formation of a previously described[7] nonstoichiometric brown nickel fluoride $NiF_{2.x}$ residue. Contrary to the pyrolysis of $(NO)_2NiF_6$, which results in the formation of $NF_3O$,[13] no evidence for the formation of the unknown compound $ClF_5O$ was observed.

The presence of $ClF_2O^+$ and $NiF_6^{2-}$ ions in $(ClF_2O)_2NiF_6$ was established by vibrational spectroscopy. The spectra of the solid showed bands characteristic for $ClF_2O^+$ (IR, 1324 vs ($\nu_1$), 700 vs, br ($\nu_2$, $\nu_5$), 502 s ($\nu_3$), 406 m ($\nu_4$), 376 m ($\nu_6$))[11] and $NiF_6^{2-}$ (IR, 625 vs ($\nu_3$), 330 m ($\nu_4$); Raman, 565 vs ($\nu_1$), 525 s, 512 ms ($\nu_2$), 308 m, 290 w ($\nu_5$))[7] with $\nu_2$ and $\nu_5$ of $NiF_6^{2-}$ showing splittings due to lifting of the degeneracies of these modes. Due to the intense color of the sample, it ws difficult to obtain Raman spectra and only the bands due to $NiF_6^{2-}$ could be observed even at −100 °C.

**Conclusion.** The above results show that $ClF_2O^+$ salts derived from unstable Lewis acids, such as $NiF_4$, can be prepared by metathetical methods. Furthermore, $(ClF_2O)_2NiF_6$ is the first example of $ClF_2O^+$ having been coupled successfully to a highly energetic anion in the form of a stable salt.

**Acknowledgment.** The authors are grateful to Drs. C. J. Schack and L. R. Grant and R. D. Wilson for their help. This work was supported in part by the Office of Naval Research.

**Registry No.** $(ClF_2O)_2NiF_6$, 91443-95-7; $ClF_2OSbF_6$, 38199-85-8; $Cs_2NiF_6$, 17218-49-4.

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(13) Bartlett, N.; Passmore, J.; Wells, E. J. *Chem. Commun.* **1966**, 213.

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## Dynamic Jahn-Teller Effects in High-Spin Trigonal-Bipyramidal Nickel(II) Complexes

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Trigonal-bipyramidal nickel(II) complexes have long been known to have a room-temperature magnetic moment distinctly smaller than the value that would be expected for a $^3E'$ ground state.[1,2] This has been attributed either to an admixture of an excited orbital doublet state,[3] which has a smaller $M_L$ value as compared to that of the ground state, or to Jahn-Teller effects.[4] Recently Hempel and Miller[5] reproposed the validity of the former hypothesis on the basis of ligand field calculations, which allowed the authors to reproduce the room-temperature magnetic moment of [NiBr(Me$_6$tren)]Br (Me$_6$tren = 2,2′,2″-tris(dimethylamino)triethylamine) and to predict a value of 3.35 $\mu_B$ for the moment at 5 K.

To our knowledge no data are available in the literature relative to low-temperature magnetic susceptibility for high-spin trigonal-bipyramidal nickel(II) complexes. Since, in principle, magnetic measurements can give some information on the energies of the spin-orbit low-symmetry split components of the ground $^3E'$ level, we decided to measure the magnetic susceptibilities of [NiBr(Me$_6$tren)]Br and [NiNCS(Me$_6$tren)]SCN·H$_2$O. For these two complexes the crystal structures are available,[4,6] and for the latter single-crystal polarized electronic spectra have been published as well.[4]

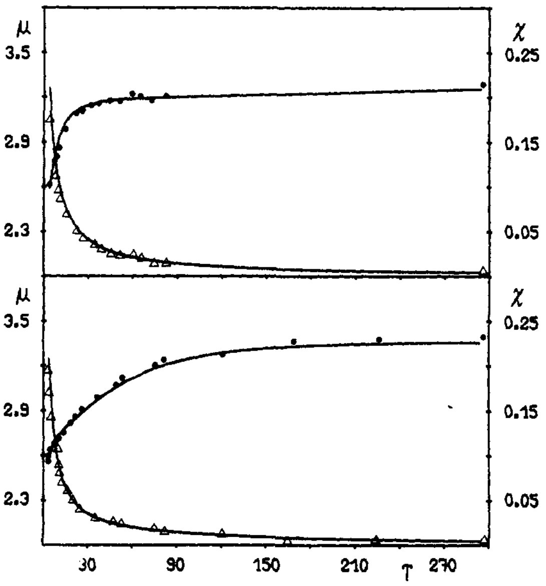

**Figure 1.** Observed values of magnetic moments (●) and susceptibility (△) for [NiBr(Me$_6$tren)]Br (bottom) and [NiNCS(Me$_6$tren)]-NCS·H$_2$O (top). The curves reproduce the calculated values with the model described in the text.

**Table I.** Best-Fit Values of Angular Overlap Parameters for [NiBr(Me$_6$tren)]Br and [*NiNCS(Me$_6$tren)*]*SCN*·H$_2$O

| | Br | | | NCS | | |
|---|---|---|---|---|---|---|
| | $r^a$ | $e_\sigma$ | $e_\pi$ | $r^a$ | $e_\sigma$ | $e_\pi$ |
| $N_{ax}$ | 2.10 | 4326 | | 2.04 | 4335 | |
| $N_1$ | 2.13 | 4350 | | 2.13 | 4270 | |
| $N_2$ | 2.13 | 4350 | | 2.08 | 4270 | |
| $N_3$ | 2.13 | 4350 | | 2.09 | 4270 | |
| X | 2.467 | 4800 | 1400 | 1.97 | 5820 | 1000 |

[a] The distance of the indicated atom to the metal ion.

The magnetic susceptibility data for the complexes were measured with two different techniques: a Faraday balance was used for [NiBr(Me$_6$tren)]Br and a vibrating-sample magnetometer for [NiNCS(Me$_6$tren)]SCN·H$_2$O. The temperature dependence of the magnetic susceptibility and of the effective magnetic moment of the two complexes (which agree with a paramagnetic behavior) is shown in Figure 1. The room-temperature moments are 3.30 $\mu_B$ for the thiocyanate and 3.42 $\mu_B$ for the bromide derivative. They decrease steadily until they become 2.61 $\mu_B$ for the former and 2.56 $\mu_B$ for the latter at 4.2 K, slightly below the spin-only value. These data appear to contrast with the predictions of previous theoretical treatments, which require much higher moments at low temperature.[5]

In order to interpret these data, the angular-overlap model (AOM) was used in the form first suggested by Gerloch.[7] The $e_\lambda$ ($\lambda = \sigma, \pi$) parameters were chosen in such a way to reproduce also the electronic transitions,[4,8] by analogy to the values reported for the similar cobalt(II) complexes.[9] The

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(1) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343.
(2) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227.
(3) Wood, J. S.; Greene, P. T. *Inorg. Chem.* **1969**, *8*, 491.
(4) Bertini, I.; Ciampolini, M.; Dapporto, P.; Gatteschi, D. *Inorg. Chem.* **1972**, *11*, 2254.
(5) Hempel, J. C.; Miller, M. E. *J. Chem. Phys.* **1981**, *75*, 2959.
(6) Di Vaira, M.; Orioli, P. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 595.
(7) Gerloch, M.; McMeeking, R. F. *J. Chem. Soc., Dalton Trans.* **1975**, 2443.
(8) Ciampolini, M.; Nardi, N.; Speroni, G. P. *Coord. Chem. Rev.* **1966**, *1*, 222.
(9) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1975**, *14*, 812.

0020-1669/84/1323-3262$01.50/0

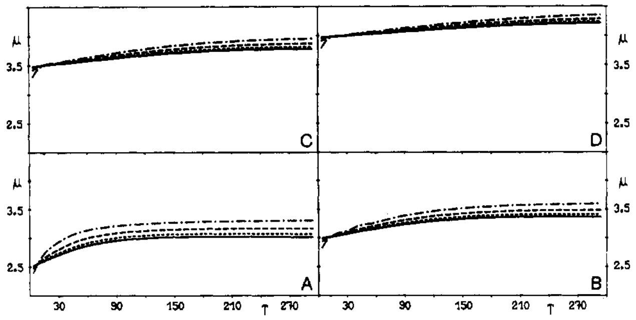

**Figure 2.** Calculated values of magnetic moments for [NiBr(Me$_6$tren)]Br for different values of $k_\parallel$ and $k_\perp$. The curves refer to $k_\perp$ = 0.25 (—), 0.50 (···), 0.75 (---), and 1.0 (-·-) with $k_\parallel$ = 0.25 (A), 0.50 (B), 0.75 (C), and 1.0 (D). The AO and Racah parameters are those reported in Tables I and II.

Table II. Best-Fit Parameters[a] for Magnetic Moments and Susceptibilities for [NiBr(Me$_6$tren)]Br and [NiNCS(Me$_6$tren)]SCN·H$_2$O

| | $B^b$ | $C^b$ | $\zeta^c$ | $k_x$ | $k_y$ | $k_z$ |
|---|---|---|---|---|---|---|
| Br | 850 | 3250 | 649 | 0.93 | 0.93 | 0.34 |
| SCN | 850 | 3250 | 649 | 0.90 | 0.94 | 0.50 |

[a] The AO parameters are those reported in Table I. [b] Racah parameters in cm$^{-1}$. [c] Spin–orbit coupling constant in cm$^{-1}$.

$e_\pi$ parameters for the nitrogen donor atoms of the tripod ligand were assumed to be zero. The bromide derivative has crystal $C_3$ symmetry, while the thiocyanate has only $C_1$ symmetry. For the calculation the geometrical parameters seen in the crystal structure were used, but no attempt was made to use different $e_\sigma$ parameters for the three equatorial donors of the thiocyanate derivatives. The best-fit values are shown in Table I. In order to reproduce the experimental magnetic susceptibility data, we first attempted to use isotropic $\zeta$, the spin–orbit coupling constant, and $k$, the Stevens orbital reduction factor.[10,11] In this hypothesis, for any set of $e_\lambda$, $k$, and $\zeta$ values the calculated magnetic moment decreases only slightly from room temperature to the 4.2 K value, as shown by the graphics in Figure 2, in agreement with previous calculations.[5] We tried then to use anisotropic $k$ values, as is common practice in EPR spectroscopy.[12] We found, as shown in Figure 2, that in order to have the magnetic moment distinctly smaller than the spin-only value at liquid-helium temperature with room-temperature magnetic moments close to the observed values it is necessary to have small $k_\parallel$ values. Increasing $k_\parallel$ raises all the curves and decreases the difference in $\mu$ at room and liquid-helium temperature. The calculated magnetic moments and susceptibilities are shown in Figure 1, and the best-fit values are given in Table II. $k_\parallel$ is required to be slightly higher for the less symmetric thiocyanate derivative.

Although anisotropic $k$ values are commonly used in the literature,it is by no means common to have such a large difference in $k_\perp$($k_x$ and $k_y$) and $k_\parallel$($k_z$), with such a small $k_\parallel$. Recently Gerloch observed that in ordder to reproduce the experimental magnetic anisotropy of pseudotetrahedral nickel(II) complexes anomalously low values of $k$ and $\zeta$ must be used,[13,14] while normal values are required for the corresponding cobalt(II) complexes. He suggested that the anomaly could be explained either by the Ham[15] effect or by the admixture of the ligand orbitals into the ground state. While, in the cases he considered, the latter could be an explanation, since he considered bromo and iodo derivatives, in our case, when essentially similar results are found for the bromo and the thiocyanate derivatives, the first explanation seems more feasible.

The Ham effect requires that the first-order orbital angular momentum matrix elements be reduced by vibronic coupling.[15] In $D_{3h}$ symmetry, the orbital E′ level has first-order orbital angular momentum only parallel to $z$; therefore, the vibronic quenching will occur only parallel to the axis, thus determining a small $k_\parallel$ value. Since no orbital angular momentum is predicted parallel to $x$ and $y$, the vibronic quenching will not operate in this case and $k_\perp$ will take the normal values expected for a nickel(II) complex. When the symmetry is lower than $D_{3h}$, the above considerations are no longer strictly valid, but they will keep much of their validity as long as the symmetry does not depart too much from $D_{3h}$. As a matter of fact, we find smaller $k_z$ values for the more symmetric bromide as compared to those for the thiocyanate derivative, suggesting a larger quenching for the former.

It seems safe to conclude therefore that the Ham effect is responsible for the low magnetic moments of high-spin trigonal-bipyramidal nickel(II) complexes, yielding a large vibronic quenching of the $z$ component of the orbital angular momentum.

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**Registry No.** [Ni(Me$_6$tren)Br]Br, 57036-60-9; [Ni(Me$_6$tren)NCS]SCN·H$_2$O, 38883-26-0.

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(10) Stevens, K. W. H. *Proc. R. Soc. London, Ser. A* **1953**, *219*, 542.

(11) In the Hamiltonian we use in the calculation, the orbital reduction parameter, $k$, is present both in the spin–orbit coupling and in the Zeeman terms.

(12) Bencini, A.; Gatteschi, D. *Transition Met. Chem.* (*Weinheim, Ger.*) **1982**, *8*, 1.

(13) Gerloch, M.; Hanton, L. R. *Inorg. Chem.* **1980**, *19*, 1962.

(14) Gerloch, M.; Hanton, L. R. *Inorg. Chem.* **1981**, *20*, 1046.

(15) Ham, F. S. *Phys. Rev. A* **1965**, *138*, 1727.

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## Synthesis of Sodium and Tetra-*n*-butylammonium Dicyanodihydroborates

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The cyanotrihydroborate ion, BH$_3$CN$^-$, has been extensively employed as a highly selective reducing agent in organic synthesis.[1] Its utility is derived in part by the electron-withdrawing cyano group, moderating its reducing ability and imparting enhanced stability in protic solvents and acidic media. A further replacement of hydride by cyano to give BH$_2$(CN)$_2^-$ would be expected to lead to further moderation of reducing ability. We have now prepared the BH$_2$(CN)$_2^-$ anion as the sodium and tetra-*n*-butylammonium salts and have carried out some preliminary experiments to assess its reducing capability in contrast with sodium cyanotrihydroborate.

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(1) For two recent reviews, see: (a) Hutchins, R. O.; Natale, N. R. *Org. Prep. Proced. Int.* **1979**, *11*, 201. (b) Lane, C. F. *Synthesis* **1975**, *135*.