H_2O$ and $\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\{2,6\text{-}(MeO)_2nic\}_2\cdot 6H_2O\}_n$ are given in Tables 2 and 3, respectively.

Table 1
Crystal data and structure refinement for $[Co(2\text{-}MeSnic)_2(H_2O)_4]\cdot 4H_2O$ and $\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\{2,6\text{-}(MeO)_2nic\}_2\cdot 6H_2O\}_n$

Compound	$[Co(2\text{-}MeSnic)_2(H_2O)_4]\cdot 4H_2O$	$\{[\{2,6\text{-}(MeO)_2nic\}_2(H_2O)_2Co(\mu\text{-}H_2O)Co(H_2O)_4(\mu\text{-}H_2O)]\{2,6\text{-}(MeO)_2nic\}_2\cdot 6H_2O\}_n$
Empirical formula	$C_{14}H_{28}CoN_2O_{12}S_2$	$C_{32}H_{60}Co_2N_4O_{30}$
Formula weight	539.44	1098.70
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	7.3182(2)	7.6184(2)
b (Å)	7.4967(4)	8.2028(2)
c (Å)	11.2936(5)	19.1793(7)
α (°)	79.080(2)	95.049(1)
β (°)	73.418(3)	95.899(1)
γ (°)	68.903(2)	107.527(2)
Z, volume (Å^3)	1, 551.41(4)	1, 1127.89(6)
D_{calc} (Mg m^{-3})	1.624	1.618
μ (mm^{-1})	1.030	0.840
$F(000)$	281	574
Diffractometer	Nonius CAD-4	Nonius CAD-4
Radiation type Mo Kα, λ (Å)	0.71073	0.71073
Temperature (K)	293(2)	173(2)
Reflections collected/unique	5132/1879	10335/3838
Refinement method	full matrix, least-squares on F^2	full-matrix, least-squares on F^2
Data/restraints/parameters	1879/0/198	3838/0/422
Goodness-of-fit on F^2	1.102	1.096
Final R indices ($I>2\sigma(I)$)	$R=0.0273$, $R_w=0.0664$	$R_1=0.0309$, $wR_2=0.0768$
Largest difference peak and hole (e Å^{-3})	0.319 and −0.396	0.603 and −0.584