Inorganica Chimica Acta, 20 (1976) L45 - L46

The Polychromism, Strictly-ordered Preparation and Monomer–Dimer Equilibrium in Copper(II) Complexes with Glycine Ethyl Ester

P. R. NORMAN and D. A. PHIPPS

Department of Chemistry, Liverpool Polytechnic, Byrom Street, Liverpool L3 3AF, U.K.

Received September 14, 1976

The study of copper complexes with α-amino acid esters as ligands has for the most part been restricted to an examination of their reactions in solution, whilst the preparation and characterisation of solid complexes has been described only briefly [1, 2]. Therefore, as part of our programme aimed at examining the changes in ligand reactivity caused by coordination, we undertook to prepare a series of these complexes. However, from our results it has become apparent that earlier reports were incomplete and required re-examination.

It has been reported [1] that the reaction of glycine ethyl ester with anhydrous copper(II) chloride, in 2:1 mol ratio, produced a green solution from which a blue solid, formulated as $[Cu^{II}(NH_2CH_2COO\ CH_2CH_3)_2]Cl_2$, could be isolated. Our initial attempts to repeat this preparation produced a series of confusing results in which a variety of bright blue, blue–green and deep green products were obtained, all having the required elemental composition and all having very similar I.R. spectra. However, despite these similarities the various products proved not to be identical and were clearly distinguished by their magnetic moments; 1.73 B.M. for the blue product typical of monomeric copper(II) species, but only 1.53 B.M. for the green product, which was taken to indicate a copper–copper interaction. The values for the blue–green products fell in between these extremes.

On closer examination it then rapidly became apparent that only two distinct products (the bright blue and deep green forms) existed, but that the relative proportions of each formed in any reaction, and hence the exact nature of the blue–green products, were greatly influenced by the experimental conditions. Thus, using ethanolic solutions of anhydrous copper(II) chloride and the ligand, the product depended not only on the reaction temperature, but also quite surprisingly, and distinctly, on the order of mixing the reactants.

At room temperature, adding the copper salt to the ligand (thereby keeping the ligand in excess) gave not a green, but rather a deep blue solution, from which a bright blue solid, identical with the complex described by earlier workers [1], was isolated. However, when the reaction was carried out at a higher temperature, the first-formed blue solution rapidly turned green, and various blue–green or even a deep green solid could then be isolated, depending on the experimental conditions. It was noted that the relative proportion of the blue form diminished as the temperature of the reaction was increased. Most remarkably, however, it was observed that by reversing the order of mixing (*i.e.* adding ligand to copper and thus keeping the copper in excess) the deep green solution was formed directly, even at room temperature, and from this solution could be isolated a deep green solid, having both the same analytical composition as the blue form and also a largely identical I.R. spectrum, but having the subnormal magnetic moment recorded earlier.

The obvious possibility of a monomer–dimer equilibrium, as suggested by these results, and particularly by the magnetic moments of the two forms, was therefore investigated further. Determinations of the relative molecular mass were made both in solution, by an isopiestic method, and also on the solid samples by mass spectrometry: Using chloroform as the solvent, the relative molecular mass of the blue form was found to be 336 (340.5 calculated for $[Cu^{II}(NH_2CH_2COO\ CH_2CH_3)_2]Cl_2$) and 590 for the green (681 calculated for the dimer). Using pyridine as the solvent, values of 236 and 650 respectively were obtained. Whilst measured and calculated values did not agree exactly, they did provide considerable encouragement for the idea of the existance of distinct monomeric and dimeric forms. Certainly, this interpretation is further supported by a later experiment in which a sample of the blue form was refluxed in ethanol, whereupon the apparent relative molecular mass of the green residue was found to be 590.

The mass spectra of the two forms provided further evidence of their nature as monomer and dimer. The blue form showed clearly a series molecular ions, with intensities corresponding to the expected isotopic abundance pattern for copper and chlorine. The green species had a spectrum which differed substantially from that of the blue; the peaks representing the molecular ions for the monomer were absent, whilst new peaks at $M/e > 600$ appeared. Although no molecular ion was apparent, a number of intense metastable peaks were present, also indicating parent ions with M/e greater than 600.

The conversion of the blue monomer to the green dimer was also found to occur on heating the solid complex. The green form melted at 78–82 °C (uncorrected) and then rapidly decomposed, whilst the blue form melted at 102 °C. Careful observation showed that immediately on melting the blue complex was converted to the green form, which then very rapidly decomposed. These events were also evident in the differential thermal analysis of the two forms, in which the green showed a simple endothermic peak at the melting point, whilst the blue showed a very sharp exothermic peak superimposed on the endothermic melting point peak at 102 °C.

The reverse reaction, the conversion of the green to the blue form could also be quite easily brought about, though only in solution, either by adding a small excess of free ligand, or by dissolving the green solid in a solvent more polar than ethanol (*i.e.* CH_3OH, DMSO *etc.*).

Whilst the tendency of copper complexes to exist in forms in which strong copper–copper interactions are possible, *i.e.* as dimers or oligomers, is well known, the existance of such distinct monomeric and dimeric species, their strictly ordered preparation and their facile interconversion are all distincly unusual. However, as a considerable number of apparently reasonable structures may be proposed for the two forms discussion of their exact structure remains fruitless without definitive (*i.e.* X-ray) evidence.

Acknowledgements

We wish to thank the S.R.C. for the award of a research grant in support of this work. We thank Dr. J. Fenerty for providing data on the differential thermal analysis of the complexes.

References

1 M. P. Springer and C. Curran, *Inorg. Chem., 2,* 1270 (1963).
2 R. W. Hay and L. J. Parker, *Aust. J. Chem., 20,* 675 (1967).