# Complexing of Tantalum Pentachloride by Chloride Ion in Fused Salt Media[1]

By Charles M. Cook, Jr.

The interaction of $TaCl_5$ with NaCl in their solutions in molten $NaFeCl_4$ was studied at 300 and 400°. The $TaCl_5$ activity, as measured by its vapor pressure, was found to vary with $TaCl_5$ and NaCl concentrations in a manner consistent with the equilibrium reaction $TaCl_5 + Cl^- \rightleftarrows TaCl_6^-$. The corresponding equilibrium constants were found to be $\log X_{TaCl_6}^- / a_{TaCl_5} X_{Cl}^- = 2.4 \pm 0.3$ at 300° and 1.7 ± 0.3 at 400°.

The first observation of the $TaCl_6^-$ anion appears to be that of Gutmann,[2] who found the compound $[Pyr \cdot POCl_2^+][TaCl_6^-]$ during an investigation of the $POCl_3$ solvent system. More recently, Morozov and his colleagues have studied the phase diagrams of the $NaCl-NbCl_5$ system[3a] and the $NaCl-TaCl_5$ system[3b] and have reported the solid compounds $NaNbCl_6$ and $NaTaCl_6$. These workers have estimated the free energies of formation of these compounds from the $NbCl_5$ and $TaCl_5$ vapor pressures above solid, powdered mixtures of $NaCl + NaNbCl_6$ and $NaCl + NaTaCl_6$, respectively.[4]

In the work described below, the reaction between tantalum pentachloride and sodium chloride in a molten salt solution

$$TaCl_5 + Cl^- = TaCl_6^- \qquad (1)$$
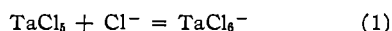
has been studied by measurement of the equilibrium $TaCl_5$ activity as a function of gross $TaCl_5$ and NaCl concentrations. The salt $NaFeCl_4$, was chosen as the solvent for this system because it is low melting, essentially inert to the reactants and dissolves both $TaCl_5$ and NaCl.

Experimental

The vapor pressure of tantalum pentachloride above a mixture containing known quantities of NaCl, $FeCl_3$ and $TaCl_5$ was measured as a function of temperature. The salt mixture was contained in a sealed, evacuated, Pyrex reaction bulb to which was attached a sickle gauge for measurement of the internal pressure. Both bulb and gauge were positioned inside a tube furnace, which was constructed of copper to minimize temperature gradients. The melt was stirred until equilibrium was reached, at which time the bulb temperature and pressure were observed.

Ingredients.—Sodium chloride (Mallinkrodt, Analytical Reagent) was weighed into the Pyrex reaction bulb and dried overnight at 480° under a stream of HCl.

Iron wire (J. T. Baker Analyzed Reagent) was placed in a silica glass side arm attached by a graded seal to the Pyrex reaction bulb. The iron was burned in a stream of chlorine (Matheson Company, Oxygen Free grade), and the ferric chloride product was quantitatively sublimed into the bulb.

Tantalum powder (Fansteel Metallurgical Company, 120–325 mesh) was placed in the silica side arm with the

iron wire, chlorinated, and the pentachloride sublimed into the reaction bulb. Traces of iron or tantalum oxides remaining after the sublimation of the chlorides were chlorinated into the bulb by treatment with phosgene. The chlorination gases were dried with $Mg(ClO_4)_2$.

After having been charged with the NaCl, $FeCl_3$ and $TaCl_5$, the reaction bulb was evacuated, backfilled with Cl_2 at approximately 60 mm. pressure, and both side arms fused shut and removed. The bulb and sickle gauge assembly was then placed in the tube furnace and connected to a pressure measuring manifold.

Temperature and Pressure.—The temperature of the molten salt mixture was measured with two chromel-alumel thermocouples held in contact with the surface of the reaction bulb by strips of glass tape. The salt melt was stirred while being held at a constant temperature for approximately 1 hr. before a final pressure–temperature reading was taken. Temperature fluctuations within the furnace due to line voltage changes were eliminated by use of a constant voltage transformer in the power source.

The use of duplicate thermocouples, the stirring of the salt melt and the elimination of sharp temperature gradients in the furnace should reduce error in the measured salt temperatures. This error has been estimated to be less than $\pm 3°$.

Pressure measurements were made over a zero to two atmosphere range by the sickle gauge between the reaction bulb and the pressure manifold. The observed pressure was that manifold pressure required to return the gauge pointer to the null position. In the majority of the runs, the gauge sensitivity was greater than ± 2 mm.; for the runs made at high $TaCl_5$ concentrations, where the pressures were higher, sturdier gauges of about ± 8 mm. sensitivity were used.

Before data were taken, the melt was held at 400° (or the maximum temperature allowed by the pressure limitations of the system) for several hours to bring about complete solution of the NaCl in the solvent. When this precaution was taken, the observed pressures equilibrated rapidly, showed no temperature–pressure hysteresis and underwent no drift with time.

Calculation of $TaCl_5$ Pressure.—The experimental data obtained from any one run consist of a series of observations of total gas pressure inside the reaction bulb as a function of temperature. The $TaCl_5$ pressure at a given temperature is the difference between the total pressure observed at this temperature and the pressure exerted by the Cl_2 initially present in the bulb, i.e., $P_{TaCl_5} = P_{Total} - P_{Cl_2}$. The Cl_2 pressure can be observed directly at low temperatures where $TaCl_5$ pressure is negligible, and P_{Cl_2} at higher temperatures was calculated from the ideal gas law.

Figure 1 shows the data from a typical run and illustrates this treatment. The solid line passes through the experimental points; the dotted line represents the chlorine gas pressure as calculated from a measurement at 25°; the dashed line represents the difference between these two pressures and accordingly is taken as the $TaCl_5$ pressure.

For those runs made at low $TaCl_5$ concentrations, the uncertainty in P_{Cl_2} is a major source of uncertainty in the values calculated for P_{TaCl_5} at 300°, since under these condi-

(1) Presented at the 11th Summer Symposium of the Division of Analytical Chemistry of the American Chemical Society, Schenectady, N. Y., 6/20/58.

(2) V. Gutmann, *Monatsh.*, **85**, 1077 (1954).

(3) (a) I. S. Morozov and B. G. Korshunov, *Zhurnal neorganiches-koi khimii*, **1**, 145 (1956); (b) I. S. Morozov, B. G. Korshunov and A. T. Simonich, *ibid.*, **1**, 1646 (1956).

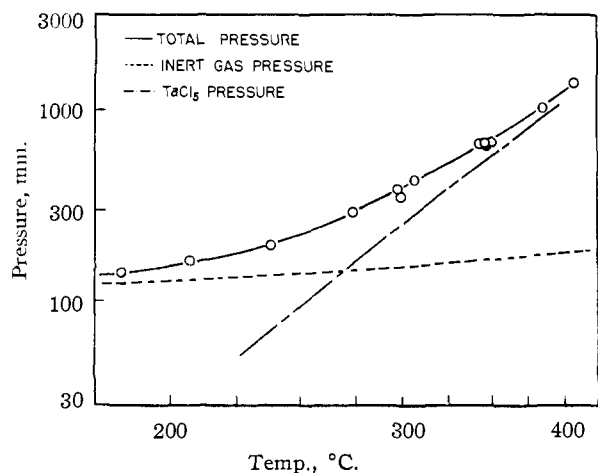(4) I. S. Morozov and A. T. Simonich, *ibid.*, **2**, 1907 (1957).

Fig. 1.—Total pressure *vs.* temperature for run 5.

tions, $P_{Cl_4} \sim P_{TaCl_5}$. The chlorine pressure correction rapidly decreases in importance with increasing temperatures and/or increasing $TaCl_5$ concentrations.

For the above procedure for calculation of the $TaCl_5$ pressure from the total pressure to be valid, the Cl_2 pressure must follow the gas law and the Fe_2Cl_6 pressure above the melt must be negligible. To demonstrate that the system fulfills these requirements, a $TaCl_5$-free mixture of initial composition $X_{FeCl_4} = 0.47$, $X_{NaCl} = 0.53$ was prepared, and the pressure above this mixture was measured from room temperature to 410°. The observed pressure was found to deviate by less than 10% from the gas law from room temperature to 410°. At the highest temperature the measured pressure was in excess of the gas law value by 10 ± 5 mm.

To establish that at the temperatures of measurement $TaCl_5$ does not react with $NaFeCl_4$ to liberate significant pressures of Fe_2Cl_6 mixtures of the same initial composition as in the above paragraph were equilibrated at 300° and at 400° with a $TaCl_5$ vapor and argon mixture that was bubbled through them. The argon exiting from the saturated melts was found to contain $TaCl_5$ that was, judging from the small amount of red coloration in the condensate, contaminated with only trace quantities of Fe_2Cl_6. Analysis of the $NaFeCl_4$-$TaCl_5$ solutions indicated the presence of 5–10 mole % $TaCl_5$ in the melts.

Discussion

The compound formed by reaction of $FeCl_3$ with $NaCl$ has been demonstrated to be $NaFeCl_4$ by Dunn[5] who found the Fe_2Cl_6 vapor pressure above mixtures of $NaCl$ and $FeCl_3$ to drop sharply to zero at $NaCl/FeCl_3$ ratios equal to or greater than unity. The similar compound $NaAlCl_4$ is well established.[6]

In this work, the solvent salt melts have all been on the $NaCl$-rich side and are considered to be $NaFeCl_4$ containing dissolved $NaCl$. In the subsequent presentation of the data the quantity $X_{Cl^-}^t$ signifies the mole fraction of the initial "free" chloride ion in the melt, *i.e.*, the number of molecules of $NaCl$ minus the number of molecules of $FeCl_3$ initially added to the sample bulb divided by the total number of ions, Na^+, $FeCl_4^-$, etc., present in the final melt. The gross mole fraction of $TaCl_5$ in the solution is similarly written $X_{TaCl_5}^t$; while the concentration of unreacted $TaCl_5$ is X_{TaCl_5}.

The vapor pressures of tantalum pentachloride at 300° above its solutions in $NaFeCl_4$–$NaCl$ are

(5) W. E. Dunn, presented at A.C.S. Del. Valley Regional Meeting, Feb. 16, 1956.
(6) E. W. Dewing. THIS JOURNAL, 77, 2639 (1955).

listed in Table I with the corresponding values of $X_{TaCl_5}^t$ and $X_{Cl^-}^t$. These data show the tantalum pentachloride vapor pressure to increase sharply with increasing $TaCl_5$ and with decreasing free chloride concentrations. The magnitude and the direction of these changes in $TaCl_5$ pressure with solution composition imply that $TaCl_5$ dissolves in the melt in part as a non-volatile chloride complex and in part as free $TaCl_5$.

TABLE I

TaCl$_5$ PRESSURE ABOVE NaFeCl$_4$-NaCl MELTS AT 300°

Run	$X_{TaCl_5}^t$	$X_{Cl^-}^t$	P_{TaCl_5}
1	0.016	0.051	14 ± 8
2	.037	.058	31 ± 5
3	.040	.058 ± 1	30 ± 5
4	.043 ± 1	.058	40 ± 6
5	.065 ± 3	.058 ± 1	260 ± 30
6	.067	.050	340 ± 30
7	.118	.054	1430 ± 200[a]
8	.114	.048	1500 ± 200[a]
9	.144	.045	2050 ± 300[a]
10	.22	.045	$P_{TaCl_5}{}^a$ equals $P_{TaCl_5}^0$
11	.048	.071	68 ± 20
12	.048	.051	43 ± 7
13	.048	.030	355 ± 25
14	.047	.010	695 ± 40

[a] Extrapolated values. $P_{TaCl_5}^0 = 3200$ mm. at 300°.

The data of run 10 show that $TaCl_5$ is not completely miscible with the solvent salt but that at some $TaCl_5$ concentration less than 22 mole % the $TaCl_5$-$NaFeCl_4$ system splits into two phases, one of which is essentially pure $TaCl_5$. The solubility limit can be estimated more accurately from the data of runs 1–9 by plotting P_{TaCl_5} *vs.* $X_{TaCl_5}^t$ and extrapolating to that gross tantalum pentachloride concentration at which the vapor pressure becomes equal to that of pure $TaCl_5$. Such a plot indicates that $P_{TaCl_5} = P_{TaCl_5}^0$ at $X_{TaCl_5}^t \sim 0.19$; at this gross tantalum pentachloride concentration most of the available chloride is in the form of $TaCl_6^-$, since $X_{Cl^-}^t = 0.045$ the free $TaCl_5$ concentration at the solubility limit accordingly is $X_{TaCl_5} \sim 0.145$.

The uncomplexed $TaCl_5$ present in the ionized $NaFeCl_4$ melt should exhibit a considerable positive deviation from Raoult's law behavior. At the solubility limit of $TaCl_5$ in $NaFeCl_4$ the activity coefficient of the uncomplexed $TaCl_5$, γ, must equal the reciprocal of the solubility. Thus from the above data $\gamma \sim (0.145)^{-1} = 6.9$. The best overall fit of the data at 300° is in fact provided by the value $\gamma = 6.5$, and accordingly the concentration of free tantalum pentachloride, X_{TaCl_5}, is taken to be equal to $P_{TaCl_5}/6.5P_{TaCl_5}^0$ at this temperature.

Figure 2 is an illustration of the behavior of increasing amounts of tantalum pentachloride dissolved in a melt containing a constant initial concentration of available chloride. The ordinate of this figure is a function of tantalum pentachloride pressure and concentration that is equivalent to the fraction of the total tantalum that is not complexed by chloride, *i.e.*, $X_{TaCl_5}/X_{TaCl_5}^t$. The abscissa represents the concentration of total $TaCl_5$ that is in excess of the free chloride ion. The plotted points represent those runs where the $X_{Cl^-}^t \sim 0.05$.
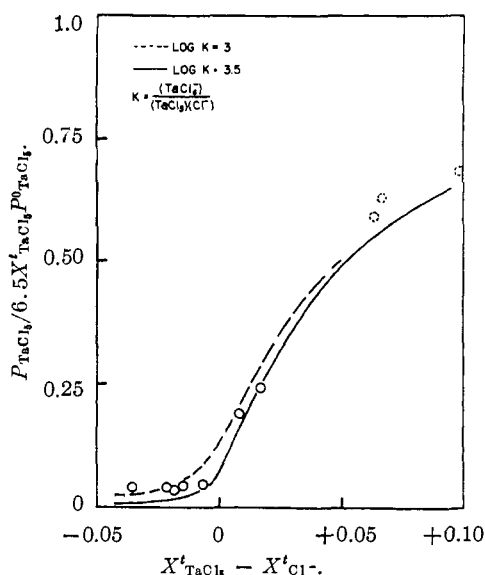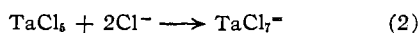
Fig. 2.—Fraction of TaCl₅ not complexed at 300° vs. TaCl₅ concentration in excess of chloride. Chloride concentration in the range $X^t{}_{Cl^-} = 0.045$ to 0.058.

The points are seen to fall along a neutralization type of curve, rising sharply when the excess NaCl has been consumed by added TaCl₅. The three dotted points, taken at high X_{TaCl_5} where the pressure limitations of the apparatus did not allow direct measurement of the pressures, represent P_{TaCl_5} values that were estimated by extrapolation.
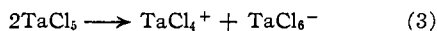
Two curves, representing the $X_{TaCl_6}/X^t{}_{TaCl_5}$ behavior to be expected if TaCl₅ reacts with chloride to yield TaCl₆⁻ according to equation 1, are presented in Fig. 2 for comparison with the plotted points. The fraction of the TaCl₅ that is uncomplexed follows the solid curve if the concentration equilibrium constant for reaction 1 is $K = X_{TaCl_6^-}/X_{TaCl_5}X_{Cl^-} = 10^{3.5}$, the dotted curve corresponds to $K = 10^3$. With the exception of the three dotted points, the experimental data are seen to fall between the two curves over a ninefold change in $X^t{}_{TaCl_5}$, with some tendency to favor the $\log K = 3$ curve at low tantalum pentachloride concentrations. The experimental results can be considered to be consistent with equation 1 where $\log K = 3.2 \pm 0.3$.

In Fig. 3 the fraction of the tantalum pentachloride that is uncomplexed is plotted, for data where $X^t{}_{TaCl_5} \sim 0.05$, against the available chloride ion concentration in the form $X^t{}_{Cl^-} - X^t{}_{TaCl_5}$. The amount of free TaCl₅ is seen to drop steadily with increasing chloride ion concentration. The points are again in agreement, over a sevenfold range of $X^t{}_{Cl^-}$, with the behavior predicted by $\log K = 3.2 \pm 0.3$, the solid line and dotted line corresponding to the $X_{TaCl_6}/X^t{}_{TaCl_5}$ behavior consistent with $K = 10^{3.5}$ and $K = 10^3$, respectively.

An attempt was made to account for the observed variation of $X_{TaCl_6}/X^t{}_{TaCl_5}$ with $X^t{}_{TaCl_5}$ and $X^t{}_{Cl^-}$ by assuming the possible complexing reactions

$$TaCl_5 + 2Cl^- \longrightarrow TaCl_7^- \qquad (2)$$

or

$$2TaCl_5 \longrightarrow TaCl_4^+ + TaCl_6^- \qquad (3)$$

or

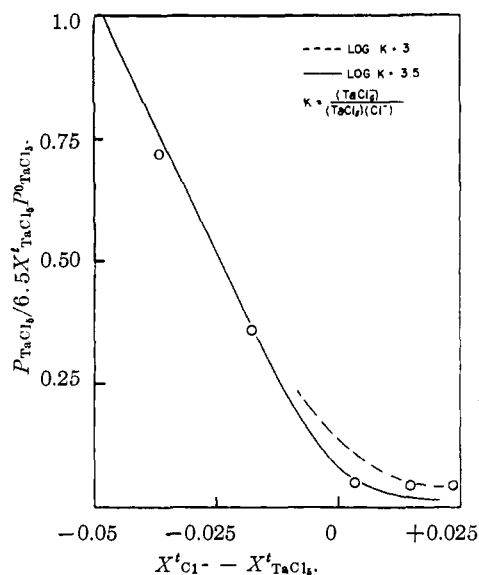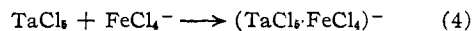$$TaCl_5 + FeCl_4^- \longrightarrow (TaCl_5 \cdot FeCl_4)^- \qquad (4)$$

Fig. 3.—Fraction of TaCl₅ not complexed at 300° vs. chloride concentration in excess of TaCl₅. Tantalum concentration constant at $X^t{}_{TaCl_5} = 0.048$.

None of these alternative reactions fit the experimental data as well as reaction 1.

The rapid increase in tantalum pentachloride pressure with temperature and the limited bursting strength of the apparatus restricted the study of the TaCl₅–Cl⁻ interaction at 400° to relatively dilute TaCl₅ solutions. As a result the TaCl₅ solubility limit in the salt melt could not be measured at this temperature and thus γ was not accurately determined.

To determine whether the complexing reaction

$$TaCl_5 + Cl^- = TaCl_6^- \qquad (1)$$
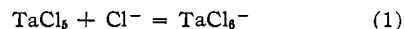
established from the experimental data observed at 300° also represents the data at 400°, the equilibrium constants $K/\gamma = X_{TaCl_6^-}/\gamma X_{TaCl_5}X_{Cl^-}$ have been calculated for the data listed in Table II. In the calculations of these constants the tantalum pentachloride activities were determined from the observed pressures by the relationship $\gamma X_{TaCl_5} = P_{TaCl_5}/P^0{}_{TaCl_5}$; the $X_{TaCl_6^-}$ and X_{Cl^-} concentrations were estimated using two assumed values of the tantalum pentachloride activity coefficient, $\gamma = 2$ and $\gamma = 5$. The data listed in Table II have been restricted to those runs where

TABLE I.

TaCl₅ PRESSURE[a] ABOVE NaFeCl₄–NaCl MELTS AT 400°

| Run	P_{TaCl_5}	$\log K/\gamma$ if $\gamma = 2$	$\log K/\gamma$ if $\gamma = 5$
1	97	1.51	1.67
2	210	1.73	1.88
3	390	1.73	1.62
4	165	1.97	2.10
5	820	1.23	1.06
11	250	1.72	1.87
12	425	1.63	2.08
		Av. 1.65	1.75

[a] $P^0{}_{TaCl_5} = 12,000$ mm. at 400°.

γX_{TaCl_5} is small compared to X_{TaCl_5} and $X^t{}_{Cl^-}$ so that $X_{TaCl_6^-}$ and X_{Cl^-} can be estimated with reason-

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 $X^t_{\text{TaCl}_6}$ or $X^t_{\text{Cl}^-}$ concentrations studied and to lie in the range log K/γ = 1.7 ± 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 ± 0.3 at 300° and to log K_1 = 1.7 ± 0.3 at 400°.

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

$$\text{NaCl(c) + TaCl}_5(\text{atm}). = \text{NaTaCl}_6(\text{c}) \qquad (5)$$
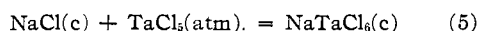
by Morozov and his co-workers with the free energy changes for the same reaction that can be estimated from the measured equilibrium constants for reaction 1. The free energy change of reaction 5 will be related to the equilibrium constant by the equation

$$\Delta F_5 = -RT \ln(a_{\text{NaTaCl}_6}/a_{\text{NaCl}}P_{\text{TaCl}_5})$$
$$= -RT \ln[(K/\gamma P^0_{\text{TaCl}_5})(\gamma_{\text{NaTaCl}_6}/\gamma_{\text{NaCl}})] \qquad (6)$$

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 relation[7]

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

Substitution into formula 6 of the measured values of K/γ, the known values of $P^0_{\text{TaCl}_5}$, 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.

(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°.[3b] 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

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

WILMINGTON, DELAWARE

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

BY C. J. BALLHAUSEN[1] AND ANDREW D. LIEHR

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 dsp² 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

(1) Visiting Scholar 1957–1958. On leave from Chemical Laboratory A, Technical University of Denmark, Copenhagen, Denmark.

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 known[2] 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 $(e_g)^4$

(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).