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Magneto-structural correlations. Rietveld refinement of the three-dimensional crystal structure of Mn(*en*)Ni(CN)$_4$ (en = ethylenediamine) and magnetic interactions through the [Ni(CN)$_4$]$^{2-}$ anion

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Abstract

Magneto-structural correlations in Mn(*en*)Ni(CN)$_4$ (en = ethylenediamine) (MENC) have been studied. The crystal structure of MENC was refined by Rietveld analysis of X-ray powder diffraction data; it is three-dimensional (3d) and is built up of [Mn(*en*)]$^{2+}$ cations with deformed octahedrally coordinated Mn(II) ($S = 5/2$) atoms and [Ni(CN)$_4$]$^{2-}$ anions containing square-planarly coordinated Ni(II) ($S = 0$) atoms. The building species are linked by bridging μ_2-cyano ligands. The characterization of magnetic properties confirmed the expected 3d nature of spin correlations by observing λ-like anomaly in specific heat at $T_c = 0.47$ K. The resulting exchange interaction $J/hc = -0.12$ cm^{-1} is somewhat smaller than that found in other complexes with the same type of exchange paths.

Keywords: Rietveld refinement; Powder diffraction; Manganese; Nickel; Cyanocomplex; Magnetic studies

1. Introduction

The molecular design of extended structures represents one of the most active fields in modern inorganic chemistry and the investigation of the relation between the structure and resulting physical properties have been the focus of intense both theoretical and experimental effort [1,2]. The preparation of materials with predictable magnetic properties represents the final aim of these studies. Apart from the fact that this successful endeavour is the final goal of molecular engineering, the preparation of such new materials may greatly help in understanding currently investigated fundamental physical phenomena, e.g., novel quantum spin states arising from geometrical frustration, mechanism of high-T_c superconductivity, nonlinear spin dynamics, etc.

Detailed experimental verification of the theoretical predictions describing the aforementioned physical phenomena ultimatively requires the investigation the dependence of the characteristic quantities in the magnetic field and at relatively high temperatures $T/J > 1$, where J represents exchange interaction. In this context, materials with moderate values of exchange coupling are of particular interest since for them high magnetic field and temperature regimes are conveniently accessible.

Structural and compositional variability of compounds containing cyano groups makes these materials appropriate for the aforementioned studies [3–8]. Indeed, selected representatives of such compounds containing [Ni(CN)$_4$]$^{2-}$ anion proved to be useful in experimental physical studies of those low dimen-

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sional magnets in which exchange interaction represents small, but not negligible perturbation [9,10].

Systematic study of using $[Ni(CN)_4]^{2-}$ anion as an exchange path requires also the investigation of the influence of number and symmetry of the magnetic orbitals to the resulting magnitude of exchange coupling. In this context compound possessing both $[Ni(CN)_4]^{2-}$ anion and Mn(II) ion may be of importance since for Mn(II) ion five magnetic orbitals are available. It should be stressed, that structural information about compounds containing both Mn(II) and $[Ni(CN)_4]^{2-}$ anion are scarce. To our knowledge, up to now only two other compounds of this type were described: clathrate $Mn(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$ [11] and $Mn(py)_2Ni(CN)_4$ (py = pyridine) both exhibiting 2d crystal structure [12]. Recently we were successful in the preparation and identification of a paramagnetic compound Mn(*en*)$Ni(CN)_4$ (MENC) but we were unsuccessful in preparation of this compound in the form of single crystals [13]. Its composition is similar to the previously studied compounds Cd(*en*)$Ni(CN)_4$ [14] and Zn(*en*)$Ni(CN)_4$ [15], respectively, which crystal structures were determined from single crystal data. Both compounds are isostructural; they exhibit three dimensional (3d) crystal structure, in which both $[M(en)]^{2+}$ (M = Zn, Cd) cation as well as $[Ni(CN)_4]^{2-}$ anion exhibit connectivities 4, and both central atoms are linked by bridging μ_2-CN^- ligands. Both these compounds are diamagnetic. As a part of our systematic studies on magneto-structural correlation in cyanocomplexes here we report the results of Rietveld refinement of the structure of MENC correlated with the results of its thermodynamic and magnetic studies.

2. Experimental section

2.1. Preparation

MENC was prepared in the form of a crystalline powder according to the procedure described in the literature [13]. Its composition was checked by the measured IR spectrum (Avatar Nicolet FT-IR Spectrophotometer).

2.2. X-ray powder diffractometry and Rietveld refinement

X-ray powder diffraction (XRD) pattern were taken from a computerized Siemens–Bruker D-500 diffractometer using backmonochromatized CuKα radiation ($\lambda(K_{\alpha 1}) = 1.540981$ Å, graphite monochromator) in the 2θ range 8–94°. The diffractogram was recorded in step mode (0.02°, 20 s).

The cell reconstruction was performed using powder data indexing program Crysfire [16]. As a result of the process the orthorhombic cell was found (possible space group *Pbna*). The lattice dimensions as well as further non-structural parameters (i.e., background, peak profile parameters including asymmetry) were next refined by the structureless (profile matching) method using Fullprof program suite [17] (Table 1). As an initial model for the full crystal structure refinement (by Fullprof), the previously reported atomic coordinates for single crystal Zn(*en*)$Ni(CN)_4$ were used [15]. During the refinement process the positions of hydrogen atoms and all displacement parameters were kept fixed and the selected interatomic distances were restrained. The refined crystal structure was analysed and validated by Platon [18]. The final Rietveld refinement fit is shown in Fig. 1. Refined structural parameters are listed in Table 2, some selected bond distances in Table 3. The schematic view of the crystal structure is shown in Fig. 2. The figures of structure were drawn using the Diamond program [19].

Table 1
Selected crystal data for MENC

Formula sum	C6 H8 Mn1 N6 Ni1
Crystal system	Orthorhombic
Space group	Pbna
Cell parameters [Å]	$a = 10.18432(11)$
	$b = 11.18705(12)$
	$c = 8.82142(9)$
Cell volume [Å^3]	$V = 1005.05(2)$
Number of form. units	$Z = 4$
Final res. parameter R_{wp}	0.103

2.3. Study of magnetic properties

The susceptibility and magnetization were investigated in a commercial SQUID magnetometer. In these measurements, inert electrical varnish was used to glue the sample into a gelcap that was held by a straw. For the susceptibility measurements, 105 G magnetic field was applied. The background correction of the signal resulting from the gelcap and straw themselves was estimated from independent run with empty gelcap.

The specific heat of MENC was scanned in a zero magnetic field using a dual-slope technique [20]. The used technique proved to be useful especially for searching anomalies in the temperature dependence of specific heat. Our study was conducted in a commercial dilution refrigerator TLE200. RuO_2 thermometer of Dale type with a nominal value 4.7 kΩ at 300 K was used as a temperature sensor after being calibrated against a LakeShore thermometer (GR 200A-50). More detailed description of the experimental setup is reported elsewhere [21].

3. Results and discussion

3.1. Structure description

The results of the Rietveld refinement have shown that MENC is isostructural with both Zn(*en*)$Ni(CN)_4$ and Cd(*en*)-$Ni(CN)_4$, and consequently its crystal structure is three dimensional (Fig. 3). The Mn(II) and Ni(II) atoms placed in the special positions with local symmetries 2 (Mn) and −1 (Ni), respectively, are linked by bridging cyano groups (Fig. 2). The Ni(II) atom is coordinated by four bridging cyano ligands in the square form, thus it is diamagnetic. The found mean Ni–C bond 1.92 Å (Table 2) is somewhat longer than the usual value of 1.86 Å [22]. The Mn(II) central atom is coordinated deformed octahedrally by one chelate bonded *en* diamine ligand and four bridging cyano ligands via N-atoms. The Mn–N bonds within the chelate ring are somewhat longer (2.40 Å) as the Mn–N(≡C) bonds (2.24 Å); these values, taking into account