A Novel Condensation Reaction Between Some Ketones and Benzil Monohydrazone in the Presence of Nickel(II) Ions

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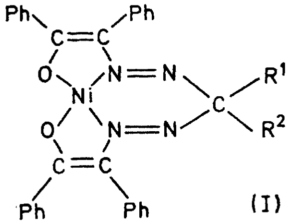
Summary The reaction between some ketones and benzil monohydrazone in the presence of nickel(II) ions has been shown to result in the formation of complexes containing a tetradentate ligand in which two benzil monohydrazone residues are linked by a single carbon atom from the ketone.

THERE has recently been considerable interest in the reactions of metal–amine complexes with carbonyl compounds.[1] Two types of reactions have been observed. In one of these, an amine group is converted into a Schiff base by condensation with the carbonyl compound, whereas the characteristic feature of the second type of reaction is the linking of amine groups by a three-carbon bridge arising from the condensation of two carbonyl compounds.



(I)

We report here the isolation of a series of nickel(II) complexes, (I), containing a tetradentate ligand in which the carbon atom from the carbonyl group of the ketone forms the sole bridge between the terminal nitrogen atoms of two benzil monohydrazone residues.

The complexes are obtained in yields up to 78% as red crystalline products on heating, in ethanol under reflux for several days, a mixture of nickel acetate, benzil monohydrazone, and a large excess of the ketone, R^1R^2CO (R^1 = Me, R^2 = Me, Et, Pr^n, Bu^n, or Ph; R^1 = Et, R^2 = Et).

The nature of the ligands has been established by i.r., ^1H n.m.r., and mass spectra. The i.r. spectra of the complexes indicate the absence of any NH_2 groups, there being no absorption between 3200—3400 cm^{-1} and only one sharp band at 1600 cm^{-1} probably associated with the phenyl group or a C=C bond of the ligand. Benzil monohydrazone itself has three strong absorption bands between 3200—3400 cm^{-1} and a medium broad band at 1620 cm^{-1}, all characteristic of the NH_2 group.

The ^1H n.m.r. spectra at 100 MHz of the complexes in CCl_4 consist of absorptions in two regions, one characteristic of the aliphatic groups centred around the absorption from methyl groups at 1·65 p.p.m. downfield from Me_4Si, the other from the hydrogens of the phenyl groups centred at −7·2 p.p.m. from Me_4Si.

The m.s. analyses of the complexes are also consistent with the suggested structure. The highest mass peaks correspond to the singly-charged parent with the expected isotopic distribution. The next highest peaks correspond to $(M - 28\text{ a.m.u.})^+$ and $(M - 56\text{ a.m.u.})^+$, suggesting fragmentation takes place by consecutive elimination of nitrogen molecules. All the complexes behaved similarly.

The di-negative ligands are co-ordinated such that the stereochemistry about the nickel(II) ion is square planar. All the complexes are diamagnetic and in benzene solution have similar spectra with absorptions at 29,100 cm^{-1} (ϵ 1·5 × 10^4), 25,600 (1·7 × 10^4), 21800sh (8·8 × 10^3), and 20,200sh (7·6 × 10^3).

In order that the single carbon atom of the ketone residue may form a bridge between the benzil monohydrazone molecules in the complex, we suggest that co-ordination to the nickel ion is through the nitrogen atoms not involved in the bridge. This results in the formation of a six-membered chelate ring: models show very little strain present in the overall structure.

The reactions whereby these complexes are produced may be described as template reactions,[2] the influence of the nickel ions being important in bringing the reactants together to form the ligands, since in the absence of the nickel ions these ligands are not obtained.

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[1] N. F. Curtis, *Coordination Chem. Rev.*, 1968, **3**, 3.

[2] D. H. Busch, *Helv. Chim. Acta*, Special Issue, 1967, 174.