# Formation of Dichlorobisaniline–Metal Complexes from *N*-Sulphinylaniline

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THE rate constant for the very slow reaction between *N*-sulphinylaniline and ethanol was determined by Janelli and Senatore[1] as $3 \cdot 6 \times 10^{-5}$ sec.$^{-1}$ at 25°. The overall equation for the reaction is:

$$PhNSO + 2EtOH \rightleftharpoons PhNH_2 + (EtO)_2SO$$
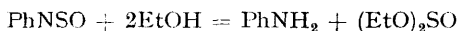
They discovered that it was base-catalysed by triethylamine.

We have found that a slight excess of *N*-sulphinylaniline in ethanolic solutions of the anhydrous metal(II) chloride of Zn, Cu, Ni, Co, and Mn resulted in the precipitation of the corresponding bisaniline complex $(PhNH_2)_2MCl_2$, M being the metal. Diethyl sulphite was isolated in at least 70% yield in each case. The complexes[2] and diethyl sulphite[3] were identified by their infrared spectra and carbon–hydrogen analyses.

$(PhNH_2)_2CuCl_2$, in 90% yield, was precipitated from a solution of $1 \cdot 8$ g. of anhydrous $CuCl_2$ in 25 ml. dry ethanol after 10 minutes. Similar yields were obtained with $NiCl_2$ (0·8 g. in 50 ml. ethanol), and $CoCl_2$ (0·8 g. in 7 ml. ethanol) after 30 and 60 min., respectively. $ZnCl_2$ (1·8 g. in 20 ml. ethanol) and $MnCl_2$ (0·6 g. in 25 ml. ethanol) gave 67% and 10% yields respectively, after 60 min. The above yields were obtained at room temperature. Heating increased the reaction rate. All manipulations, save for the isolation of diethyl sulphite were carried out in a dry, inert atmosphere. Before usage, ethanol was deoxygenated.

These results suggest that the above metal(II) chlorides catalyse the reaction between *N*-sulphinylaniline and ethanol. Preliminary kinetic studies have confirmed this view and a thorough kinetic investigation of the reaction mechanism is now in progress.

[1] L. Jannelli and L. Senatore, *Ann. Chim. (Italy)*, 1965, **55**, 988.
[2] A. J. Jungbauer and C. Curran, *Spectrochim. Acta*, 1965, **21**, 641.
[3] A. Simon, H. Kriegsmann, and H. Butz, *Chem. Ber.*, 1956, **89**, 2390.