

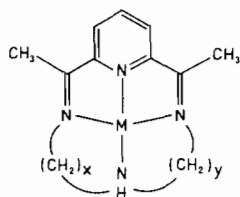
Macrocycle Formation. A CR Isomer Containing Five- and Seven-Membered Chelate Rings

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Recently we discussed¹ the preparation of complexes of ligands x,y-CR, following work by Busch² on the original CR macrocycle (x = y = 3 in the Figure).



Ring strain explained our inability to close the 2,3-CR macrocycle, a similar observation having been made earlier³ in the case of 2,2-CR, but well-defined compounds of 3,4-CR with Ni(II), Cu(II) and Zn(II) were prepared¹ together with some methyl-Co(III) complexes.⁴ We predicted¹ that 2,4-CR should be stable, but were unable to obtain the parent triamine for metal template⁵ reaction with 2,6-diacetylpyridine. The present availability of the compound (I.C.N. Pharmaceuticals) and the recent publication of its stability constants with Ni(II), Zn(II) and Cu(II),^{6,7} have led us to investigate the formation of the macrocycle.

Several attempts at preparing its Ni(II) and Zn(II) complexes by the usual method (A of ref. 1) were unsuccessful, only tarry, apparently polymeric products being obtained. However, at pH 8.2 in ethanol-water (70 °C, 8 hr) the Cu(II) complex formed readily and was isolated in good yield as its diperchlorate salt and dried *in vacuo*. Found: C, 34.9; H, 4.3; N, 10.9; Cu·C₁₅H₂₂N₄·2ClO₄ requires: C, 34.6; H, 4.3; N, 10.8%. The absence of a ν_{O-H} band around 3500 cm⁻¹ in the i.r. spectrum confirms the anhydrous character of the complex. This is in contrast to the Cu(II) complexes of CR and 3,4-CR.^{1,2} A single, sharp ν_{N-H} at 3240 cm⁻¹, the absence of ν_{C=O}, and two ν_{C=N} bands at 1615 and 1650 cm⁻¹ confirm the formation of the macro-

cycle. Two exocyclic C=N stretches are expected due to the grossly asymmetric structure of the ligand. The blue aqueous solution of the compound absorbs at 591 nm (ε = 1.6 × 10²), which compares well with the CR and 3,4-CR Cu(II) complexes.¹ The reflectance spectrum contains a broad peak at 610 nm. The room temperature magnetic moment of the solid is 1.84 B.M., indicating that the complex is magnetically dilute.

A small amount of a green compound was filtered from the original Cu(II) reaction mixture. Its analysis and i.r. spectrum indicate an oligomeric species wherein the triamine and diketone have reacted in a 1:2 mol ratio, the product binding Cu(II) and precipitating as the perchlorate salt. An apparently similar, yellow-brown, amorphous product of a 2:3 reaction was isolated from the Ni(II) condensation performed in dilute solution at 50 °C using an extended reaction time.⁸

In the ternary complex¹ of triamine, diacetylpyridine and metal ion the primary amino groups can form Schiff-base linkages both inter- and intramolecularly; the former producing the macrocycle, the latter oligomeric species. The equilibrium constants for protonation of the coordinated triamine indicate⁶ that only in the case of Cu(II) are all three nitrogen atoms bound to the metal. This is in keeping with the high stability constants found generally for Cu(II) with polyamine ligands,⁹ and explains our observation that the intra-molecular reaction is particularly favoured when Cu(II) is employed.

References

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