Magnetic properties of paramagnetic one-dimensional chains where first transition metals are infinitely aligned with metal–metal bonds

([1]*Graduate School of Engineering, Gifu University*, [2]*Faculty of Engineering, Gifu University*)
○Atsushi Takamori,[1] Kazuhiro Uemura [2]
Keywords: Magnetic Behavior; One-dimensional Chain; Hetero-metal; Multinuclear Complex

Heteronuclear metal string complexes (HMSCs), where two or three metals are regularly aligned as several strings with metal–metal bonds, have been the focus of attention due to their potential applications, which are not found in extended metal atom chains comprised of homometals. The well-known synthetic approach to obtain these HMSCs is a template method utilizing multidentate ligands. In contrast, Pt-assisted extension has been the focus of attention because the combination of Pt and desired metals (= M) afforded heterometallic Pt–M complexes. Recently, we reported trinuclear complexes *trans*-$[Pt_2M(piam)_4(NH_3)_4](ClO_4)_2$ (**1-M**, piam = pivalamidate, M = Mn, Co, Ni, and Cu) are dimerized to be hexanuclear complexes Pt–M–Pt···Pt–M–Pt, showing magnetic interactions through –Pt···Pt– bonds.[1,2] Although the inner Pt atoms of Pt–M–Pt complexes metallophilic interact each other, the outer ones did not, resulted in the finite HMSCs. In this study, we will show crystal structures and physical properties for infinite one-dimensional chains aligned as ···Pt–M–Pt···Pt–M–Pt···, which were successfully obtained by changing the bridging ligand from piam to acetamidate (= acam).

Simply mixing *trans*-$[Pt(acam)_2(NH_3)_2]$, MCl_2 (M = Co, Ni, and Cu), and $NaClO_4$ in adequate solvent afforded single-crystals of *trans*-$[Pt_2M(acam)_4(NH_3)_4](ClO_4)_2$ (**2-M**). Single-crystal X-ray analyses revealed that each trinuclear complex is extended to be one-dimensional chains, with the close Pt···Pt distances of about 3.47–3.61 Å (Figure 1). Considering the chemical formulae, the formal oxidation states of M are Co(+2), Ni(+2), and Cu(+2). XPS and EPR measurements resulted in that M in **2-M** have high-spin states with unpaired electrons. Temperature dependence of magnetic susceptibilities for **2-Co** and **2-Ni** showed antiferromagnetic behaviors through –Pt···Pt– bonds separated by about 8.8 Å, with $J = -9.5$ (**2-Co**) and -13.5 (**2-Ni**) cm^{-1}. In contrast, **1-Cu** showed weak ferromagnetic behavior with $J = 0.14$ cm^{-1}.

1) Takamori, A.; Uemura, K. *Inorg. Chem.*, **2022**, *61*, 5762–5778. 2) Uemura, K.; Takamori, A. *Coord. Chem. Rev.*, **2022**, *471*, 214736.

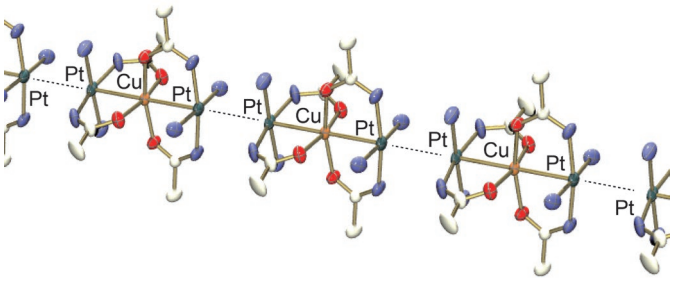

Figure 1. Crystal structure of **2-Cu**.