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metal ions, the preference for maintaining a ligand field with as many hard-base donor ligands as possible appears to be thermodynamically more favorable than formation of smaller molecular weight units with more M–P bonding. The fact that these complexes are unique in their high molecularity without leading to insoluble polymers should be noted inasmuch as simple molecular carboxylato complexes containing more than four metal atoms appear to be unknown.[32]

Acknowledgment. A grant from the Lehigh University Forum, which supported the initial stages of this investigation, and the assistance of F. A. Cotton in making possible the crystal structure determinations are gratefully acknowledged.

Registry No. $Ni_6(Ph_2PCH_2CH_2CO_2)_{12}$, 86711-95-7; $Co_6(Ph_2PCH_2CH_2CO_2)_{12}$, 86711-96-8.

Supplementary Material Available: A stereoscopic view of the $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ molecules and tables of structure factors, thermal vibration parameters, and bond distances and angles in the phenyl rings (28 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Synthesis of 4-Methylthiazole Complexes of Copper(II) Chloride. Structure of a Mixed-Valent Dimer, $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$

WAYNE E. MARSH, WILLIAM E. HATFIELD, and DEREK J. HODGSON*

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The reaction of 4-methylthiazole (4-Metz), C_3H_5NS, with copper(II) chloride has been investigated. A total of six new complexes has been identified, five of which are discussed in detail. These include the copper(II)–copper(II) dimers $[Cu(4\text{-Metz})_2Cl_2]_2$, $[Cu(4\text{-Metz})_2Cl_2]_2 \cdot 2CH_3OH$, and $[Cu(4\text{-Metz})(DMF)Cl_2]_2$, the copper(II) monomer $[Cu(4\text{-Metz})_3Cl_2]$, and the mixed-valent copper(II)–copper(I) dimer $[Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3]$. The crystal structure of the mixed-valent dimer is discussed in detail. The complex, $Cu_2(C_3H_5NS)_4Cl_3$, crystallizes in the monoclinic space group $P2_1/n$ with four binuclear species in a cell of dimensions $a = 10.957$ (2) Å, $b = 15.457$ (3) Å, $c = 15.104$ (2) Å, and $\beta = 108.61$ (1)°. The structure has been refined to a final value of the weighted R factor of 0.035 on the basis of 2543 independent data with $I \geq 3\sigma(I)$. The geometry at the Cu(II) center is distorted tetragonal pyramidal, while that at the Cu(I) center is pseudotetrahedral. The two copper centers are bridged by two chloride ligands, the Cu(I)–Cu(II) separation being 3.244 (1) Å.

Introduction

The investigation of the reaction chemistry of 4-methylthiazole with copper(II) chloride has produced several products that not only show some uncommon coordination properties at copper but also indicate some reduction–oxidation chemistry that has not been observed in similar systems of the type CuA_2X_2 (where A is a monodentate ligand and X is a halide). Initial interest in this study was centered on the preparation, and subsequent structural and magnetic characterization, of the dimeric complex $[Cu(4\text{-Metz})_2Cl_2]_2$, which would be analogous to the dimeric copper(II) bromide complex of 4-methylthiazole.[1] However, by use of a synthetic procedure similar to that used for preparing the bromide complex, at least six products were formed and, as a result, several new avenues of study were initiated. Of particular interest was the discovery of a mixed-valence dimer, $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$, which represents a reduction of the parent Cu(II)/Cu(II) dimer with a corresponding loss of chloride ion. This observation is reminiscent of the behavior of a variety of biological macromolecules containing binuclear active sites[2-9] and their synthetic models.[10-17]

Experimental Section

Synthesis of $[Cu(4\text{-Metz})_2Cl_2]_2$ (1). Compound **1** can be prepared in several ways, and depending on certain modifications of the general procedure, other products can be obtained as well (vide infra). For specifically isolating **1**, the following procedure was developed. Copper(II) chloride dihydrate was dehydrated under a vacuum and in the presence of the drying agent P_4O_{10}, and the resultant anhydrous copper(II) chloride was kept in a desiccator until used. The methanol used in the synthesis was distilled over $Mg(OMe)_2$ for 1 h and deaerated with dry N_2 before use. The ligand 4-methylthiazole was obtained from Aldrich Chemical Co. and used without further purification. The complex was prepared by dissolving 1.344 g (0.01 mol) of anhydrous $CuCl_2$ in 20 mL of methanol under a N_2 atmosphere and by adding to this solution under N_2 2.975 g (0.03 mol) of the ligand in methanol. The mixture was stirred constantly for about 10 min and then filtered. The blue-green precipitate that had formed was collected, rinsed with ether, and sealed in small vials to prevent decomposition. The solution was sealed under N_2 and placed in the freezer unit of a refrigerator or allowed to evaporate at room temperature under a steady flow of N_2 for crystallization purposes. The first crystals formed and the initial precipitate were **1** and usually came out of solution immediately; extended periods of crystallization yielded other products (vide infra). Anal. Calcd for $Cu(C_8H_{10}N_2S_2)Cl_2$: C, 28.88; H, 3.03; N, 8.42. Found: C, 28.74; H, 3.03; N, 8.24.

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Table I. Positional Parameters for $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu(II)	0.02053 (6)	0.25043 (5)	−0.04930 (5)	C2D	−0.1605 (6)	0.1061 (4)	−0.1212 (4)
Cu(I)	0.23466 (8)	0.11631 (6)	−0.07453 (6)	C4D	−0.2375 (5)	0.2277 (4)	−0.1937 (4)
Cl(1)	0.0980 (1)	0.2447 (1)	−0.1767 (1)	C5D	−0.3330 (5)	0.1723 (5)	−0.2378 (4)
Cl(2)	0.1303 (1)	0.1110 (1)	0.0385 (1)	C6D	−0.2320 (6)	0.3206 (5)	−0.2130 (4)
Cl(3)	−0.0909 (1)	0.2996 (1)	0.0463 (1)	H2A	0.290 (3)	0.256 (3)	0.105 (3)
S1A	0.3797 (2)	0.3890 (1)	0.1216 (1)	H5A	0.295 (3)	0.502 (3)	0.038 (2)
S1B	0.5825 (2)	0.2776 (1)	−0.0358 (1)	H6A	0.065 (5)	0.507 (4)	−0.083 (3)
S1C	0.0686 (2)	−0.1165 (1)	−0.2440 (1)	H6A′	0.067 (4)	0.442 (3)	−0.134 (3)
S1D	−0.3017 (2)	0.0709 (1)	−0.1957 (1)	H6A″	−0.034 (5)	0.442 (4)	−0.073 (4)
N3A	0.1673 (4)	0.3295 (3)	0.0137 (3)	H2B	0.380 (4)	0.262 (3)	−0.122 (3)
N3B	0.4063 (4)	0.1721 (3)	−0.0319 (3)	H5B	0.678 (4)	0.204 (3)	0.095 (3)
N3C	0.1748 (4)	0.0224 (3)	−0.1670 (3)	H6B	0.558 (7)	0.102 (5)	0.156 (5)
N3D	−0.1371 (4)	0.1879 (3)	−0.1265 (3)	H6B′	0.431 (5)	0.076 (3)	0.122 (3)
C2A	0.2716 (6)	0.3086 (4)	0.0796 (4)	H6B″	0.489 (6)	0.033 (4)	0.078 (4)
C4A	0.1701 (5)	0.4164 (4)	−0.0080 (4)	H2C	0.091 (4)	−0.057 (3)	−0.112 (3)
C5A	0.2786 (7)	0.4563 (4)	0.0452 (5)	H5C	0.142 (4)	−0.067 (3)	−0.358 (3)
C6A	0.0603 (6)	0.4536 (4)	−0.0833 (4)	H6C	0.281 (4)	0.080 (3)	−0.332 (3)
C2B	0.4339 (6)	0.2361 (5)	−0.0778 (4)	H6C′	0.221 (6)	0.140 (4)	−0.285 (4)
C4B	0.5105 (5)	0.1537 (4)	0.0442 (4)	H6C″	0.339 (5)	0.098 (4)	−0.251 (4)
C5B	0.6120 (6)	0.2042 (5)	0.0515 (5)	H2D	−0.102 (4)	0.072 (3)	−0.084 (3)
C6B	0.5049 (7)	0.0825 (5)	0.1092 (5)	H5D	−0.400 (4)	0.182 (3)	−0.282 (3)
C2C	0.1104 (6)	−0.0447 (4)	−0.1558 (4)	H6D	−0.299 (4)	0.338 (3)	−0.272 (3)
C4C	0.1930 (5)	0.0189 (4)	−0.2534 (4)	H6D′	−0.235 (4)	0.356 (3)	−0.172 (3)
C5C	0.1413 (7)	−0.0516 (5)	−0.3024 (4)	H6D″	−0.154 (4)	0.332 (3)	−0.222 (3)
C6C	0.2630 (6)	0.0889 (5)	−0.2812 (4)				

Synthesis of $[Cu(4\text{-Metz})_2Cl_2]_2\cdot 2CH_3OH$ (2). Dark blue crystals of **2** can be prepared by modifying slightly the preparation given above for **1**. After the reaction sequence is followed to yield the filtrate, the solution can be placed in the freezer unit of a refrigerator for crystallization to occur. As stated above, the first crystals formed are **1**, but if these are allowed to stand in solution for approximately 24 h, none of these original crystals remain and only dark blue well-defined crystals are present. Elemental analyses of these crystals were inconsistent, showing a range from 0.56 to 0.75 mol of methanol/mol of copper. While a possible explanation of this observation is the presence of a variable, nonstoichiometric amount of methanol in the crystals, the more probable deduction is that some of the methanol had escaped before the analyses were performed and that the original stoichiometry was 1:1. This conclusion is consistent with the observed crystal structure and with observations of the behavior of these crystals when exposed to air.[18]

Synthesis of $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$ (3). Here again, the preparation of this mixed-valent dimer is essentially the same as presented above for the initial reaction. After the filtrate is obtained, the solution is sealed under a N_2 atmosphere and allowed to stand for 2–3 days, after which a slow stream of dry N_2 is blown over the solution. After several hours of slow evaporation, dark green well-defined crystals begin forming, and when the evaporation procedure is continued until only a small amount of solution remains, many crystals of **3** are obtained. One of these crystals of appropriate size and quality was chosen for the X-ray analysis. This product was also prepared by running the same reaction but using freshly distilled ethanol instead of methanol; the product was confirmed by X-ray analysis on a single crystal.

Synthesis of $[Cu(4\text{-Metz})(DMF)Cl_2]_2$ (4). Complex **4** can be prepared from either **1** or **2** or by dissolving these products in a minimum amount of *N*,*N*-dimethylformamide and placing the solution in the freezer unit of a refrigerator. After a few days, crystals appear that are green and are of reasonable quality. The complex can also be brought out of solution by the addition of ether, whereupon a light green powder forms. Alternatively, complex **4** can be made by dissolving the starting complexes in a mixture of methanol and DMF that contains a ratio of DMF to added complex of at least 1:1. Here again, crystals form by cooling the solution or by evaporation of the solution at room temperature. Some of the compound prepared as described was washed with ether, allowed to dry in air, and sent for analysis. Anal. Calcd for $Cu(C_7H_{12}N_2SO)Cl_2$: C, 27.41; H, 3.94; N, 9.13. Found: C, 27.21; H, 3.75; N, 8.79.

Synthesis of $Cu(4\text{-Metz})_3Cl_2$ (5). Compound **5** was made by using the general procedure described above for **1** except that a larger excess of 4-Metz was used and the reaction mixture was not placed under a N_2 atmosphere. The solution was placed in the freezer unit of a refrigerator, and after a few days, light green crystals formed. Crystals of this complex can also be obtained by starting with complex **4** and adding a methanol solution containing 4-methylthiazole.[18]

X-ray Data Collection and Reduction. A prismatic crystal of the mixed-valent dimer **3** was placed on an Enraf-Nonius CAD4 automated diffractomer; preliminary analysis indicated that the crystals were monoclinic. The observed systematic absences of $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$) uniquely indicated the space group $P2_1/n$, which was confirmed by the subsequent successful refinement of the structure. On the basis of a least-squares fit of the diffractometer settings of 25 reflections, the cell constants were determined to be $a = 10.957$ (2) Å, $b = 15.457$ (3) Å, $c = 15.104$ (2) Å, and $\beta = 108.61$ (1)°; the observations were made with use of Mo Kα radiation ($\lambda(K\alpha_1) = 0.7093$ Å) at 20 °C. The density of the crystals as measured by flotation in a tetrahydrofuran/iodomethane solution was found to be 1.72 g cm^{-3}, which agrees well with the calculated value of 1.726 g cm^{-3} based upon four formula units per cell and a molecular weight of 630.06.

A unique set of diffraction data ($\pm h,+k,+l$) was collected by using Mo Kα radiation and a graphite monochromator. The diffracted intensities and their estimated standard deviations were corrected for Lorentz–polarization effects but not for absorption. A total of 5436 independent data with $2\theta(\text{Mo}) \leq 55°$ were processed, of which 2543 had $I \geq 3\sigma(I)$; only these latter data were used in the refinement of the structure.

Solution and Refinement of the Structure. The solution of the structure was achieved by using MULTAN with 375 reflections having $E \geq 1.86$. An E map, calculated for the solution with the highest combined figure of merit, revealed the positions of the copper and chlorine atoms. Least-squares refinement with the corresponding difference Fourier maps yielded the locations of the other non-hydrogen atoms. All computer programs were those provided by Enraf-Nonius in their SDP package; the atomic scattering factors are taken from ref 19. All least-squares calculations were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ where the weights w were assigned as $4F_o^2/\sigma^2(I)$. Isotropic least-squares refinement gave values of the usual agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ of 0.092 and 0.095, respectively; anisotropic refinement reduced R_1 to 0.054 and R_2 to 0.051. A difference Fourier map showed the positions of all of the hydrogen atoms. The final cycle of least-squares refinement using isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for

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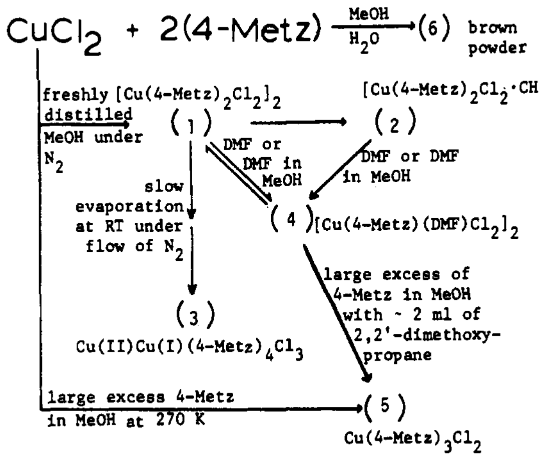
Scheme I



all other atoms converged to final values of R_1 and R_2 of 0.043 and 0.035, respectively. The final difference Fourier map was featureless, with no peak higher than 0.29 e $Å^{-3}$. The positional parameters derived from the final cycle, along with their standard deviations, as estimated from the inverse matrix, are presented in Table I. Lists of the atomic thermal parameters and observed and calculated structure amplitudes are available as supplementary material.

Discussion of the Reaction Scheme

The reaction of 4-methylthiazole with anhydrous copper(II) chloride in methanol has produced six different products, depending on the treatment of the initial reaction solution or on the treatment of the resultant products. The synthesis showing the production of each compound is given in Scheme I. As shown, if the reaction was run without excluding water, the primary product **6** was a brown precipitate that formed immediately. By comparison with similar reactions,[18] this compound was presumed to be a tetrameric species of general formula $Cu_4OL_4Cl_6$. This undesired product can be eliminated entirely by using freshly distilled methanol and by carrying out the reaction under a nitrogen atmosphere. When this was done, the initial product[18] formed was the dimeric complex **1**; the blue-green platelike crystals formed after only a few hours. This compound has displayed unusual reactivity, both in solution and in the solid state; the crystals were observed to decompose when exposed to the atmosphere, and when left in solution, they served as a basis for the formation of several other complexes. One of these compounds, **2**, was formed after approximately 24 h at the reduced temperature of 270 K. The crystals were dark blue parallel planar units, and an X-ray analysis of one crystal showed it to consist of a dimeric unit similar to the parent compound **1** but with the addition of one independent molecule of methanol per unit cell.[18] This compound displayed rapid decomposition when taken out of solution, probably due to the loss of the methanol.

Presumably, it is the reactivity of the parent dimer, **1**, in conjunction with other factors, that brings about the chemical reduction of this dimer to product **3**; this new compound formed as dark green well-defined crystals and was shown by X-ray analysis to be a mixed-valent dimer, $Cu^{II}Cu^{I}$(4-Metz)$_4$Cl$_3$. Crystals of this compound can also be formed from ethanol if the precautions listed above for the initial reaction are followed.

In working with complexes **1** and **2**, we observed that dissolving either of these products in *N,N*-dimethylformamide (DMF) initiated a reaction whereupon a very stable green substance formed. Later reactions showed that the same product could be obtained from a mixture of DMF in methanol and that crystals of good size and quality could be made. These crystals were shown by analysis and by an X-ray study to be **4**; the complex consisted of a symmetric dimeric unit with one independent 4-methylthiazole and one *N,N*-dimethylformamide ligand coordinated to the copper in a cis fashion.[18]

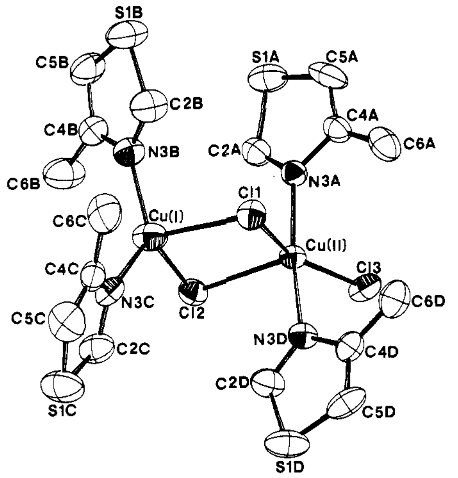


Figure 1. View of the mixed-valent dimer $Cu^{II}Cu^{I}$(4-Metz)$_4$Cl$_3$. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

Table II. Internuclear Separations (Å) in $Cu^{II}Cu^{I}$(4-Metz)$_4$Cl$_3$

Cu(II)–Cl(1)	2.340 (1)	Cu(I)–Cl(1)	2.662 (2)
Cu(II)–Cl(2)	2.613 (1)	Cu(I)–Cl(2)	2.340 (2)
Cu(II)–Cl(3)	2.298 (2)	Cu(I)–N3B	1.981 (4)
Cu(II)–N3A	2.002 (4)	Cu(I)–N3C	1.976 (5)
Cu(II)–N3D	1.998 (4)	S1B–C2B	1.675 (6)
S1A–C2A	1.694 (6)	C2B–N3B	1.297 (7)
C2A–N3A	1.294 (7)	N3B–C4B	1.366 (6)
N3A–C4A	1.386 (6)	C4B–C5B	1.334 (8)
C4A–C5A	1.353 (8)	C4B–C6B	1.489 (9)
C4A–C6A	1.482 (9)	C5B–S1B	1.690 (7)
C5A–S1A	1.681 (8)	S1C–C2C	1.682 (7)
S1D–C2D	1.687 (6)	C2C–N3C	1.296 (7)
C2D–N3D	1.297 (7)	N3C–C4C	1.382 (6)
N3D–C4D	1.382 (6)	C4C–C5C	1.337 (8)
C4D–C5D	1.352 (8)	C4C–C6C	1.462 (10)
C4D–C6D	1.469 (9)	C5C–S1C	1.693 (7)
C5D–S1D	1.685 (8)	Cu(II)–Cu(I)	3.244 (1)

Further investigation showed that the reaction could be reversed to synthesize the parent dimer **1** and, subsequently, **2** by taking dimer **4** and adding to it a solution of 4-methylthiazole in methanol in a ratio of ligand to complex of slightly greater than 1:1. If an excess of 4-methylthiazole was used in conjunction with a small amount of 2,2′-dimethoxypropane, a dehydrating agent, the product **5** was formed. Crystals of this complex were light green and were shown to be monomeric.[18] This complex can also be prepared from the initial reaction if a large excess of 4-methylthiazole is used and if the reaction mixture is open to the atmosphere at a reduced temperature of 270 K.

Description of the Structure of $Cu^{II}Cu^{I}$(4-Metz)$_4$Cl$_3$ (3)

The complex consists of dimeric $Cu^{II}Cu^{I}$(4-Metz)$_4$Cl$_3$ units that are well separated from each other. A view of the dimeric unit is given in Figure 1. Owing to the mixed-valence character of the dimer and the inequality of the coordination spheres around each copper center, the bridging Cu_2Cl_2 unit does not have to be planar and, in fact, the best least-squares plane through the bridging atoms Cu(II), Cu(I), Cl(1), and Cl(2) shows deviations from this plane of −0.087, −0.086, 0.086, and 0.087 Å, respectively. The nonplanar nature of the bridging atoms is also indicated by a dihedral angle of 12.3° between the two planes defined by Cu(II)/Cl(1)/Cl(2) and Cu(I)/Cl(1)/Cl(2). Other differences within the bridging unit can be seen in the bond distances and angles given in Tables II and III, respectively.

As can be seen in Figure 1 and from examination of Tables II and III, the geometry at the copper(II) center is severely

Table III. Internuclear Angles (deg) in $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$

Cl(1)–Cu(II)–Cl(2)	99.04 (5)	Cl(1)–Cu(I)–Cl(2)	97.67 (5)
Cl(1)–Cu(II)–Cl(3)	159.15 (6)	Cl(1)–Cu(I)–N3B	99.43 (14)
Cl(1)–Cu(II)–N3A	88.12 (12)	Cl(1)–Cu(I)–N3C	98.00 (14)
Cl(1)–Cu(II)–N3D	88.55 (12)	Cl(2)–Cu(I)–N3B	114.35 (14)
Cl(2)–Cu(II)–Cl(3)	101.81 (5)	Cl(2)–Cu(I)–N3C	111.21 (15)
Cl(2)–Cu(II)–N3A	95.26 (13)	N3B–Cu(I)–N3C	128.03 (19)
Cl(2)–Cu(II)–N3D	93.96 (13)	Cu(I)–N3B–C2B	121.2 (4)
Cl(3)–Cu(II)–N3A	90.37 (12)	Cu(I)–N3B–C4B	129.3 (4)
Cl(3)–Cu(II)–N3D	89.60 (13)	C2B–N3B–C4B	109.5 (5)
N3A–Cu(II)–N3D	170.58 (18)	N3B–C2B–S1B	117.0 (5)
Cu(II)–N3A–C2A	126.3 (4)	C2B–S1B–C5B	87.6 (3)
Cu(II)–N3A–C4A	123.6 (4)	S1B–C5B–C4B	112.4 (5)
C2A–N3A–C4A	110.1 (5)	C5B–C4B–N3B	113.5 (6)
N3A–C2A–S1A	116.5 (5)	C5B–C4B–C6B	125.9 (7)
C2A–S1A–C5A	88.2 (3)	N3B–C4B–C6B	120.7 (6)
S1A–C5A–C4A	112.8 (5)	Cu(I)–N3C–C2C	124.5 (4)
C5A–C4A–N3A	112.5 (6)	Cu(I)–N3C–C4C	125.6 (4)
C5A–C4A–C6A	128.5 (6)	C2C–N3C–C4C	109.9 (5)
N3A–C4A–C6A	119.0 (6)	N3C–C2C–S1C	116.5 (5)
Cu(II)–N3D–C2D	125.9 (4)	C2C–S1C–C5C	88.1 (4)
Cu(II)–N3D–C4D	123.4 (4)	S1C–C5C–C4C	112.4 (5)
C2D–N3D–C4D	110.7 (5)	C5C–C4C–N3C	113.0 (6)
N3D–C2D–S1D	115.5 (5)	C5C–C4C–C6C	127.8 (7)
C2D–S1D–C5D	89.1 (3)	N3C–C4C–C6C	119.2 (6)
S1D–C5D–C4D	111.8 (5)	Cu(II)–Cl(1)–Cu(I)	80.56 (5)
C5D–C4D–N3D	112.9 (6)	Cu(II)–Cl(2)–Cu(I)	81.61 (5)
C5D–C4D–C6D	126.6 (6)		
N3D–C4D–C6D	120.5 (5)		

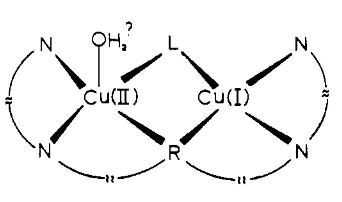
distorted tetragonal pyramid, with the basal plane consisting of two trans nitrogen atoms from 4-Metz ligands and two trans chloride ions while the apical site is occupied by the chloride ligand Cl(2). The distortions from tetragonal-pyramidal geometry are considerable but are less severe than those of a trigonal-bipyramidal model. On the basis of the tetragonal-pyramidal model, for example, the trans N3A–Cu(II)–N3D is 170.6 (2)°, which is a typical value for complexes of this type, but the trans Cl(1)–Cu(II)–Cl(3) angle is only 159.2 (1)°. Alternatively, the four basal ligands deviate markedly from coplanarity, with Cl(1) and Cl(3) being 0.129 and 0.128 Å, respectively, above the plane while N3A and N3D are both 0.129 Å below the plane. As is common in tetragonal-pyramidal complexes, the copper(II) atom lies out of the plane by 0.29 Å in the direction of the apical atom, Cl(2). This highly distorted geometry is in contrast to that observed in $[Cu(4\text{-Metz})_2Br_2]_2$, in which the geometry is very close to that of an idealized tetragonal pyramid;[1] however, other copper(II) chloride complexes of the type $[CuL_2Cl_2]_2$ have distorted geometries about the copper center similar to that observed in this complex.[18,20,21]

The view of the dimer shown in Figure 1 shows that the geometry about the copper(I) ion, Cu(I), is a distorted-tetrahedral arrangement. The six angles subtended at Cu(I), which are listed in Table III, confirm this description and show that the largest distortion is the N3B–Cu(I)–N3C angle of 128.0°. The average value of these angles is 108.1°, which agrees well with the expected value of 109.5°. Also, examination of dihedral angles between the planes formed by Cu(I)/Cl(1)/Cl(2) and Cu(I)/N3B/N3C, Cu(I)/Cl(1)/N3B and Cu(I)/Cl(2)/N3C, and Cu(I)/Cl(1)/N3C and Cu(I)/Cl(2)/N3B shows values of 89.9, 88.5, and 88.5°, respectively. These angles are very close to the 90° value expected for an ideal-tetrahedral arrangement.

The Cu–Cl and Cu–N bond distances observed in $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$ are typical for bis(μ-chloro)-bridged complexes.[18,20,21] The Cu(II)–N3A and Cu(II)–N3D bond distances are slightly longer than the corresponding Cu(I)–N3B and Cu(I)–N3C distances; the former are 2.002 (4) and 1.998 (4) Å while the latter distances are 1.981 (4) and 1.976 (5) Å, respectively. The difference of ~0.02 Å may simply be due to the decreased steric interaction around the 4-coordinate Cu(I) atom as opposed to the 5-coordinate Cu(II) atom. The basal Cu(II)–Cl distances are 2.340 (1) and 2.298 (2) Å, with the distance to the bridging atom Cl(1) being the longer. The axial Cu(II)–Cl(2) distance of 2.613 (1) Å is also within the previously observed range for these complexes and is very close to the distance found in other copper(II) chloride complexes of 4-methylthiazole.[18] Owing to the absence of an inversion center in the molecule, the Cu(I)–Cl distances are not required to be equivalent to the corresponding Cu(II)–Cl distances but, in fact, the bond lengths are similar, with the Cu(I)–Cl(2) distance being 2.340 (2) Å and the Cu(I)–Cl(1) distance being 2.662 (2) Å. The bridging angles Cu(II)–Cl(1)–Cu(I) and Cu(II)–Cl(2)–Cu(I) are, by comparison, somewhat different, having values of 80.56 (5) and 81.61 (5)°, respectively; these angles are considerably smaller than the values found in other bis(μ-chloro) complexes.[18,20,21] Also, the Cu(II)–Cu(I) distance of 3.244 (1) Å is significantly smaller than the shortest observed Cu(II)–Cu(II) separation of 3.416 Å found in $[Cu(PAN)Cl_2]_2$.[20] Presumably, these differences are due to the presence of the 4-coordinate copper(I) center, which would provide less steric bulk in this dimer, as opposed to other dimeric complexes having two 5-coordinate copper(II) centers. The bond distances and angles within the 4-methylthiazole ligands are normal, as can be seen in Tables II and III. Each of the four independent rings (A, B, C, D) is planar, with no atom deviating from the respective least-squares plane by more than 0.004 Å (A), 0.003 Å (B), 0.004 Å (C), and 0.006 Å (D). The exocyclic methyl carbon atom attached to rings A and D deviates from the respective planes by 0.023 and 0.011 Å while the methyl carbon atoms on the other two rings are within the plane defined by their respective 5-membered ring.

Conclusions

The abundance of synthetic chemistry produced by reacting 4-methylthiazole with copper(II) chloride has created several research directions that may provide added input into research areas such as biological modeling, catalytic processing, and magnetic–structural correlations. The identification of the mixed-valent dimer, $Cu^{II}Cu^{I}/(4\text{-Metz})_4Cl_3$, may be significant in the study of half-met hemocyanin where a binuclear Cu(II)/Cu(I) species having an endogenous and an exogenous ligand bridging the metal centers has been suggested.[2,3,9,10] The dimer presented here is remarkably similar to the suggested structure of the half-met form.[2,3]



In the half-met derivative, the nitrogen donors in the copper coordination spheres are from histidine groups present in the protein, the L group is some exogenous ligand, and R represents an endogenous ligand. In studies of mollusc and arthropod hemocyanins, various ligands, such as NO_2^-, Cl^-, CN^-, SCN^-, and others, are being investigated as the possible exogenous bridging unit, L. Since the complex $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$ is the only mixed-valent copper dimer with monodentate ligands whose synthesis has been reported to date, this complex may provide a unique opportunity for investigating certain properties exhibited by the hemocyanins.

Of the products formed in the above synthesis, three of the complexes represent dimeric copper(II) units that have the

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capability of interacting magnetically. As has been stated elsewhere,[21] a major goal in research on bis(μ-halo) copper(II) dimers is the study of the relationship between structure and magnetism, and the preparation of **1**, **2**, and **4** is a contribution to this analysis, which will be more thoroughly discussed in a subsequent publication.

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Supplementary Material Available: Listings of atomic thermal parameters and of observed and calculated structure amplitudes (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Isoelectronic Molecules with Triple Bonds to Metal Atoms (M = Mo, W): Crystal and Molecular Structures of Tri-*tert*-butoxytungsten Ethylidyne and Nitride

MALCOLM H. CHISHOLM,* DAVID M. HOFFMAN, and JOHN C. HUFFMAN

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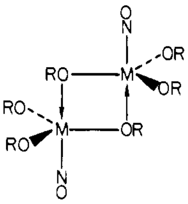
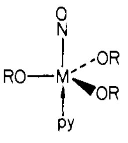
The crystal and molecular structures of $(t\text{-BuO})_3W{\equiv}CMe$ and $(t\text{-BuO})_3W{\equiv}N$ have been determined. In both compounds, tungsten is in a trigonal-bipyramidal geometry with the M≡X function in an axial position. The ethylidyne compound has a centrosymmetric structure involving two trigonal-bipyramidal units joined along a common axial–equatorial edge by a pair of bridging O-*t*-Bu ligands. The nitrido compound is a linear polymer involving alternating short (1.74 (1) Å) and long (2.66 (1) Å) W–N distances corresponding to localized triple and weak dative bonds, respectively. These molecules are members of a more extensive series of compounds containing M≡X functions, where X = NO and $M(OR)_3L$ and M = Mo and W, and structural comparisons are made. For X = CMe, N, and NO trigonal-bipyramidal geometries are found, whereas Lewis base adducts of $M_2(OR)_6$ compounds favor square-based pyramidal geometries with the M≡M bond in the apical position. Crystal data at −160 °C for $(t\text{-BuO})_3W{\equiv}CMe$: $a = 10.317$ (3) Å, $b = 9.517$ (3) Å, $c = 10.891$ (3) Å, $\alpha = 98.90$ (2)°, $\beta = 67.05$ (2)°, $\gamma = 115.24$ (2)°, $Z = 1$, $d_{\text{calcd}} = 1.604$ g cm^{-3} in space group $P\bar{1}$. $(t\text{-BuO})_3W{\equiv}N$: $a = 10.159$ (2) Å, $b = 10.159$ (2) Å, $c = 8.801$ (2) Å, $\gamma = 120.00$ (1)°, $Z = 2$, $d_{\text{calcd}} = 1.761$ g cm^{-3} in space group $P6_3cm$.

Introduction

It has previously been noted[1,2] that NO reacts with hydrocarbon solutions of $M_2(OR)_6$ (M≡M) compounds, where M = Mo[3] and W,[4] to cleave the M≡M bond. In a formal sense, the M≡M bond consisting of one σ and two π components is replaced by two metal–ligand triple bonds, M≡N→O. The structures of $[Mo(O\text{-}i\text{-}Pr)_3NO]_2$[1] and $W(O\text{-}t\text{-}Bu)_3(NO)(py)$[2] are depicted by I and II, which emphasize the trigonal-bipyramidal coordination of the metal atom.



I



II

The recent syntheses[5] of compounds of formula $(t\text{-BuO})_3W{\equiv}CMe$ and $(t\text{-BuO})_3W{\equiv}N$ by cleavage of the W≡W bond in reactions of $W_2(O\text{-}t\text{-}Bu)_6$ with MeC≡CMe and MeC≡N, respectively, provide access to an extensive series of isoelectronic molecules containing the M≡X function supported by strongly π-donating ligands. We show here that the structures of these molecules fall into one of two classes: trigonal bipyramids when X = CMe, N, and NO and square-based pyramids when X = $M(OR)_3L$.

Table I. Fractional Coordinates for the $[(t\text{-BuO})_3W{\equiv}CMe]_2$ Molecule

atom	10^4x	10^4y	10^4z
W(1)	1522.0 (2)	4969.8 (3)	3529.4 (2)
C(2)	3055 (7)	4378 (7)	2792 (6)
C(3)	4365 (9)	3879 (10)	2159 (8)
O(4)	2535 (5)	7147 (5)	3305 (4)
C(5)	4080 (7)	8306 (8)	2752 (7)
C(6)	5061 (9)	8174 (10)	3427 (10)
C(7)	3944 (10)	9849 (9)	3032 (10)
C(8)	4708 (10)	8022 (11)	1254 (8)
O(9)	257 (5)	3826 (5)	2531 (4)
C(10)	259 (7)	2680 (7)	1498 (6)
C(11)	1709 (9)	3393 (10)	262 (7)
C(12)	192 (12)	1252 (9)	2002 (9)
C(13)	−1171 (8)	2329 (10)	1208 (8)
O(14)	−693 (5)	5723 (5)	4639 (4)
C(15)	−1212 (8)	6532 (8)	3970 (7)
C(16)	−173 (9)	6860 (9)	2523 (7)
C(17)	−2841 (8)	5433 (10)	4046 (8)
C(18)	−1147 (9)	8046 (8)	4684 (8)

Results and Discussion

Crystals of $(t\text{-BuO})_3W{\equiv}CMe$ were grown by vacuum sublimation, and from an X-ray study, the molecular structure was found to be of type I. An ORTEP view of the molecule is shown in Figure 1. Atomic positional parameters are given in Table I, and pertinent bond distances and angles are reported in Table II. Complete listings of bond distances and angles and anisotropic thermal parameters are available in the supplementary material.

The association by alkoxy bridge formation is very weak, as evidenced by the extremely long W–O (axial) bond distance, 2.484 (4) Å, which occurs with little lengthening of the equatorial W–O bond. Compare W–O = 1.934 (4) Å for the equatorial bridging O-*t*-Bu bond with W–O = 1.89 (1) Å (averaged) for the two other W–O-*t*-Bu ligands. The W–O bridging axial distance, 2.484 (4) Å, may be compared with the related Mo–O distance, 2.195 (6) Å, in $[(i\text{-PrO})_3MoNO]_2$,[1]

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