

TABLE V  
DEGREE OF ASSOCIATION OF MAGNESIUM BROMIDE IN  
DIETHYL ETHER AND TETRAHYDROFURAN

Degree of association	Solvent	Ref.
1.05	Diethyl ether	14
1.09 1.17	Diethyl ether	15
1.00	Tetrahydrofuran	15

most Grignard solutions is largely monomeric  $\text{RMgX} \cdot 2(\text{ether})$ , in accordance with the recent vapor pressure measurements of the ethyl Grignard solution<sup>17</sup> and the species found in the solid state of phenylmagnesium bromide dietherate.<sup>3</sup>

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## The Magnetic Properties of Nickel(II) Complexes Containing a Macrocyclic Ligand and the Existence of a High Spin–Low Spin Equilibrium

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The effect of an axial perturbation produced by a series of anions on the magnetic properties of a nickel(II) ion in the planar field produced by a closed macrocyclic ligand containing four donor nitrogen atoms, tetra-benzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, has been examined. With  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ , and  $\text{B}(\text{C}_6\text{H}_5)_4^-$ , the resultant complexes are diamagnetic and therefore have singlet ground states. With  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{NCS}^-$ , the resultant complexes exhibit moments consistent with triplet ground states. However, for the anions  $\text{Cl}^-$  and  $\text{Br}^-$ , moments intermediate between these two extremes were observed. Measurements of the variation of magnetic susceptibility as a function of temperature between 110 and 300°K. were made. An equilibrium between singlet and triplet states has been assumed to explain the non-Curie–Weiss temperature dependence of the chloride and bromide salts. The calculated enthalpy values for the chloride and bromide are comparable with thermal energies. The entropy changes are small, as expected, but not that predicted by change in spin multiplicity alone.

### Introduction

The effect of a series of ligands of increasing strength on the spin state of certain transition metal ions is expected to produce high-spin compounds for weak field ligands and low-spin compounds for strong field ligands. Consequently, the magnetic moments of such metal complexes are expected to lie in the region of the two extremes, this indeed being the case with the majority of examples. However, a number of complexes of iron, cobalt, and nickel exhibit magnetic moments which lie between these two extremities. The temperature dependence of the magnetic susceptibilities of such compounds would not be expected to follow the usual Curie–Weiss behavior because the apparent magnetic moments of the anomalous compounds are expected to be strongly temperature dependent.

The assumption of an equilibrium between high- and low-spin isomers to explain anomalous magnetic behavior is not new and was proposed by Bozza<sup>1</sup> as long ago as 1933. Cambi and Szego,<sup>2</sup> also around this time, used this concept to explain the anomalous room temperature magnetic moments and non-Curie–Weiss temperature dependence of the magnetic susceptibilities of a series of iron(III) complexes with dialkyl dithiocarbamates. Recent work<sup>3</sup> has confirmed the anomalous room temperature magnetic moments for these compounds. Cambi also proposed an equilibrium between isomers with one and three unpaired electrons to explain the temperature dependence of susceptibility of some cobalt(II) complexes.<sup>4</sup> Theorell and Ehrenberg<sup>5</sup> and George, Beetlestone, and Griffith<sup>6</sup> obtained

spectral and magnetic data for ferrimyoglobin fluoride, cyanide, and hydroxide. Measurements of the magnetic susceptibility between 1 and 30° showed that the susceptibilities of both the high-spin fluoride and the low-spin cyanide follow the Curie law, but that of the hydroxide shows a non-Curie temperature dependence. This was interpreted as arising from an equilibrium between high- and low-spin forms, spectral data being presented to substantiate this conclusion.

The room temperature magnetic moments of some octahedral cobalt(II) complexes with  $\alpha$ -diimines obtained by Figgins and Busch<sup>7</sup> are “intermediate” in value, and an equilibrium mixture of isomeric high-spin and low-spin forms was again suggested. Variation of the magnetic moment of bis(2,6-pyridinedial dihydrazone)cobalt(II) iodide between 80 and 373°K. was explained on the basis of a thermal equilibrium between doublet and quartet states.<sup>8</sup> Other examples of this type of equilibrium for cobalt(II) complexes containing similar ligands have recently been observed by Curry, Burke, and Busch,<sup>9</sup> and Stoufer.<sup>10</sup>

Spin-state isomerism in the case of nickel(II) has been a subject of interest and contention for a number of years. Maki<sup>11</sup> first reported the phenomenon for salicylaldehyde complexes. Her interpretation, as extended by Ballhausen and Liehr,<sup>12</sup> required that the relative energies of the singlet and triplet states be very sensitive to the nature of two ligands located axially, above and below the metal atom which is otherwise bound to a planar array of donor atoms. Most simply, so long as the axial ligands compare closely

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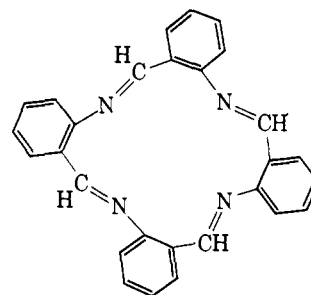
in their binding strength to the in-plane ligands, the structure is grossly octahedral and the triplet state lies lowest. As the axial ligand-field strength is decreased, the singlet state drops in energy relative to the triplet. Thus, at some particular point in relative axial-in-plane ligand field strengths, the singlet and triplet states should coexist.

Intermediate magnetic moments have been reported for many years since the observation of French, Magee, and Sheffield<sup>13</sup> that the solid diamagnetic complex bis(formylcamphorethylenediamine)nickel(II) displayed a moment of 1.9 B.M. in methanol. The formation of six-coordinate species by the addition of two polar solvent molecules was proposed to account for the solution paramagnetism of some salicylaldehyde complexes,<sup>14,15</sup> and Basolo and Matoush<sup>16</sup> were able to isolate crystalline six-coordinate complexes containing 2 moles of pyridine. The partial paramagnetism observed for solid diamagnetic nickel(II) complexes in "noncoordinating" solvents has been more difficult to explain. Molecular weight data, n.m.r. studies, and the concentration dependence of the magnetic moment in inert solvents have supplied evidence that molecular association is responsible for the anomalous magnetic properties of some nickel(II) salicylaldehyde complexes.<sup>17,18</sup> The proposal of a square-planar-tetrahedral equilibrium in inert solvents was made a number of years ago.<sup>14,15</sup> The existence of this phenomenon was demonstrated by Phillips and co-workers for some bis(N,N-disubstituted aminotroponimine)nickel(II) complexes.<sup>19</sup> This type of equilibrium has also been proposed in the cases of some substituted salicylaldehyde nickel(II) complexes<sup>18a,20,21</sup> and some compounds containing substituted phosphine ligands.<sup>22</sup> The existence of an equilibrium in inert solvents between diamagnetic planar, paramagnetic polymer, and paramagnetic tetrahedral forms has been proposed for some 3- and 4-substituted N-arylsalicylaldehyde nickel(II) complexes.<sup>23</sup>

Goodgame and Venanzi<sup>24</sup> examined the axial perturbation by anions X in complexes  $NiL_4X_2$ , where  $L_4$  represents a planar field produced by four neutral donors, from two bidentate ligands. Complexes with anions of negligible or low-coordinating ability are diamagnetic while those of medium to good coordinating power exhibit room temperature magnetic moments consistent with octahedral or weakly tetrag-

onal nickel(II) complexes. No examples were obtained with intermediate room temperature magnetic moments, the data merely dividing the complexes into two groups, those with singlet ground states and those with triplet ground states. The magnetic crossover occurs abruptly between the chloride and bromide derivatives for bis(N,N-diethylethylenediamine)nickel(II) complexes and between the iodide and bromide derivatives for bis(N,N-dimethylethylenediamine)nickel(II) complexes. Recently, Holt, Bouchard, and Carlin<sup>25</sup> found that dichlorotetrakis(N,N'-diethylthiourea)nickel(II) has an anomalous room temperature magnetic moment and a non-Curie-Weiss temperature dependence, which was attributed to a singlet-triplet equilibrium in the solid phase. The bromide derivative, which is diamagnetic at room temperature, becomes weakly paramagnetic at higher temperatures.

We wish to report a study of the magnetic properties resulting from an axial perturbation by anions of a system with a planar field produced by a closed macrocyclic ligand containing four nitrogen donor atoms, tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine,<sup>26,27</sup> later referred to as TAAB.



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## Experimental

The preparation and characterization of the metal complexes containing the macrocyclic ligand have been reported elsewhere.<sup>27</sup> All samples used had analyses and infrared spectra consistent with the formulas assigned. The chloride and bromide salts were precipitated from aqueous solution several times by the addition of the appropriate acid. Infrared spectra, analyses, and room temperature magnetic moments were identical within experimental error after each precipitation. The chloride derivative was also made by bubbling hydrogen chloride gas into a methanolic solution of the perchlorate salt. The measured room temperature magnetic moment was within experimental error ( $\pm 0.02$  B.M.) of that obtained by the previously mentioned procedure and recorded in Table I; its infrared spectrum was also identical with that obtained previously.

TABLE I  
ROOM TEMPERATURE MAGNETIC PROPERTIES

Compound	Temp., °K.	$\chi_M \times 10^6$	$\mu_{eff}$ , B.M.
Ni(TAAB)(ClO <sub>4</sub> ) <sub>2</sub>	300	-35	a
Ni(TAAB)(BF <sub>4</sub> ) <sub>2</sub>	300	-122	a
Ni(TAAB)[B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ] <sub>2</sub>	300	-206	a
Ni(TAAB)Br <sub>2</sub> ·H <sub>2</sub> O	293	614	1.47
Ni(TAAB)Cl <sub>2</sub> ·H <sub>2</sub> O	293	931	1.68
Ni(TAAB)I <sub>2</sub>	299	4000	3.21
Ni(TAAB)(NO <sub>3</sub> ) <sub>2</sub>	301	4250	3.22
Ni(TAAB)(NCS) <sub>2</sub>	302	3960	3.21

<sup>a</sup> Small residual paramagnetism was observed in all cases.

Magnetic measurements were made at room temperature for the perchlorate, fluoroborate, tetraphenylborate, chloride, bromide, iodide, nitrate, and thiocyanate salts by the Gouy method

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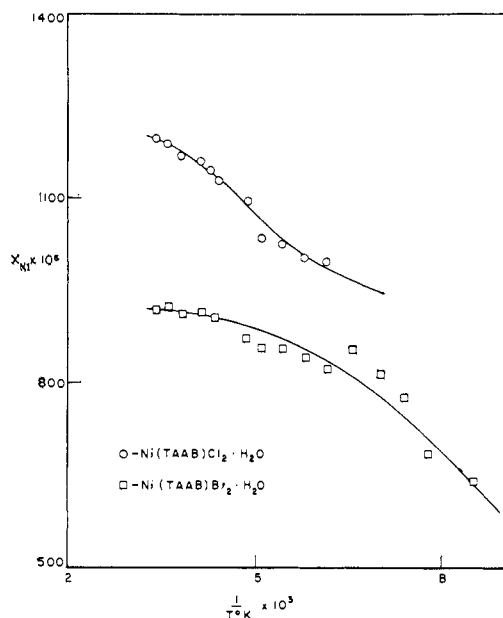


Fig. 1.—Variation of the magnetic susceptibility with the reciprocal of temperature.

using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as standard. Measurements of the variation of magnetic susceptibility as a function of temperature between 110 and 300°K. were made for the chloride, bromide, iodide, and thiocyanate salts using an apparatus constructed by Burke<sup>28</sup> and based on that of Figgis and Nyholm.<sup>29</sup> Diamagnetic corrections for the ligands and anions were calculated from Pascal's constants.<sup>30</sup> The susceptibilities have been determined with a precision of somewhat better than 1%.

### Results and Discussion

The results of room temperature magnetic measurements are recorded in Table I. These data show an increase of the magnetic moment from diamagnetism through intermediate moments to complete paramagnetism as the strength of the axial perturbation is increased. With anions of poor coordinating ability, *viz.*,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{B}(\text{C}_6\text{H}_5)_4^-$ , the resultant complexes are diamagnetic and therefore have singlet ground states. With anions of greater coordinating ability, *viz.*,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{NCS}^-$ , the resultant complexes exhibit moments consistent with triplet ground states. However, with certain anions, *viz.*,  $\text{Cl}^-$  and  $\text{Br}^-$ , moments intermediate between these two extremes were observed. During this change from singlet to triplet ground states, it appears reasonable to assume that the in-plane ligand field remains essentially constant, infrared spectra due to the ligand being the same for the perchlorate as for the thiocyanate except for some very small changes in position of some bands. In view of the strong intramolecular, nonbonded interactions within the macrocycle, any substantial alteration in the metal-donor bond would be expected to cause alterations in such infrared modes as the out-of-plane C-H deformations and the C=N stretching vibrations. Visible reflectance spectra on solid samples are consistent with the associated changes in spin of the ground state.<sup>27</sup> The spectra of the  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ , and  $\text{B}(\text{C}_6\text{H}_5)_4^-$  compounds are consistent with the presence of a planar nickel(II) species, while those of

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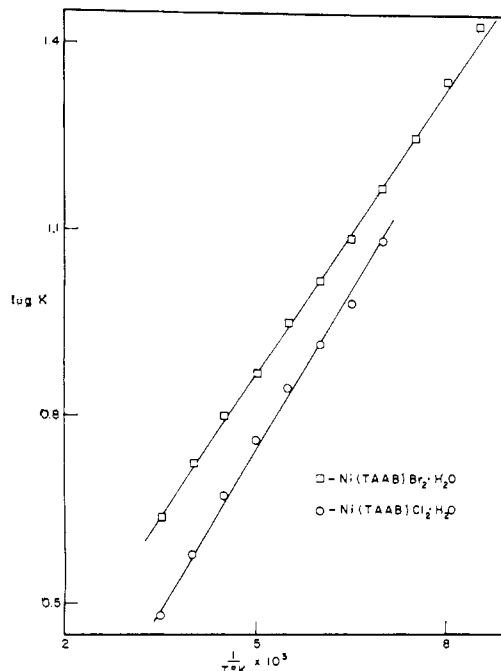
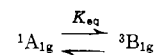


Fig. 2.—Variation of  $\log K_{\text{eq}}$  with the reciprocal of temperature.

the iodide,  $\text{NO}_3^-$ , and  $\text{NCS}^-$  suggest octahedral or tetragonal nickel(II) species. The chloride and bromide show features of both types of spectra.

The results of the determination of the temperature dependence of the magnetic susceptibilities for the chloride and bromide derivatives are summarized in Table II and presented graphically in Fig. 1. The values observed show the phenomenon to be reversible. The results obtained at low temperature for the chloride appear to suggest a leveling of the magnetic susceptibility toward a temperature-independent value as is to be expected when the singlet state predominates. For a small range of ligand field strengths, on either side of the singlet-triplet ground state "cross-over" point, the energy separation between the singlet and triplet states should have a value comparable with thermal energies. The equilibrium arising from thermal distribution between the singlet and triplet states can be written



The equilibrium constant  $K_{\text{eq}}$  can be calculated from  $K_{\text{eq}} = N_{\text{H}}/N_{\text{L}}$ , where  $N_{\text{L}}$  and  $N_{\text{H}}$  represent the mole fractions of the low- and high-spin forms, respectively. These mole fractions can be calculated from the measured magnetic moment at any temperature, assuming the moment of the compound in the high-spin state to be 3.2 B.M., and that of the substance in the low-spin state to be 0.5 B.M. (residual paramagnetism). These values are based on the measured values of the moment at room temperature for the thiocyanate (high spin) and perchlorate (low spin) salts of the cation. The enthalpy and entropy changes for the equilibrium have been calculated by determining  $K_{\text{eq}}$  at a number of temperatures and constructing a graph of  $\log K_{\text{eq}}$  vs.  $1/T$  (°K.). The plot of  $\log K_{\text{eq}}$  vs.  $1/T$  produced a straight line for both the chloride and bromide (Fig. 2). Values of  $+800 \pm 10$  (278  $\text{cm}^{-1}$ ) and  $+700 \pm 10$   $\text{cal. mole}^{-1}$  (245  $\text{cm}^{-1}$ ) were obtained for the enthalpies of the chloride and bromide, respectively.

TABLE II  
THE TEMPERATURE DEPENDENCE OF  
MAGNETIC SUSCEPTIBILITIES

Ni(TAAB)Cl <sub>2</sub> ·H <sub>2</sub> O			Ni(TAAB)Br <sub>2</sub> ·H <sub>2</sub> O		
Temp., °K.	$\chi_{Ni} \times 10^6$	$\mu_{eff}$	Temp., °K.	$\chi_{Ni} \times 10^6$	$\mu_{eff}$
163.0	998	1.14	117.2	641	0.78
173.2	963	1.18	129.0	681	0.84
184.5	1019	1.23	135.3	775	0.92
196.2	1034	1.29	142.2	813	0.97
204.7	1093	1.34	152.7	855	1.03
213.6	1054	1.35	161.8	819	1.04
226.8	1125	1.43	173.2	838	1.08
234.4	1144	1.47	184.8	850	1.13
243.6	1157	1.51	196.6	852	1.16
262.0	1169	1.57	206.5	867	1.20
278.2	1188	1.63	230.1	903	1.30
293.0	1195	1.68	243.4	911	1.34
			260.7	913	1.39
			275.7	926	1.43
			292.6	917	1.47

The  $\Delta H$  values are comparable with thermal energies ( $\Delta E = kT = 208 \text{ cm.}^{-1}$  at  $300^\circ\text{K.}$ ), so that small temperature changes result in differing populations of the  $^3B_{1g}$  and  $^1A_{1g}$  states, and consequently differing magnetic moments.

To conform to the theory of Ballhausen<sup>31</sup> and Ballhausen and Liehr,<sup>12</sup> the entropy changes should be positive for the equilibrium reaction as written above. The total electronic degeneracy of the  $^3B_{1g}$  state is 3 and that of the  $^1A_{1g}$  state is 1, hence the entropy change should be  $R \ln 3$  or  $+2.15 \text{ e.u.}$  The observed entropy changes of  $+0.57 \text{ e.u.}$  for the chloride and  $-0.45 \text{ e.u.}$  for the bromide are small, as expected, but not that predicted by change in spin multiplicity alone. An effect contributing a small negative entropy change must also be included to account for the observed values.

The role of the water molecule in the chloride and bromide complexes is not fully understood. The infrared spectra show a broad band around  $3400 \text{ cm.}^{-1}$  and a shoulder about  $1650 \text{ cm.}^{-1}$  both in determinations with KBr disks and Nujol mulls. No absorptions characteristic of coordinated water could be found at lower energies.<sup>32</sup>

An interesting result of these magnetic studies is the apparent anomalous order of the halide ions in ligand

field strength; *viz.*,  $I > Cl > Br$ . Apparently, in this case, iodide behaves as a better coordinating agent than chloride and bromide and therefore produces a high-spin complex. For first-row transition metals, the order of increasing ligand field strength is usually  $NCS > NO_3 > Cl > Br > I$ , iodide being near the low end of the spectrochemical series. From the electronic spectra of these compounds,<sup>27</sup> the halides appear in their normal positions in the spectrochemical series. In fact, the low-energy triplet-triplet absorption occurs as follows:  $NCS$ , 10,500;  $NO_3$ , 8900;  $Cl \cdot H_2O$ , 8800;  $Br \cdot H_2O$ , 8300; and  $I$ , 8100  $\text{cm.}^{-1}$ .

The water molecule may play an active role in affecting the ligating efficacy of chloride and bromide, for all the other salts are anhydrous (see Table I and ref. 27). It is possible that the molecule of water is hydrogen bonded to the smaller halide in such a way that the interaction of that ion with the metal atom is limited. In this regard it should be mentioned that considerable difficulty has attended attempts to produce the anhydrous salts; *e.g.*, vacuum drying appears to result in the elimination of hydrogen halide. Concluding from the spectral data that the halides exhibit a normal spectrochemical order when the triplet is the ground state, it is assumed that, for the singlet state, the water molecule may be hydrogen bonded to the halide<sup>24</sup> and that the axial ligand field due to the halide is thereby reduced sufficiently to produce a singlet ground state. The equilibrium would therefore involve both a change in electronic structure and an alteration in the anion-water interaction. The process envisioned may provide the small negative entropy change required to explain the experimental data.

Other examples of tetragonal nickel complexes have been reported in which water molecules appear to change the spin state of the nickel atom, although no intermediate magnetic moments were produced.<sup>24,33,34</sup> The function of the water molecule in all these systems appears to be unusual, and possibly similar. The phenomenon is certainly worthy of further investigation.

**Acknowledgment.**—The financial support of the National Institutes of Health is gratefully acknowledged.

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