THE CONVERSION OF BENZOYLHYDRAZINE TO 1,2-DIBENZOYLHYDRAZINE CATALYSED BY NICKEL(II) OR COPPER(II) ACETATE

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Summary

When excess benzoylhydrazine is added to nickel(II) acetate in butanol at room temperature, 1,2-dibenzoylhydrazine is produced. The same product is formed when copper(II) acetate is used, but not when either metal is present as its chloride salt.

Benzoylhydrazine complexes of a range of metals are known. The named ligand co-ordinates in a bidentate fashion, through the oxygen atom and the terminal nitrogen atom. It may behave as a neutral ligand^{1,2}, or as an anionic ligand by losing one or more protons^{1,2,3}. 1,2-dibenzoylhydrazine forms a similar range of complexes^{4,5}. In one case, it is reported³ that one of these organic molecules can be converted to a complexed form of the other. Specifically, 1,2-dibenzoylhydrazine reacts with $[\text{ReOCl}_3(\text{PPh}_3)_2]$ in ethanol in the presence of acid to yield ethylbenzoate and $[\text{Re}(N_2\text{COPh})\text{Cl}_2(\text{PPh}_3)_2]$, a complex of benzoylhydrazine (3-). Here we report a reaction which produces interconversion in the opposite sense. This method of forming 1,2-dibenzoyl-hydrazine has been briefly mentioned elsewhere¹.

Complexes of benzoylhydrazine are usually prepared^{2,3} by refluxing together the appropriate metal salt and the ligand in ethanol, with the reagents present in the molar ratio of 1:2. The complexes produced contain metal and ligand in the same ratio. We find that butanol solutions containing benzoylhydrazine (0.5 M) and metal(II) chloride (0.07 M) yield, on standing at room temperature, precipitates of tris-complexes, $\left[ML_3\right]Cl_2$; where L represents benzoylhydrazine and M = Fe, Co, Ni or Zn. Precipitates do not form when M = Mn or Cu. These complexes are well characterised by spectroscopic, magnetic and analytical data. When analogous experiments are attempted using nickel(II) or copper(II) acetates, the products are markedly different. This difference is well illustrated in the case of the nickel salts. When benzoylhydrazine is added to a butanol solution of either nickel salt, the solution quickly takes a blue colouration. However the acetate solution slowly undergoes a further colour change, becoming brown. On standing

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overnight the chloride solution yields a fine, sky blue precipitate of the tris-benzoylhydrazine complex; whereas white needle like crystals separate out from the acetate solution. These white crystals which, in mass, represent most of the benzoylhydrazine originally added, have been identified by analysis, melting point, mass spectrometric and infrared spectroscopic studies as 1,2-dibenzoylhydrazine. When the butanol is removed from the filtrate under reduced pressure, a brown oil is obtained which can be crystallized only with difficulty. This material contains at least two components. Part of the brown product dissolves rapidly in ethanol, leaving behind a small quantity of a red solid. The ethanol soluble solid has not been completely characterised; but available data, including analysis, suggest that it is the polymeric complex of nickel(II) and 1,2-dibenzoylhydrazine(1-), [Ni (PhCONNHCOPh)]n.

Benzoylhydrazine is also converted to 1,2-dibenzoylhydrazine by copper(II) acetate under the same conditions, although the conversion is slower. Cobalt (II) acetate does not appear to effect the conversion, but merely forms a complex of benzoylhydrazine.

We believe that this reaction occurs as the result of the nucleophilic attack of a free benzoylhydrazine molecule on the carbonyl carbon atom of a co-ordinated molecule of the same compound. Such a process should be enhanced by co-ordination to a positively changed metal ion. We have, as yet, no firm opinion on the difference in behaviour of the chloride and acetate salts. However we note that the related aroylhydrazine ligands, (RCH \approx N.NH.CO.Ar), give octahedral complexes with nickel(II) chloride, but give square planar complexes with nickel(II) and copper(II) acetate⁶. The mechanism suggested by us differs from that advanced by Alcock, Baker and Diamantis¹. These authors found that the dibenzoyl product was produced by heating benzoylhydrazine with cupric chloride in water or ethanol. This reaction was accompanied by reduction of copper(II) to copper(I). We consider it to be unlikely that an analogous reduction of nickel(II) could take place; and so favour a scheme involving nucleophilic attack or coordinated ligand, rather than a process involving an oxidation-reduction reaction between metal and ligand. Further studies are being undertaken to extend and elucidate the observations reported herein.

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