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Reactions of Coordinated Complexes I. The Reaction of Bis(acetylacetonato)Nickel(II) with Carbon Disulfide[1]

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The reaction of bis(acetylacetonato)nickel(II), ($Ni(AcAc)_2)_3$, with carbon disulfide, followed by extraction with anhydrous ether yields a reddish brown solid, found on analysis to have the same composition as ($Ni(AcAc)_2)_3$. The $Ni(AcAc)_2$ species is confirmed by infrared spectra. In addition, the mass spectra are identical, each containing a peak at m/e 256 corresponding to $Ni(AcAc)_2$ monomer. Number averaged molecular weight determinations yield a value corresponding to four $Ni(AcAc)_2$ units per molecule. The presence of square planar nickel species is shown by magnetic susceptibility measurements. The UV–visible spectrum of the product is typical of those containing square planar nickel. The spectrum in the near-IR confirms the presence of octahedral nickel. The ratio of square planar to octahedral species is shown to be one to three. On the basis of the experimental observations, a structure of the product is proposed.

Introduction

The stereochemistry of nickel(II) complexes encompasses various structural types, the most common being octahedral, tetrahedral, and square planar. Although the majority of these compounds are characteristic of one of these simple types, many compounds exhibit so called anomalous behavior which can best be described as having characteristics of two or more of the above simple types. The behavior of these complexes is, in many cases, dependent on the concentration, solvent, and temperature conditions. For example, in some nickel(II) salicylaldimine complexes, the solid form is diamagnetic whereas in donor solvents, partial or complete paramagnetism is observed.[2] It has been shown that this behavior is due to an equilibrium between the planar monomeric species and an associated form containing paramagnetic nickel species.[3] Similar configurational equilibria between planar species and tetrahedral forms have been demonstrated in bis-bidentate complexes with bulky substituted groups.[4,5,6]

There are some examples where one molecule contains nickel(II) ions in two different stereochemical configurations at the same time. One form of bis(meso-stilbenediamine)nickel(II) dichloracetate is known to contain both planar diamagnetic species and octahedral paramagnetic nickel in a one to two ratio.[7]

Certain four coordinate monomeric complexes tend to polymerize under specific conditions to give six coordinate species. Such a complex is bis(acetylacetonato)nickel(II), ($Ni(AcAc)_2)_3$, which is trimeric in the solid state and in noncoordinating solvents up to 200° C. It is cleaved to six coordinate tetragonal monomers by donor solvents such as water or pyridine.[8] In these solvents the acetylacetonate ligands are in a planar configuration about the nickel ion and the donor molecules are *trans* to each other.

In the present work, a configurational isomer of ($Ni(AcAc)_2)_3$ is prepared by the reaction of the trimer with carbon disulfide. The product is a tetramer in the solid state and in noncoordinating solvents. It contains both octahedral paramagnetic nickel species and square planar diamagnetic species. Further, it is found that there is only one square planar nickel in the molecule and three octahedral species. There also appears to be an equilibrium in solution between the square planar species and a tetrahedral form.

Experimental

Bis(acetylacetonato)nickel(II), ($Ni(AcAc)_2)_3$, is prepared by the reaction of nickel chloride hexahydrate with acetylacetone.[9] It is dried over phosphorus pentoxide *in vacuo* at 78° C for twenty four hours. Reagent grade carbon disulfide and anhydrous ether were used without further purification.

Twenty grams of anhydrous ($Ni(AcAc)_2)_3$ were added to 200 ml carbon disulfide, stoppered and left for two weeks. During this time, the mixture changed from pale green to red–brown and a precipitate formed. The solvent was flash evaporated and the residue was extracted with anhydrous ether. Flash evaporation of the ether yielded a brick red powder.

Since the product tended to pick up water upon standing, it was dried over phosphorus pentoxide *in vacuo* at 78° overnight. All experimental determinations with the exception of the elemental analysis were performed on the anhydrous form. (If allowed to stand uncovered in air for several hours, calculations show that the product picks up two molecules of water per molecule of product. Because of this problem, and because samples were sent out for elemental analysis, it was felt that more accurate results would be obtained by doing the elemental analysis on the hydrated form. Anal. Calcd. for $Ni(C_5H_8O_2)_2 \cdot 2H_2O$: Ni, 20.04; C, 41.00; H, 6.19; Found: Ni, 20.13; C, 40.69; H, 5.95.

Measurements of the molecular weight of the compound were determined on a Perkin–Elmer Model 115 Osmometer using benzene as the solvent.

Infrared spectra were obtained as KBr pellets on a Perkin–Elmer Model 457. Magnetic susceptibility measurements were obtained on both $(Ni(AcAc)_2)_3$ and the product in the solid state[10] and in solution. The solution state measurements were obtained in benzene and carbon tetrachloride using the method of Evans.[11] The instrument used was an Hitachi–Perkin–Elmer 60 MHz NMR. Tetramethylsilane was used as the reference in all measurements.

Ultraviolet and visible spectra were taken on a Beckman Acta III Spectrophotometer. Measurements were done in carbon tetrachloride solutions.

Near-IR measurements were obtained on a Perkin–Elmer Model 350 Spectrophotometer.

Mass spectral data was obtained on the solid using an Hitachi–Perkin–Elmer Model 270 Mass Spectrometer.

Discussion

A value of 1030 was obtained for the molecular weight of the product. This corresponds to a molecular formula of $(Ni(AcAc)_2)_4$ which has a molecular weight of 1024. By itself, this piece of data is not enough to establish a tetramer as the structure of the compound because a mixture of several oligomers might easily lead to the same result by this number averaged method. Further, the work of San Filippo *et al.*[12] showed the determinations taken on a weight averaged basis can yield vastly different results. They pointed out that a number averaged determination of $(Ni(AcAc)_2)_3$ yielded a value equivalent to the trimer, but a weight averaged method gave a value of 2220. They point out that this indicates that the average configuration in solution is the trimer but there may actually be a broad distribution of oligomers. This same situation has also been suggested for $Co(AcAc)_2$.[13] Whether or not there is actually *only* tetramers present or a distribution of oligomers is not known and the experimental data that have been obtained cannot distinguish between the possibilities. Thin layer chromatography showed the presence of only one compound but this does not rule out the possibility of oligomerization.

The infrared spectroscopic data shows that the same organic species are present in both the product and in $(Ni(AcAc)_2)_3$. The mass spectra were also identical both of which had peaks at m/e 256 as the species of highest molecular weight. This corresponds to Ni $(AcAc)_2$ monomer, which is to be expected in polymeric species such as are present here.

The UV–visible spectrum of the product is typical of those of square planar complexes having one medium intensity ($\approx 10^3$) transition around 490 nm giving the complex its characteristic red–brown color. The molar absortivity is typical of many square planar complexes particularly those containing organic ligands.[14]

The near-IR of $(Ni(AcAc)_2)_3$ contains a low broad peak centered at about 1.10μ. A spectrum run on the tetramer also showed a peak in this area centered at 1.13μ. Since the trimer contains only octahedral nickel, this peak confirms the presence of octahedral nickel in the tetramer (see Figure 1).

As was stated previously, the molecular weight determinations yielded an average value equivalent to a tetrameric species of $Ni(AcAc)_2$. Further the UV–visible spectrum shows the presence of square planar nickel. Magnetic moment determinations were done to further substantiate these observations. The solid state magnetic moment of $(Ni(AcAc)_2)_3$ was found to be 3.26 and that of the product, 2.85. The smaller moment of the product is explaned by the presence of square planar nickel which is diamagnetic. A quantitative prediction can be made of the relative magnitudes of the two moments. Since the magnetic susceptibility of a compound is a function of its molecular weight, the magnetic moment is a function of the square root of the molecular weight, because $\mu = 2.83 \sqrt{\chi^{\text{corr}}\, T}$. If it is assumed that there is one square planar nickel species present in the molecule, then the magnetic moment of $(Ni(AcAc)_2)_3$ should equal $\sqrt{4/3}$ times the magnetic moment of the product, since the product has four $Ni(AcAc)_2$ units per molecule of which three are paramagnetic. If the measured magnetic moment of the product, 2.85, is multiplied by $\sqrt{4/3}$, the result, 3.29, is in good agreement with the measured value of the magnetic moment of $(Ni(AcAc)_2)_3$, 3.26.

Thus there is corroborative evidence suggesting the existence of both square planar nickel and octahedral nickel in the complex in a ratio of 1:3.

Table I gives the values obtained for the magnetic moment, of the product and of $(Ni(AcAc)_2)_3$ in benzene and in carbon tetracholoride solutions.

There are several important features of the above data. First, the magnetic moment of $(Ni(AcAc)_2)_3$ agrees very well with the solid state moment (3.26). Although the moments of the product are in all cases

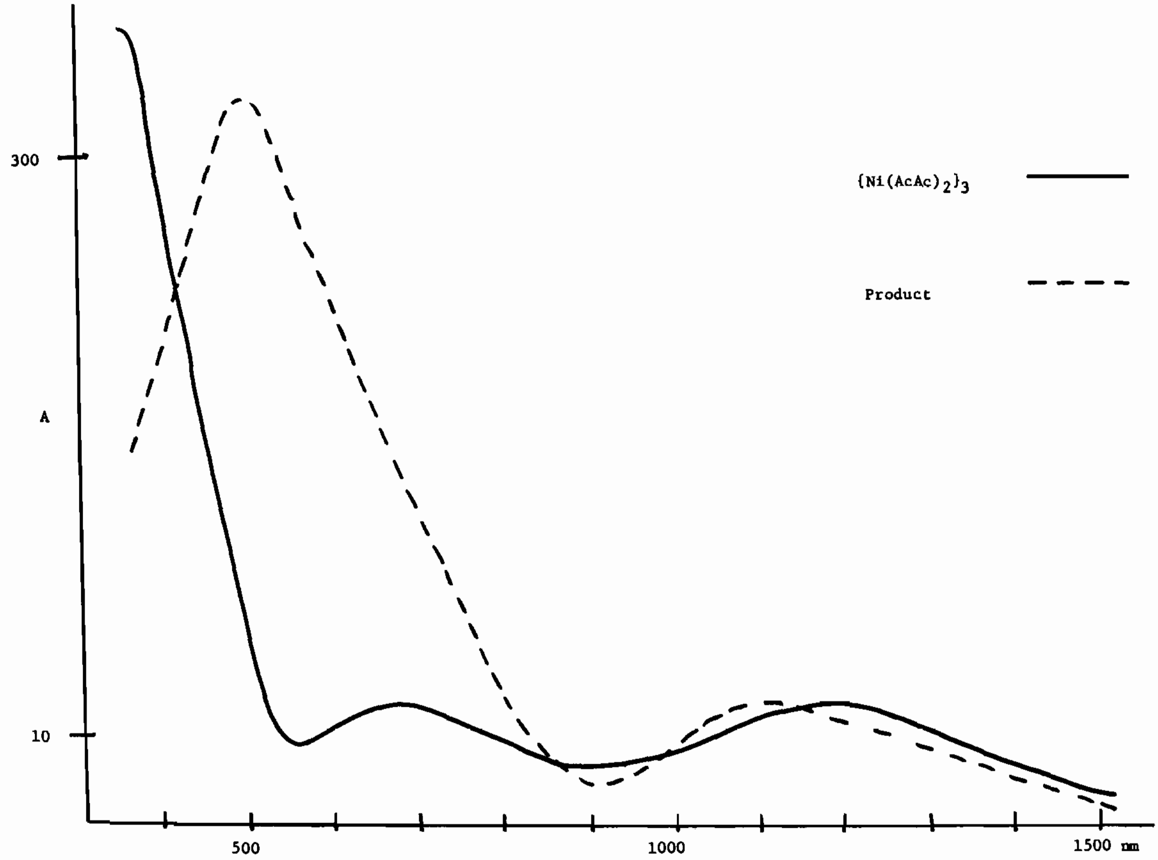

Figure 1. Ultraviolet and near-IR absorption spectra of $(Ni(AcAc)_2)_3$ and product. The relative absorbances of the two compounds are not to scale with respect to each other. The spectra were obtained in carbon tetrachloride. The concentration of each was 25 g/liter.

TABLE I. Solution State Magnetic Moments of the Product and $(Ni(AcAc)_2)_3$ at 34° C.

	CCl_4	C_6H_6
Product	3.08	3.03
$(Ni(AcAc)_2)_3$	3.16	3.20
$(Ni(AcAc)_2)_3$ [15]	3.12	3.24

less than those of the trimer, they are too high to be explained by the tetrameric configuration containing one square planar nickel species. This behavior can be explained by postulating a configurational equilibrium in solution between the square planar species and a tetrahedral species which can be achieved by a flexion about the inter-nickel axis. The tetrameric nickel(II) ion thus formed has a paramagnetic moment equivalent to two unpaired electrons. Thus the magnetic moment would be higher in such a case than it would be if only the square planar species were present as in the solid state. Further, a study of the temperature dependence of the magnetic moment in the range 34–154° C showed no fit to the Curie–Weiss Law, a fact suggested by the presence of configurational equilibrium such as is present here. Table II is a compilation of the temperatures vs. magnetic moment over this range.

TABLE II. Temperature vs. Magnetic Moment of the Product.

Temperature (° C)	(Magnetic Moment)
34	2.90
44	2.86
54	2.77
64	2.79
74	2.81
84	2.80
94	2.78
104	2.56
114	2.57
124	2.60
134	2.61
144	2.64
154	2.59

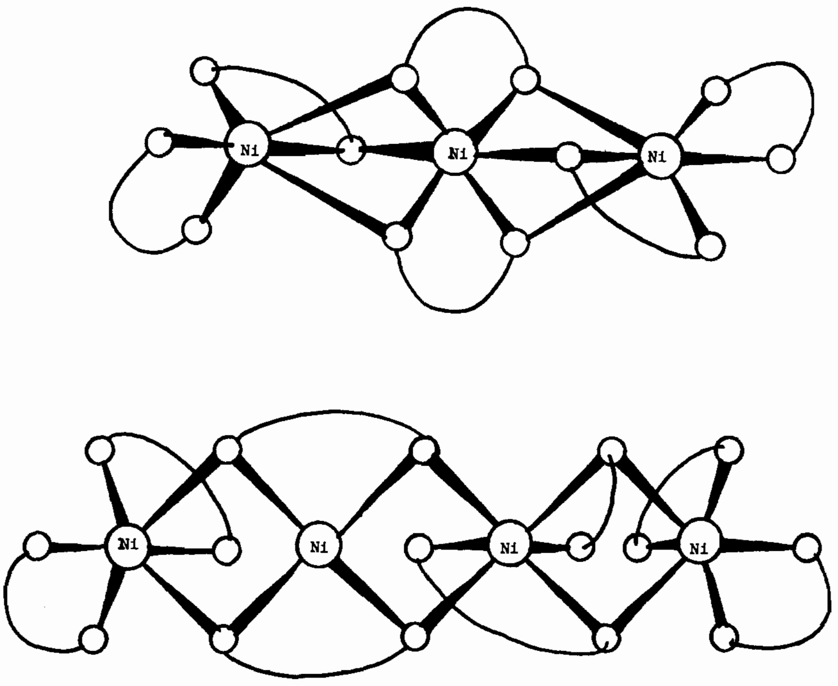

Figure 2. Structure of $(Ni(AcAc)_2)_3$ and proposed structure for product $(Ni(AcAc)_2)_4$.

On the basis of the experimental evidence presented here it is possible to propose a structure for this product (Figure 2). It is a new configurational isomer of $(Ni(AcAc)_2)_3$ that is tetrameric and contains one square planar nickel species. The other three $Ni(AcAc)_2$ units are essentially octahedral owing to the presence of bridging oxygens like those present in the trimer. The square planar nickel species must be in the interior of the molecule (it cannot be terminal) and contains two vacant bonding positions *trans* to each other. These provide sites for the molecule to pick up or give up two molecules of water.

It would be desirable to corroborate the proposed structure with X-ray crystal analysis data. We have been unsuccessful thus far in growing suitable crystals. The proposed structure must therefore remain proposed until such data is available.

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