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LETTER

Addition of Methanol to Dicyanamide in the Cu(II) Coordination Sphere: Structure of Bis{bis(methoxycarbimido)aminato}copper(II)

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During investigation of the system Cu(II)–N(CN)$_2^-$–py–CH_3OH–H_2O (py = pyridine), violet red crystals of a copper(II) complex were separated. The formation of a dicyanamide complex of pyridine is excluded on the basis of analytical as well as IR data. It has been shown that metal ions (e.g. Zn^{2+}, Cu^{2+}) catalyse the addition of 2 moles methanol to dicyanamide to form bis(methoxycarbimido)amine, HN=C(OCH_3)NH·(OCH_3)C=NH [1, 2]. An analogous reaction might occur under the conditions of our system, too. Therefore, an X-ray diffraction study was undertaken in order to elucidate the structure of the compound obtained and the chemical reaction of its synthesis.

Experimental

The system $Cu(NO_3)_2$, $KN(CN)_2$, CH_3OH, pyridine and water in the molar ratios 1:2:30:25:60 was left to stand. After several days, the blue colour of the solution changed and violet–red crystals separated. *Anal.* Calc. for $C_8H_{16}N_6O_4Cu$: C, 29.68; H, 4.98; N, 25.95; Cu, 19.62. Found: C, 29.91; H, 5.03; N, 25.78; Cu, 19.54%.

A total of 707 independent non-zero observed reflexions with $I > 3\sigma(I)$ were measured on a Syntex $P2_1$ diffractometer. Intensities were corrected for the Lorenz and polarization factors and experimental absorption effect. The structure was solved by Patterson functions, completed through the SHELX76 system [3] and refined by a least-squares procedure on F_{obs} to conventional $R = 0.031$ and $R_w = 0.030$. The maximal feature in the final difference map was 0.21 e Å^{-3}.

The infrared spectrum was recorded on a Specord M80 spectrophotometer (4000–400 cm^{-1}) using KBr pellets, while the electronic spectrum in the visible region was recorded on a Specord M40 spectrophotometer from Nujol mulls spread on Whatman 1.

Results and Discussion

The compound under study is thermally very stable; its decomposition begins only from 200 °C. It is only soluble in hot toluene and slightly so in hot benzene; in the other usual solvents it is practically insoluble.

Crystals of the compound are monoclinic, space group $P2_1/n$, $a = 9.973(3)$, $b = 5.657(1)$, $c = 11.578(3)$ Å, $\beta = 99.73(2)°$, $F(000) = 336$, $D_m = 1.62$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1.67$ g cm^{-3}, μ(Cu Kα) = 2.52 mm^{-1}.

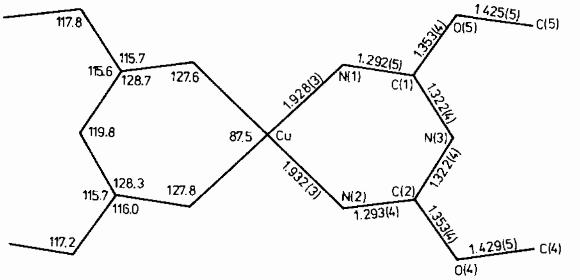

Fig. 1. The molecular structure of Cu(BMCA)$_2$. The bond lengths are in Å, angles in °.

The structure consists of discrete Cu(BMCA)$_2$ units where BMCA = bis(methoxycarbimido)aminate anion (Fig. 1), held together by van der Waals interactions and hydrogen bonds. The copper atom is located in the centre of symmetry and is square-planar coordinated by four nitrogen atoms, forming a relatively very stable six-membered metallocycle. The C–N distances of 1.292(5) and 1.322(4) Å indicate a strongly delocalizated π-bonding system (length of single C–N bond is 1.49 Å; length of partially double C–N bond is 1.32 Å). The methoxy groups are out of the mean plane. There are two molecules in the unit cell which are nearly parallel and lie approximately in the *xz* plane.

In the IR spectrum of Cu(BMCA)$_2$, the very strong bands with their maxima at 1606 cm^{-1} (and shoulder at 1614 cm^{-1}) and at 1375 cm^{-1} are assigned to the ν(C=N) and ν(C–N) vibrations,

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respectively. Characteristics of other middle IR data for the solved structure are ν(NH) (3364ms, 3348ms cm^{-1}), δ(NH) (1558vs cm^{-1}), $\delta_{as,s}(CH_3)$ (1470vs, 1443ms, 1405s cm^{-1}), and ν_{as}(COC) (1203s, 1194s cm^{-1}) vibrations [4].

The electronic spectrum exhibits a broad ligand field band with a maximum at 2.04 μm^{-1} and an expressive shoulder at *c.* 1.79 μm^{-1}. The energies of the highest d ← d transitions are in agreement with a strong coplanar field produced by the CuN_4 chromophore [5]. Nevertheless, the occurrence of the low-energy shoulder indicates that the lowest d ← d transition is well separated in energy from the highest ones*, which makes it different from some other coplanar CuN_4 chromophores [5].

One is justified in supposing that in the reaction system used, $Cu\{N(CN)_2\}_2(py)_2$ is primarily formed, in which the $N(CN)_2^-$ anion is coordinated through its cyanide nitrogen to Cu^{II} [1]. The reorganized electron density makes favourable conditions for a nucleophilic attack of methanol to cyanide carbons which have some positive charge, and a hydrogen transfer connected with the formation of imine groups. The bonding abilities of the new anionic ligands allow the formation of six-membered metallocycles, while the pyridine ligands are removed from the coordination sphere. It should be noted that $Cu(BMCA)_2$ contains identical ligands as the analogous zinc complex, which has been prepared in other way by Rembarz *et al.* [2].

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*This problem will be solved at a later date.

References

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