Structure and Magnetic Properties of a Dimerized Trinuclear Ni String Complex

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Metal string complexes, composed of a linear polymetallic core surrounded by the multidentate organic ligands, have attracted great interest for the study of metal–metal interactions and the application as conductive molecular nanowires.[1] Since the first report of the metal string complex $Ni_3Cl_2(dpa)_4$ (dpa^- = dipyridylamido anion),[2] various kinds of Ni^{II} string complexes have been synthesized.[3] However, there is no report of connecting several metal string units. Here, we synthesized a novel dimerized Ni string complex $[Ni_6Cl_2(dpa)_8](I_5)_2{\cdot}0.25I_2$ (**1**), and investigated its physical properties.

1 was synthesized by a reaction of the trinuclear complex $Ni_3Cl_2(dpa)_4$ and I_2 in mesitylene, and its molecular structure was determined from single-crystal X-ray study (**Figure 1a**). Two trinuclear moieties are bridged by a chloride to form the dimer structure, and this is the first example that two Ni string units are connected and isolated. The valence of all Ni ions in a dimer was confirmed to be divalent according to the charge balance, bond length analysis and X-ray photoelectron spectroscopy. Optical studies and DFT calculations revealed the electronic absorption bands and a vibration mode characteristic of a dimer structure. Moreover, in the solid state, the dimer string units align one-dimensionally in an MMMXMMMX (M = Ni and X = Cl) manner, leading to the intra- and inter-dimer antiferromagnetic interactions (**Figure 1b**). Details are discussed.

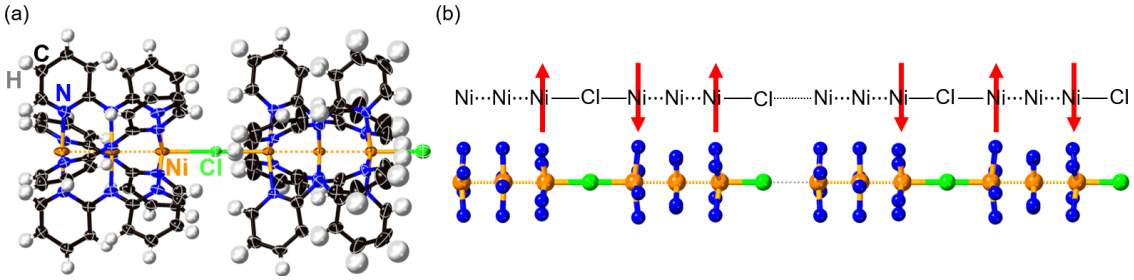

Figure 1. (a) Molecular structure of **1** at 100 K. The thermal ellipsoids are drawn with a 50% probability, and counter anions are omitted for clarity. (b) The spin arrangements of **1** in the solid state. Red allows denote the $S = 1$ spins.

1) F. A. Cotton *et al*., *Multiple Bonds Between Metal Atoms*. Springer: Boston (2005).
2) T. J. Hurley *et al*., *Inorg. Chem.* **1968**, *7*, 33.
3) P. Braunstein *et al*., *Chem. Rev.* **2021**, *121*, 7346.