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Preparation and Crystal Structure of a New Hetero-metal Mixed Valence Cu^{II}- Pt^{IV} Complex with One Dimensional Chain Structure $[Cu(en)_2][PtCl_2(en)_2](ClO_4)_4$

Hiroki OSHIO,* Koshiro TORIUMI, and Shunji BANDO
Institute for Molecular Science,
Okazaki National Research Institutes, Myodaiji, Okazaki 444

Bis(ethylenediamine)copper(II) trans-dichlorobis(ethylenediamine)platinum(IV) perchlorate was prepared and the halogen-bridged linear chain structure has been determined by X-ray diffractometry. The copper and platinum complexes are stacked alternately in the chain. Temperature dependence of the magnetic susceptibility and EPR data indicate no strong magnetic interaction between copper atoms.

One dimensional halogen bridged M^{II}-M^{IV} mixed valence complexes, which are analogous to the so called Wolffram's red salt, have been extensively studied, because they have an extremely strong electron-lattice coupling within a chain structure.1) This type of compounds consists of either a pair of the complexes having the same metal ions with different oxidation states or a combination of two kinds of complexes having different diamagnetic metal ions in platinum groups on each oxidation state.1) It is well known that charge transfer properties between two metal ions or molecules can be used to design a molecular ferromagnet.2) If paramagnetic hetero-metal ions can be introduced to such chain systems, a study of the charge transfer properties between hetero-metal ions can be made. Here the synthesis, molecular structure, and magnetic properties of the title compound (**1**) are reported.

Red needle crystals were grown by slow evaporation of an aqueous solution (5 cm^3) containing $[PtCl_2(en)_2]Cl_2$ (1 mmol), $[Cu(en)_2]Cl_2 \cdot 2H_2O$ (1 mmol), and $NaClO_4$ (4 mmol).

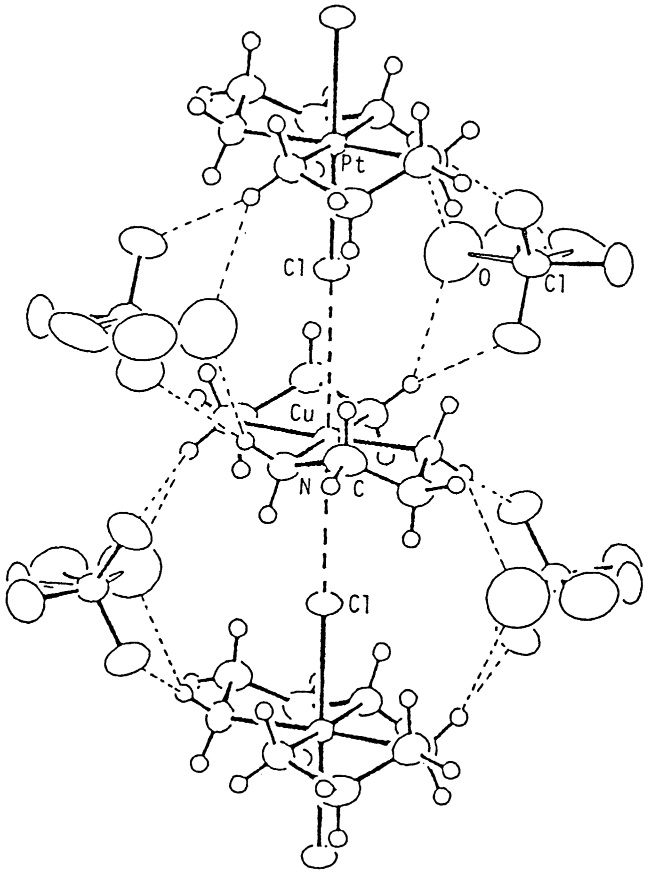

Fig. 1. ORTEP view of the compound **1**. There are disorders on the bridged chlorine atom and oxygen atoms of the perchlorate anion. One of the disordered chlorine atoms erased from the figure.

The X-ray crystal structure analysis reveals a chloro-bridged linear chain structure, which is isomorphous with the halogen-bridged M^{II}-M^{IV} mixed valence compound of $[M(en)_2][MX_2(en)_2](ClO_4)_4$ (M=Pt, Pd; X=Cl, Br).[4] As shown in Fig. 1, the octahedral six-coordinate $Pt^{IV}Cl_2(en)_2$ and square-planar four-coordinate $Cu^{II}(en)_2$ units are arranged alternately, constructing a linear chain structure along the b-axis. The alternating structure was confirmed by the diffuse scatterings corresponding to the one-dimensional periodicity with a repeating unit, $\cdots Cu^{II}\cdots Cl\text{-}Pt^{IV}\text{-}Cl\cdots$. However, as has been observed for the analogous M^{II}-M^{IV} mixed valence compounds,[4] the bridging chlorine atoms are positionally disordered at two sites equidistant from the midpoint between two metal sites with an occupancy factor of 0.5. The Pt^{IV} and Cu^{II} atoms are also disordered at the metal site, and cannot be distinguished from each other. The Pt/Cu ratio in the metal site has been determined to be 1.11/0.89 by the full-matrix least-squares calculation. The nonstoichiometric structure can be interpreted by a partial substitution of the Cu^{II} complex by the Pt^{II} one during preparation.

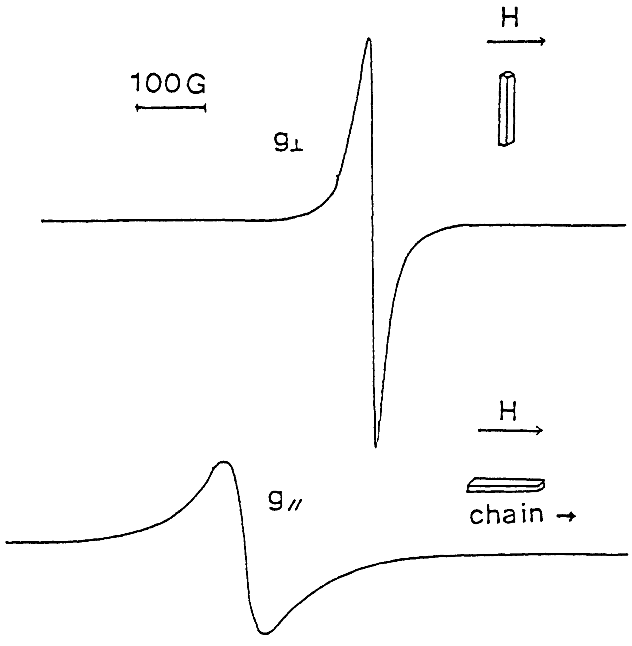

Fig. 2. Single crystal X-band EPR spectrum of the compound **1** measured at 10 K. Aligned crystals were oriented in the b-axis (linear chain axis) parallel and perpendicular to the external field.

In a similar manner to the structural analysis of the Wolffram's red salt analogs,[4)] it can be considered that the shorter metal to Cl distance (2.313(3) Å) corresponds to the Pt^{IV}-Cl distance, whereas the longer one (3.081(3) Å) to the Cu^{II}···Cl distance. These are similar to the values for $[Pt^{II}(en)_2][Pt^{IV}Cl_2(en)_2]$-$(ClO_4)_4$ (**2**), that is, 2.318 and 3.085 Å for the Pt^{IV}-Cl and Pt^{II}···Cl, respectively.[4)] The bond length ratios of M^{IV}-Cl to M^{II}···Cl, which is a measure of the electron-lattice interaction in the homo-metal system,[5)] are 0.751 for both **1** and **2**. On the other hand, the interatomic distance between copper and bridged halogen atoms is extremely long compared with a macrocylic tetraaminecopper complex which has an apical Cu-Cl distance of 2.716(11)Å.[6)] Optical studies, which provide informations about the charge transfer properties between the platinum and copper centers, are currently under way.

A single crystal EPR spectrum measured at 10 K is shown in Fig. 2. Hyperfine splitting and zero-field splitting were not observed. Anisotropic g values are obtained; 2.048 and 2.167 for perpendicular and parallel components, respectively, and the principal axis of the g tensor is parallel to the chain direction (b axis). The EPR spectrum indicates that an electron spin on the copper atom occupies the $d_{x^2-y^2}$ orbital which is perpendicular to the chain direction. The temperature dependence of the magnetic susceptibility for the compound 1 was also measured in the temperature range (2.7-300 K). The susceptibility obeys the Curie-Weiss law with 0.415 emu mol^{-1} K and -1.2 K for the Curie and Weiss constants, respectively. Both the EPR and magnetic data show that there is no strong magnetic interaction between the paramagnetic copper ions. It is suggested that a paramagnetic metal ion, which has an electron spin in a d_{z^2} orbital, should be introduced into the chain system in order to achieve strong magnetic interactions through the bridged halogen atom.

References

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3)Crystal data are : $C_8H_{32}N_8O_{16}Cl_6CuPt$, orthorhombic, Icma, Z=2, a=13.645(1), b=10.787(1), c=9.645(1) Å, V=1419.6(2) $Å^3$, D_x=2.30 g cm^{-3} (considering the populations of metal atoms), D_m=2.28 g cm^{-1}, μ(MoKα)=66.0 cm^{-1}. Intensity data were collected at room temperature with graphite monochromated MoKα radiation by using a crystal with dimensions of 0.33x0.13x0.06 mm^3. The structure was refined by a full-matrix least-squares technique including occupancy factors of the metal ions. The weighting scheme is w= $[\sigma_c^2+(0.020|Fo|)^2]^{-1}$. Final R and R_w values are 0.025 and 0.039, respectively, for 991 absorption corrected reflections ($|Fo|>3\sigma(Fo)$). Anal. Found: C,10.19; H,3.36; N,11.83%. Calcd for $C_8H_{32}N_8O_{16}Cl_6Cu_{0.89}Pt_{1.11}$: C,9.78; H,3.28; N,11.41%.

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