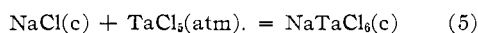


able certainty despite uncertainty in γ . The values of the K/γ constants, reported in Table II, are seen to be only slightly sensitive to the choice of γ , to remain constant over the $X_{\text{TaCl}_6}^+$ or X_{Cl^-} concentrations studied and to lie in the range $\log K/\gamma = 1.7 \pm 0.3$.

Thus the vapor pressures of tantalum pentachloride above its solutions in NaFeCl₄-NaCl mixtures appear to be consistent at 300 and 400° with the complexing reaction 1. The association constants $K_1 = X_{\text{TaCl}_6^-}/a_{\text{TaCl}_6}X_{\text{Cl}^-}$, are equal to $\log K_1 = 2.4 \pm 0.3$ at 300° and to $\log K_1 = 1.7 \pm 0.3$ at 400°.

It is of interest to compare the free energy values calculated for the reaction



by Morozov and his co-workers with the free energy changes for the same reaction that can be estimated from the measured equilibrium constants for reaction 1. The free energy change of reaction 5 will be related to the equilibrium constant by the equation

$$\begin{aligned} \Delta F_5 &= -RT \ln(a_{\text{NaTaCl}_6}/a_{\text{NaCl}}P_{\text{TaCl}_5}) \\ &= -RT \ln[(K/\gamma P_{\text{TaCl}_5}^0)(\gamma_{\text{NaTaCl}_6}/\gamma_{\text{NaCl}})] \quad (6) \end{aligned}$$

where γ_{NaTaCl_6} and γ_{NaCl} are the activity coefficients of dissolved NaTaCl₆ and NaCl in molten NaFeCl₄, with the standard states of both dissolved salts being the pure crystal. The activity coefficient ratio $\gamma_{\text{NaTaCl}_6}/\gamma_{\text{NaCl}}$ can be approximated by

the relation⁷

$$\gamma_{\text{NaTaCl}_6}/\gamma_{\text{NaCl}} = \exp \left[\int_{1081^\circ}^T (L_{f(\text{NaCl})}/RT^2) dT - \int_{743^\circ}^T (L_{f(\text{NaTaCl}_6)}/RT^2) dT \right] \quad (7)$$

Substitution into formula 6 of the measured values of K/γ , the known values of $P_{\text{TaCl}_5}^0$, and of values of $\gamma_{\text{NaTaCl}_6}/\gamma_{\text{NaCl}}$ estimated by formula 7 yields the calculated values $\Delta F_5 = -2.6 \pm 0.7$ kcal./mole at 300°; $\Delta F_5 = +0.5 \pm 0.7$ kcal./mole at 400°. Morozov's group reports $\Delta F_5 = -1.9$ and $+1.0$ kcal./mole at these temperatures.

Acknowledgments.—The author wishes to thank Mr. W. M. Johnston for analytical data, the Pigments Department of E. I. du Pont de Nemours & Company for permission to release these results and Dr. J. O'M. Bockris and Dr. G. W. Watt for helpful criticism.

(7) In the use of this relation the assumption is made that solutions of NaCl and of NaTaCl₆ in liquid NaFeCl₄, with the standard states of the solutes taken as the hypothetical supercooled liquids at temperature T , deviate from ideality approximately to an equal extent. This assumption would appear to be reasonable since it appears that many simple salt mixtures do not, in the absence of complexing by the solvent, deviate markedly from ideal behavior.

Values of $L_{f(\text{NaCl})}$, the heat of fusion of NaCl, as a function of temperature were calculated from data in N. B. S. Bulletin 500.

The melting point of NaTaCl₆ has been reported as 470°. The heat of fusion of NaTaCl₆ is not known, and, for the purpose of these calculations, has been estimated from $L_{f(\text{NaCl})}$ and the ratio of the melting points. Thus

$$L_{f(\text{NaTaCl}_6)} \sim L_{f(\text{NaCl})} [743^\circ/1081^\circ] = 4.7 \text{ kcal./mole}$$

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

Some Comments on the Anomalous Magnetic Behavior of Certain Ni(II) Complexes

By C. J. BALLHAUSEN¹ AND ANDREW D. LIEHR

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The magnetic and spectral properties of tetra-coördinated Ni(II) complexes are discussed in the light of the modern theory of ligand fields. It is pointed out that for such Ni(II) complexes there exist both strong experimental evidence and convincing theoretical arguments against (a) the existence of dsp^2 bonding, and (b) the existence in solutions and melts of planar-tetrahedral conformational equilibria. Equations governing the magnetic susceptibility of partially paramagnetic planar Ni(II) systems are derived and their usefulness in determining the singlet-triplet energy separation is underlined. Some conjectures concerning the nature of the famous Lifschitz salts of nickel are presented and an interesting analogy between these compounds and the recently characterized copper alkanoates is noted.

Introduction

The tetra-coördinated complexes of Ni(II) have occupied a prominent position in the development of the theory of inorganic complex ions. They have been frequently cited as prime examples for the "magnetic criterion of bond type" and have hence been classified as planar or tetrahedral accordingly as they are dia- or paramagnetic. Indeed, the anomalous magnetic susceptibilities exhibited by solutions and melts of certain tetracoördinated Ni(II) complexes have been explained as due to the establishment of a dynamic equilibrium between these two conformations. In this note we wish to point out that the modern theory of inorganic complexes, the ligand field theory, offers an alternative interpretation of the anomalous magnetic behavior of tetra-coördinated Ni(II) complexes and that

extremely useful information concerning the low lying energy levels of these complexes may be obtained from studies of the variation of the magnetic susceptibility with temperature.

Theory

As is well known² the imposition of a ligand field splits the fivefold degeneracy of the transition metal 3d electronic orbitals in a manner characteristic of the spatial symmetry of the attached ligands. In Fig. 1 is depicted this splitting for the cases here of interest. If one neglects configuration interaction, the ground electronic state of a weakly tetragonal Ni(II) complex may be written as either $(e_g)^4(b_{2g})^2(a_{1g})^2$ (*diamagnetic*) or $(e_g)^4$

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(2) See for example, the following recent review articles: (a) J. S. Griffith and L. E. Orgel, *Quart. Rev.*, **11**, 381 (1957) (non-mathematical); W. E. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956) (mathematical).

$(b_{2g})^2(a_{1g})^1(b_{1g})^1$ (*paramagnetic*); and the ground electronic state of a strongly tetragonal Ni(II) complex may be likewise written as either $(e_g)^4$ ($a_{1g})^2(b_{2g})^2$ (*diamagnetic*) or $(e_g)^4(a_{1g})^2(b_{2g})^1(b_{1g})^1$ (*paramagnetic*). Thus we see that even for a rigorously square planar Ni(II) complex it is possible to have a paramagnetic ground state. This situation is entirely analogous to that which gives rise to the "low-spin" complexes of Fe(III), Co(III), etc.^{2,3}

If we assume that it is sufficient to consider only the first four electronic states of a Ni(II) complex to obtain the correct *qualitative* behavior of tetragonal Ni(II) complex ions, we may write the appropriate zero-order wave functions as (see Fig. 1)

(a) Weak tetragonality

$$\begin{aligned} {}^1A_{1g}: & |(z^2)(z^2)| \\ {}^3B_{1g}: & |(z^2)(x^2 - y^2)| \\ {}^1B_{1g}: & 2^{-1/2} \{ |(z^2)(x^2 - y^2)| - |(\bar{z}^2)(x^2 - y^2)| \} \\ {}^1A_{1g}: & |(x^2 - y^2)(x^2 - y^2)| \end{aligned}$$

(b) Strong tetragonality

$$\begin{aligned} {}^1A_{1g}: & |(xy)(\bar{xy})| \\ {}^3A_{2g}: & |(xy)(x^2 - y^2)| \\ {}^1A_{2g}: & 2^{-1/2} \{ |(xy)(x^2 - y^2)| - |(\bar{xy})(x^2 - y^2)| \} \\ {}^1A_{1g}: & |(x^2 - y^2)(x^2 - y^2)| \end{aligned} \quad (1)$$

where a bar indicates spin $-1/2$. It is to be strongly emphasized that we are here not necessarily implying that the electronic wave functions (z^2) , $(x^2 - y^2)$ and (xy) are the pure nickel 3d atomic orbitals $3d_{z^2}$, $3d_{x^2-y^2}$ and $3d_{xy}$. We wish only to indicate by our notation that the orbitals in question are generalized wave functions having the same symmetry properties as the corresponding nickel atomic orbitals. In equation 1 we have, in the interests of economy, suppressed the explicit mention of the six Ni(II) electrons occupying the two lowest ligand field levels.⁴

An appropriate choice of the zero of energy leads to the following expressions for the energy spectrum of the tetragonal Ni(II) complexes

(a) Weak tetragonality

$$\begin{aligned} {}^1A_{1g}: & \begin{vmatrix} 4(F_2 + 9F_4) - E & 4F_2 + 15F_4 \\ 4F_2 + 15F_4 & 2\Delta_1 + 4(F_2 + 9F_4) - E \end{vmatrix} = 0 \\ E & = 4(F_2 + 9F_4) + \Delta_1 \pm \{(4F_2 + 15F_4)^2 + \Delta_1^2\}^{1/2} \\ {}^1B_{1g}: & E = 21F_4 + \Delta_1 \\ {}^3B_{1g}: & E = -(8F_2 + 9F_4) + \Delta_1 \end{aligned} \quad (2)$$

(b) Strong tetragonality

$$\begin{aligned} {}^1A_{1g}: & \begin{vmatrix} 4(F_2 + 9F_4) - E & 35F_4 \\ 35F_4 & 2\Delta_2 + 4(F_2 + 9F_4) - E \end{vmatrix} = 0 \\ E & = 4(F_2 + 9F_4) + \Delta_2 \pm \{(35F_4)^2 + \Delta_2^2\}^{1/2} \\ {}^1A_{2g}: & E = 4F_2 + F_4 + \Delta_2 \\ {}^3A_{2g}: & E = 4F_2 - 69F_4 + \Delta_2 \end{aligned} \quad (3)$$

In equations 2 and 3 the quantities F_k , ($k = 2, 4$), are the well-known Condon and Shortley parameters⁵ and the Δ_k , ($k = 1, 2$), are the single

(3) J. H. Van Vleck, *J. Chem. Phys.*, **3**, 807 (1935); J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, **7**, 167 (1935).

(4) We have here assumed that the excitation of these six electrons requires considerably more energy than for the excitation of the remaining two electrons. This is quantitatively a very poor approximation for the weak tetragonality case, but, even in this case, leads to very instructive qualitative results.

(5) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, 1953, pp. 176-177.

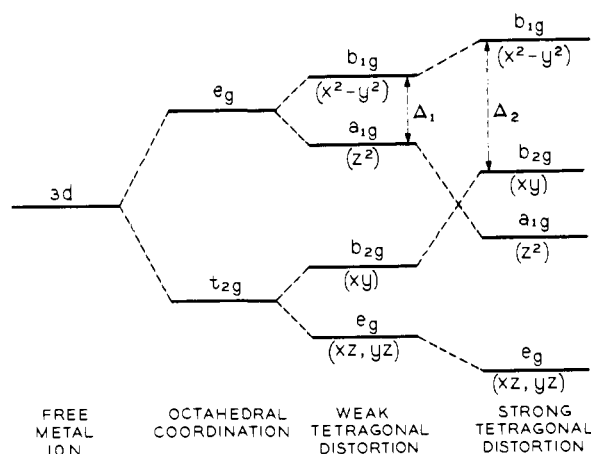


Fig. 1.—Energy level correlation diagram for weakly and strongly tetragonally distorted transition metal complexes. Hexa-coordinated Ni(II) complexes with non-equivalent groups along the z -axis exemplify weakly distorted complexes, and bidentate tetra-coordinated Ni(II) complexes with either no axial groups or with foreign groups along the perpendicular (z) axis exemplify strongly distorted complexes.

electron orbital separations depicted in Fig. 1. We thus see that on the basis of this calculation we should expect the following spectral lines

(a) Weak tetragonality

(1) paramagnetic

$$\begin{aligned} \nu_1 & = E_1({}^1A_{1g}) - E({}^3B_{1g}) = 3(4F_2 + 15F_4) - \{(4F_2 + 15F_4)^2 + \Delta_1^2\}^{1/2} \\ \nu_2 & = E({}^1B_{1g}) - E({}^3B_{1g}) = 2(4F_2 + 15F_4) \approx 11,000 \text{ cm.}^{-1} \\ \nu_3 & = E_2({}^1A_{1g}) - E({}^3B_{1g}) = 3(4F_2 + 15F_4) + \{(4F_2 + 15F_4)^2 + \Delta_1^2\}^{1/2} \end{aligned} \quad (4)$$

(2) diamagnetic

$$\begin{aligned} \nu_1 & = E({}^3B_{1g}) - E_1({}^1A_{1g}) = -3(4F_2 + 15F_4) + \{(4F_2 + 15F_4)^2 + \Delta_1^2\}^{1/2} \\ \nu_2 & = E({}^1B_{1g}) - E_1({}^1A_{1g}) = -(4F_2 + 15F_4) + \{(4F_2 + 15F_4)^2 + \Delta_1^2\}^{1/2} \\ \nu_3 & = E_2({}^1A_{1g}) - E_1({}^1A_{1g}) = 2\{(4F_2 + 15F_4)^2 + \Delta_1^2\}^{1/2} \end{aligned} \quad (5)$$

(b) Strong tetragonality

(1) paramagnetic

$$\begin{aligned} \nu_1 & = E_1({}^1A_{1g}) - E({}^3A_{2g}) = 3(35F_4) - \{(35F_4)^2 + \Delta_2^2\}^{1/2} \\ \nu_2 & = E({}^1A_{2g}) - E({}^3A_{2g}) = 2(35F_4) \approx 7,000 \text{ cm.}^{-1} \\ \nu_3 & = E_2({}^1A_{1g}) - E({}^3A_{2g}) = 3(35F_4) + \{(35F_4)^2 + \Delta_2^2\}^{1/2} \end{aligned} \quad (6)$$

(2) diamagnetic

$$\begin{aligned} \nu_1 & = E({}^3A_{2g}) - E_1({}^1A_{1g}) = -3(35F_4) + \{(35F_4)^2 + \Delta_2^2\}^{1/2} \\ \nu_2 & = E({}^1A_{2g}) - E_1({}^1A_{1g}) = -(35F_4) + \{(35F_4)^2 + \Delta_2^2\}^{1/2} \\ \nu_3 & = E_2({}^1A_{1g}) - E_1({}^1A_{1g}) = 2\{(35F_4)^2 + \Delta_2^2\}^{1/2} \end{aligned} \quad (7)$$

It is evident from equations 2 and 3 that the conditions for the appearance of diamagnetism in both the weak and strong tetragonality cases are

(a) Weak tetragonality

$$E({}^3B_{1g}) > E({}^1A_{1g}), \text{ or, } \Delta_1 > 8^{1/2}(4F_2 + 15F_4) \quad (8)$$

(b) Strong tetragonality

$$E({}^3A_{2g}) > E({}^1A_{1g}), \text{ or, } \Delta_2 > 8^{1/2}(35F_4) \quad (9)$$

If we take F_2 and $10F_4$ to be about⁶ 1000 cm.⁻¹ these conditions become $\Delta_1 > 15,000$ cm.⁻¹ and $\Delta_2 > 9,900$ cm.⁻¹

Discussion of Weakly Tetragonal Ni(II) Complexes.—It is obvious that our simplified treatment will not correctly predict the absorption spectra of weakly tetragonal Ni(II) complexes. Such complexes are more correctly viewed as slightly perturbed octahedral complex ions.⁷⁻⁹ However, our treatment does graphically illustrate the possibility of the existence of magnetic quenching or promotion in weakly tetragonal complexes. We believe¹⁰ that it is by this mechanism that the diamagnetic planar Ni(II) chelates attain partial paramagnetic character when dissolved in strongly polar solvents such as methyl alcohol, pyridine, etc., rather than by conformational equilibria.¹¹ If this be the case the molar susceptibility of such solutions should be given by

$$\chi_M = \frac{2g^2\beta^2N}{3kT} \left\{ 1 + \frac{1}{3} \exp \left[\frac{h\nu_1}{kT} \right] \right\}^{-1} + N\alpha \quad (10)$$

where g is the Landé factor for the ${}^3B_{1g}$ state, N Avogadro's number, k the Boltzmann constant, β the Bohr magneton, $N\alpha$ the temperature independent part of the susceptibility and $h\nu_1$ the energy separation of the diamagnetic ground state, ${}^1A_{1g}$, and the low-lying excited triplet state, ${}^3B_{1g}$ (see equation 5). As no detailed susceptibility *vs.* temperature studies have been as yet carried out on such solutions, we have not been able to verify this predicted behavior.

Discussion of Strongly Tetragonal Ni(II) Complexes.—Of much greater intrinsic interest are the predictions our model yields for strongly tetragonal Ni(II) complexes. Here we should expect valid prognostications of both the spectra and the magnetic properties of such complexes, and, in all probability, a truer description of their actual electronic structure than the time-honored dsp^2 specification.¹² Indeed, as it has been decisively proven by McGarvey¹³ that Cu(II) planar complexes (at least those which he personally investigated) are not dsp^2 in electronic structure, one may probably safely infer that the same conclusions hold true for the corresponding diamagnetic planar Ni(II) systems. Hence, let us now consider the behavior of the magnetic sus-

ceptibility expected of strongly tetragonal Ni(II) complexes on the basis of our model.

Now equation 10 is a perfectly general expression for the magnetic susceptibility of any electronic system possessing both a low-lying singlet and a low-lying triplet state.¹⁴ Hence, we should expect the strongly tetragonal as well as the weakly tetragonal Ni(II) complexes to exhibit a magnetic susceptibility obeying equation 10. As both the sign and the magnitude of the energy separation¹⁵ $h\nu_1$ for strongly tetragonal systems is intimately connected with the tetragonality parameter, Δ_2 , we see that the behavior of diamagnetic planar Ni(II) complexes will be quite sensitive to changes in bond lengths and bond angles^{7,8b,16} as well as to solvation effects.^{8b-10} Indeed, the decrease in the effective crystalline field seen by such Ni(II) complexes on melting or on dissolution in "non-complexing" solvents may well lower the numerical value of the tetragonality parameter Δ_2 (recall $\Delta_2 > \sim 10,000$ cm.⁻¹, for diamagnetism) such that $h\nu_1$ is now comparable with thermal energies. In this event the complex will become partially paramagnetic. We believe that it is by this mechanism that diamagnetic planar Ni(II) complexes attain partial paramagnetic behavior on melting¹⁷ and on dissolution,^{11,18} rather than by any extensive change in conformation, such as is implied in the current assumption¹⁹ of planar-tetrahedral equilibria. Moreover, if the tetragonality parameter, Δ_2 , is less than 10,000 cm.⁻¹ the ${}^3A_{2g}$ state will become the ground electronic state (see equation 9) and the planar complex will be paramagnetic with a magnetic moment μ of around three Bohr magnetons. This is undoubtedly what happens when diamagnetic planar Ni(II) complexes are dissolved in solvents like pyridine.¹⁰

If our conjectures concerning the nature of four coordinated Ni(II) complexes are correct, we should expect that paramagnetic planar Ni(II) complexes (for example, the bis-salicylaldehyde and bisacetylacetone²⁰) should show either no crystal field bands in the near infrared and visible, or only a few weak spin-forbidden bands (see Fig. 2). On the other hand, we should expect¹⁰ that the diamagnetic (and partially paramagnetic) planar Ni(II) complexes to show one, or possibly two (the second may be masked by the very strong ligand absorption bands²¹) crystal field bands ($\epsilon < 10^2$). This is what is actually observed.^{10,11,18}

(6) L. E. Orgel, *J. Chem. Phys.*, **23**, 1819 (1955).

(7) C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat-fys. Medd.*, **29**, No. 8 (1955).

(8) (a) Claudio Furlani, *Z. physik. Chem. (Frankfurt) [N. F.]*, **10**, 291 (1957); (b) *Gazz. chim. ital.*, **88**, 279 (1958); (c) C. Furlani and G. Morpurgo, Trieste Università Istituto Di Chimica, Pubblicazione N. 21, 1958.

(9)(a) Gilda Maki, *J. Chem. Phys.*, **28**, 651 (1958); (b) **29**, 162 (1958); (c) **29**, 1129 (1958).

(10) Gilda Maki (private communication) has also come to this conclusion by means of a much more elaborate calculation. Indeed, she has shown that no tetrahedral model is consistent with both the spectra and magnetic properties of these complex ions. See Gilda Maki, "The Energy Levels of Transition Elements of $3d^{2(z)}$ Type: Spectra, Magnetic Properties, Geometry and Bonding in Complexes, Thesis, University of California, 1957, pp. 231-236 and also ref. 9 (c).

(11) B. Willis and D. P. Mellor, *THIS JOURNAL*, **69**, 1237 (1947); S. Fujii and M. Sumitani, *Sci. Repts. Tohoku Imp. Univ., First Series*, **37**, 49 (1953); H. C. Clarke and A. L. Odell, *J. Chem. Soc. (London)*, **1955**, 3431.

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, pp. 118-123.

(13) B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956).

(14) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, 1932, pp. 189-190.

(15) For strongly tetragonal complexes this is the energy separation of the ${}^3A_{2g}$ and the low-lying ${}^1A_{1g}$ state (see Equation 7).

(16) H. Hartmann and H. Fischer-Wasels, *Z. physik. Chem. (Frankfurt) [N. F.]*, **4**, 298 (1955).

(17) L. Sacconi, R. Cini and F. Maggio, *THIS JOURNAL*, **79**, 3933 (1957); see also L. Sacconi, P. Paoletti and R. Cini, *ibid.*, **80**, 3583 (1958).

(18) L. Sacconi, P. Paoletti and G. Del Re, *ibid.*, **79**, 4062 (1957).

(19) The dipole moment measurements of Sacconi, Paoletti and Del Re¹⁸ afford additional evidence against this mechanism.

(20) Electron diffraction studies of the vapor phase of this complex by S. Shibata (*Bull. Chem. Soc. (Japan)*, **30**, 753 (1957)) show it to be planar. However, an X-ray powder diagram study by the same author (*ibid.*, **842** (1957)) yielded inconclusive, if not actually ambiguous, results. An incomplete single crystal X-ray study which fixes only the number of Ni atoms per unit cell has been reported by G. J. Bullen (*Nature*, **177**, 537 (1956)).

(21) L. Sacconi, P. Paoletti and F. Maggio, *THIS JOURNAL*, **79**, 4067 (1957).

Some Speculations on the Lifschitz Complexes.—

This subsection might more appropriately be called "the tale of the blue and the yellow." Lifschitz, Bos and Dijkema²²⁻²⁴ have prepared a number of tetra-coördinated complexes of Ni(II) with stilbenediamine (1,2-diphenylethylenediamine, *stien*) and with monophenylethylenediamine (*phenen*) of the general composition Ni[*stien* or *phenen*]₂X₂. Dependent upon the nature of the anion and also upon the occluded molecules of solvation, these compounds form either blue (paramagnetic) or yellow (diamagnetic) crystals, which in many cases are interconvertible. With the single exception of Ni[*phenen*]₂(NO₃)₂, all such complexes which are salts of the strongest mineral acids (HClO₄, H₂SO₄, HCl, etc.) may form a blue (paramagnetic) modification only in the solvated state (for example, Ni[*phenen*]₂(ClO₄)₂·2H₂O), if at all.²⁵ This behavior is readily understood on the basis of the strong tetragonality theory developed above. The anions of the strong acids are weak bases and, so, produce only a small axial perturbation on the planar *stien* and *phenen* complexes. Thus these are diamagnetic with one, or possibly two, crystal field bands in the visible, as is observed.^{7,8b} In those cases where the axial direction is not sterically blocked,²⁵ the addition of polar solvate of crystallization produces a sufficient perturbation to invert the (planar) singlet and triplet electronic states (a decrease in the magnitude of Δ_2 due to a "pseudo" octahedral²⁶ coördination) and causes the complex to simultaneously change its color and magnetism. The blue modification of anhydrous Ni[*phenen*]₂(NO₃)₂ occurring at elevated temperatures is most probably a thermally induced crystalline transformation, possible due to the close axial approach of the planar NO₃⁻ groups (thus becoming "pseudo" octahedral).²⁶

Of considerably more interest are the salts of Ni[*stien*]₂X₂ where the anion X⁻ is from a weak acid of the type RCO₂H, (R = H⁻, CH₃⁻, CHCl₂⁻, etc.). These complexes have been shown by Hein and Müller²⁷ to possess an anhydrous blue (paramagnetic) modification and *two* yellow (diamagnetic) modifications. Only one of these yellow forms (I) may be "reversibly" converted into a blue modification.²⁸ The second yellow form (II), which is immediately produced on dissolution of the

(22) I. Lifschitz, J. G. Bos and K. M. Dijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939).

(23) I. Lifschitz and J. G. Bos, *Rec. trav. chim.*, **59**, 407 (1940).

(24) I. Lifschitz and K. M. Dijkema, *ibid.*, **60**, 581 (1941).

(25) Steric effects are extremely important in determining when a blue modification will be formed on the occlusion of solvate of crystallization. This is dramatically demonstrated by the fact that the dihydrate of the *meso-stien* chloride of Ni(II) is yellow (diamagnetic)²⁷ while the hydrates of the *racemic* and *active stien*²¹ and of the *phenen*²⁴ chloride are blue (paramagnetic).

(26) That is, these complexes are then better viewed as weakly tetragonal complex ions in which case they should be, by our previous considerations, blue and paramagnetic. The proposal that the blue Ni(II) *stien* complexes are best viewed as pseudo octahedral has also been suggested recently by C. Furlani.^{8b}

(27) Fr. Hein and H. Müller, *Z. anorg. allgem. Chem.*, **283**, 172 (1956).

(28) As all known weakly tetragonal ("pseudo" octahedral) Ni(II) complexes are blue and paramagnetic (thus Δ_1 never satisfies eq. 8), it is impossible to say *a priori* whether the blue form obtained in the reverse reaction is structurally identical with the original blue modification. Indeed, for the salts here under consideration the second blue modification may well be different from the original.

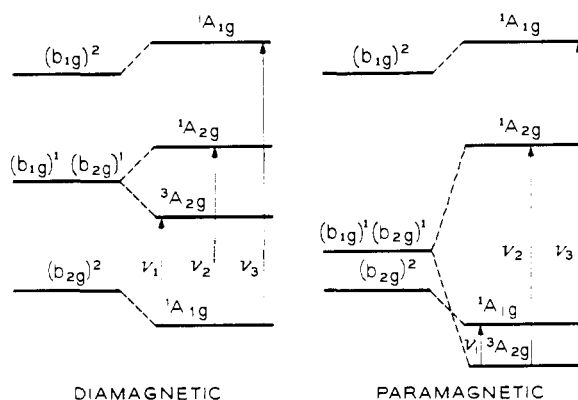


Fig. 2.—Energy level diagrams for the paramagnetic and diamagnetic forms of strongly tetragonal Ni(II) complexes.

blue modification in polar solvents, is the stable form of this complex. We believe that this stable yellow form (II) of Ni[*stien*]₂X₂ is planar and that the anhydrous blue modification is a pseudo-octahedral complex formed by -CO₂⁻ bridges, perhaps having the formula [Ni₂[*stien*]₄(RCO₂)₂⁺⁺(RCO₂⁻)₂. We attribute the "unstable" yellow form I to the solid phase break-up of the RCO₂⁻ bridges, accompanied, perhaps, by the formation of planar Ni[*stien*]₂⁺⁺ groups.²⁹ If this be the case, these Ni(II) complexes are the analogs of the recently characterized RCO₂⁻ bridged Cr(II)³⁰ and Cu(II)³¹⁻³³ complexes.

Conclusion

We hope that the ideas and speculations presented in this paper will stimulate further experimental and theoretical studies of these fascinating compounds. It seems that a great deal of concrete information concerning the nature of the electronic structure of these complexes could be obtained from both detailed susceptibility measurements and from optical, electron spin resonance and nuclear magnetic resonance studies, not to mention the immense clarification of their properties that would be afforded by single crystal³⁴ X-ray structural an-

(29) It is significant that the yellow form I exists only in the solid phase and is converted back into a blue modification only by the occlusion of polar solvents or by heat.²⁷ It dissolves in non-polar solvents with a yellow color, presumably forming here the stable yellow form II. Both yellow forms (I and II) when dissolved in boiling formamide retain their color and are also inert toward the addition of dimethylglyoxime (DMG). On the other hand, the blue forms when dissolved in the same media change color and will quantitatively precipitate out Ni(DMG)₂.²⁷

(30) C. Furlani, *Gazz. chim. ital.*, **87**, 876 (1957).

(31) The analogy with the Cu(II) systems is quite startling. Equation 10 also governs their magnetic behavior (see B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956), and R. L. Martin and H. Waterman, *ibid.*, 2545 (1957)), although the origin of the energy separation, $h\nu_1$, is quite different (indeed, $h\nu_1$ might well be negative for the Ni(II) complexes). Also, as has been shown recently by R. L. Martin and A. Whitley (*ibid.*, 1394 (1958)), the Cu(II) bridged systems retain their identity in non-polar solvents, such as dioxane and benzene, but are immediately decomposed by polar solvents, with a simultaneous change of both color and magnetism.

(32) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468 (1958).

(33) S. Yamada, H. Nakamura and R. Tsuchida, *Bull. Chem. Soc. (Japan)*, **30**, 953 (1957); **31**, 303 (1958); R. Tsuchida, S. Yamada and H. Nakamura, *Nature*, **181**, 479 (1958).

(34) Although the tetrahedral structure has been invoked to explain paramagnetic tetracoördinated Ni(II) complexes for more than twenty-five years, we have only been able to find one such X-ray substantiated case, Ni(Ph₂P)₂X₂, (X = I, Br, Cl). See L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

alyses. It is not improbable that the results of such researches might lead to a view of their basic

(35) NOTES ADDED IN PROOF.—Dr. S. C. Nyburg of the Department of Chemistry, University College of North Staffordshire (private communication) is at present performing X-ray structural analyses of these complexes. Bridged complexes of V(III) with RCO_2^- groups have been characterized recently by B. Jezowska-Trzebiatowska and L.

electronic structure totally different from that here presented.³⁵

Pajdowski, *Roczniki Chemii*, **31**, 769 (1957). A stable paramagnetic isomer of bis (N-methylsalicylaldimine) Ni(II) has been reported by C. M. Harris, S. L. Lenzer and R. L. Martin, *Australian J. Chem.*, **11**, 331 (1958).

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Proton Magnetic Resonance Spectra of Malic Acid and its Salts in Deuterium Oxide^{1,2}

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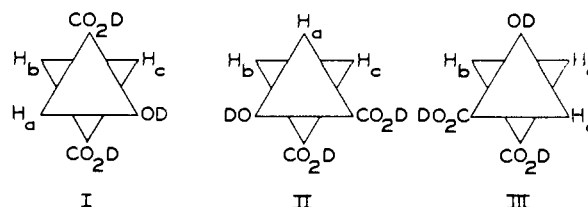
After exchange with deuterium oxide, malic acid and its salts represent systems of three non-equivalent protons. The structures of the proton magnetic resonance spectra obtained can be approximated quite well by use of the recently developed theories for the case in which one of the chemical shifts is large with respect to the two others and to the three coupling constants. It is possible to identify the chemical shifts with particular protons and the coupling constants with particular pairs by use of high resolution experiments on the monodeuterio-L-malate produced enzymatically. The monodeuterio-L-malate produced by hydrating fumarate by fumarase is that diastereomer in which the protons are gauche when the carboxyl groups are *trans*, as shown earlier by proton resonance experiments on the solid acid. The changes in chemical shifts and coupling constants with concentration and degree of neutralization of malic acid have been studied. Better resolution is obtained when the cation is potassium rather than lithium or sodium.

Introduction

The high resolution proton magnetic resonance spectra of simple organic compounds provide a means for determining the positions of deuterium atoms substituted for hydrogen atoms and for analyzing mixtures of the various partially deuterated species produced by exchange or in the course of various reactions. The L-malate formed from fumarate by the action of pig heart fumarase in D_2O contains one atom of deuterium in the methylene group,³ and proton resonance experiments on the solid acid at -196° show that the two protons are in the gauche position⁴ provided that the carboxyl groups are in the *trans* position. A study of the high resolution spectra of malic acid and the enzymatically prepared monodeuterio-L-malic acid and their salts was undertaken in order to provide the basis for the analysis of mixtures of partially deuterated malic acids arising in the acid and base catalyzed hydrations of fumarate.

Analysis of the high resolution spectra of two-spin systems for the case in which the difference in chemical shifts is of the order of magnitude of the coupling constant is well known.⁵⁻⁷ Analysis of the high resolution spectra for systems of three protons recently has been described in detail⁸⁻¹⁰ for the

approximation that $|\nu_b - \nu_a| \gg |\nu_c - \nu_b|$, $|A_{ab}|$, $|A_{ac}|$, $|A_{bc}|$, where the ν 's are the n.m.r. frequencies and the A 's are coupling constants. For malic acid the subscripts designate the various protons as indicated by



According to this nomenclature the monodeuterio-L-malic acid produced enzymatically is represented by $\text{H}_2\text{D}_c\text{M}$.

Experimental

The carboxyl and hydroxyl protons of recrystallized¹¹ malic acid and its salts were exchanged out and replaced by deuterons. The dry sample was dissolved in D_2O , the water sublimed out and the process then repeated two times. The sample then was dissolved in 99.5% D_2O , usually to give a concentration of 2 *M*, and sealed in a 5 mm. (o.d.) tube.

The spectra were observed at a nominal frequency of 40 megacycles using a Varian V-4300 n.m.r. spectrometer equipped with a superstabilizer. The cooling water for the magnet coils was circulated from a thermostat at 25° controlled to $\pm 0.03^\circ$. The spectra were recorded with the sample spinning under a variety of experimental conditions. In order to determine chemical shifts with respect to H_2O , small capillaries containing water were placed in the n.m.r. tubes, or ground coaxial tubes¹² were used. The separations of the lines from the water resonance peak were measured using the sideband resonances produced by audiomodulation of the magnetic field.¹³ The audio oscillator was checked at intervals with a Hewlett Packard Electronic Counter (Model 524B). By recording sidebands of appropriate spacing and intensity with either the Sanborn or Varian recorders, it was possible to reproduce shifts of the order of 100 c.p.s. with an average deviation of less than 1%.

(11) C. Frieden, R. G. Wolfe and R. A. Alberty, *ibid.*, **79**, 1523 (1957).

(12) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

(13) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 608 (1951).

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(2) This research was supported by grants by the National Science Foundation and by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation.

(3) H. F. Fisher, C. Frieden, J. S. McKinley McKee and R. A. Alberty, *THIS JOURNAL*, **77**, 4436 (1955).

(4) T. C. Farrar, H. S. Gutowsky, R. A. Alberty and W. G. Miller, *ibid.*, **79**, 3978 (1957).

(5) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

(6) M. K. Banerjee, T. P. Das and A. K. Saha, *Proc. Roy. Soc. (London)*, **226A**, 490 (1954).

(7) W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

(8) G. A. Williams and H. S. Gutowsky, *J. Chem. Phys.*, **25**, 1288 (1956).

(9) H. J. Bernstein, J. A. Pople and W. G. Schneider, *Canadian J. Chem.*, **35**, 65 (1957).

(10) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *THIS JOURNAL*, **79**, 4596 (1957).