Structural Characterization of Dichloro[2-(2-methylaminoethyl)pyridine]copper(II)

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The crystal and molecular structure of dichloro[2-(2-methylaminoethyl)pyridine]copper(II), $CuCl_2(C_8N_2H_{12})$, has been determined from three-dimensional X-ray counter data. The complex crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in a cell of dimensions $a = 19.627$ (9), $b = 8.288$ (3), and $c = 6.520$ (2) Å. The observed and calculated densities are 1.68 (2) and 1.694 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a value of the conventional R factor (on F) of 0.025 for 908 data having $F^2 > 3\sigma(F^2)$. The complex consists of tetragonal pyramids which are linked by single chloride bridges, the axial chloride on one copper atom being in the basal plane of an adjacent copper. The bridging Cu–Cl distances are 2.300 (2) and 2.785 (2) Å while the terminal distance is 2.267 (1) Å and the Cu–Cl–Cu bridging angle is 113.58 (5)°. The geometry of the MAEP ligand is intermediate between the values reported for other aminoethylpyridine complexes. The singly bridged polymeric nature of this complex is unique for systems of the type $CuLX_2$.

Introduction

The synthesis of complexes of the formulation $Cu(AEP)X_2$ (where AEP is 2-(2-aminoethyl)pyridine and X is a halide) was first reported by Uhlig and Maaser, who suggested that these complexes were probably dihalogen-bridged dimers with tetragonal-pyramidal geometry at the copper centers.[1] Our recent structural investigations of $Cu(AEP)Cl_2$ and $Cu(AEP)Br_2$, however, have demonstrated that these complexes are best described as six-coordinate polymers which contain monohalogen-bridged chain interactions in addition to the predicted dimeric structure; moreover, both of these types of aggregation are very weak, with apical Cu–Br distances of 3.57 and 3.71 Å in the bromo complex[2] and values of 3.50 and 3.52 Å in the chloro analog.[3] Consequently, the magnetic properties of $Cu(AEP)X_2$ are somewhat complex, since there are two separate pathways for possible spin–spin coupling.[4]

In an attempt to remove this structural complexity and thereby allow a more rigorous treatment of the magnetic properties of the complex, we have synthesized the methylated complex $Cu(MAEP)Cl_2$, where MAEP is 2-(2-methylaminoethyl)pyridine. The presence of the methyl group might be expected to prevent six-coordination at the copper by blocking approach from one direction; an analogous structural change is observed in the complexes $Cu(py)_2X_2$ (py = pyridine) and $Cu(pic)_2X_2$ (pic = 2-picoline = 2-methylpyridine), the former being six-coordinated polymers[5,6] while the latter are five-coordinated dimers.[7,8] Thus, we anticipated that $Cu(MAEP)Cl_2$ might be a dichloro-bridged dimer. The structures of a number of such systems have been investigated in the hope of correlating the structural and magnetic properties of this significant class of complexes,[7,9–15] and we felt that an analysis of the structure of $Cu(MAEP)Cl_2$ would further aid us toward that goal. In view of the wide variety of structural types reported for other complexes of formulation $CuLX_2$ (where L is bidentate) or CuA_2X_2 (where A is unidentate),[2,3,5–8,10,15–20] however, it is apparent that other structural possibilities exist for $Cu(MAEP)Cl_2$.

Experimental Section

The complex was prepared by the slow addition of 0.392 g (0.003 mol) of MAEP in 20 ml of absolute methanol to a solution of 1.01 g (0.006 mol) of $CuCl_2\cdot2H_2O$ in 20 ml of absolute methanol. Blue-green crystals precipitated within a few hours. Anal. Calcd for $CuCl_2N_2C_8H_{12}$: C, 35.52; H, 4.44; N, 10.35. Found: C, 35.46; H, 4.48; N, 10.29. On the basis of Weissenberg and precession photography, the crystals were assigned to the orthorhombic system; the observed systematic absences of $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd are only consistent with space group $P2_12_12_1$ (D_2^4). The cell constants, obtained by least-squares methods, are $a = 19.627$ (9), $b = 8.288$ (3), and $c = 6.520$ (2) Å; these observations were made at 22° with the wavelength assumed as λ(Cu $K\alpha_1$) 1.5405 Å. A density of 1.694 g cm^{-3} calculated for four formula units per cell is

in good agreement with the value of 1.68 (2) g cm^{-3} observed by flotation in bromoform–benzene solutions. Necessarily, in space group $P2_12_12_1$ no crystallographic symmetry is imposed on monomeric units in the cell.

Diffraction data were obtained from a prismatic crystal with faces (100), ($\bar{1}$00), (110), ($\bar{1}\bar{1}$0), (1$\bar{1}$0), ($\bar{1}$10), (201), ($\bar{2}$0$\bar{1}$), (301), and (30$\bar{1}$). The separations between opposite pairs of faces were as follows: (100) and ($\bar{1}$00), 0.023 cm; (110) and ($\bar{1}\bar{1}$0), 0.037 cm; (1$\bar{1}$0) and ($\bar{1}$10), 0.013 cm; (201) and ($\bar{2}$0$\bar{1}$), 0.050 cm; (301) and (30$\bar{1}$), 0.046 cm. The crystal was mounted roughly parallel to the crystallographic c axis, and intensity data were collected on a Picker four-circle automatic diffractometer using Cu $K\alpha$ radiation filtered through a 0.5-mil Ni foil at a takeoff angle of 1.5°. The receiving aperture was 5.0 × 5.0 mm and was placed 32 cm from the crystal. Data were collected in the θ–2θ scan mode at a rate of 1°/min; peaks were scanned from 0.65° below the calculated $K\alpha_1$ peak position to 0.65° above the calculated $K\alpha_2$ peak position. Stationary-counter, stationary-crystal backgrounds were collected for 10 sec at both ends of each scan. The pulse height analyzer was set for an approximately 90% window centered on the Cu $K\alpha$ peak.

A unique data set having $2° < 2\theta° < 125°$ was collected, a total of 978 independent intensities being recorded. The intensities of three standard reflections, monitored after every 100 reflections, showed no systematic decline as a function of exposure time. The data were processed by the method of Ibers and coworkers,[21] the standard deviations being estimated from their formula[21]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + p^2I^2]^{1/2}$$

and the value of p being assigned as 0.045. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization effects and for absorption. The absorption coefficient for these atoms using Cu $K\alpha$ radiation is 71.6 cm^{-1}, and for the sample chosen the transmission coefficients were in the range of 0.147–0.325.[22] Of the 978 data collected, 908 were greater than 3 times their estimated standard deviations; only these data were used in the subsequent structure analysis and refinement.

Solution and Refinement of Structure

The position of the copper atom was determined from a three-dimensional Patterson function, and two cycles of least-squares refinement of this position were run. All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c the atomic scattering factors for Cu, Cl, and N were from Cromer and Waber,[23] those for C from Ibers,[24] and those for H from Stewart, Davidson, and Simpson.[25] The effects of the anomalous dispersion of Cu and Cl were included in calculations of F_c,[26] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer and Liberman.[27]

The locations of the remaining nonhydrogen atoms were obtained from subsequent difference Fourier syntheses; isotropic least-squares refinement of these 13 atoms led to values of the conventional agreement factors $R_1 = \sum ||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ of 0.081 and 0.118, respectively. Anisotropic refinement of these same atoms gave $R_1 = 0.043$ and $R_2 = 0.062$. The positions of 12 hydrogen atoms were located in a subsequent

Table I. Heavy-Atom Positional Parameters for Cu(MAEP)Cl$_2$

Atom	x	y	z
Cu	0.18015 (3)	0.00948 (6)	0.05746 (9)
Cl(1)	0.29092 (5)	-0.05137 (14)	0.14268 (18)
Cl(2)	0.15563 (5)	-0.25598 (13)	0.01726 (20)
N(1)	0.1990 (2)	0.2357 (4)	0.1692 (6)
N(2)	0.0819 (2)	0.0679 (5)	0.0030 (5)
C(1)	0.0454 (2)	0.1548 (5)	0.1384 (8)
C(2)	-0.0230 (2)	0.1880 (7)	0.1010 (9)
C(3)	-0.0530 (2)	0.1344 (7)	-0.0728 (11)
C(4)	-0.0165 (2)	0.0475 (7)	-0.2129 (9)
C(5)	0.0510 (2)	0.0143 (6)	-0.1686 (7)
C(6)	0.0824 (2)	0.2182 (7)	0.3217 (8)
C(7)	0.1414 (3)	0.3268 (6)	0.2592 (10)
C(8)	0.2393 (3)	0.3359 (6)	0.0277 (10)

difference Fourier synthesis, and a least-squares calculation in which the hydrogen atoms were not refined while the nonhydrogen atoms were refined anisotropically gave values of R_1 and R_2 of 0.036 and 0.054, respectively. The decision not to allow the hydrogen atom parameters to vary was forced upon us by the limited number of available data. The present refinement involved 908 data and 118 variables; inclusion of the isotropic refinement of 12 hydrogen atoms would have given rise to 166 variables and a ratio of observations to variables of only 5.47:1. Hence, the hydrogen atoms were assigned isotropic thermal parameters of 4.5 Å^2 and were not varied. Examination of the low-order data suggested to us that they were suffering from secondary extinction, and a correction of the type described by Zachariasen was applied; this resulted in values of 0.033 and 0.052 for R_1 and R_2, respectively.[28,29]

At this stage of the refinement the model was checked to see if the correct enantiomer had been selected. Since only a single form (*hkl*) of the data had been collected, a least-squares calculation was run in which the Miller indices *hkl* were replaced by $\bar{h}\bar{k}\bar{l}$ for all reflections. This brought about a marked reduction in R_1 and R_2, with final values of 0.025 and 0.039, respectively; this great improvement in R_2 convinced us that this reversed model is correct.

In the final cycle of least-squares no atomic parameter underwent a shift of more than 0.25 times its estimated standard deviation, which is taken as evidence that the refinement had converged. The value of R_2 showed no abnormal dependence on sin θ or on $|F_o|$, which suggested that our weighting scheme was appropriate. A final difference Fourier was featureless, with no peak higher than 0.38 e Å^{-3}. The final value of the extinction coefficient[29] was 1.1 (1) × 10^{-7}. The positional and thermal parameters derived from the final least-squares cycle are presented in Tables I and II; a list of observed and calculated structure amplitudes is available.[30] For the convenience of the reader, the positions of the hydrogen atoms as calculated on the basis of tetrahedral geometry at the extracyclic C and N atoms and trigonal geometry at the pyridine atoms with C–H and N–H bond lengths of 1.08 and 1.03 Å, respectively, are shown in Table III along with the values observed in the Fourier map.

Description of the Structure

The complex consists of polymeric (Cu(MAEP)Cl$_2$)$_x$ chains in which the units are linked by single Cu–Cl–Cu bridges; the chains run along the crystallographic c axis. A view of one segment of the polymer is given in Figure 1. The coordination
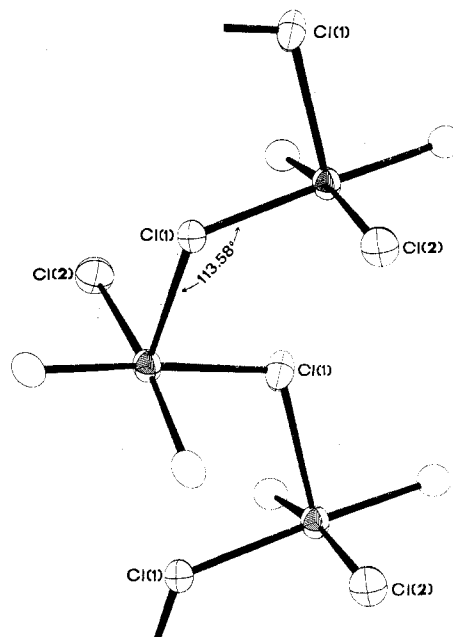

Figure 1. View of the polymeric, singly bridged chain in Cu(MAEP)Cl$_2$. The Cu atoms are shown as shaded ellipsoids, Cl atoms as sectioned ellipsoids, and N atoms as open ellipsoids. The crystallographic c axis is vertical in the figure.
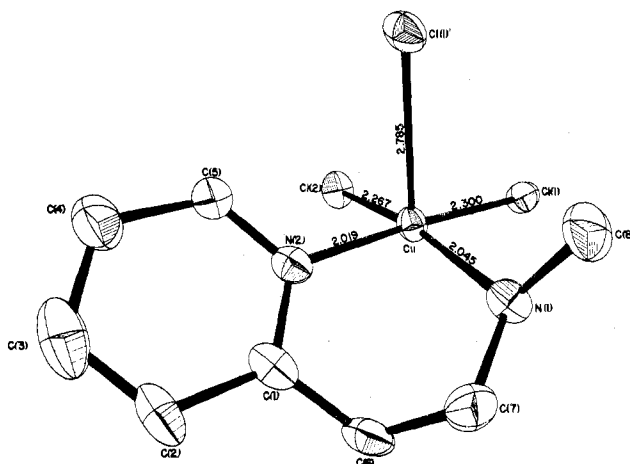

Figure 2. Coordination geometry around one copper atom in Cu(MAEP)Cl$_2$. Atom Cl(1)′ is related to Cl(1) by the 2$_1$ screw parallel to c.

around the copper centers is approximately tetragonal pyramidal, the base being formed by two cis nitrogen atoms from the MAEP ligand and two chlorides while the axial site is occupied by another chloride. The chain is propagated through the axial chloride Cl(1)′, which is part of the base of the

Table II. Thermal Parameters for Cu(MAEP)Cl$_2$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00134 (2)	0.00893 (10)	0.01950 (19)	0.00033 (3)	-0.00008 (4)	0.00016 (11)
Cl(1)	0.00153 (2)	0.0159 (2)	0.0193 (3)	0.00120 (5)	-0.00090 (7)	-0.0036 (2)
Cl(2)	0.00241 (3)	0.0091 (1)	0.0275 (3)	-0.00040 (5)	-0.00022 (9)	0.0014 (2)
N(1)	0.00174 (9)	0.0094 (5)	0.0219 (10)	0.0007 (2)	0.0002 (3)	0.0014 (6)
N(2)	0.00170 (9)	0.0114 (5)	0.0185 (9)	0.0006 (2)	0.0005 (3)	0.0014 (6)
C(1)	0.0017 (1)	0.0110 (7)	0.0224 (11)	0.0006 (2)	0.0015 (4)	0.0051 (9)
C(2)	0.0015 (1)	0.0175 (9)	0.031 (2)	0.0013 (3)	0.0018 (4)	0.0056 (10)
C(3)	0.0014 (1)	0.0187 (10)	0.042 (2)	0.0001 (3)	-0.0004 (5)	0.011 (1)
C(4)	0.0017 (1)	0.0175 (9)	0.029 (1)	-0.0004 (3)	-0.0007 (4)	0.004 (1)
C(5)	0.0017 (1)	0.0165 (8)	0.020 (1)	0.0001 (3)	-0.0003 (3)	-0.0001 (9)
C(6)	0.0022 (1)	0.0173 (9)	0.020 (1)	0.0023 (3)	0.0011 (4)	-0.0026 (9)
C(7)	0.0026 (1)	0.0116 (7)	0.030 (2)	0.0006 (3)	0.0002 (4)	-0.006 (1)
C(8)	0.0030 (1)	0.0113 (7)	0.032 (2)	-0.0017 (3)	0.0018 (5)	-0.000 (1)

[a] The form of the anisotropic ellipsoid is exp$[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Hydrogen Atom Positions in Cu(MAEP)Cl$_2$

Atom	Obsd[a]			Calcd[b]		
	x	y	z	x	y	z
H(2)	-0.052	0.237	0.191	-0.052	0.257	0.211
H(3)	-0.104	0.129	-0.125	-0.106	0.160	-0.101
H(4)	-0.036	-0.011	-0.351	-0.040	0.006	-0.354
H(5)	0.081	-0.047	-0.235	0.080	-0.057	-0.276
H(6)	0.099	0.138	0.398	0.102	0.118	0.409
H(6)'	0.051	0.262	0.398	0.047	0.286	0.415
H(7)	0.158	0.369	0.406	0.159	0.390	0.393
H(7)'	0.139	0.429	0.126	0.123	0.413	0.147
H(8)	0.239	0.456	0.100	0.241	0.457	0.084
H(8)'	0.203	0.343	-0.080	0.216	0.339	-0.123
H(8)''	0.288	0.255	-0.021	0.291	0.290	0.013
H(N1)	0.223	0.179	0.227	0.225	0.225	0.305

[a] The observed positions are from a difference Fourier map; these positions were included in the structure factor calculations. [b] These positions are calculated on the basis of normal geometry (see text) and are probably more reliable than the observed values.

Table IV. Interatomic Distances in Cu(MAEP)Cl$_2$

Atoms	Dist, Å	Atoms	Dist, Å	Atoms	Dist, Å
Cu-Cu'	4.263 (2)	N(2)-C(1)	1.346 (6)	C(5)-N(2)	1.348 (6)
Cu-Cl(1)	2.300 (2)	C(1)-C(2)	1.392 (6)	C(1)-C(6)	1.493 (7)
Cu-Cl(2)	2.267 (1)	C(2)-C(3)	1.353 (9)	C(6)-C(7)	1.523 (7)
Cu-Cl(1)'	2.785 (2)	C(3)-C(4)	1.366 (9)	C(7)-N(1)	1.481 (6)
Cu-N(1)	2.045 (4)	C(4)-C(5)	1.383 (6)	N(1)-C(8)	1.472 (7)
Cu-N(2)	2.019 (3)				

Table V. Interatomic Angles in Cu(MAEP)Cl$_2$

Atoms	Angle, deg	Atoms	Angle, deg
Cl(1)-Cu-Cl(2)	90.90 (5)	N(2)-C(1)-C(2)	120.2 (5)
Cl(1)-Cu-N(1)	86.8 (1)	C(1)-C(2)-C(3)	120.2 (5)
Cl(1)-Cu-N(2)	176.0 (2)	C(2)-C(3)-C(4)	120.3 (4)
Cl(1)-Cu-Cl(1)'	93.97 (4)	C(3)-C(4)-C(5)	117.9 (5)
Cl(2)-Cu-N(1)	165.7 (1)	C(4)-C(5)-N(2)	122.6 (5)
Cl(2)-Cu-N(2)	90.5 (1)	C(5)-N(2)-C(1)	118.8 (4)
Cl(2)-Cu-Cl(1)'	92.98 (5)	Cu-N(1)-C(7)	118.1 (3)
N(1)-Cu-N(2)	90.9 (1)	C(7)-N(1)-C(8)	111.8 (3)
N(1)-Cu-Cl(1)'	101.2 (1)	Cu-N(2)-C(1)	121.4 (3)
N(2)-Cu-Cl(1)'	89.7 (1)	N(2)-C(1)-C(6)	117.1 (4)
Cu-Cl(1)-Cu'	113.58 (5)	C(1)-C(6)-C(7)	111.3 (4)
Cu-N(1)-C(8)	113.0 (4)	C(6)-C(7)-N(1)	112.7 (4)
		C(2)-C(1)-C(6)	122.7 (5)

adjacent tetragonal pyramid. A view of the coordination about one copper atom is shown in Figure 2. The base is not exactly planar, the trans atoms Cl(1) and N(2) lying 0.10 Å above the best least-squares plane through the four ligating atoms while Cl(2) and N(1) lie 0.10 Å below it. As is commonly observed in tetragonal-pyramidal complexes,[31] the metal atom lies 0.16 Å above the plane toward the axial ligand.

The interatomic distances and angles of importance are presented in Tables IV and V, respectively. The equatorial Cu-Cl distances of 2.300 (2) and 2.267 (1) Å are normal, with the distance to the terminal atom Cl(2) shorter than that to the bridging atom Cl(1), as expected. As is usually found in copper(II) complexes, the apical Cu-Cl(1)' distance is longer than the equatorial separations, and the value of 2.785 (2) Å found here is in the range reported for a variety of dimeric and polymeric copper(II) complexes.[3,5,7,10,15] The Cu-N separations of 2.019 (3) and 2.045 (4) Å are also normal, with the distance to the aromatic nitrogen N(2) again shorter than that to the extracyclic nitrogen N(1).

The coordination of the MAEP ligands may be compared to that found for a number of other substituted amino-ethylpyridine complexes.[2,3,32-39] As in all of these examples, the six-membered chelate ring formed by N(1), N(2), C(1), C(6), C(7), and Cu retains the classic "boat" geometry. The base portion of the boat approximates planarity, with an average deviation from the best four-atom least-squares plane of 0.074 Å, while Cu and C(6) are 0.68 and 0.72 Å above this

plane. Hence, in the present case the boat is much more symmetric than in the seven previously documented examples.[33-39] Moreover, since in the three cases[33,35,38] in which the copper atom is further from the plane than is C(6) the N(1)-Cu-N(2) angle is acute (86.5–86.9°) while in the four in which the reverse is true the angle is obtuse (94.6–96.7°), it would appear that in the present case the N(1)-Cu-N(2) would be predicted to be close to (but greater than) 90°; the observed value of 90.9 (1)° is entirely consistent with this conclusion. The earlier suggestion[35] that the N(1)-Cu-N(2) angle is acute unless the axial coordination is relatively strong should presumably be modified, since in Cu(AEP)$_2$(NCS)$_2$ this angle is 86.9°; the correlation appears to be between the flatness of the "bow" or "stem" of the boat and this chelating angle, although in six-coordinated complexes C(6) is usually flattened (i.e., displaced only a small distance from the plane) to avoid interactions between its hydrogen atoms and the axial ligand. In the present case, approach to the sixth coordination site of the copper is impaired by H(6). As in the other complexes, the pyridine ring is roughly planar, with no atom deviating from the least-squares plane by more than 0.012 Å. The bond lengths and angles in the ring and in the extracyclic aminoethyl group are also in the normal range.[32-39]

The nature of the aggregation in this complex is quite different from that found in other systems of the type CuLX$_2$ (where L is bidentate) or CuA$_2$X$_2$ (where A is unidentate). In [Cu(AEP)Cl$_2$]$_x$, there are both doubly bridged pairwise interactions and singly bridged chains, with both of these interactions being extremely weak (Cu-Cl separations of 3.522 and 3.504, respectively); the resulting geometry at the copper is roughly octahedral.[3] In the present case there are no pairwise interactions, and the singly bridged chains are much more strongly bound (Cu-Cl distance 2.785 Å) than in the AEP complex. The Cu-Cl(1)-Cu angle at the bridge in this case is 113.58 (5)°. As is evident from an examination of Figure 2, the absence of a sixth ligand in the copper sphere is not due to the presence of the methyl group on N(1) since this group is on the same side of the basal plane as the axial ligand. It appears possible, however, that approach to the sixth coordination site of copper is hindered by the bridging chloride which links the next two copper atoms in the chain (see Figure 1). Nonetheless, it is not clear why the MAEP complex adopts a geometry which is radically different from that of the AEP complex.

Other complexes of the types CuLX$_2$ and CuA$_2$X$_2$ show a variety of different geometries. Thus, for example, the complexes Cu(tmen)X$_2$ (tmen = N,N,N',N'-tetramethyl-ethylenediamine)[15,40] and Cu(pic)$_2$X$_2$ (pic = 2-methyl-pyridine)[7,8] are comprised of doubly halogen-bridged dimers, Cu(py)$_2$X$_2$ (py = pyridine or its 4-substituted derivatives)[5,6,19,20] and α-Cu(NH$_3$)$_2$X$_2$[18] are doubly halogen-bridged chains, and Cu(teen)Cl$_2$ (teen = N,N,N',N'-tetraethyl-ethylenediamine)[17] and Cu(diMepy)$_2$X$_2$ (diMepy = 2,3-di-methylpyridine)[16] are monomers. The singly bridged chain observed in Cu(MAEP)Cl$_2$, however, is unique for complexes of this formulation as far as we are aware.

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Crystal Structure and Molecular Geometry of μ-Carbonyl-bis(μ-hexafluoroisopropylidenimino)-hexacarbonyldimanganese(*Mn–Mn*), [(CF₃)₂C═N]₂Mn₂(CO)₇, a Complex with Bridging Alkylidenimino Ligands

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The complex μ-carbonyl-bis(μ-hexafluoroisopropylidenimino)-hexacarbonyldimanganese(*Mn–Mn*), [(CF₃)₂C═N]₂Mn₂(CO)₇, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with a = 9.298 (5) Å, b = 26.614 (19) Å, c = 9.543 (8) Å, β = 121.00 (5)° and V = 2024.2 Å³; ρ(obsd) = 2.06 (1) and ρ(calcd) = 2.080 g cm⁻³ for mol wt 634.0 and Z = 4. X-Ray diffraction data complete to 2θ = 45° (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer and the structure was solved via the use of the Patterson, Fourier, and least-squares refinement techniques. The positions of all atoms have been accurately determined, the resulting discrepancy indices being R_F = 10.91% and R_{wF} = 6.23% for all 2630 reflections or R_F = 5.17% and R_{wF} = 5.67% for the 1512 data with $I \geq 3\sigma(I)$. The [(CF₃)₂C═N]₂Mn₂(CO)₇ molecule consists of two Mn(CO)₃ groups which are held together by two bridging [(CF₃)₂C═N] ligands, one bridging carbonyl ligand, and a Mn–Mn bond 2.518 (2) Å in length. The molecule is thus a member of the series (OC)₃M(μ-X)₃M(CO)₃, of which the founder member is Fe₂(CO)₉. An unexpected feature of the [(CF₃)₂C═N]₂Mn₂(CO)₇ molecule is the highly asymmetric ("semibridging") nature of the bridging carbonyl ligand, for which Mn(1)–CO = 1.944 (9) Å and Mn(2)–CO = 2.173 (9) Å. This asymmetry is apparently compensated by a small, but significant, contrary asymmetry in Mn–N distances to the two bridging [(CF₃)₂C═N] ligands.

Introduction

Transition metal complexes containing alkylidenimino ligands, R₂C═N–, have been known for some time.[1] Crystallographic studies on two such species have been reported previously. Thus, (*p*-tol)₂C═N—N═C(*p*-tol)₂ reacts with Fe(CO)₅, yielding the bridging alkylidenimino complex [(*p*-tol)₂C═N]₂Fe₂(CO)₆, which has been shown[2,3] to have the structure I (R = *p*-tol). A species with a terminal alkylidenimino ligand has also been investigated; (π-C₅H₅)-Mo(CO)₂[N═C(CMe₃)₂], II, has an almost linear Mo–N–C skeleton and a short Mo–N distance of only 1.87 Å.[4]

Alkylidenimino ligands can coordinate to a single central atom in two distinct ways. Thus, in some silicon[5] and titanium[6] complexes, the M–N–C system is bent, with sp²-hybridized nitrogen (see III) while in some molybdenum[4] (see II) and

I   II
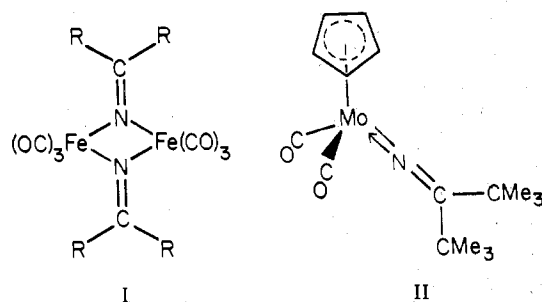
boron[7-9] species, the M–N–C system is linear, with sp-hybridized nitrogen (see IV). These two cases have been treated in terms of the alkylidenimino ligand behaving as a one- and three-electron donor, respectively. This