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Metamagnetism and long range ordering in μ-1,3 bridging transition metal thiocyanato coordination polymers

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ABSTRACT

Reaction of $M(SCN)_2$ (M = Mn, Fe, Ni) with pyridine (pyr) in aqueous solution at room temperature leads to the formation of the literature known pyridine-rich 1:4 compounds of composition $[M(SCN)_2(\text{pyridine})_4]$ (M = Mn (**1-Mn**), Fe (**1-Fe**), Ni (**1-Ni**)) reported recently. On heating, the 1:4 compounds decompose into their corresponding pyridine-deficient 1:2 compounds of composition $[M(SCN)_2(\text{pyridine})_2]_n$ (M = Mn (**2-Mn**), Fe (**2-Fe**), Ni (**2-Ni**)) which decompose on further heating. In the crystal structure of the pyridine-deficient 1:2 compounds the metal cations are coordinated by four N-atoms of two pyridine ligands and two N-bonded thiocyanato anions, each in mutually *trans* orientation, and by two S-atoms of two adjacent thiocyanato anions in a slightly distorted octahedral geometry. The thiocyanato anions bridge the metal cations into one-dimensional (1D) polymeric chains. IR spectroscopic investigations on the pyridine-deficient 1:2 compounds are in agreement with the presence of μ-1,3 bridging thiocyanato anions. Magnetic measurements of the pyridine-rich 1:4 compounds show only Curie–Weiss paramagnetism whereas for the pyridine-deficient 1:2 compounds an antiferromagnetic ordering for $[Mn(NCS)_2(\text{pyridine})_2]_n$ (**2-Mn**) and metamagnetic behavior for $[Ni(NCS)_2(\text{pyridine})_2]_n$ (**2-Ni**) is found. For $[Cu(NCS)_2(\text{pyridine})_2]_n$ (**2-Cu**) Curie–Weiss paramagnetic behavior is observed. $[Fe(NCS)_2(\text{pyridine})_2]_n$ (**2-Fe**) shows metamagnetic behavior, which was already investigated but remeasured for a more detailed characterization.

1. Introduction

Recently, much effort has been made in the development and exploration of novel functional materials with well-defined properties [1–14]. The combination of pure inorganic metal salts with organic spacer ligands resulted in a rich diversity of coordination polymers, metal organic frameworks or inorganic–organic hybrid composites with interesting and promising, e.g. photochemical or magnetic properties [15–34]. In this context compounds that show cooperative magnetic exchange interactions like, e.g. antiferro- or ferromagnetism are usually observed in two-dimensional (2D) and three-dimensional (3D) coordination polymers with bridging organic co-ligands and bridging small-sized anions. Moreover, for possible future applications materials are needed in which the magnetic behavior can be tuned or switched as function of external parameters. This also includes metamagnetic compounds that show different magnetic properties above and below a critical magnetic field. Moreover, for a more detailed understanding and the optimization of such materials the systematic exploration of the magneto-structural correlations and their implementation in the rational design of materials with magnetic exchange interactions is absolutely needed.

However, in contrast to the higher-dimensional materials, magnetic exchange of adjacent spin carriers can also be observed in zero-dimensional (OD) and one-dimensional (1D) compounds, so called single molecule magnets (SMMs) or single chain magnets (SCMs). In these compounds the magnetic coupling is mediated through superexchange interactions and they show superparamagnetic behavior above a blocking temperature T_B and slow relaxation of the magnetization below T_B [35,36]. In this context it is noted that slow relaxation of magnetization can also be found in 2D systems if the magnetic chains are separated through large and magnetic non-interacting bidentate co-ligands [37].

In our own research our interest is focused on the magnetic properties of 1D and 2D compounds predominantly based on transition metal thio- and selenocyanates. In the course of our systematic investigations we have found that such compounds can selectively be prepared by thermal decomposition reactions of suitable precursor compounds in which the metal cations are octahedrally coordinated by two *N*-terminal bonded anions and four N-donor co-ligands [38–47]. On heating a part of the co-ligands are irreversible be removed leading to 1D and 2D compounds with μ-1,3 bridging anions and modified magnetic exchange interactions. This approach is especially useful in those cases where the compounds

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with bridging anions cannot be prepared in solution but is also of importance for the exploration of such compounds. In the course of our work we have investigated the pyridine-deficient 1D compounds $[Co(NCX)_2(pyridine)_2]_n$ (X = S, Se), which were prepared by thermal decomposition of the pyridine-rich 0D precursor complexes of composition $[Co(NCX)_2(pyridine)_4]$ (X = S, Se). Surprisingly both compounds show single chain magnetic behavior which were the first examples for the occurrence of these rare phenomena in thio- and selenocyanates [48,49]. However, for further magneto-structural investigations in this class of compounds also investigations on the magnetic properties of the corresponding compounds with transition metal cations out of the first transition metal period are needed. Therefore we synthesized compounds of composition $[M(NCS)_2(pyridine)_2]_n$ (M = Mn, Fe, Ni) by thermal decomposition of their literature known pyridine-rich precursor compounds $[M(NCS)_2(pyridine)_4]$ (M = Mn (**1-Mn**), Fe (**1-Fe**), Ni (**1-Ni**)) [50–54]. In this context it is mentioned that the structures of corresponding compounds of composition $[M(NCS)_2(pyridine)_2]_n$ (M = Cu (**2-Cu**), Ni (**2-Ni**)) [55,56] are already described in literature, so that the thermal decomposition products can be easily identified. It also has to be announced that compound **2-Fe** was already magnetically investigated by Foner et al. [57] in 1975 and metamagnetic behavior was found but the ferromagnetic state was not further investigated. Therefore additional magnetic measurements were also being performed for this compound in order to prove if, e.g. SCM behavior is found as it was observed for the first time for the homospin Fe(II) compound $[Fe_9(chp)_{12.4}(O_2CMe)_{5.6}]_n$ (chp = 6-chloro-2-pyridinolate) by Przybylak et al. [58]. Here, we report on our investigations.

2. Material and methods

2.1. Materials

$Ni(SCN)_2$ and $MnCl_2{\cdot}2H_2O$ were obtained from Alfa Aesar. $FeCl_2{\cdot}4H_2O$ and KNCS were obtained from Sigma-Aldrich and pyridine was obtained from Riedel-de Haën. Solvents were used without further purification. Crystalline powders of compounds **1-Fe**, **1-Mn**, **1-Ni** and **2-Cu** were prepared by stirring the reactants in appropriate solvents at room temperature. The residues were filtered off and washed with ethanol and diethylether and dried in air. The purity of all compounds was checked by X-ray powder diffraction (Figs. S18–S21 in the supplementary information) and elemental analysis.

2.2. Synthesis of [tetrakis(pyridine-κN)-bis(thiocyanato-κN)-iron(II)] (*1-Fe*)

The literature known compound **1-Fe** was prepared according to a different procedure by the reaction of $FeCl_2{\cdot}4H_2O$ (198.8 mg, 1.00 mmol), KNCS (194.4 mg, 2.00 mmol) and pyridine (632.8 mg, 8.00 mmol) in water (4.00 mL). Yield: 256.4 mg (52.5%). *Anal.* Calc. for $C_{22}H_{20}FeN_6S_2$ (488.4): C, 54.10; H, 4.13; N, 17.21; S, 13.13. Found: C, 54.54; H, 4.10; N, 17.16; S, 13.09. IR (KBr): 2067 (s), 1598 (s), 1486 (w), 1442 (s), 1212 (w), 1068 (w), 1037 (w), 1005 (w), 765 (w), 755 (w), 712 (m), 700 (m), 625 (w), 483 (w), 428 (w), 419 (w) cm^{-1}.

2.3. Synthesis of [tetrakis(pyridine-κN)-bis(thiocyanato-κN)-manganese(II)] (*1-Mn*)

The literature known compound **1-Mn** was prepared according to a different procedure by the reaction of $MnCl_2$ (125.8 mg, 1.00 mmol), KNCS (194.4 mg, 2.00 mmol) in pyridine (2.65 mL, 32.90 mmol). Yield: 111.9 mg (23.0%). *Anal.* Calc. for $C_{22}H_{20}N_6MnS_2$ (487.5): C, 54.20; H, 4.14; N, 17.24; S, 13.15. Found: C, 54.46; H, 4.13; N, 17.47; S, 13.52. IR (KBr): 2060 (s), 1598 (s), 1486 (m), 1442 (s), 1213 (m), 1068 (m), 1034 (m), 1005 (m), 765 (m), 754 (m), 712 (s), 700 (s), 623 (m), 481 (w), 421 (w), 414 (w) cm^{-1}.

2.4. Synthesis of [tetrakis(pyridine-κN)-bis(thiocyanato-κN)-nickel(II)] (*1-Ni*)

The literature known compound **1-Ni** was prepared according to a recipe given in the literature by the reaction of $Ni(SCN)_2$ (174.9 mg, 1.00 mmol) and pyridine (632.8 mg, 8.00 mmol) in water (2.00 mL) [50]. Yield: 246.8 mg (50.23%). *Anal.* Calc. for $C_{22}H_{20}N_6NiS_2$ (491.3): C, 53.79; H, 4.10; N, 17.11; S, 13.05. Found: C, 53.02; H, 3.96; N, 17.07; S, 13.29. IR (KBr): 2082 (s), 1599 (s), 1487 (m), 1443 (s), 1212 (m), 1069 (m), 1039 (m), 1008 (m), 768 (m), 757 (m), 713 (s), 700 (s), 626 (m), 483 (w), 437 (w), 429 (w) cm^{-1}.

2.5. Synthesis of catena-poly[bis(pyridine-κN)-bis(thiocyanato-κN,κS)-copper(II)] (*2-Cu*)

The literature known compound **2-Cu** was prepared according to a different procedure by the reaction of $CuCl_2{\cdot}2H_2O$ (170.5 mg, 1.00 mmol) and KNCS (194.4 mg, 2.00 mmol) in pyridine (0.50 mL, 6.45 mmol) and subsequent precipitation in water (1.50 mL). Yield: 249.6 mg (73.87%). *Anal.* Calc. for $C_{12}H_{10}CuN_4S_2$ (337.9): C, 42.65; H, 2.98; N, 16.58; S, 18.98. Found: C, 42.86; H, 2.85; N, 16.82; S, 19.32. IR (KBr): 2092 (s), 1603 (m), 1486 (w), 1445 (m), 1214 (w), 1070 (w), 1042 (w), 1015 (w), 759 (w), 693 (m), 638 (w), 478 (w), 435 (w) cm^{-1}.

2.6. Synthesis of catena-poly[bis(pyridine-κN)-bis(thiocyanato-κN,κS)-iron(II)] (*2-Fe*)

This compound was isolated in the first heating step (see Section 3.2) of compound **1-Fe**. Yellow well-shaped single-crystals suitable for X-ray structure determination were obtained in a mixture with unknown phases by reaction of $FeCl_2{\cdot}4H_2O$ (0.50 mmol, 99.40 mg) and KNCS (1.00 mmol, 97.20 mg) with pyridine (0.25 mmol, 20.20 μL) in 1.50 mL of water at room temperature. Calculated for the ligand-deficient compound **2-Fe**. *Anal.* Calc. for $C_{12}H_{10}FeN_4S_2$ (330.2): C, 43.65; H, 3.05; N, 16.91; S, 19.42. Found: C, 43.76; H, 2.87; N, 16.44; S, 19.62. IR (KBr): 2093 (s), 1600 (m), 1486 (w), 1442 (m), 1215 (w), 1070 (w), 1039 (w), 1010 (w), 755 (w), 696 (m), 629 (w), 472 (w), 422 (w) cm^{-1}.

2.7. Synthesis of catena-poly[bis(pyridine-κN)-bis(thiocyanato-κN,κS)-manganese(II)] (*2-Mn*)

This compound was isolated in the first heating step (see Section 3.2) of compound **1-Mn**. Colorless well-shaped single-crystals suitable for X-ray structure determination were obtained in a mixture with unknown phases by reaction of $MnCl_2{\cdot}2H_2O$ (1.00 mmol, 162.00 mg), KNCS (2.00 mmol, 194.40 mg) and pyridine (0.50 mmol, 40.3 μL) in 1.50 mL of ethanol at room temperature. Calculated for the ligand-deficient compound **2-Mn**. *Anal.* Calc. for $C_{12}H_{10}MnN_4S_2$ (329.3): C, 43.77; H, 3.06; N, 17.01; S, 19.47. Found: C, 43.99; H, 3.02; N, 16.85; S, 19.72. IR (KBr): 2090 (s), 1598 (m), 1486 (w), 1441 (m), 1215 (w), 1069 (w), 1038 (w), 1007 (w), 760 (w), 697 (m), 626 (w), 475 (w), 419 (w) cm^{-1}.

2.8. Synthesis of catena-poly[bis(pyridine-κN)-bis(thiocyanato-κN,κS)-nickel(II)] (*2-Ni*)

This compound was isolated in the first heating step (see Section 3.2) of compound **1-Ni**. Calculated for the ligand-deficient compound **2-Ni**. *Anal.* Calc. for $C_{12}H_{10}N_4NiS_2$ (333.1): C, 43.28;