N-Allylprazole as a Ligand. III.*) The Crystal and Molecular Structure of (1-Allyl-3,5-dimethylpyrazole)-copper(I) Chloride

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The crystal structure of (1-allyl-3,5-dimethylpyrazole)copper(I) chloride, $CuCl(C_8H_{12}N_2)$, has been determined by the three-dimensional X-ray analysis. The crystal is triclinic, space group $P\bar{1}$; $a=8.442(4)$, $b=8.873(6)$, $c=8.112(3)$ Å, $\alpha=103.44(3)$, $\beta=116.42(3)$, $\gamma=63.37(3)°$ and $Z=2$. The structure was refined to an R value of 0.056 for 1196 collected reflections. The complex has a dimeric structure in which the copper(I) ion is surrounded quasi-tetrahedrally by two bridging chlorines, a pyrazole-nitrogen and the olefinic part of the allyl group. The C=C bond distance (1.34 Å) scarcely shows any increase upon coordination to the metal. The olefin plane is almost perpendicular to the Cu-olefin bond axis and shows no significant bendings of the olefinic atoms out of the plane.

We have reported that *N*-allylpyrazole forms complexes with transition metals and in certain metal complexes (M=Cu(I), Ag(I)[1], Pd(II) and Pt(II)[2]) the coordination of the olefin site of the allyl group was indicated. In the Cu(I) and Ag(I) complexes, the coordination of the allyl site was evidenced by the decrease of the C=C vibration frequencies in the solid state. It is well known that Cu(I) ion easily forms complexes with olefins and together with Ag(I) presents the extreme of the transition metal-olefin compounds, in which the σ-donation of the olefinic electrons to the metal might be predominant. Up to present, however, the crystal structures of only a few Cu(I)-olefin complexes have been determined by the X-ray analysis and sufficient structural data are uavailable for the discussion. We now report the crystal structure of CuCl(admp (admp=1-allyl-3,5-dimethylpyrazole), one of the chelate olefin complex of Cu(I).

Experimental

The crystals of CuCl(admp) were grown from an ethanol solution as described in Ref. 1. They were stable in air. Oscillation and Weissenberg photographs were taken to determine the cell dimensions and the space group of the crystals, using the Cu$K\alpha$ radiation ($\lambda=1.5418$ Å).

Crystal data: $CuClC_8H_{12}N_2$, MW=235.1; triclinic, $a=8.442(4)$, $b=8.873(6)$, $c=8.112$ (3) Å, $\alpha=103.44(3)°$, $\beta=116.42(3)°$, $\gamma=63.37(3)°$, $V=486.1$ Å^3; $Z=2$, $D_m=1.67$ g cm^{-3}, $D_x=1.61$ g cm^{-3}; $\mu=0.47$ cm^{-1}; space group $P\bar{1}$.

The intensities of the reflections were measured on a Rigaku automated four-circle diffractometer. The dimensions of the specimen used for the data collection were about $0.1\times0.3\times0.5$ mm. The ω-2θ scan technique was employed. The scan speed was 2°/min in 2θ. The background counts of ten seconds duration were taken at both limits of the scan. The Mo$K\alpha$ radiation ($\lambda=0.71068$ Å) monochromated by a graphite crystal was used. Three standard reflections were measured during the data collection to check any deterioration of the crystal. Independent 1196 reflections ($|F_o|\geq3\sigma(|F_o|)$) were collected up to $2\theta=50°$.

The structure was solved by the conventional heavy atom method. Copper and chlorine atoms were found on a three dimensional Patterson map. All the carbon and nitrogen atoms were located from the successive Fourier and difference syntheses. The parameters of these atoms were refined by a block-diagonal least-squares method to $R=0.091$ with the isotropic temperature factors and to a $R=0.064$ with anisotropic ones. The calculated hydrogen positions were affirmed by the difference syntheses including six methyl hydrogens. Their parameters were refined using isotropic temperature factors. The final R value was 0.056. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[3] Calculations were performed by a HITAC 8800/8700 computer at the Computer Centre of this University, using a local version of the Universal Crystallographic Computation Program System, UNICS.[4]

Description of the Structure

The final atomic parameters are listed in Table 1. The molecular and crystal structures of CuCl(admp) are shown in Figs. 1 and 2. The interatomic distances and bond angles within a molecule are listed in Tables 2 and 3. No unusual intermolecular proximity in the adjacent units is observed.

The complex has a centrosymmetric dimeric structure in which each copper atom is surrounded quasi-tetrahedrally by two bridging chlorines, a nitrogen and an olefinic part of the allyl group (Fig. 1). The olefinic carbons C7 and C8 are 2.13(1) Å and 2.15(1) Å apart

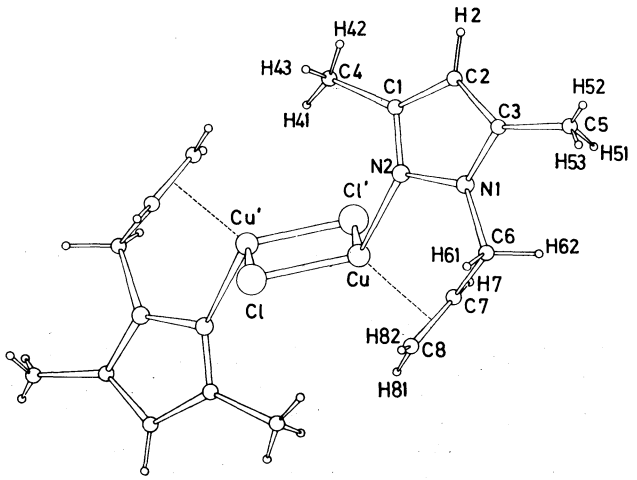

Fig. 1. The molecular structure of CuCl (admp).

* Part II, see Ref. 2.

Table 1(a). Final and temperature parameters for nonhydrogen atoms with their standard deviations in parentheses ($\times 10^4$)

Atom	x	y	z	B_{11}[a)]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	−829(2)	260(2)	1504(2)	217(3)	162(3)	179(3)	−100(2)	77(2)	10(2)
Cl	1673(4)	781(4)	1828(4)	187(6)	191(5)	145(5)	−106(5)	51(5)	−11(4)
N1	−2013(11)	−1432(10)	3011(10)	149(19)	132(15)	125(17)	−60(14)	49(15)	5(12)
N2	−514(12)	−1779(10)	2570(11)	168(20)	145(16)	139(18)	−71(15)	66(15)	−2(13)
C1	364(14)	−3458(12)	2500(13)	154(23)	123(18)	114(20)	−28(16)	32(17)	14(14)
C2	−566(14)	−4188(13)	2915(13)	176(25)	148(20)	119(20)	−58(18)	30(18)	13(15)
C3	−2103(14)	−2863(12)	3216(12)	173(23)	138(18)	102(19)	−78(17)	24(17)	19(14)
C4	2140(17)	−4301(15)	2053(18)	222(30)	191(25)	283(33)	−49(22)	144(27)	4(22)
C5	−3634(16)	−2848(15)	3712(16)	206(27)	198(23)	219(27)	−107(21)	92(22)	16(19)
C6	−3209(15)	358(13)	3276(14)	190(25)	118(18)	185(24)	−49(17)	91(20)	1(16)
C7	−3514(16)	1362(13)	1786(16)	199(27)	120(19)	227(27)	−48(19)	101(23)	−2(17)
C8	−2869(16)	2583(13)	2167(16)	235(28)	116(18)	253(28)	−55(19)	140(24)	−13(18)

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

Table 1(b). Final positional and temperature parameters for hydrogen atoms

Atom	$x\times 10^3$	$y\times 10^3$	$z\times 10^3$	B(A^2)	Atom	$x\times 10^3$	$y\times 10^3$	$z\times 10^3$	B(A^2)
H41	213(18)	−367(16)	146(17)	7.0(35)	H53	−365(15)	−234(13)	466(14)	4.5(27)
H42	208(19)	−525(16)	149(18)	8.0(38)	H61	−244(19)	72(17)	431(18)	8.0(38)
H43	333(18)	−451(15)	323(17)	6.9(35)	H62	−452(13)	40(11)	318(12)	2.8(22)
H2	−20(13)	−537(11)	288(12)	2.5(20)	H7	−425(14)	125(12)	82(13)	3.4(23)
H51	−476(14)	−233(12)	292(13)	3.6(24)	H81	−317(16)	322(14)	124(15)	5.2(29)
H52	−332(14)	−403(12)	386(14)	4.0(25)	H82	−216(14)	275(12)	343(13)	3.3(23)

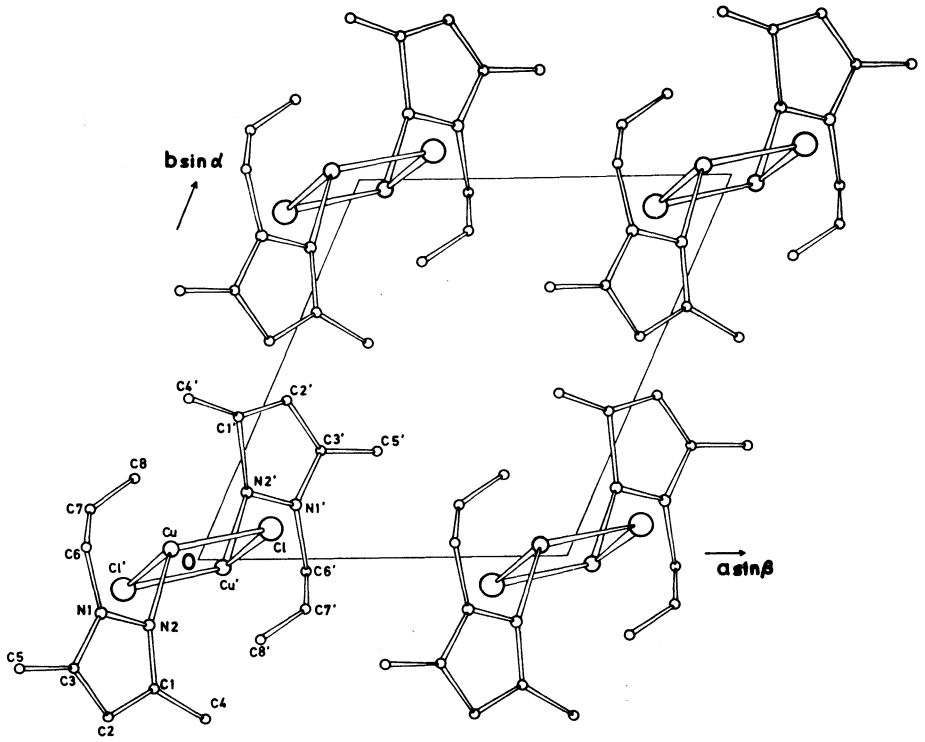

Fig. 2. The crystal structure of CuCl(admp) projected along the c-axis.

from Cu respectively. The distance between Cu and M, the middle point of C7–C8, is 2.03 Å, which indicates an evident bonding of Cu and olefin (Fig. 3). The dihedral angle between the two planes Cl–Cu–Cl′ and N2–Cu–M is 105.2°, and deviates to some extent from the theoretical 90° of a regular tetrahedron. Chlorine is bonded unequivalently to two copper atoms, 2.525(3) Å apart from one copper and 2.252(4) Å apart from the other. The pyrazole ring and two methyl carbons C4 and C5 make a perfect plane, from which the vectors Cu–N2 and C6–N1 are bent 15.8° and 2.9° respectively to the opposite directions of the plane.

The bond length of the coordinated C=C double bond is 1.34(2) Å. The vector Cu–M is perpendicular

Table 2. Interatomic distances (Å) with their standard deviations in the parentheses

Cu–Cu′	3.172(3)	C2–H2	0.95(10)
Cu–Cl	2.252(4)	C4–H41	0.82(18)
Cu–Cl′	2.525(3)	C4–H42	0.89(14)
Cu–N2	2.045(11)	C4–H43	1.00(14)
Cu–C7	2.126(13)	C5–H51	0.85(8)
Cu–C8	2.151(11)	C5–H52	0.98(12)
N1–N2	1.351(15)	C5–H53	0.81(11)
N2–C1	1.334(12)	C6–H61	0.92(13)
C1–C4	1.513(18)	C6–H62	1.05(13)
C1–C2	1.393(24)	C7–H7	0.77(8)
C2–C3	1.380(16)	C8–H81	0.92(14)
C3–C5	1.509(23)	C8–H82	0.95(9)
C3–N1	1.357(19)		
N1–C6	1.478(11)		
C6–C7	1.529(20)		
C7–C8	1.338(20)		

Table 3. Bond angle (degree)

Cl–Cu–Cl′	97.01(14)	C1–C4–H41	109(11)
Cu–Cl–Cu′	82.99(11)	Cl–C4–H42	104(10)
N2–Cu–Cl	123.35(32)	C1–C4–H43	109(8)
N2–Cu–Cl′	98.29(31)	H41–C4–H42	116(15)
N2–N1–C6	118.0(10)	H41–C4–H43	108(14)
N2–N1–C3	111.6(9)	H42–C4–H43	111(13)
C3–N1–C6	130.4(11)	C1–C2–H2	123(6)
Cu–N2–N1	111.5(6)	C3–C2–H2	131(6)
Cu–N2–Cl	139.0(9)	C3–C5–H51	111(8)
N1–N2–C1	105.9(10)	C3–C5–H52	107(7)
N2–C1–C4	120.3(12)	C3–C5–H53	113(9)
N2–C1–C2	110.4(12)	H51–C5–H52	115(11)
C2–C1–C4	129.2(11)	H51–C5–H53	104(12)
C1–C2–C3	105.9(12)	H52–C5–H53	108(11)
C2–C3–C5	130.9(14)	N1–C6–H61	105(10)
C2–C3–N1	106.2(13)	N1–C6–H62	107(6)
C5–C3–N1	122.9(11)	C7–C6–H61	103(10)
N1–C6–C7	108.4(10)	C7–C6–H62	112(6)
C6–C7–C8	122.9(11)	H61–C6–H62	121(12)
		C6–C7–H7	115(9)
		C8–C7–H7	121(9)
		C7–C8–H81	120(8)
		C7–C8–H82	115(7)
		H81–C8–H82	125(11)

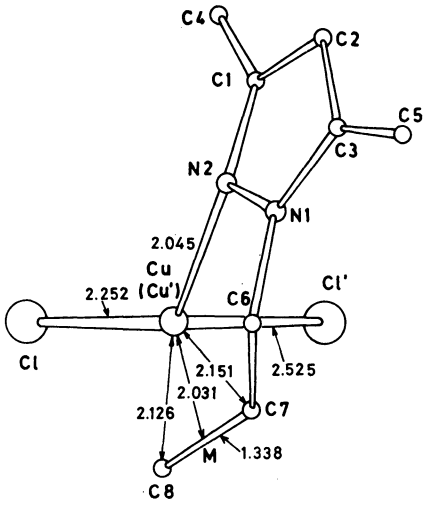

Fig. 3. The structure of the coordination sphere projected along the Cu–Cu′ axis.

to the C7–C8 bond (88.9(15)°). The deviations of the olefinic atoms from their least-squares plane are less than 0.1 Å and any distinctive features such as a bending out of the plane are not observed. The angle between this plane and Cu–M axis is 87.8°.

Discussion

Preceding studies by Bennett and co-workers have revealed that phosphine-olefin and arsine-olefin type of ligands successfully form stable olefin complexes with a number of transition metals,[5] making much use of the coordination ability of the donor atom. Among them, the structures of Mo(0),[6] Fe(0),[7] Ag(I)[8] and Rh(I)[9,10] complexes have been determined by the single crystal X-ray analysis, whereby a bridging bidentate in the Ag(I) complex and chelating bi- or quadridentate coordination in other complexes were known. Our nitrogen-olefin type ligand, admp, shows an analogous ability of the complex-formation with several transition metals to these chelate olefin type ligands.

As for Cu(I), several N-olefin,[11] P-olefin and As-olefin[12] complexes are known. They were assumed to contain a chelating bidentate coordination but none of them has been devoted to the X-ray analysis. With respect to the simple olefin complexes, up to now, the crystal structures of only three Cu(II)-olefin complexes have been determined by the X-ray analysis. The tetrahedral coordination form is found in CuCl(1,5-cyclooctadiene) dimer,[13] in which Cu is surrounded quasi-tetrahedrally by two bridging chlorines and two C=C moieties. Another coordination form is found in CuCl(1,3,5,7-cyclooctatetraene)[14] and CuCl (2,5-norbornadiene),[15] where two chlorines and one C=C make a trigonal plane around the central copper. The molecular structure of our admp complex, a dimeric tetrahedral coordination, is very analogous to that of the cyclooctadiene complex.

The most remarkable characteristic of the metal-olefin bond present in Cu(I)-admp is that the bond length of the coordinated C=C (1.34(2) Å) is scarcely increased compared with those of the free olefins (1.33—1.35 Å) and the C=C sp^2 plane scarcely shows a distortion upon coordination to Cu. In many metal-olefin complexes, a significant increase of the C=C distance upon complex formation is observed and hence regarded as the most important structural evidence to be explained in the metal-olefin bond nature. For instance, in above cited Fe(0) complex,[7] the bond length of the coordinated C=C is 1.45(2) Å, while that of the uncoordinated C=C is 1.33(2) Å. In Ag(I)[8] and Mo[6] complexes, the coordinated C=C shows a length of 1.41(6) Å and 1.39(2) Å respectively. This indicates that in Cu(I)-admp the metal-olefin interaction may be very weak.

It is known that Cu(I) and Ag(I) are able to form complexes with olefins which mainly consist of the σ-donation of the olefinic electrons to the metal. The IR spectra of Cu(I)- and Ag(I)-admp show the lowering shifts of the ν(C=C) band in the solid states but in solutions, free ν(C=C) and little change of

^{1}H-NMR of the olefinic protons are observed, which may be due to the liberation of the metal-olefin bond. Similar trends of the ^{1}H-NMR were noticed in the P-olefin and As-olefin type complexes of these metals. Such a lability in the Cu(I)-olefin and Ag(I)-olefin bonds is frequently observed.[16,17] It also indicates a weak metal-olefin interaction in these olefin complexes.

The weak metal-olefin interaction of CuCl(admp) is very likely but there remains some curiosity behind. The former X-ray studies on the crystal structures of Cu(I)- and Ag(I)-olefin compounds have reported the small but significant increases of the coordinated C=C bond distances.[18] Hence the metal-olefin interaction in CuCl(admp) should be considered to be particularly weak, although the stretching frequency, ν(C=C), is lowered by 103 cm^{-1}, which is much larger than those of Ag(I)-olefin (50—75 cm^{-1}) and is one of the largest value among the Cu(I)-olefin complexes (80—100 cm^{-1}).[11,12,19] Since the data are too limited and some are old, more investigations of many Cu(I)-olefin complexes will be required, in order to find the reason of this contradiction.

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