

FIVE COORDINATION OF COPPER(II)*

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This communication describes the isolation of a possible five-coordinated copper(II) complex of 4-methylpyridine with copper(II) acetylacetonate.

Graddon (1959) gave spectrophotometric evidence for the formation of five-coordinated complexes of substituted pyridines with copper(II) acetylacetonate. However, Traill (1960) considers that Graddon's suggestion of the formation of a five-coordinated copper(II) complex is "not the only possible interpretation, nor the most probable one". This criticism by Traill is not in accord with recent findings.

Such findings suggest that the five-coordination of copper(II) is unusual but not unknown. Llewellyn and Waters (1960) have shown that the structure of *NN'*-disalicylidene-*propane-1,2*-diamine copper(II) monohydrate contains five-coordinated copper with a pyramidal configuration. The structure of another five-coordinated copper(II) compound, terpyridyl copper(II) chloride dihydrate, was reported by Corbridge and Cox (1956). They contend that there is no doubt that its structure is essentially the same as that of the zinc compound—a distorted trigonal bipyramid. Further, Hall and Waters (1960) have shown that in *NN'*-disalicylidene-ethylenediamine copper, each copper atom is five-coordinated with a pyramidal arrangement of ligands. The same five-coordination of copper has been shown by Frasson, Bardi, and Bezzi (1959) in the dimer of copper(II)bis(dimethylglyoxime).

Because of Graddon's claim the above preparation was attempted. The ligand chosen as the most likely to form a stable compound with copper(II) acetylacetonate was 4-methylpyridine. According to Sacconi, Lombardo, and Paoletti (1958) this ligand has a high electron density on the nitrogen atom.

Experimental

Copper(II) acetylacetonate was prepared by the method of Jones (1959). The light blue crystalline solid was recrystallized from chloroform (Found: Cu, 24.4%. Calc. for $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$: Cu, 24.3%).

Copper(II) acetylacetonate (1 g) was dissolved in B.D.H. 4-methylpyridine (about 15 ml) and refluxed for 30 min. On cooling the green solution, irregular hexagonal blue-green plates were obtained. These were dried between filter paper and transferred to a closed container. Washing even with cold dry benzene decomposed the complex. Analysis was carried out on single large crystals (Found: C, 53.9; H, 5.9; N, 3.9; Cu, 18.0%. Calc. for $\text{CuC}_{16}\text{H}_{21}\text{O}_4\text{N}$: C, 54.1; H, 6.0; N, 4.0; Cu, 17.9%). On standing in air it also slowly reverted to the pale blue colour of copper(II) acetylacetonate. Analysis was carried out on this residue, the carbon and hydrogen values being high due to the little 4-methylpyridine still present (Found: C, 47.3; H, 5.6; N, <0.5%. Calc. for $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$: C, 45.9; H, 5.4%).

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Note added in Proof.—Graddon and Watton (1960) discuss further evidence for the structure of 1 : 1 adducts of cupric β -diketone chelates with heterocyclic bases.

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