COPPER(II) COMPLEXES OF N-METHYLGLUCAMIDE
AND
PHOSPHOTHIOIC-N-METHYLGLUCAMIDE AMIDES

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SUMMARY

The N-acylhydrazine grouping, R.CO.NH.NH₂, as exemplified by N-benzyolhydrazine, N-acetylhydrazine and N-propionylhydrazine can coordinate in the keto form to copper(II), giving rise to bis-chelates of the type L₂CuX₂ (X = Cl⁻, NO₃⁻, CLO₄⁻, SO₄²⁻) containing five-membered rings. In addition to these compounds displaying effectively the normal coordination number of four for copper(II), N-benzyolhydrazine complexes of the type L₃CuX₂ and L₄CuX₂ were isolated and some information on the manner in which the ligands are coordinated was obtained from visible and infrared spectroscopy.

The isopropylidene derivatives of the above N-acylhydrazines are also able to form keto complexes. A proton can be removed from these ligands giving rise to neutral bis-complexes. It was found that in these complexes the coordination number of copper(II) could be expanded to five (or six) by the formation of monoaquo and mono- or bis-heterocyclic base adducts. Equilibrium constants for the addition of pyridine, 4-methylpyridine and 2-methylpyridine to bis-(N-isopropylidene-N'-benzoylhydrazino)copper(II) and bis-(N-isopropylidene-N'-propionylhydrazino)copper(II) in benzene solution were measured.
spectrophotometrically and indicated that the addition of one molecule of base is mainly responsible for large shifts in the visible region spectra.

The visible region spectra of the above classes of chelate were determined and used as a guide to the stereochemistry of the copper(II) complexes of the series of \( N,N \)-diaacyldihydrazine ligands, \((\text{CH}_2)_n(\text{CONH})_2\), from \( n = 0 \) to \( 10 \). As the value of \( n \) increases in such a series, the stereochemistry of the chelates formed would be expected to vary from a bis-bidentate polymeric structure through a tridentate to a quadridentate type structure.

Three series of chelates were examined.

1. **Complexes of \( N,N \)-diaacyldihydrazine ligands coordinated in the keto form.** The lower members of the series \( (n = 0,1) \) form complexes of the type \( \text{LOxX}_2 \cdot 0.5\text{H}_2\text{O} \) \((\text{X} = \text{Cl}^-, \text{SO}_4^{2-})\) from acid solution. Such complexes could have a polymeric structure, but the coordination of anions or water molecules would appear likely, producing monomers. Preparations from neutral solution resulted in the spontaneous liberation of hydrogen ions, producing precipitates of somewhat variable composition but approximating to the formulation \( \text{L}_2\text{CuX}_2 \cdot 2\text{H}_2\text{O} \). When \( n = 2 \) to \( 6 \), \( \text{LOxX}_2 \cdot 0.5(\text{or} 1)\text{H}_2\text{O} \) complexes were produced and from \( n = 7 \) to \( 10 \), anhydrous complexes were obtained. For the higher members of the series \( \text{L}_2\text{CuX}_2 \cdot 2\text{H}_2\text{O} \), type complexes are apparently more stable.
(II)

(2) Complexes of N,N'-diisopropylidene-N'-W'-
diacidhydrazine ligands coordinated in the keto form.

When \( n = 0 \), the complex \( LCu_2Cl_2 \cdot 0.5H_2O \) was formed. The remaining members \( n = 1 \) to 10 formed \( LCu_2 \cdot 0.5(\text{or } 1)H_2O \) type complexes. Coordination of halide in the fifth or sixth position of copper(II) is a feature of this class of complexes and gives rise to a band at approximately 25,000 cm\(^{-1}\), which is absent in the perchlorate complexes. A spectrophotometric study of the \( n = 4 \) complex indicated that in pure water, acetone is hydrolysed from the molecule, while in nearly pure acetone the coordination of chloride ion has a large perturbing effect on the spectrum.

(3) Complexes of N,N'-diisopropylidene-N'-W'-
diacidhydrazine ligands coordinated in the enol form.

When \( n = 0 \), a polymeric complex \( LCu \) was obtained. From \( n = 2 \) to 4, \( LCu \cdot H_2O \) complexes were formed. The similarity of the visible spectra of the \( n = 3 \) and 4 complexes to the anhydrous N-isopropylidene-N'-acyl-
diacidhydrazine complexes indicated that water was not coordinated in the apical positions of the copper(II) ion. When \( n = 5 \) or 6, both anhydrous complexes and monohydrates containing apically coordinated water were obtained. A structure in which the ligands are bia-bidentate, forming dimers, would appear to be in best agreement with the spectra of this series of complexes. For the \( n = 4 \) complex, the
formation of a monopyridinate showing the spectral effects of apically coordinated pyridine would preclude the possibility of a tridentate configuration. Further information on this problem was obtained by examination of the spectra of some complexes of tridentate ligands containing pyridine in the fourth coordination position.

In discussing the effects of solvents on the visible spectrum of bis-(acetylacetonate)copper(II), it was suggested that the changes may best be accounted for by resolution of the spectra into only two Gaussian components. Such a procedure would indicate \(d_{2}\) to have the highest energy (for positive hole transitions) in a square planar configuration, and to be most affected by apical coordination of solvent molecules.