

Communications

$(C_2H_5)_4NCu_2Cl_4$: An Ordered, Mixed-Valence $(Cu_2Cl_4)_n^{2-}$ Chain

Sir:

Mixed-valence inorganic systems have been of substantial interest to inorganic chemists in the past several decades. This has included studies of electron-transfer reactions in mixed-valence dimer systems with the emphasis on reaction rates and intervalence charge-transfer spectra¹ and linear-chain compounds, where the presence of variable oxidation states can lead to high electrical conductivity. For mixed Cu(I)–Cu(II) systems, the coordination geometries of the two species are generally quite distinctly different, and thus the mixed valence is stabilized by stereochemical effects.³ An exception to this is a series of ternary copper sulfides that, though formally mixed-valence Cu(I)–Cu(II) systems, appear to be in reality mixed-valence sulfur compounds.⁴ In the copper chloride system, the classical mixed-valence system is the $Co(NH_3)_6CuCl_5$ – $[Co(NH_3)_6]_4Cu_5Cl_{17}$ system.⁵ The former contains square-pyramidal $CuCl_5^{3-}$ ions⁶ while the latter consists of clusters of corner-shared $CuCl_4^{3-}$ tetrahedra.⁷ A continuous range of Cu(I):Cu(II) ratios appears to exist. Other mixed-valence copper chloride salts also contain distinctly different coordination sites for the two valence states.⁸ In this paper, the preparation and crystal structure of an ordered, mixed-valence Cu(I)–Cu(II) linear-chain salt are described in which the coordination geometries for the two oxidation states are quite similar.

The compound was prepared as a byproduct of our crystal growth of single crystals of $(TEA)_4Cu_4Cl_{12}$ (TEA = tetraethylammonium).⁹ Crystals of the latter were grown by a simplified temperature gradient technique,¹⁰ in which the solvent was an ethyl acetate–nitromethane mixture. Crystal growth was continued over a period of 18 months. At the end of this period, examination

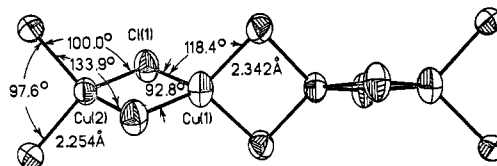


Figure 1. View of a portion of the $(Cu_2Cl_4)_n^{2-}$ chain in $(C_2H_5)_4NCu_2Cl_4$.

of the residue in the bottom of the tubes reveals a few dozen deep blue needle crystals. After removal, the surfaces of the crystals gradually (over a period of several months) changed to reddish orange upon exposure to air.

An X-ray structure determination¹¹ showed the crystals to be tetragonal with two independent copper atoms on special positions and the one independent chlorine atom in the asymmetric unit. The copper atom designated as Cu(1) was located at $(\frac{1}{4}, \frac{1}{4}, 0)$ at a site of S_4 symmetry, while Cu(2) was at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ with D_2 site symmetry. The chlorine atoms are located so as to define a bridged chain structure parallel to the c axis with distorted-tetrahedral geometry for each copper atom (Figure 1). Difference electron density syntheses revealed an atom at $(\frac{1}{4}, \frac{1}{4}, z)$ ($z \approx \frac{5}{8}$) with additional adjacent peaks identifiable as a disordered TEA ion. Since the site symmetry at the nitrogen atom in the space group $P4/ncc$ is C_4 , the disorder is a necessity. Significant bond distances and angles are given in Figure 1. Lists of data collection parameters, of all positional and thermal parameters, and of bond distances and angles, as well as a listing of observed and calculated structure factors, are available as supplementary material.

The observed stoichiometry dictates that $(TEA)Cu_2Cl_4$ is a mixed-valence Cu(I)–Cu(II) system but does not indicate whether or not the valences are localized. Structurally, it is clear that two distinctly different copper sites exist. Cu(1) has S_4 site symmetry with Cu–Cl distances of 2.342 (1) Å and with two Cl–Cu–Cl angles of 92.8 (1)° and four of 118.4 (1)°. These distances and angles are consistent with expectations for four-coordinate copper(I).¹⁴ On the other hand, Cu(2) has D_2 site symmetry with

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- (11) Crystals are tetragonal, in group $4/mmm$ and space group $P4/ncc$, with $a = 11.131$ (1) Å and $c = 17.400$ (2) Å (based on 25 accurately centered reflections with $30^\circ < 2\theta \leq 40^\circ$). One complete octant of data ($h, k, l \geq 0$; 205 reflections with $2\theta \geq 55^\circ$) was collected at 295 K, which yielded 894 unique reflections ($R_{merge} = 0.023$), of which 572 had $F \geq 3\sigma(F)$. A Syntex P2₁ diffractometer, upgraded to Nicolet P3 specifications, with a graphite monochromator was used for data collection¹² ($\lambda = 0.71069$ Å, bisecting geometry, ω scan). With $Z = 4$, $\rho_{calcd} = 1.73$ g cm⁻³ ($M_r = 399.2$). The crystal measured $0.1 \times 0.1 \times 0.4$ mm³, and an empirical absorption correction assuming an ellipsoidally shaped crystal was made ($\mu = 34.5$ cm⁻¹, maximum and minimum transmission of 0.746 and 0.644, respectively). Final least-squares refinement¹³ gave $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0513$ for the 3σ data set (0.103 for all reflections) and $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2} = 0.0428$ for the 3σ data set (0.0571 for all reflections).
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shorter Cu-Cl distances of 2.254 (1) Å and two angles at 97.6 (1)°, two at 100.0 (1)°, and two at 133.9 (1)°. This distortion is typical of CuCl_4^{2-} ions in the presence of non-hydrogen-bonding cations, as is the observed bond distance.¹⁵ Thus it is clear structurally that the Cu(I) and Cu(II) ions are localized at sites Cu(1) and Cu(2), respectively. Since the geometries of the two sites are so similar, this material would be best described as a type IIb mixed-valence system in the Robin and Day classification.¹⁶

The intense blue color of this salt, in contrast to the normal yellow to red color of copper(II) chloride salts, deserves comment. Although sufficient sample is not available to obtain a spectrum, the blue would imply a strong absorption in the low-energy end of the visible region. The band is strongly polarized along the crystal *c* axis, that is, along the chain direction. The logical origin of this band would likely be an intervalence charge-transfer transition. Further work will be carried out as soon as a repeatable synthetic scheme is worked out.

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Supplementary Material Available: Tables of data collection parameters, positional and isotropic thermal parameters of non-hydrogen atoms, bond lengths and angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom positional and thermal parameters and a stereographic view of the unit cell contents (8 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of $[\text{Fe}(\text{dbt})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ and Related S-Bonded Thiophene Complexes

Sir:

Hydrodesulfurization and hydroliquefaction are two essential steps in the effective utilization of abundant, high-sulfur coal.^{1,2} These reactions are catalyzed by a variety of metal compounds, usually heterogeneously. Organometallic compounds, including $[\text{Fe}(\text{CO})_5]$, $[\text{Fe}_2(\text{CO})_4(\text{Cp})_2]$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$), and $[\text{Mo}(\text{CO})_6]$, are effective coal hydroliquefaction catalysts, alone or in the presence of added sulfur.^{2,3} These carbonyls have also demonstrated hydrodesulfurization activity with coal⁴ and coal model

compounds.^{4,5} The thiophenes, especially dibenzothiophene (dbt), are the best model compounds for organically bound sulfur in coal,⁶ yet the transition-metal coordination chemistry of thiophene ligands is not well investigated.

Chromium,⁷ manganese,⁸ iron,⁹ ruthenium,¹⁰ rhodium, and iridium¹¹ form η^5 -complexes with certain thiophenes, especially tetramethylthiophene, and η^6 -complexes with the arene rings of benzothiophenes have been reported.¹² Thiophenes are weak S-donor ligands. A few S-bonded complexes of thiophene and 2,5-dimethylthiophene are known for iron¹³ and ruthenium,¹⁴ but these are not fully characterized because they are so labile. Incorporating thiophenes into chelating ligands leads to some increase in stability. $[\text{RuCl}_2\{\text{P}(4\text{-MeC}_6\text{H}_4)_2(\text{SC}_2\text{H}_7)_2\}]_2$ with a chelating phosphine-dibenzothiophene ligand has been prepared and structurally characterized.¹⁵ Copper and silver form structurally characterized complexes with chelating imide-thiophene ligands in which the thiophenes interact only weakly with the metals.¹⁶ Thus, there are few good models for the attachment of thiophenes to metallic catalysts via sulfur, a bonding mode believed to be the first step in catalytic desulfurization of coal.¹⁷ We report here the preparation and structure of an iron-dibenzothiophene complex in which the thiophene is not part of a chelating ligand system.

Displacement of isobutene from $[\text{Fe}(\eta^2\text{-H}_2\text{C}=\text{CMe}_2)(\text{CO})_2(\text{Cp})][\text{BF}_4]$ ¹⁸ by dibenzothiophene (dbt), thiophene (th), benzo-

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