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ON THE STRUCTURE AND PROPERTIES OF 2-COPPER-1-(DIMETHYLAMINOMETHYL)FERROCENE

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Summary

Some properties of 2-copper-1-(dimethylaminomethyl)ferrocene [1] have been studied (thermal decomposition, decomposition by strong HCl) and the crystal structure of this organocopper compound has been determined.

2-Copper-1-(dimethylaminomethyl)ferrocene has been obtained by the action of 2-lithium-1-(dimethylaminomethyl)ferrocene on the complex of dimethylaminomethylferrocene with copper iodide. The possibility of employing the new reagent for the synthesis of 2-aryldimethylaminomethylferrocenes and substituted diferrocenyls [2] has been indicated.

The first organocopper compound in the ferrocene series is a red crystalline substance which is fairly stable in air and insoluble in the majority of organic solvents. Yet the simultaneous presence of an organic solvent, such as benzene, and water, brings about a very slow decomposition of 2-copper-1-(dimethylaminomethyl)ferrocene (I). (Dimethylaminomethylferrocene and corresponding substituted diferrocenyls have been detected in the organic layer.) Thermal decomposition carried out in boiling xylene for 2 h under argon also yielded dimethylaminomethylferrocene along with traces of the products of doubling of dimethylaminomethylferrocenyl radicals. Heating in air up to 170°C or treatment by strong HCl at room temperature leads to rapid decomposition of I with the formation of the same reaction products.

A complete X-ray structural study was carried out in order to establish the molecular geometry of 2-copper-1-(dimethylaminomethyl)ferrocene (I). Crystals of I are tetragonal, $a = 15.389(2)$, $c = 10.278(1)$ Å, $V = 2434.0(8)$ Å^3, M = 305.7 $D_m = 1.67$, $D_c = 1.68$ g cm^{-3} for $Z = 8$, space group $P\bar{4}2_1c$. Intensities of 761 reflections have been measured with an automatic diffractometer "Syntex-$P2_1$" (λ Mo-K_α, graphite monochromator, θ—2θ-scan). In the subsequent calculations 540 reflections with $F^2 \geqslant 2\sigma$ were used, disregarding absorption. The structure was solved by the direct method according to MULTAN programme and refined by the full-matrix anisotropic least squares method to $R = 0.060$. Atomic coordinates and anisotropic temperature factors are given in Table 1. Table 2 gives values of bond lengths and angles.

Complex I in the crystal has a tetrameric structure. Within ±0.042(4) Å copper atoms form an almost planar square whereas substituted cyclopentadienyl rings serve as bridging ligands, each at the expense of only one of its carbon atoms (Fig. 1). Nitrogen atoms do not participate in the coordination of copper atoms since the shortest intramolecular distance Cu. . .N is 3.09(2) Å, i.e. it appreciably exceeds the values of ~2.0 Å, common to ammine complexes of copper. This peculiarity of structure I seems rather unusual though it may evidently be accounted for by the general steric overcrowding in the molecule.

In general a square-clusters form is not typical of atoms of transition and post-transition metals and has been reported only for complex $[Me_3SiCH_2Cu]_4$ (II) [3] where there is a similar grouping of Cu atoms with four alkyl bridges, with bond lengths Cu—Cu (2.443(3) in I and 2.417 Å in II) and Cu—C (2.05(3) in I and 2.02 Å in II) differing insignificantly in the two complexes. However, while in II the bridging carbon atoms are practically co-planar with the Cu_4 cluster plane, in I they are alternatively displaced from this mean plane in opposite directions. Planar arrangement of Cu atoms was also found in $[Cu(MeNNNMe)]_4$ [4] although here a parallelogram and not a square is found. Cu—Cu—Cu angles are 112.1 and 67.7° and the shortest Cu—Cu distances are 2.66 Å, which is considerably greater than in I or II.

The tetrametic cluster $[(MeC_6H_3CH_2NMe_2)Cu]_4$ (III) [5] which is similar in structure to I and II, exhibits, however, a tetrahedral butterfly conformation skeleton. Amino-substituted phenyl rings with an average Cu—C distance of 2.06 Å serve here as bridging ligands. In contrast to I, the N atom in III takes part in the coordination by the Cu atom (Cu—N is 2.19 Å) thus making it pentacoordinate.

The Fe atom in structure I seems to be the fifth ligand as the Cu—Fe distance is 2.945(5) Å, which may indicate a weak metal—metal interaction, although

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL FACTORS (in form $T = \exp[-1/4 \times 10^{-1}(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)]$)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1100(2)	223(2)	−41(4)	25(2)	24(2)	51(2)	−1(1)	2(3)	1(2)
Fe	2682(3)	−550(3)	−1160(5)	19(2)	35(2)	53(2)	3(2)	6(2)	3(2)
N	325(15)	−1815(17)	−2765(20)	31(15)	77(17)	17(12)	−20(13)	−3(11)	−1(12)
C(1)	1009(17)	1510(16)	472(37)	17(16)	21(15)	127(37)	4(13)	−21(18)	2(18)
C(2)	1630(20)	−1327(16)	−1793(32)	61(21)	10(15)	66(20)	18(13)	40(19)	−5(15)
C(3)	2448(18)	−1842(17)	−1691(27)	41(18)	39(17)	50(17)	22(14)	12(16)	14(15)
C(4)	2814(17)	−1751(18)	−352(25)	37(15)	60(18)	33(21)	20(14)	22(16)	28(16)
C(5)	2242(15)	−1220(16)	459(29)	9(12)	32(15)	100(26)	15(12)	23(15)	33(17)
C(6)	3833(25)	−203(25)	−1978(65)	34(21)	27(20)	203(50)	−7(19)	42(29)	12(28)
C(7)	3176(37)	−22(37)	−2709(48)	124(45)	79(37)	121(37)	40(32)	48(32)	−13(33)
C(8)	2696(27)	642(27)	−2181(50)	51(24)	61(27)	95(32)	−26(21)	−48(27)	58(26)
C(9)	2973(29)	709(21)	−956(52)	56(26)	22(18)	155(42)	−29(16)	42(24)	47(25)
C(10)	3742(25)	238(24)	−651(36)	39(19)	41(19)	115(35)	10(17)	−30(21)	−15(20)
C(11)	1016(16)	−1202(23)	−2909(28)	−3(13)	106(23)	43(17)	9(16)	−5(14)	14(19)
C(12)	501(22)	−2683(21)	−3056(31)	103(28)	28(16)	86(23)	42(19)	0(21)	−26(19)
C(13)	−292(20)	−1514(17)	−3681(26)	58(19)	48(17)	47(15)	−25(14)	−12(18)	−6(16)

TABLE 2

BONDLENGTHS *d* (Å) AND BOND ANGLES *ω* (°)

Bond	*d*	Bond	*d*	Angle	*ω*	Angle	*ω*
Cu—Cu′	2.443(4)	C(1)—C(2)	1.45(3)	Cu′—Cu—Cu‴	89.9(2)	C(2)—C(1)—C(5)	115.0(1.5)
Cu—Fe	2.945(5)	C(2)—C(3)	1.49(4)	Fe—Cu—Cu‴	157.8(2)	C(1)—C(2)—C(3)	102.7(2.1)
Cu—C(1)	2.05(4)	C(3)—C(4)	1.49(4)	Fe—Cu—Cu′	97.6(2)	C(2)—C(3)—C(4)	109.5(2.3)
Cu′—C(1)	2.05(4)	C(4)—C(5)	1.46(4)	C(1)—Cu—Cu′	53.5(1)	C(3)—C(4)—C(5)	110.6(2.3)
Fe—C(1)	2.06(4)	C(5)—C(1)	1.51(3)	C(1)—Cu—Cu‴	140.8(2)	C(4)—C(5)—C(1)	102.0(1.9)
Fe—C(2)	2.12(3)	C(6)—C(7)	1.29(7)	C(1)—Cu′—Cu	53.3(1)	Av. C—C—C	108.0(2.0)
Fe—C(3)	2.09(3)	C(7)—C(8)	1.37(7)	C(1)—Cu—Cu‴	139.2(2)	C(7)—C(6)—C(10)	110.6(4.4)
Fe—C(4)	2.04(3)	C(8)—C(9)	1.33(7)	C(1)—Cu—Fe	44.5(1)	C(6)—C(7)—C(8)	110.6(4.8)
Fe—C(5)	2.07(3)	C(9)—C(10)	1.42(6)	C(1′)—Cu′—Fe	123.1(2)	C(7)—C(8)—C(9)	105.0(4.2)
Fe—C(6)	2.03(4)	C(10)—C(6)	1.53(7)	C(1)—Cu—C(1′)	165.8(4)	C(8)—C(9)—C(10)	115.7(4.0)
Fe—C(7)	1.94(5)	Av. C—C	1.44(5)	Cu—C(1)—Cu′	73.2(1.0)	C(9)—C(10)—C(6)	96.1(3.4)
Fe—C(8)	2.11(4)	C(2)—C(11)	1.50(4)	C(2)—C(11)—N	107.8(2.4)	Av. C—C—C	107.6(4.1)
Fe—C(9)	2.00(3)	C(11)—N	1.43(4)	C(11)—N—C(12)	117.6(2.4)	C(11)—C(2)—C(1)	126.2(2.3)
Fe—C(10)	2.10(4)	C(12)—N	1.40(4)	C(11)—N—C(13)	102.4(2.2)	C(11)—C(2)—C(3)	130.9(2.6)
Av. Fe—C	2.06(4)	C(13)—N	1.42(4)	C(12)—N—C(13)	107.5(2.3)		

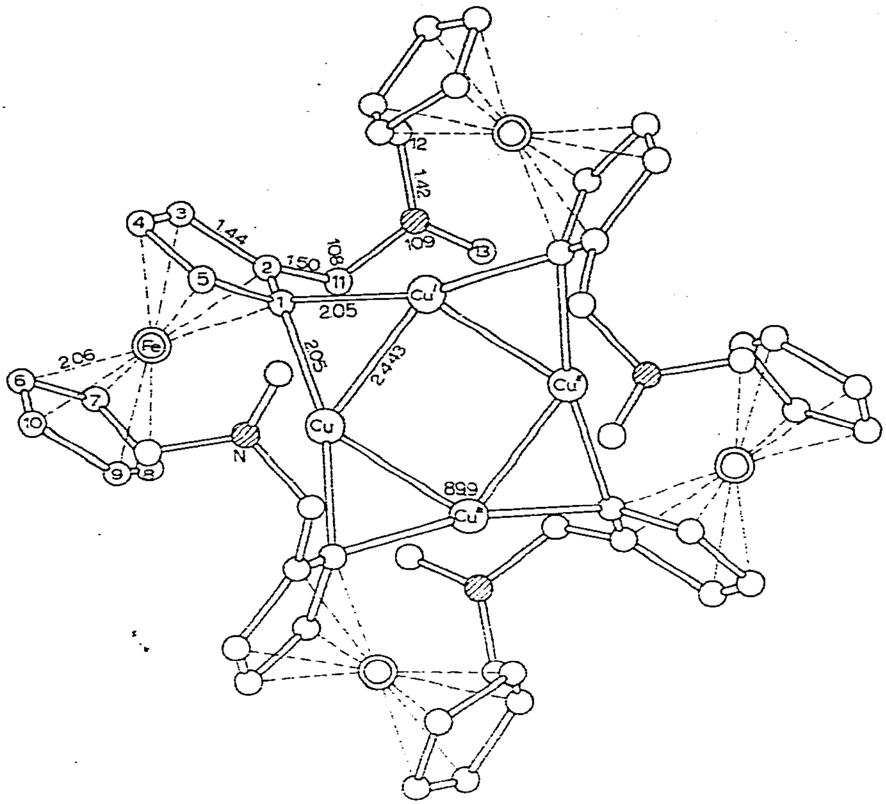

Fig. 1.

this value exceeds the sum 2.69 Å of the covalent radii of the Cu and Fe atoms which are 1.35 [6] and 1.34 Å [7] respectively. The molecular structure of I resembles in this respect that of $[C_5H_5FeC_5H_4Au_2(PPh_3)_2]^+$ (IV), where the ferrocenyl ligand also plays an unusual bridging function, yet the Au—Fe distance of 2.818 Å in cation IV is almost equal to the sum of the radii while the bridging carbon atom of the pentadienyl ring is situated asymmetrically relative to the Au atoms (the Au—C distances are 2.13 and 2.27 Å). It is noteworthy that the bridging ring in IV has an envelope-like conformation and the rings in the sandwich are not parallel, their dihedral angle being 16° whereas in I the cyclopentadienyl ligands are planar and the dihedral angle is only 6.5°.

The geometric characteristics of the ferrocene nucleus in I are normal and average distances for Fe—C (2.06(4) Å) and C—C (1.44(5) Å) are close to those found for ferrocene and its derivatives. The valence configuration of the nitrogen atoms is distorted pyramidal (angles C—N—C are 117(2), 103(2) and 107(2)°; an average C—N bond length is 1.42(4) Å). The methylene carbon atoms are in the planes of the corresponding cyclopentadienyl rings; the C(11)—C(2) bond length is 1.50(4) Å, the C—C—N angle is 108(2)°.

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