

Crystal Structure and Electronic Spectroscopy of Bis(hydrazinium) Hexachlorotricuprate(2I,II): a Cu(I)-Cu(II) Mixed-Valence System Exhibiting Intervallence Charge Transfer

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Received May 23, 1990

The crystal structure of the mixed-valence Cu(I)-Cu(II) salt $(N_2H_5)_2Cu_3Cl_6$ has been determined. The compound crystallizes in the monoclinic space group $P2_1/a$ with $a = 5.797$ (3) Å, $b = 12.749$ (7) Å, $c = 7.471$ (3) Å, and $\beta = 93.31$ (4)°, and the X-ray diffraction data were refined to final values of $R = 0.0736$ and $R_w = 0.0829$. The salt of 2:1 Cu(I):Cu(II) stoichiometry consists of chains of stacked planar $CuCl_3^{2-}$ anions ($Cu^I-Cu^I = 2.901$ Å) that are linked together into a two-dimensional network through coordination to the Cu(II) ions. The Cu(II) ions have a distorted 4 + 2 octahedral coordination in which the basal plane consists of two chloride ions (from $CuCl_3^{2-}$ anions in adjacent chains) and two hydrazinium ions. The axial sites contain chloride ions from two additional $CuCl_3^{2-}$ anions in the same pair of chains. Near-IR-visible absorption spectroscopy, which shows a broad intervalence absorption band covering the visible region of the spectrum, and EHMO calculations support a Robin and Day type II classification for this compound. The EHMO calculations also indicate the presence of only very weak Cu(I)-Cu(I) interactions along the stacks of $CuCl_3^{2-}$ anions.

Introduction

This laboratory has recently taken an interest in mixed-valence copper halide compounds,¹ particularly those which fall into Robin and Day classes II and III.² The title compound, synthesized several years ago by Hatfield and co-workers,³ was reported to exhibit some class II properties; the crystals were dark in color, and a very broad absorption band through the entire visible range was observed. The compound was also characterized by using infrared, magnetic susceptibility, and elemental analysis techniques. It is from these data that Hatfield et al. proposed the formulation $[Cu^{II}(N_2H_5)_2Cl_2][Cu^I Cl_3]_2$ for this mixed-valence compound. The most important question to be addressed in this paper is whether the system is a localized or delocalized one; we will argue that the title compound is a Robin and Day class II compound. Results from near-IR and visible absorption spectra and EHMO calculations will be used to support this view.

There has also been recent interest in the literature concerning the nature of copper(I) interactions.⁴ These works deal with $d^{10}-d^{10}$ interactions between copper(I) atoms displaying bond distances ranging from 2.35 to 3.18 Å. All of these compounds have bridging ligands between the neighboring copper(I) ions, and this complicates the matter of sorting out any contributions of Cu(I)-Cu(I) interactions to the bonding. The mixed-valence salt treated in this paper represents the first case of a relatively short (2.901 Å), non-ligand-bridged, copper(I)-copper(I) contact. The results from the EHMO calculations will be used to show the role of these contacts in the overall bonding picture.

Experimental Section

Synthesis. The compound was synthesized as described elsewhere in the literature.³ The synthesis yielded what appeared to be black needles, but when crushed and viewed under a microscope, they were actually deep red.

X-ray Structure Determination. A crystal with dimensions $0.32 \times 0.15 \times 0.11$ mm was mounted on a thin glass fiber. The data collection was carried out on a fully automated R3m diffractometer employing Cu K α radiation ($\lambda = 1.54178$ Å) and a graphite monochromator.⁵ The orientation matrix and lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections with high Bragg angles. Two standard reflections (011, 140) were monitored every 96

Table I. Crystallographic Data for $[Cu^{II}(N_2H_5)_2Cl_2][Cu^I Cl_3]_2$

chem formula: $H_{10}Cl_6Cu_3N_4$	space group: $P2_1/a$ (No. 14)
fw = 465.4	$T = 22$ °C
$a = 5.797$ (3) Å	$\lambda = 1.54178$ Å
$b = 12.749$ (7) Å	$\rho_{calcd} = 2.83$ g/cm ³
$c = 7.471$ (3) Å	$\mu = 201.55$ cm ⁻¹
$\beta = 93.31$ (4) Å	transm coeff = 0.22-0.91
$V = 551.3$ (5) Å ³	$R(F_o) = 0.0736$
$Z = 2$	$R_w(F_o) = 0.0829$

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for $[Cu^{II}(N_2H_5)_2Cl_2][Cu^I Cl_3]_2$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Cu(1)	1882 (3)	2456 (1)	7694 (2)	23 (1)
Cu(2)	5000	0	10000	13 (1)
Cl(1)	1988 (5)	4247 (2)	7696 (3)	15 (1)
Cl(2)	2243 (5)	1686 (2)	10430 (4)	16 (1)
Cl(3)	1754 (5)	1510 (3)	5145 (4)	18 (1)
N(1)	2542 (17)	-492 (8)	8142 (13)	18 (4)
N(2)	3134 (19)	-1232 (9)	6871 (15)	26 (4)

^aThe equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Distances (Å) and Angles (deg) for $[Cu^{II}(N_2H_5)_2Cl_2][Cu^I Cl_3]_2$ ^a

Cu(2)-Cl(2)	2.709 (3)	Cu(1)-Cl(2)	2.266 (3)
Cu(2)-N(1)	2.030 (10)	Cu(1)-Cl(3)	2.251 (3)
Cu(2)-Cl(1b)	2.333 (3)	Cu(1)-Cu(1a)	2.901 (1)
Cu(1)-Cl(1)	2.285 (4)		
Cl(2)-Cu(2)-N(1)	86.0 (3)	Cl(1)-Cu(1)-Cl(2)	115.5 (1)
Cl(2)-Cu(2)-Cl(1c)	85.4 (1)	Cl(1)-Cu(1)-Cl(3)	122.4 (1)
Cl(2)-Cu(2)-Cl(1b)	94.6 (1)	Cl(2)-Cu(1)-Cl(3)	121.9 (1)
N(1)-Cu(2)-Cl(1b)	88.8 (3)	Cl(1)-Cu(1)-Cu(1a)	89.3 (1)
Cl(1b)-Cu(2)-Cl(1c)	180.0 (1)	Cl(2)-Cu(1)-Cu(1a)	93.3 (1)
Cl(2)-Cu(2)-Cl(2a)	180.0 (1)	Cl(3)-Cu(1)-Cu(1a)	92.1 (1)
N(1)-Cu(2)-N(1a)	180.0 (1)	Cu(1)-Cl(1b)-Cu(2a)	113.4 (1)
N(1)-Cu(2)-Cl(2a)	94.0 (3)	Cu(2)-Cl(2)-Cu(1)	105.1 (1)
Cl(1b)-Cu(2)-Cl(2a)	85.3 (1)	Cu(2)-N(1)-N(2)	118.9 (7)
Cl(1b)-Cu(2)-N(1a)	91.2 (3)		

^aa denotes transformation by \bar{x} , \bar{y} , \bar{z} , b denotes transformation by $\bar{x} + 1/2$, $y + 1/2$, \bar{z} , and c denotes transformation by $x + 1/2$, $\bar{y} + 1/2$, \bar{z} .

reflections and showed no systematic variation. The intensities of 669 reflections were measured by using an ω scan (1.3° range) with speeds varying from 4 to 29.3° min⁻¹. (The 1.3° scan range was used because preliminary peak scans revealed some broad peaks; however, no twinning was observed among the peaks showing the largest $|\Delta/\sigma|$ values.) Following the data reduction, 563 unique reflections remained, with 535 having $|F| > 3\sigma$. The positions of all Cu and Cl atoms were found via direct methods, with the nitrogen atoms being found from subsequent

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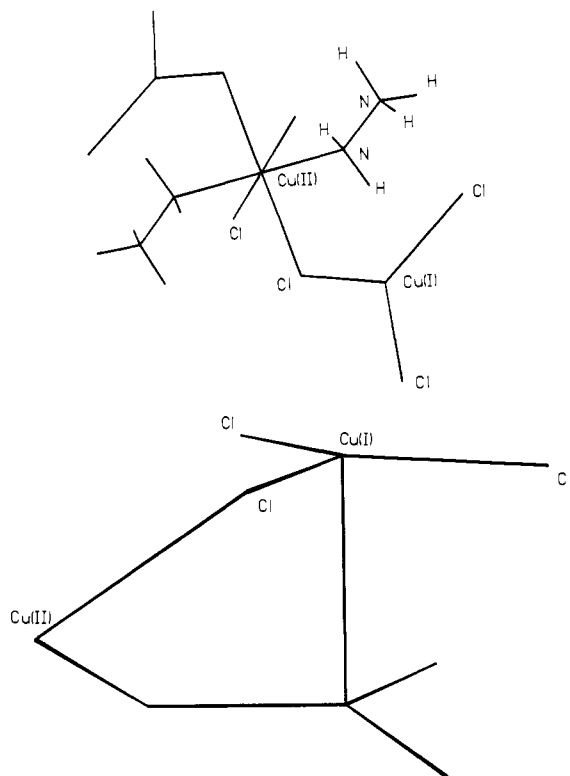


Figure 1. Fragments used in the EHTMO calculations: (a, top) to probe optical properties; (b, bottom) to probe Cu(I)–Cu(I) interactions.

electron difference synthesis. All non-hydrogen atoms were refined anisotropically to final values of $R = 0.0736$ and $R_w = 0.0829$. The final refinement included 68 least-squares parameters with a mean value of $|\Delta/\sigma| = 0.001$ and $g = 0.00402$. The goodness of fit was 1.802, and the final difference map showed a residual of $1.5 e/\text{\AA}^3$ near Cu(1). The hydrogen atoms were refined isotropically with the N–H distances fixed at 0.96 Å and isotropic thermal parameters fixed at 1.2 times the equivalent isotropic thermal parameter of the nitrogen atom to which they were bonded. An absorption coefficient of 201.5 cm^{-1} was calculated, and empirical absorption corrections were applied, resulting in a transmission range of 0.22–0.91. All data reduction, including Lorentz and polarization corrections, structure solution and refinement, and graphics, were performed by using SHELXTL 5.1 software.⁶ Crystallographic data may be found in Table I. Atomic coordinates and isotropic thermal parameters are listed in Table II, and bond angles and distances in Table III. Additional structural details may be found in the supplementary material.

Absorption Spectroscopy. The absorption spectroscopy was carried out on a Perkin-Elmer 1700X FTIR spectrometer in the region from 3000 to $12\,000 \text{ cm}^{-1}$ and on a Perkin-Elmer 330 in the region from $12\,000$ to $22\,000 \text{ cm}^{-1}$. Diffuse reflectance was the technique employed on both instruments, with the aid of standard Perkin-Elmer accessories. The samples were run as powdered mixtures of the title compound and KBr. There was no color difference observed between ground sample and ground sample plus KBr when viewed under a microscope, indicating that no reaction between the title compound and the KBr matrix occurred.

Calculations. The extended Huckel molecular orbital calculations were performed by using the EHT program available from QCPE.⁷ The basis set included the $\text{Cu}^{\text{II}}(\text{N}_2\text{H}_5)_2\text{Cl}_4$ moiety, with 4 + 2 geometry, plus the two $\text{Cu}^{\text{I}}\text{Cl}_2$ species bonded to the equatorial chloride atoms of the 4 + 2 anion (Figure 1a). The parameters for this calculation were taken from the paper by Hoffmann dealing with another Cu(I)/Cu(II) halide compound under study in this laboratory.⁸ These calculations were used to lend insight into the optical properties of the compound. The calculations performed to uncover the nature of the Cu(I)–Cu(I) interaction used a basis set containing two $\text{Cu}^{\text{I}}\text{Cl}_2$ monomers linked by a Cu(II) ion (Figure 1b). The same parameters were used in this calculation as well.

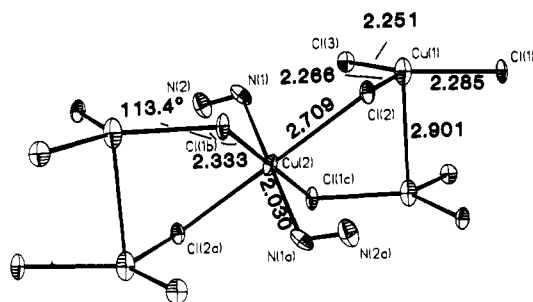


Figure 2. Illustration of the structure showing thermal ellipsoids as viewed from the c direction.

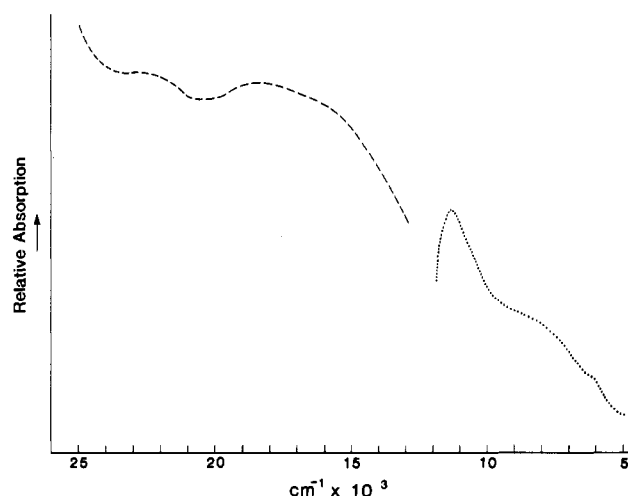


Figure 3. Absorption spectrum for the title compound. The dotted line spectrum was taken on a Perkin-Elmer 1700X FTIR spectrometer and the dashed line spectrum was taken on a Perkin-Elmer 330 UV-vis-near-IR instrument. The method of diffuse reflectance was used to collect both spectra.

Results

Structure Description. This structure may be most simply described by first laying down a framework of $\text{Cu}^{\text{I}}\text{Cl}_3^{2-}$ anions and then linking these units together with $\text{Cu}^{\text{II}}\text{Cl}_2(\text{N}_2\text{H}_5)_2^{2+}$ dications.

The copper(I) part of this structure consists of infinite chains of staggered, trigonal-planar, $\text{Cu}^{\text{I}}\text{Cl}_3^{2-}$ monomers (Cu–Cu distance = 2.901 (1) Å). Adjacent $\text{Cu}^{\text{I}}\text{Cl}_3^{2-}$ anions assume a staggered configuration. These $\text{Cu}^{\text{I}}\text{Cl}_3^{2-}$ units are only slightly distorted from a perfect trigonal-planar geometry: the copper(I) ion is only 0.06 Å out of the plane defined by its ligands, and the Cl–Cu–Cl angles are 115.5 (1), 122.4 (1), and 121.9 (1)°. The Cu–Cl distances range from 2.251 (3) to 2.285 (4) Å. The chain, which runs along the a axis, shows a slight antiphase distortion (Cu–Cu angle = 175.4°).

The coordination polyhedra of the copper(II) ions, each located on a center of inversion, serve to bridge adjacent copper(I) chains in the b direction. The copper(II) ion assumes a normal 4 + 2 elongated octahedral coordination geometry (Figure 2). In the equatorial positions are two chlorine atoms (from adjacent chains) bonded at 2.333 (3) Å and two nitrogen atoms (from hydrazinium ions) at 2.030 (10) Å. Chlorine atoms from the same two neighboring chains occupy apical positions of the $\text{Cu}^{\text{II}}\text{Cl}_4(\text{N}_2\text{H}_5)_2^{2+}$ cation at a distance of 2.709 (3) Å.

Absorption Spectroscopy. The diffuse-reflectance spectrum of the title compound showed strong absorption throughout the entire visible range, but several maxima could be observed. A very broad peak, with an approximate width of 5000 cm^{-1} , was centered at $18\,200 \text{ cm}^{-1}$. A sharp maxima was observed at $11\,500 \text{ cm}^{-1}$, with a broad shoulder at about 8000 cm^{-1} . An extremely intense absorption begins at about $25\,000 \text{ cm}^{-1}$, with a shoulder at approximately $22\,000 \text{ cm}^{-1}$. This spectrum is shown in Figure 3.

Theoretical Calculations. The extended Huckel calculations, carried out on the copper(I) fragment pictured in Figure 1b, gave

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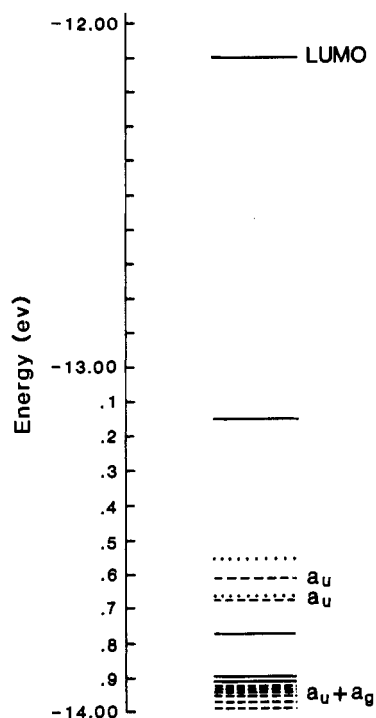


Figure 4. Energy level diagram as calculated via an EHMO calculation on the fragment shown in Figure 1a. The diagram is explained fully in the text.

an overlap population of 0.0097 between adjacent copper(I) centers.

The extended Huckel calculations carried out on the copper(II) fragment shown in Figure 1b yielded a very broad block of d orbitals. An energy level diagram of these orbitals is shown in Figure 4. The molecular orbitals in this diagram are of three types: those primarily centered on the Cu(II) center (solid lines), those primarily centered on the Cu(I) center (dashed lines), and those centered on both copper(II) and copper(I) centers (dotted lines). All of these orbitals also contain significant ligand orbital contributions, particularly from the bridging Cl ligands. The LUMO is almost exclusively copper(II) $d_{x^2-y^2}$ in character, with contributions from the $p\sigma$ orbitals on the atoms in the equatorial plane.

Discussion

The crystal structure of this mixed-valence Cu(I)/Cu(II) chloride salt reveals a unique linear chain system consisting of stacks of trigonal planar CuCl_3^{2-} anions with close [2.901 (1) Å] contacts between the Cu(I) ions in the stack. Stability is conferred to the structure by the formation of Cu(I)–Cl–Cu(II)–Cl–Cu(I) linkages, both between and within chains. The local geometries of the local Cu(I) and Cu(II) ions are not unusual. The existence of coordinated cationic ligands is rare, but not unknown.⁹ Trigonal coordinations for the Cu(I) species are also known,¹⁰ although relatively rare with simple halide ligands.

The presence of a direct Cu(I)–Cu(I) linkage without the presence of sterically constricting bridging ligands is quite unusual. An analogous chain of bicoordinate Ag(I) species has been found in an ethylenediamine complex of AgNO_3 (Ag–Ag = 3.15 Å), while the same authors have reported a dimeric tricoordinate Ag(I) species in a 2-(aminomethyl)pyridine–metachloridine complex (Ag–Ag = 3.28 Å).¹¹ Allowing for the difference in radii (~0.15 Å) between Cu and Ag, the M–M interactions would appear to be quite comparable in these systems.

We postulate that the Cu(II) species is playing a large role in the Cu(I) chain formation. It has been put forth by Hoffmann¹²

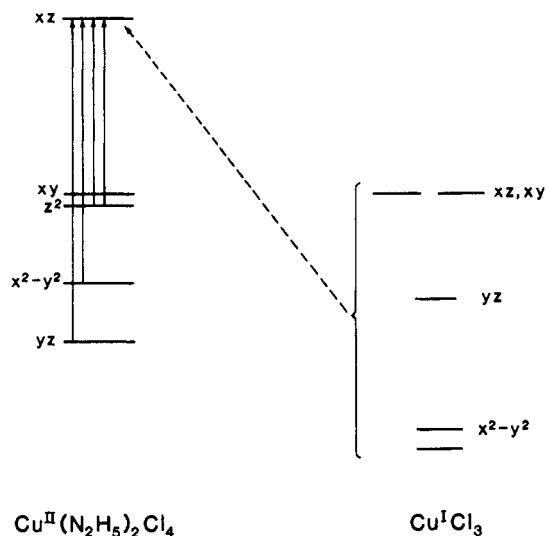


Figure 5. Diagram showing the d-orbital energy levels of the copper(I) and copper(II) chromophores placed side by side.

that the factors contributing to the geometry in a bridged structure are, in order of decreasing importance, the geometry of the monomer, the symmetry-conditioned coupling of the bridging ligands, and the metal–metal bonding interaction. The EHMO calculations show an overlap population of 0.0097 between the two Cu(I) ions in the $\text{Cu}_2\text{Cl}_4^{4-}$ unit. This would indicate only a very weak attractive interaction between the neighboring copper(I) ions in the infinite chain, and this attraction surely accounts for only a small part of the impetus driving the chain formation. Thus, the bridging $\text{Cu}^{\text{II}}(\text{N}_2\text{H}_5)_2\text{Cl}_2^{2-}$ network must help stabilize the structural features leading to direct Cu(I)–Cu(I) interactions. However, this network can in no way be thought to force this interaction as in other Cu(I) complexes where the unusually short Cu–Cu distances are a result of constraints imposed by bidentate bridging ligands.

The structural results of this study are not conclusive as to whether the system falls into class I or class II of the Robin and Day scheme. The copper(I) and copper(II) ions sit in sites of very different symmetry, the copper(II) species in sites of $4 + 2$ symmetry and the copper(I) ions in sites of $3 + 2$ symmetry. Under this criteria the compound fits into class I. However, the presence of the bridging chloride ion leaves the question open.

The absorption spectroscopy can be used to make a case for class II behavior. The copper(II) chromophore is expected to be blue. This conclusion is based on the blue color of the compound (hydrazinium)₂CuCl₄·2H₂O. This compound has also been studied by Hatfield et al.³ and is postulated to be a six-coordinate Cu–(N₂H₅)₂Cl₄ species with coordinated hydrazinium cations. The $\text{Cu}^{\text{I}}\text{Cl}_3^{2-}$ chromophore is colorless. The broad band centered at 18 200 cm^{-1} is a band not observed in either chromophore and is thus an excellent candidate for an intervalence charge-transfer band.

The EHMO calculations lend insight into the nature of the broad absorption in the visible region. It is instructive to first consider the set of d-block orbitals from the copper(II) and copper(I) chromophores placed side by side. This scheme is shown in Figure 5. The typical copper(II) d–d transitions are shown with solid lines on the left side of the diagram. In addition to these transitions, several intervalence charge-transfer transitions, denoted with a dashed line, are possible. This picture presents a spectrum with copper(II) d–d and intervalence charge-transfer transitions intermixed at the low-energy region of the spectrum. It also shows an IVCT band at higher energy. The EHMO calculations agree with this simple picture, and the energy level diagram is shown in Figure 4. The same trend is observed; the copper(II) d levels and the copper(I) d levels are present in about the same order. In addition there are some levels which show strong character on

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both metal centers. In the symmetry of the problem, C_i , there are two irreducible representations: a_u and a_g . The LUMO, along with all other orbitals showing copper(II) character, must belong to the irreducible representation a_g . The copper(I) orbitals may belong to either representation, and the symmetries of these energy levels are denoted in Figure 4. The transitions arising from the a_u copper(I) orbitals will be of the strongest intensity. The transitions originating on the a_g copper(II) orbitals will be much weaker, since they occur via a vibronic mechanism. The broad absorption at $18\,200\text{ cm}^{-1}$ is tentatively assigned to the transitions arising from the $a_g + a_u$ copper(I) orbitals at the bottom of the energy level diagram. Below $12\,500\text{ cm}^{-1}$ are the typical copper(II) d–d transitions, with the sharp maximum at about $11\,000\text{ cm}^{-1}$ attributable to transitions arising from the copper(I) a_u orbitals lying among the copper(II) d orbitals. Unfortunately, the nature of the sample precludes further investigation of this hypothesis via polarized spectroscopy.

There has been some work performed on analogous systems which support the above assignments. In the salts $\text{Cu}^{\text{II}}(\text{NH}_3)_4(\text{Cu}^{\text{I}}\text{Br}_2)_2$ and $\text{Cu}^{\text{II}}(\text{NH}_3)_4(\text{Cu}^{\text{I}}\text{Cl}_2)_2 \cdot \text{H}_2\text{O}$, the copper halide chains, consisting of edge-sharing CuCl_4^{2-} tetrahedra, are cocrystallized parallel to stacks of square-planar $\text{Cu}^{\text{II}}(\text{NH}_3)_4^{2+}$ ions.^{13a} The square-planar copper(II) ions are isolated from the copper(I) halide chains, with no ligands in the axial positions for the bromide and water molecules in the axial positions (2.73 \AA) in the chloride. In the iodide analogue, $\text{Cu}^{\text{II}}(\text{NH}_3)_4(\text{Cu}^{\text{I}}\text{I}_2)_2$, the square-planar Cu(II) ions serve to bridge the copper(I) iodide chains and thus have iodide ions in the axial positions.^{13b} In other words, in the chloride and bromide salts the plane of the $\text{Cu}(\text{NH}_3)_4^{2+}$ ion is perpendicular to the copper(I) halide chain axis, but in the iodide

salt this plane is tilted, allowing the bridging iodide ions in the copper(I) chain to occupy the axial positions in the $\text{Cu}^{\text{II}}(\text{NH}_3)_4^{2+}$ ion. The chloride and bromide salts are both violet, a fact explained by the d–d transitions in a square-planar field of ammonia ligands. The iodide, however, is deep green, a result which the authors attribute to an intervalence charge transfer. The bridging network in the iodide salt is somewhat similar to that of the title compound, with the latter having additional shorter bridges involving the equatorial chloride ions. The fact that a significant change in the color of the iodide is brought on by such a weak bridge further supports the above intervalence assignments.

Conclusions

The crystal structure, absorption spectroscopy, and EHMO calculations all support a class II Robin and Day classification for the title compound. The crystal structure reveals a chloride bridge between the Cu(I) and Cu(II) centers in this salt, a result which points to an interaction between the metal centers. The EHMO calculations performed show a mechanism for the intervalence charge transfer to occur; a purely Cu(II) LUMO molecular orbital with several lower lying molecular orbitals showing strong Cu(I) character. The broad absorption band, centered in a region where no absorption exists for either the Cu(I) or Cu(II) chromophore taken separately, supports such a picture.

Acknowledgment. This research was supported by NSF Grant DMR-8803382 and PRF Grant 20215-AC3-C. The X-ray diffraction facility was established through funds provided by NSF Grant CHE-8408407 and The Boeing Co.

Supplementary Material Available: Tables of X-ray data collection parameters, atomic coordinates and isotropic thermal parameters for non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom positions and isotropic thermal parameters (3 pages); a structure factor table (4 pages). Ordering information is given on any current masthead page.

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Contribution from the Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19880-0328, and Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

EPR Spectra of $(\text{C}_5\text{Me}_5)\text{MoCl}_2(\text{PMe}_3)_2$ in Solution and in Single Crystals of $(\text{C}_5\text{Me}_5)\text{MoCl}(\text{PMe}_3)_2(\text{N}_2)^{\dagger}$

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Received August 3, 1989

EPR spectra of the d^3 species $\text{Cp}^*\text{MoCl}_2(\text{PMe}_3)_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) have been observed both in solution at 173 K and in orthorhombic single crystals of $\text{Cp}^*\text{MoCl}(\text{PMe}_3)_2(\text{N}_2)$ at 77 K. $\text{C}_{16}\text{H}_{33}\text{ClMoN}_2\text{P}_2$ is orthorhombic, of space group $P2_12_12_1$, with $a = 14.7195(11)\text{ \AA}$, $b = 16.4715(16)\text{ \AA}$, $c = 8.9180(6)\text{ \AA}$, $V = 2162.2(3)\text{ \AA}^3$, $Z = 4$, $R = 0.052$, and $R_w = 0.060$ for 1833 reflections. The matrices of g and the ^{95}Mo hyperfine interaction indicate that the unpaired spin population resides primarily in the $4d_{z^2}$ orbital of the molybdenum atom. However, considerable anisotropy was also apparent in the ^{31}P hyperfine interactions, whence it is concluded that some unpaired spin is to be found in the phosphorus 3p orbitals. These conclusions confirm recent Fenske–Hall type molecular orbital descriptions of the model compound $\text{CpMoCl}_2(\text{PH}_3)_2$.

Introduction

In the course of our research into the synthesis of early-transition-metal complexes containing terminal PR_2^- ligands,¹ we attempted to prepare new, low-valent W and Mo starting materials such as the 16-electron compound " $\text{Cp}^*\text{MoCl}(\text{PMe}_3)_2$ ". Instead of the latter, we obtained² dark blue crystals of the 18-electron dinitrogen complex $\text{Cp}^*\text{MoCl}(\text{PMe}_3)_2(\text{N}_2)$ contaminated with the red-brown, 17-electron complex $\text{Cp}^*\text{MoCl}_2(\text{PMe}_3)_2$. Upon finding crystals of the two compounds to be isomorphous, we undertook

a single-crystal EPR study of the paramagnetic dichloro compound doped into diamagnetic crystals of the dinitrogen complex.

A general EHMO bonding analysis of CpML_4 piano stool complexes has been reported previously,³ and a recent Fenske–Hall calculation⁴ by Poli et al. on $\text{CpMoCl}_2(\text{PH}_3)_2$ implicated Mo–P

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