Crystal and magnetic structure of the two-dimensional coordination polymers CoCl₂(bpy−d8) and NiCl₂(bpy−d8)

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Abstract. Neutron diffraction studies of polycrystalline samples of the two-dimensional coordination polymers CoCl₂(bpy−d8) and NiCl₂(bpy−d8) (bpy−d8 = 4,4′-bipyridine, fully deuterated) were carried out at various temperatures in order to determine their chemical and magnetically ordered structures. For both compounds, an orthorhombic structure, space group Pban (No. 50), was observed in which infinite chains of (−CoCl₂−) or (−NiCl₂−) units were cross-linked by the bipyridine ligands. Previous magnetic susceptibility studies of Co- and NiCl₂(bpy) revealed long-range antiferromagnetic ordering below 5.0 and 8.5 K, respectively. From the low-temperature neutron diffraction data, a simple magnetic moment arrangement was deduced in which the metal ions are ferromagnetically coupled within the metal–chloride chains and nearest-neighbor chains couple antiferromagnetically. At 1.5 K, ordered moments of 2.8(2) and 4.0(2)µB, respectively, were observed with a moment orientation along the metal–bpy–metal bridges.

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In the search for new pathways towards molecular magnetic materials [1–3], the assembly of new types of metal coordination polymers has played an important role in recent years [4]. Several bifunctional ligands have proven to be well-suited building blocks for the assembly of one- to three-dimensional network structures and for the mediation of magnetic exchange interactions. Recently, two-dimensional metal coordination polymers with the general formula MCl₂(bpy), with M = (Fe, Co, Ni) and bpy = 4,4′-bipyridine, have been synthesized [5]. In these compounds, infinite chains of (−MCl₂−) units are cross-linked by the rod-like bpy ligands yielding a two-dimensional network. Magnetic susceptibility data revealed a dominant ferromagnetic exchange interaction between the metal centers associated with the (−MCl₂−) chains. Long-range antiferromagnetic ordering was observed for all compounds below 5–10 K [5], indicative of antiferromagnetic interchain interactions.

In this work we describe neutron diffraction studies of deuterated CoCl₂(bpy−d8) and NiCl₂(bpy−d8) from which new information on the crystal and magnetically ordered structure is deduced and the role of bpy for the interchain magnetic interaction is clarified.

1 Experiment

Microcrystalline samples of both compounds (each ≈ 200 mg in weight) were synthesized by a hydrothermal route described in [5] using bpy-d8 (98% D) purchased from Campro Scientific (Berlin), anhydrous CoCl₂ and NiCl₂ (Strem Chemicals, 99 + %), and D₂O (Aldrich Chemical Co., 99.9% D) as solvent. Phase purity was checked by X-ray powder diffraction (impurity level < 2%). Magnetization measurements using an MPMS Squid magnetometer (Quantum Design) showed that the deuterated samples show behavior identical to that reported for the non-deuterated ones. Neutron diffraction was carried out at various temperatures between 1.5 and 300 K at the Berlin Neutron Scattering Center using the diffractometers E6 (high-flux) and E9 (high-resolution), with neutron wavelengths of 2.448(4) and 1.7964(10) Å, respectively. The samples were cooled in a ⁴He-Flow cryostat. Rietveld analysis of the diffraction data was carried out using Fullprof [6].

2 Results and discussion

Figure 1 shows the high-resolution powder diffraction pattern recorded at 6 K and a blow-up of the data for 6 and 300 K for CoCl₂(bpy−d8). The patterns for 6 and 300 K are very similar, showing that the crystal structures are essentially the same at both temperatures. Similar data (not shown) were measured for NiCl₂(bpy−d8).

Previously, from X-ray diffraction on single crystals of non-deuterated Co- and NiCl₂(bpy), an orthorhombic
The result of the corresponding Rietveld refinement of the neutron diffraction data is shown in Fig. 1 as a solid line. The resulting structural parameters are listed in Table 1, and the crystal structure is depicted in Fig. 2. The single pyridine rings appear perfectly flat, as expected for chemical reasons. This may be regarded as a proof of validity of the assumptions made prior to the refinement. The new structural information deduced from the neutron diffraction data is the tilt of the two
pyridine rings from the [001] plane by ±15°. This behavior is not uncommon, as demonstrated by related examples [7, 8].

Figure 3 shows the neutron diffraction patterns recorded with the instrument E6 at 1.5 and 6 K (10 K) for CoCl$_2$ (bpy−d8) (NiCl$_2$ (bpy−d8)) and a blow-up of the difference between these diffractograms. The magnetic Bragg reflections ($hkl$) can be identified and are indexed on the basis of the crystallographic unit cell using integer values for $h$, $k$, and $l$. Therefore, the magnetic and crystallographic unit cells are identical. Specifically, there is no doubling of the unit cell along $c$. This already shows that along the (–MCl$_2$–) chains the moments are arranged ferromagnetically. Since the overall spin arrangement is antiferromagnetic, we may conclude that nearest-neighbor chains couple antiferromagnetically.

For both compounds, CoCl$_2$ (bpy−d8) and NiCl$_2$ (bpy−d8), the intensity of the strongest magnetic reflection, (100), was determined for various temperatures. It becomes smaller with increasing temperature and vanishes above the corresponding magnetic transition temperatures, 5.0 and 8.5 K. No intensity is observed at the (010) position, which suggests that the ordered moments are oriented $\parallel b$, i.e., along the bpy bridges. The Rietveld refinement of the difference pattern was carried out assuming this simple spin arrangement. For the refinement, only the magnitude of the ordered magnetic moment and the background parameters were allowed to vary. All other parameters were taken from the fit of the nuclear Bragg pattern recorded at 10 K. The fits are shown in Fig. 3 as the curve through the data points. Comparison of the intensities of the nuclear and magnetic Bragg reflections results in an ordered magnetic moment of 2.8(2) and 2.0(2)$\mu_B$ for CoCl$_2$ (bpy−d8) and NiCl$_2$ (bpy−d8), respectively, at 1.5 K. These values are somewhat smaller than the full Co and Ni moments, presumably due to zero-field splitting effects. The resulting magnetic structure is shown schematically in Fig. 4.

3 Conclusion

The present neutron diffraction study yielded important information on the crystal structure of Co- and NiCl$_2$ (bpy−d8) that is superior to that from previous X-rays studies. From the observed magnetic structure in these compounds, we infer a ferromagnetic coupling associated with the intrachain interaction through Cl bridges. The observed three-dimensional arrangement of the magnetic moments points to a significant antiferromagnetic interchain coupling. It is interesting to note that chains linked by the bpy ligands show a ferromagnetic spin arrangement, and therefore these ligands appear not to be responsible for the interchain magnetic interaction. In the related system Co(ox)(bpy), antiferromagnetic arrangement of Co–ox chains linked by bpy was observed [7], which is opposite to the behavior in the present case. We therefore conclude that any magnetic interaction mediated through the bpy ligands is too weak to have an effect on the magnetic spin arrangement.

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References

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