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CHEMISTRY DEPARTMENT, UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA

Pressure in Coordination Chemistry. I. Nickel(II) Salicylaldimines and Aminotroponeimineates

By A. H. EWALD AND E. SINN

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The anomalous magnetic and spectroscopic behavior of a number of N-substituted Ni(II) salicylaldimine and aminotroponeimine complexes in solution has been examined over a range of pressures. The susceptibility of the aminotroponeimineates is found to decrease with pressure, indicating that the planar, diamagnetic form of the complex has a smaller volume in solution than the tetrahedral form. The susceptibility of the salicylaldimine complexes, on the other hand, is found to increase with pressure indicating that the associated complexes are formed with a decrease in volume. For *n*-alkyl but not *sec*-alkyl salicylaldimines the contribution of a planar-tetrahedral equilibrium to the pressure dependence is negligible.

Introduction

In recent years many coordination compounds have been shown to deviate, in the solid state and in solu-

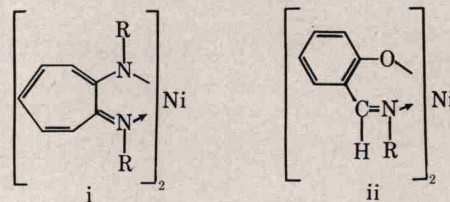
tion, from the Curie and Curie-Weiss laws for magnetic susceptibility. The mechanisms giving rise to these deviations may be divided into four main types.

One type occurs when the electron-pairing energy of a complex lies between the ligand field strengths of possible high-spin and low-spin forms and results in a high-spin $\rightleftharpoons$ low-spin equilibrium which has been observed in a number of different systems.¹⁻⁴ A second type arises from the antiferromagnetic interaction between the unpaired electrons of two or more metal atoms in a complex.^{5,6} The last two mechanisms depend on the changes in ligand field energy when the conformation about the central atom changes, either by association of monomeric complex molecules or by reorientation of the ligands in a planar $\rightleftharpoons$ tetrahedral conformational equilibrium. In the present paper we shall be concerned mainly with the effect of pressure on these last two mechanisms. Similar studies will be reported on the crossover and antiferromagnetic equilibria.^{2,7}

In several series of complexes⁸⁻¹¹ deviations from normal diamagnetic or paramagnetic behavior have been found to be the result of the coordination of the metal atom of one complex with donor atoms of other molecules in such a way that the metal atom achieves pseudo-octahedral coordination. Such association occurs, for example, in solutions of *N*-alkyl-substituted salicylaldehyde^{8,9} and β -diketone complexes of Ni(II). In some related compounds, such as the *N*-*sec*-alkyl-salicylaldehydes,¹²⁻¹⁴ a tetrahedral (paramagnetic) $\rightleftharpoons$ planar (diamagnetic) conformational equilibrium plays a major part in addition to the associative equilibrium. Where these two equilibria coexist, their pressure dependence and temperature dependence are opposite; a rise in temperature favors the planar, monomeric species compared with the associated species and also favors the tetrahedral species over the planar. (This is not necessarily true in all cases; *e.g.*, in the *t*-butyl complex the planar form is the higher energy form.¹²⁻¹⁴) Increasing pressure has, broadly speaking, the same effect as decreasing temperature. As a result their relative contributions can sometimes be sorted out, particularly with the assistance of other results, such as nmr contact shifts.

It cannot be predicted *a priori* whether the associative or the conformational equilibrium will be more important under various conditions of temperature and pressure, since the effect of pressure depends entirely on the relative volumes of the species which coexist in solution. However the contributions of the

two equilibria can be separated by analogy arguments if one examines related systems for which it is known that only one of the equilibria plays a part.



Some Ni(II) aminotroponeimineates (i) form solutions with anomalous magnetic properties which have been shown¹⁵ to result entirely from planar $\rightleftharpoons$ tetrahedral equilibria. Pressure measurements on such solutions have shown (Figure 1) a decrease in susceptibility with increasing pressure; this indicates that the equilibrium is shifted toward the planar, diamagnetic form. Solutions of nickel(II) *N*-*n*-alkylsalicylaldehyde (ii), on the other hand, show paramagnetism at atmospheric pressure which increases with increasing pressure. If the initial paramagnetism is due in part to the presence of some tetrahedral molecules, their concentration, by analogy with the aminotroponeimineates, will be reduced by an increase in pressure. Thus the *n*-alkyl salicylaldehydes form a group in which only the associative equilibrium has any significant effect on the magnetic properties. Because of the important bearing of the measurements on the aminotroponeimineates on the interpretation of the studies made on salicylaldehydes, the results for the two groups are presented together.

Pyridine Adducts.—Solutions of many planar Ni(II) complexes can become paramagnetic by forming adducts with strongly coordinating solvents such as pyridine. Probably all four-coordinated salicylaldehydes combine with pyridine to some extent; most form stable bispyridine adducts^{16,17} but some, such as the parent bis(salicylaldehyde)nickel(II),¹⁷ bis(*o*-phenylenediiminosalicylaldehyde)nickel(II), and bis(3,4-diminotoluenesalicylaldehyde)nickel(II), are not fully paramagnetic even in pyridine solution. This results from an equilibrium between the planar complexes and their octahedral pyridine adducts. The effects of temperature and pressure on this equilibrium are qualitatively the same as those on the associative equilibrium discussed above.

Experimental Section

A Gouy method was used for the magnetic measurements (*cf.* ref 1). A beryllium-copper (Berylco 25) sample tube, with a moving piston carrying a Bridgman seal, was used to contain the compressed samples in solution or suspension. Water,¹⁸ benzene,¹⁸ nickel chloride solution,¹⁸ and cesium tetrachlorocobaltate solution¹⁹ were used for the magnetic calibrations. Pressures inside the tube were calibrated as in ref 1 by observing the known phase transitions of carbon tetrachloride, benzene, and bromo-

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