

Synthesis, crystal structure and magnetic properties of heterodimetallic $\text{Re}^{\text{IV}}\text{Cu}^{\text{II}}$ complexes.

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Streszczenie

The two rhenium(IV)-copper(II) heterometallic complexes $[\text{CuL}\beta][\text{ReCl}_4(\text{ox})]\cdot\text{DMF}$ (1) and $[(\text{CuL}\alpha)_2\text{Cl}][\text{ReCl}_4(\text{ox})]\text{Cl}$ (2) ($\text{L}\beta = \text{N-dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclo-tetradeca-4,11-diene}$ and $\text{L}\alpha = \text{N-dl-5,7,7,12,12,14-hexa-methyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene}$) were synthesized, and the crystal structures of both compounds were determined at 173(2) K. Complex 1 crystallizes in a monoclinic space group $P2_1$, with $a = 9.365(2)$ Å, $b = 15.150(2)$ Å, $c = 10.776(1)$ Å, $\beta = 110.01(1)^\circ$, $Z = 2$, whereas 2 crystallizes in an orthorhombic space group $Pca2_1$ with $a = 16.660(5)$ Å, $b = 16.017(5)$ Å, $c = 17.066(5)$ Å, and $Z = 4$. The $\text{CuL}\beta$ macro-cycle cation is approximately planar and coordinated from above and below by $[\text{ReCl}_4(\text{ox})]_2^-$ units through the bis(bidentate) oxalato ligands. It features an oxalato-bridged heterometallic $\text{Re}^{\text{IV}}\text{-Cu}^{\text{II}}$ zigzag chain, the shortest intrachain metal-metal distances are $\text{Re}\cdots\text{Cu} = 5.568(2)$ and $5.870(2)$ Å in the direction of the b axis. The crystal structure of 2 consists of dinuclear complex cations $[(\text{CuL}\alpha)_2\text{Cl}]^{3+}$ with $[\text{ReCl}_4(\text{ox})]_2^-$ and isolated Cl^- as counter anions. Cu atoms in $\text{CuL}\alpha$ are only fivefold coordinated in a square pyramidal surrounding, and the cations $(\text{CuL}\alpha)_2^+$ are connected in pairs by chloride. The intramolecular $\text{Cu}\cdots\text{Cu}$ separation is $4.885(3)$ Å, the shortest $\text{Re}\cdots\text{Cu}$ distance is $7.612(3)$ Å. The magnetic behavior of 1 and 2 has been investigated over the temperature range 1.7–300 K. Compound 1 behaves like a ferrimagnetic $\text{Cu}^{\text{II}}\text{-Re}^{\text{IV}}$ dimetallic, one-dimensional chain with intrachain antiferromagnetic coupling. Compound 2 shows weak anti-ferromagnetic interactions within the $\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}$ units.

Słowa kluczowe

Rhenium(iv), Chain structures, Copper(ii), Heterometallic complexes

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