Perturbation of the Electronic Structure of a Copper(II) ion by a $Cu^{I}Cl$ Moiety in a Class I Mixed Valence Copper Complex, $Cu^{II}(Me_5dien)Cl_2(Cu^{I}Cl)$

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A new mixed valence copper complex $Cu^{II}(Me_5dien)Cl_2(Cu^{I}Cl)$ (**2**) was obtained from the reaction of CuCl with $Cu^{II}(Me_5dien)Cl_2$ (**1**) in acetonitrile. The structures of **1** and **2** have been determined by single-crystal X-ray diffraction analyses. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.374(5)$ Å, $b = 17.155(3)$ Å, $c = 23.806(5)$ Å, $\beta = 94.40(4)°$, $Z = 8$, and $V = 3398(1)$ Å^3 while compound **2** crystallizes in orthorhombic space group *Pbcn* with $a = 14.71(1)$ Å, $b = 16.06(2)$ Å, $c = 13.38(1)$ Å, $Z = 8$, and $V = 3159(5)$ Å. The $Cu^{II}(Me_5dien)Cl_2$ unit in both compounds has a similar distorted square-pyramidal geometry. The $Cu^{I}Cl$ moiety in **2** is attached to the Cu^{II} unit via two bridging chlorine atoms and has a distorted trigonal planar geometry. UV−vis and EPR spectroscopic studies and molecular orbital calculations established the presence of significant perturbation of the $Cu^{I}Cl$ unit to the electronic structure of the Cu(II) ion in compound **2**.

Introduction

Mixed valence copper complexes have been of great interest to chemists for a long time because they display intriguing physical and chemical properties, provide valuable information on electron-transfer mechanisms, and serve as possible models for copper proteins.[1] Mixed valence copper complexes were categorized into three classes, based on the coordination geometry of the formal Cu(I) and Cu(II) ions.[1a] In class I the copper(I) and copper(II) centers have distinctly different geometries which are typical for each oxidation state. In class III all copper ions have the same geometry and the copper(I) and copper(II) centers are indistinguishable. In class II compounds the geometries of Cu(I) and Cu(II) are nearly identical but distinguishable, a somewhat ambiguous definition. Efforts were made to further distinguish these three classes of mixed valence copper complexes by their electronic properties, in addition to the copper geometry. While it has been well documented that class II and class III compounds usually display significant d−d interactions and characteristic d → d charge transfer bands between the Cu(I) and Cu(II) centers,[1e,2] causing the intense color of these compounds, there have been few reports supporting the presence of perturbation by a Cu(I) ion to the electronic structure of a Cu(II) ion in a class I environment.[3,4] Recently, we have discovered a new mixed valence copper complex $Cu^{II}(Me_5dien)Cl_2(Cu^{I}Cl)$ (**2**) (Me_5dien = *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine) with a distinct class I structure. This compound can be obtained readily via the reaction of $Cu^{II}(Me_5dien)Cl_2$ (**1**) with $Cu^{I}Cl$ in a 1:1 ratio. The geometry of the copper(II) center in compound **1** and **2** is similar. However, the electronic structures of the copper(II) ion in **1** and **2** appear to be quite different; compound **1** is blue while compound **2** is black-green. With the anticipation that the electronic structural difference of these two compounds could be caused by by d−d interactions between Cu(I) and Cu(II) ions in **2** which is rare among class I mixed valence copper complexes, we conducted a comparative investigation on the structures and electronic properties of compound **1** and **2**. The results of our study are reported herein.

Experimental Section

All reactions were performed in an inert nitrogen atmosphere using a dual manifold Schlenk line and Schlenk flasks. Electron spin resonance spectra were recorded on a Brüker ESP 300E spectrometer at X-band frequency. UV−vis spectra were recorded on a Gilford Response UV−vis spectrometer interfaced with a IBM computer. The transmission spectra of the solid samples were taken using a nujol mixed powder sample pressed on a quartz glass slide. Elemental analyses were done by Canadian Microanalytical Service, Delta, British Columbia. Solvents were reagent grade, distilled from appropriate drying agents under N_2 prior to use. Copper(II) chloride, copper(I) chloride, and *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (Me_5dien) were purchased from Aldrich.

Preparation of $Cu^{II}(Me_5dien)Cl_2$ (1). $CuCl_2$ (100 mg, 0.74 mmol) and *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (129 mg, 0.74 mmol) were added to a flask containing 10 mL of dichloromethane. A light blue solution was obtained. After being stirred for 3 h at 23 °C. The solution was concentrated to about 5 mL *in vacuo*. After this was allowed to stand at 0 °C for 24 h, light blue crystals of **1** were obtained in nearly quantitative yield.

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Table 1. Crystallogrpahic Data

	$C_9H_{23}N_3Cl_2Cu\cdot{}^1/_2CH_2Cl_2$ (**1**)	$C_9H_{23}N_3Cl_3Cu_2$ (**2**)
fw	349.95	406.75
space group	$P2_1/n$	*Pbcn* (No. 61)
a, Å	8.347(5)	14.705(11)
b, Å	17.155(3)	16.06(2)
c, Å	23.806(5)	13.380(11)
β, deg	94.40(4)	90
V, Å^3	3398(1)	3159(5)
Z	8	8
D_c, g cm^{-3}	1.37	1.71
μ, cm^{-1}	17.41	31.8
T, °C	23	23
λ, Å	0.710 69	0.710 69
transm coeff	0.70−1.00	0.64−1.00
no. of measd reflns	6201	2708
no. of obsd. reflns	1454 ($I > 3.00\ \sigma(I)$)	1125 ($I > 3.00\ \sigma(I)$)
R^a	0.067	0.048
$R_w{}^b$	0.065	0.041
goodness-of-fit,^{c} *S*	2.21	1.94

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$, $w = 1/\sigma^2(F_o)$. [c] $S = (\sum w(|F_o| - |F_c|)^2/(N_o - N_v))^{1/2}$. N_o = number of observations, N_v = number of variables.

Preparation of Cu^{II}(Me$_5$dien)Cl$_2$(Cu^{I}Cl) (2). $CuCl_2$ (100 mg, 0.74 mmol) and *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (129 mg, 0.74 mmol) were added to a flask containing 10 mL of acetonitrile at 23 °C. A light blue solution was obtained. After 3 h, CuCl (74 mg, 0.74 mmol) was added and the solution became dark purple-blue. The solution was stirred for additional 2 h. After being concentrated to about 5 mL and kept at 0 °C for 24 h, the solution yielded black-green crystals of compound **2** (42 mg, yield 0.21 mmol, 28%. Additional product can be isolated with further concentration of the solution). Mp: 196 °C. Anal. Calcd for $C_9H_{23}N_3Cl_3Cu_2$: C, 26.58; H, 5.70; N, 10.33. Found: C, 26.81; 5.52; N, 10.38.

Compound **2** was also obtained in good yield from the reaction of **1** with CuCl in a 1:1 ratio in CH_3CN.

X-ray Diffraction Analysis. The blue crystal of compound **1** (0.10 × 0.20 × 0.20 mm) was obtained from a CH_2Cl_2/hexane solution while the dark green crystal of compound **2** (0.20 × 0.30 × 0.30 mm) was grown from a concentrated CH_3CN solution. The crystals were mounted on glass fibers and sealed with epoxy glue. Data were collected over the 2θ range of 3−50° at 23 °C on a Rigaku AFC6S diffractometer using graphite-monochromated Mo Kα radiation and operating at 50 kV and 35 mA. Three standard reflections were measured every 147 reflections. All data processing was performed on a Silicon Graphics computer using the TEXSAN crystallographic software package. All data were corrected for Lorentz−polarization effects and absorption (empirical absorption correction). Neutral atom scattering factors were taken from Cromer and Waber.[5]

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ while compound **2** crystallizes in the orthorhombic space group *Pbcn* (No. 61), uniquely determined by the systematic absences. The positions of metal atoms in both compounds were determined by direct methods. All non-hydrogen atoms were located by subsequent difference Fourier syntheses. The positions of hydrogen atoms were calculated and their contributions in structure factor calculations were included. There are two independent molecules of compound **1** and one CH_2Cl_2 solvent molecule in the asymmetric unit of crystal **1**. Metal, chlorine, and nitrogen atoms in **1** and all non-hydrogen atoms in **2** were refined anisotropically. The details of crystallographic analyses are given in Table 1.

Table 2. Important Positional and Isotropic Thermal Parameters

atom	*x*	*y*	*z*	*B*(eq),^{a} Å^2
		Compound **1**		
Cu(1)	0.9204(3)	0.1959(2)	0.9586(1)	2.84(8)
Cu(2)	0.6629(4)	0.1495(2)	0.2064(1)	2.98(8)
Cl(1)	0.9676(7)	0.1247(4)	1.0491(2)	3.8(2)
Cl(2)	0.6998(8)	0.2661(4)	0.9804(3)	4.4(2)
Cl(3)	0.4873(7)	0.1880(4)	0.2821(2)	4.2(2)
Cl(4)	0.6074(9)	0.0182(4)	0.2046(3)	4.7(2)
N(1)	0.783(2)	0.125(1)	0.9033(7)	2.5(5)
N(2)	1.114(2)	0.150(1)	0.9174(7)	2.8(5)
N(3)	1.075(2)	0.290(1)	0.9755(8)	3.8(6)
N(4)	0.891(2)	0.132(1)	0.2503(8)	4.4(6)
N(5)	0.752(2)	0.260(1)	0.1878(8)	3.3(6)
N(6)	0.509(2)	0.170(1)	0.1359(7)	2.6(5)
C(1)	1.076(3)	0.321(2)	1.034(1)	6.3(8)
C(2)	1.024(3)	0.359(2)	0.937(1)	4.2(6)
C(3)	1.232(3)	0.264(2)	0.961(1)	5.4(7)
C(4)	1.219(3)	0.213(2)	0.909(1)	3.8(6)
C(5)	1.038(3)	0.117(2)	0.866(1)	4.9(7)
C(6)	0.890(3)	0.071(2)	0.878(1)	3.9(6)
C(7)	0.661(3)	0.080(2)	0.934(1)	5.1(7)
C(8)	0.687(3)	0.172(1)	0.861(1)	3.9(6)
C(9)	1.202(3)	0.083(2)	0.950(1)	4.9(7)
C(10)	0.881(3)	0.100(2)	0.307(1)	5.6(7)
C(11)	0.987(3)	0.078(2)	0.217(1)	4.7(6)
C(12)	0.971(3)	0.208(2)	0.251(1)	5.3(7)
C(13)	0.931(3)	0.252(1)	0.196(1)	4.0(6)
C(14)	0.694(3)	0.277(1)	0.128(1)	3.6(6)
C(15)	0.523(3)	0.254(1)	0.122(1)	4.1(6)
C(16)	0.341(3)	0.152(2)	0.146(1)	5.1(7)
C(17)	0.552(3)	0.123(1)	0.085(1)	4.4(6)
C(18)	0.700(3)	0.325(1)	0.225(1)	4.6(7)
		Compound **2**		
Cu(1)	0.70937(9)	0.10976(8)	0.1103(1)	2.24(3)
Cu(2)	0.6077(1)	−0.0286(1)	0.2786(2)	4.48(5)
Cl(1)	0.6348(2)	0.1034(2)	0.2922(3)	3.66(8)
Cl(2)	0.6740(2)	−0.0276(2)	0.0899(3)	3.36(8)
Cl(3)	0.5632(2)	−0.1493(2)	0.3187(3)	5.10(10)
N(1)	0.8429(6)	0.0844(6)	0.1515(8)	2.8(2)
N(2)	0.7472(6)	0.2319(5)	0.1045(8)	2.3(2)
N(3)	0.6033(6)	0.1496(6)	0.0189(8)	2.6(2)
C(1)	0.8556(8)	0.0292(7)	0.240(1)	3.6(3)
C(2)	0.8882(8)	0.0469(9)	0.064(1)	4.3(4)
C(3)	0.8837(7)	0.1656(8)	0.175(1)	3.3(3)
C(4)	0.8490(7)	0.2337(7)	0.102(1)	3.4(3)
C(5)	0.7172(8)	0.2784(7)	0.195(1)	3.4(3)
C(6)	0.7090(8)	0.2670(8)	0.014(1)	3.4(3)
C(7)	0.6087(8)	0.2411(8)	0.009(1)	3.3(3)
C(8)	0.617(1)	0.1109(8)	−0.082(1)	4.7(4)
C(9)	0.5118(8)	0.1257(8)	0.060(1)	4.2(4)

[a] $B(\mathrm{eq}) = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Results and Discussion

Syntheses and Crystal Structures. Compound **2** can be obtained readily via either the direct reaction of Cu^{II}Cl$_2$ and Cu^{I}Cl with Me$_5$dien in a 1:1:1 ratio or the reaction of Cu^{II}(Me$_5$dien)Cl$_2$ (**1**) with Cu^{I}Cl in a 1:1 ratio in CH_3CN. Compound **2** is stable in CH_3CN but undergoes decomposition in solvents such as CH_2Cl_2 and THF. Compound **1** is a simple mononuclear complex, but surprisingly the structure of this compound and the analogous bromide compound have not been reported in the literature. For comparison purpose, the structures of both **1** and **2** were determined by single-crystal X-ray diffraction analysis. Important positional and thermal parameters are given in Table 2. Selected bond lengths and angles are listed in Table 3. ORTEP diagrams showing the structures of **1** and **2** are given in Figure 1 and 2, respectively. There are two independent molecules of **1** in the asymmetric unit with identical structures. Therefore, the structural parameters are given for only one of them (Cu(1)).

The Me$_5$dien ligand in **1** and **2** is coordinated to the copper(II) center as a tridentate ligand. The Cu(II) center in compound **1** has a distorted square pyramidal geometry with the Cl(1) atom on the axial position and Cl(2), N(1), N(2), and N(3) on the basal plane (Cu(1)−Cl(1) = 2.480(6) Å, Cl(2)−Cu(1)−N(2)

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[5] Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2A.

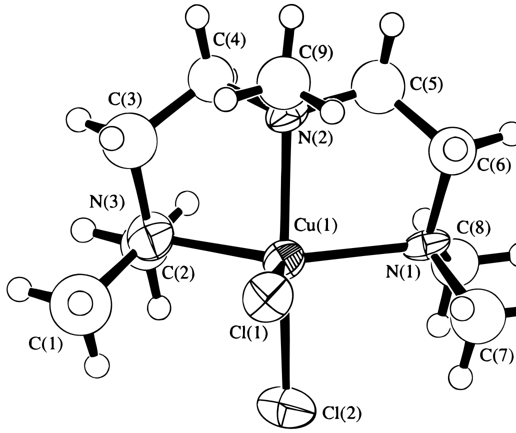

Figure 1. ORTEP diagram showing the structure of one of two independent molecules of **1** with labelling scheme and 50% thermal ellipsoids.

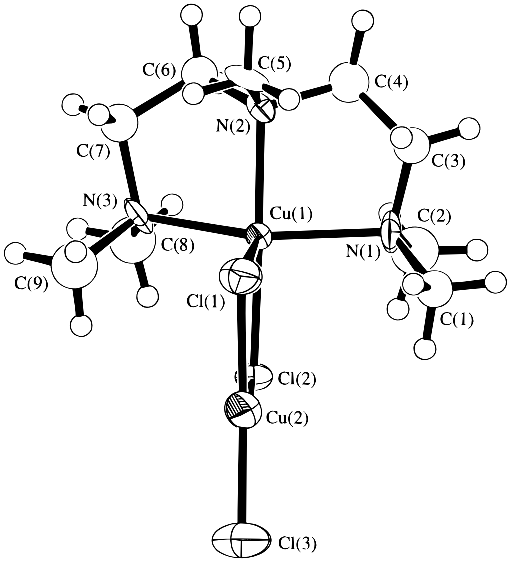

Figure 2. ORTEP diagram showing the structure of compound **2** with labelling scheme and 50% thermal ellipsoids.

Table 3. Selected Bond Lengths (Å) and Angles (deg)

Compound **1**			
Cu(1)−Cl(2)	2.292(7)	Cu(1)−Cl(1)	2.480(6)
Cu(1)−N(3)	2.08(2)	Cu(1)−N(2)	2.11(2)
Cu(1)−N(1)	2.08(2)		
Cl(1)−Cu(1)−Cl(2)	98.0(2)	Cl(2)−Cu(1)−N(3)	92.8(6)
Cl(2)−Cu(1)−N(2)	163.8(5)	Cl(2)−Cu(1)−N(1)	92.0(5)
Cl(1)−Cu(1)−N(3)	99.1(5)	Cl(1)−Cu(1)−N(2)	98.2(5)
Cl(1)−Cu(1)−N(1)	108.0(5)	N(3)−Cu(1)−N(2)	83.9(7)
N(1)−Cu(1)−N(3)	151.6(7)	N(2)−Cu(1)−N(1)	83.7(7)
Compound **2**			
Cu(1)−Cl(1)	2.671(4)	Cu(1)−Cl(2)	2.283(3)
Cu(1)−N(1)	2.080(9)	Cu(1)−N(2)	2.041(8)
Cu(1)−N(3)	2.083(9)	Cu(2)−Cl(1)	2.164(4)
Cu(2)−Cl(2)	2.707(4)	Cu(2)−Cl(3)	2.115(4)
Cu(1)−Cu(1)−Cl(2)	88.8(1)	Cl(1)−Cu(1)−N(1)	98.0(3)
Cl(1)−Cu(1)−N(2)	100.6(3)	Cl(1)−Cu(1)−N(3)	103.9(3)
Cl(2)−Cu(1)−N(1)	93.3(3)	Cl(2)−Cu(1)−N(2)	170.6(3)
Cl(2)−Cu(1)−N(3)	93.2(3)	N(1)−Cu(1)−N(2)	86.6(4)
N(1)−Cu(1)−N(3)	157.3(4)	N(2)−Cu(1)−N(3)	83.5(4)
Cl(1)−Cu(2)−Cl(2)	90.3(1)	Cl(1)−Cu(2)−Cl(3)	158.9(2)
Cl(2)−Cu(2)−Cl(3)	110.7(1)	Cu(1)−Cl(1)−Cu(2)	92.1(1)
Cu(1)−Cl(2)−Cu(2)	88.6(1)		

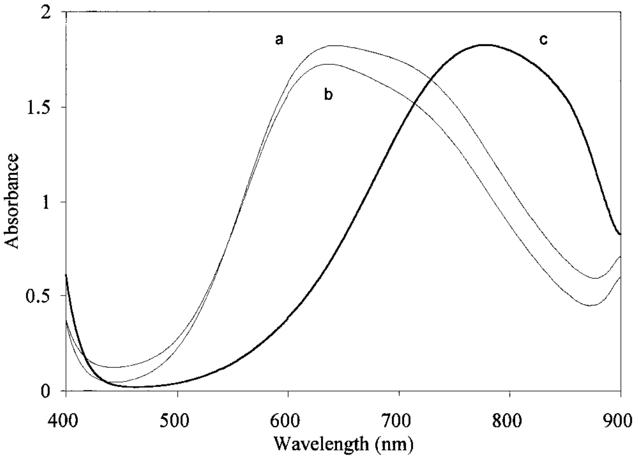

Figure 3. UV−vis spectra recorded in CH_3CN (0.01 M): (a) compound **2**, (b) compound **1** + CuCl, (c) compound **1**.

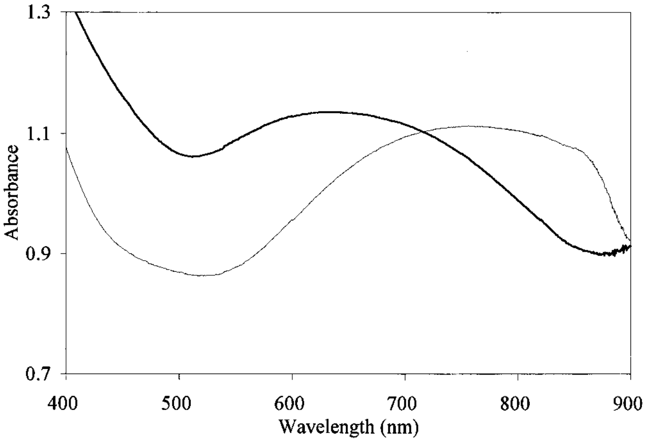

Figure 4. UV−vis spectra of the powder samples of compound **1** and compound **2** (dark line) recorded in Nujol.

= 163.8(5)°, N(1)−Cu(1)−N(3) = 151.6(7)°). Similar structures have been observed in previously reported copper(II) halides containing a tridentate nitrogen ligand.[6] The Cu(II) geometry in compound **2** is similar to that of **1**. The axial position in **2** is occupied by Cl(1) (Cu(1)−Cl(1) = 2.674(4) Å) with a bond length much longer than the Cu(1)−Cl(1) distance in **1**. The basal plane of the Cu(II) center in **2** is more planar than that in **1**, as indicated by the N(1)−Cu(1)−N(3) and N(2)−Cu(1)−Cl(2) angles (157.3(4) and 170.6(3)°) which can be attributed to the weaker axial Cu(1)−Cl(1) bond. The $Cu^{I}Cl$ moiety in **2** is attached to the Cu^{II} unit via two bridging chlorine atoms (Cu(2)−Cl(1) = 2.164(4) Å, Cu(2)−Cl(2) = 2.707(4) Å). The Cu(2)−Cl(3) bond length (2.115(4) Å) is slightly shorter than that of Cu(2)−Cl(1) (2.164(4) Å). The geometry of the Cu(2) center could be described as a distorted trigonal plane which is quite common for a Cu(I) ion.[2a] The geometry of the Cu(II) center in **2** is apparently perturbed by the $Cu^{I}Cl$ moiety. The formation of the Cu(2)−Cl(1) bond is believed to be responsible for the lengthening of the axial Cu(1)−Cl(1) bond, the most significant change from **1** to **2**.

Examples of mixed valence copper complexes are plentiful. However, most of the previously reported mixed valence copper complexes involve bidentate or multidentate ligands as the bridging ligand for the Cu(II) and Cu(I) centers.[1−3] Only a few examples of mixed valence copper complexes where the Cu(II) and Cu(I) centers are linked together via monodentate halide ligands have been reported.[2d,4,7] According to the crystal

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(6) (a) Arriortua, M. I.; Mesa, J. L.; Rojo, T.; Debaerdemaeker, T.; Porter, D. B.; Stratemeier, H.; Reinen, D. *Inorg. Chem.* **1988**, *27*, 2976. (b) Nepveu, F.; Walz, L. *Acta Crystallogr., C*, **1985**, *41*, 332. (c) Veldhuis, J. B. J.; Driessen, W. L.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1986**, 537.

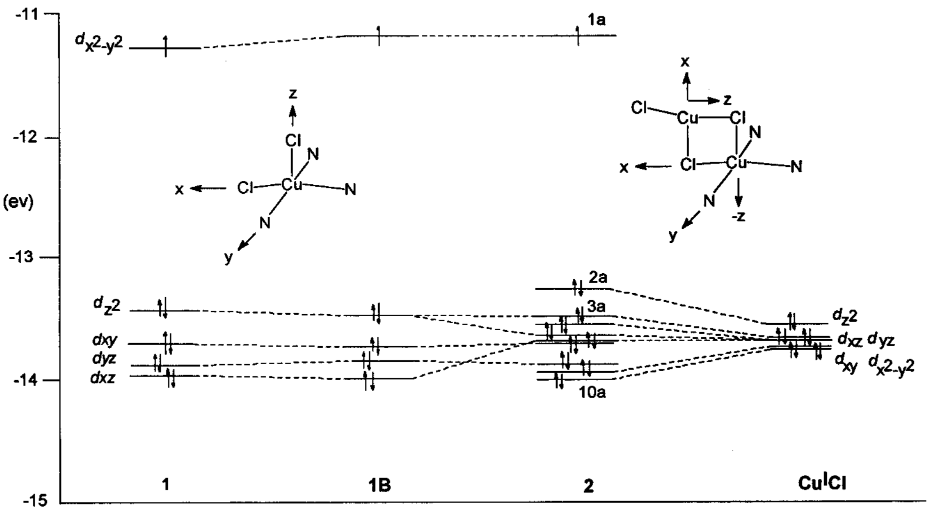

Figure 5. Energy level diagram showing the relative energy levels of d orbitals in compounds **1**, **2** and the Cu(II) portion in **2** treated as an independent molecule (**1B**).

structure, compound **2** would belong to the class I mixed valence copper complexes, where there are distinct geometries for Cu(II) and Cu(I) ions and the unpaired electron is localized on the Cu(II) center. If compound **2** indeed behaves like a class I compound, based on previous studies, one would expect that the copper(II) ion has similar electronic structures in **1** and **2**, since the coordination environment of the Cu(II) ion in both compounds is essentially identical. However, interestingly, compounds **1** and **2** display different colors: **1** is light blue while **2** is black-green. To understand the electronic structures of these two compounds, molecular orbital calculations (extended Hückel) and spectroscopic studies were performed.

Spectroscopic Studies and the Electronic Structures of 1 and 2. The solution and solid UV−vis spectra of compounds **1** and **2** in the 400−900 nm region are shown in Figure 3 and 4, respectively. The solution spectra are similar to those of the solid, except that the absorption of compound **2** in the solid spreads almost the entire visible region, which is in agreement with its dark black-green color. In solution compound **1** has a maximum at 777 nm ($\epsilon = 180$ M^{-1} cm^{-1}) while compound **2** has a maximum at 643 nm ($\epsilon = 175$ M^{-1} cm^{-1}), which are typical of d → d transitions and account for the color difference of these two compounds (the Cl → Cu charge transfer bands in these two compounds appear at much higher energy (<430 nm) and do not overlap with the d → d transition bands). Both compounds also appear to have absorptions in the near-infrared region which may also be related to the d electrons. However, owing to the limitation of our instrument, those absorption bands could not be measured. The addition of Cu^ICl to the solution of compound **1** results in the spectrum of **1** changing to that of compound **2** (Figure 3). If the structures of the Cu(II) portion in **1** and **2** can be considered as essentially identical, the ligand field effect on the Cu(II) ion in both compounds should be similar. The d → d absorption difference of **1** and **2** could then be related to the Cu^ICl moiety which could perturb the energy levels of the d orbitals of the Cu(II) center in **2**.

In order to better understand the nature of these d → d absorption bands, molecular orbital calculations were performed for both compounds **1** and **2**. These calculations were of the extended Hückel type[8] and employed the weighed H_{ij} formalism.[9] The molecular geometries employed for these calculations were taken directly from the crystal structural data. The z axis in compound **1** was placed along the Cu(1)−Cl(1) vector while the local z axes for the Cu(1) and Cu(2) atoms in compound **2** were placed along the Cu(1)−Cl(1) vector and the Cu(2)−Cl(1) vector, respectively. The energy levels of molecular orbitals dominated by the d orbitals are shown in Figure 5. (The correlation lines indicate only the d orbitals which contribute significantly to the MOs of **2**. No correlation lines are drawn for those d orbitals giving minor contributions to the MOs of **2**.) For demonstration purpose, the five d orbitals of the Cu^ICl unit whose energy levels are arbitrarily placed are also included in the diagram. The calculation results show that the unpaired electron in both compounds occupies the $d_{x^2-y^2}$ orbital. The addition of the Cu^ICl unit to **1** results in significant change of the d energy levels of the Cu^{II} center in **2**. The $d_{x^2-y^2}$ and d_{xz} levels rise, the d_{z^2} and d_{xy} levels decrease, while the energy of the d_{yz} orbital remains the same, which is consistent with the d → d transition energy of **2** being higher than that of **1** observed in the UV−vis spectra. In addition, significant mixings of the d orbitals from both Cu^I and Cu^{II} centers are present, even though there is essentially no net overlap between the d orbitals of the two copper centers in **2**. For example, there are significant contributions from both copper centers in orbitals 3a and 5a in compound **2** (Figure 6). The MO calculation results suggest that in compound **2** not only the d → $d_{x^2-y^2}$ transitions on the Cu(II) center but also the d → $d_{x^2-y^2}$ charge transfer from the Cu^I center to the Cu^{II} center could also occur and contribute to the absorption band at 643 nm. Intervalence charge transfer

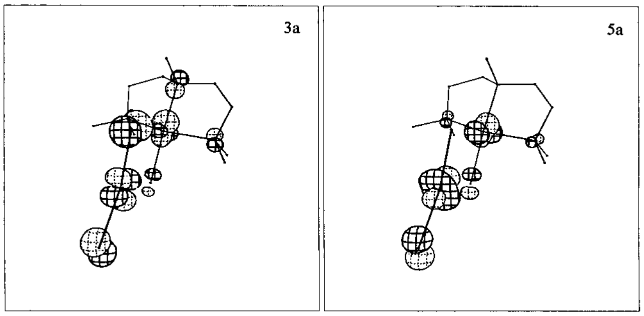

Figure 6. Diagrams for molecular orbitals 3a and 5a of compound **2**.

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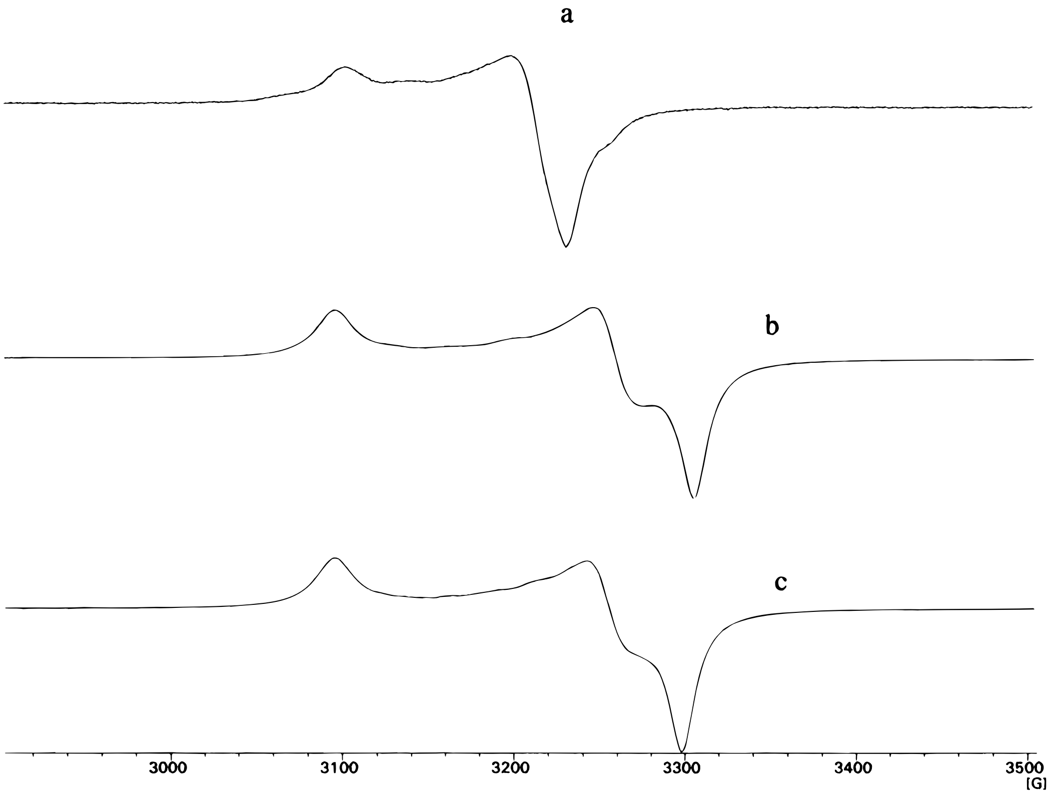

Figure 7. EPR diagram for the powder samples of compounds **1** and **2**: (a) compound **1** at 77 K; (b) compound **2** at 298 K; (c) compound **2** at 77 K.

is not common among mixed valence copper complexes with a distinct class I environment, but has been observed previously.[4]

One may argue that the dramatic different UV−vis spectra of compounds **1** and **2** are caused by the lengthening of the axial Cu(1)−Cl(1) bond in **2** (0.2 Å longer than that in **1**) and the change of the bond angles on the Cu(II) basal plane. We therefore performed EHMO calculation on the portion of $Cu^{II}(Me_5dien)Cl_2$ in **2** using crystal parameters from **2**. The calculation results show that the energy of the $d_{x^2-y^2}$ orbital indeed increases and the energy of the d_{z^2} decreases, following the same pattern as in **2**. However, the d_{xy}, d_{xz}, and d_{yz} orbitals remain essentially at the same levels to those in **1** (**1B** in Figure 5). We therefore believe that the structural difference could contribute in causing the change of the electronic structure of the Cu(II) unit in **2**, but the *d* orbital contribution from the Cu(I) center may also be present. A more detailed theoretical investigation employing a higher level molecular orbital calculation method than EHMO could be very useful in clarifying this matter.

EPR spectra for powder samples of compounds **1** and **2** were recorded at 77 and 298 K. The powder spectra of **1** at 77 K and 298 K are identical and have two peaks (Figure 7). Simulation of both spectra yielded three *g* values ($g_x = 2.077$, $g_y = 2.088$, $g_z = 2.220$). The powder spectra of **2** at 77 and 298 K are essentially identical (Figure 7). Three anisotropic *g* values ($g_x = 2.050$, $g_y = 2.075$, $g_z = 2.183$) are well resolved, which is in agreement with the crystal structure. The hyperfine coupling for both compounds are not visible in the spectra which could be caused by intermolecular exchange interactions. Since **1** and **2** have a distorted square pyramidal geometry with $d_{x^2-y^2}$ being the ground state, the *g* value difference in **1** and **2** in the powder spectra can be related to the energy difference of $d_{x^2-y^2} - d_{xy}$, $d_{x^2-y^2} - d_{yz}$, and $d_{x^2-y^2} - d_{xz}$ in these two compounds.[10] According to the EHMO calculation results, the $\Delta E(d_{x^2-y^2} - d_{xy})$ (2.525 ev) in **2** is larger than that in **1** (2.383 ev), consistent with the g_z values being smaller in **2** than that in **1**. EHMO calculation results also suggest that the Cu^ICl moiety in **2** introduces a larger anisotropy of the d_{xz} and d_{yz} orbitals of the Cu(II) ion than that in **1**, via some degree of interaction with the d_{xz} orbital of the Cu(II) center (The $d_{xz} - d_{yz}$ separation is 0.105 eV in **1** and 0.171 eV in **2**), which is in agreement with the larger g_x and g_y separation in **2**. The g_z values of the powder samples for both compounds are somewhat smaller than those typically observed for a copper(II) ion[11] which could be attributed to some intermolecular spin interactions.

Conclusion

The addition of a Cu^ICl moiety to the complex $Cu^{II}(Me_5dien)Cl_2$ (**1**) causes some structural variation of the Cu(II) portion and a dramatic change of the Cu(II) ion's electronic structure. Both structural variation and the d orbital interference of the Cu(I) ion may be responsible for the change of the electronic structure of the Cu(II) ion.

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Supporting Information Available: Tables of complete lists of positional, isotropic, and anisotropic thermal parameters and bond lengths and angles, and an ORTEP diagram showing the two independent molecules and the CH_2Cl_2 solvent molecule in the crystal lattice of **1** (16 pages). Ordering information is given on any current masthead page.

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