

Nickel(II) in a Weak Tetragonal Field

Sir:

There has recently been considerable interest in the apparently four-coordinate nickel(II) complexes which exhibit anomalous magnetic moments in solution or in the melt. This behavior has been ascribed to: (a) the formation of six-coordinate species by the addition of two polar solvent molecules,^{1,2} (b) a square-planar-tetrahedral equilibrium in inert solvents,^{3,4} (c) solute-solute association,^{5,6} and (d) an equilibrium between spin-paired and spin-free planar nickel(II) species.^{7,8} While examples of the first three mechanisms are well known,¹⁻⁶ the last, while potentially of interest from the standpoint of obtaining information concerning the electronic structure of Ni(II), has not previously been reported. The difficulty in examining this type of behavior has been the unavailability heretofore of a Ni(II) complex which illustrates this phenomenon. We wish to report our studies on a system where nickel, in the crystalline phase, is found predominantly in the diamagnetic state, with a thermally accessible triplet state.

Dichlorotetrakis(N,N'-diethylthiourea)nickel(II) is green at room temperature and is presumed to be *trans*-octahedral in the solid state on the basis of comparison with other substituted thiourea complexes.⁹ The recrystallized compound is diamagnetic and blue at low temperature (77-194°K.) and attains partial paramagnetism, reversibly, as the temperature is raised; data obtained by the Gouy method are summarized in the first two columns of Table I. We are

TABLE I
MAGNETIC MOMENTS AND DERIVED QUANTITIES FOR [Ni(detu)₄Cl₂]

Temp., °K.	μ , B.M. ^a	N_1	N_3	K	ΔE , ^b cm. ⁻¹
280	1.10	0.88	0.12	0.14	605
290	1.22	0.85	0.15	0.17	580
300	1.33	0.82	0.18	0.21	555
310	1.46	0.79	0.21	0.27	525
320	1.57	0.76	0.24	0.33	495
330	1.69	0.72	0.28	0.40	465
340	1.81	0.67	0.33	0.48	435
350	1.93	0.63	0.37	0.59	400
360	2.05	0.58	0.42	0.72	360
370	2.17	0.53	0.47	0.88	315

^a Read from a least-squares plot of 30 points over the range 270-370°K. ^b Calculated from eq. 10 of ref. 7.

forced to conclude that, in [Ni(detu)₄Cl₂], the nickel resides in a weak tetragonal field,⁷ and that the magnetic moment is governed only by the thermal population of a low-lying paramagnetic level.

- (1) F. Basolo and W. R. Matoush, *J. Am. Chem. Soc.*, **75**, 5663 (1953).
- (2) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431, 3435 (1955).
- (3) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).
- (4) (a) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); (b) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).
- (5) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).
- (6) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).
- (7) C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959).
- (8) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162, 1129 (1958).
- (9) Yellow [Ni(tu)₄Cl₂] (tu is thiourea) is *trans*-octahedral,¹⁰ and yellow [Ni(etu)₄Cl₂] (etu is ethylenethiourea) is also *trans*-octahedral.¹¹ Substitution of N,N'-diethylthiourea (detu) is assumed not to change the gross geometry of the coordination sphere: we hope to settle this question by complete crystal structure analysis. The compound is prepared by reaction of NiCl₂·6H₂O with diethylthiourea in butanol and is a nonconductor in solution. *Anal. Calcd.*: C, 36.22; H, 7.23; Found: C, 36.21; H, 7.55.
- (10) A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).
- (11) Unpublished work by S. L. Holt, Jr. in this laboratory.

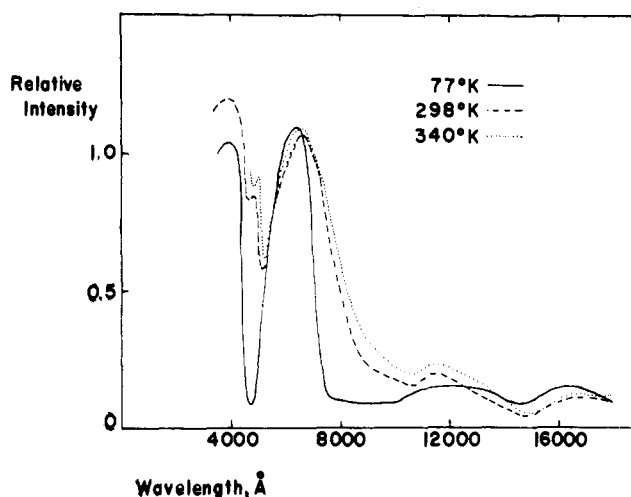
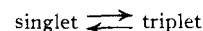


Fig. 1.—Reflectance spectra of [Ni(detu)₄Cl₂] as a function of temperature.

The analogous blue-green bromo and green iodo compounds are diamagnetic at room temperature, but the bromo compound appears to become feebly paramagnetic at higher temperatures (100°). Since chloride is closer to N,N'-diethylthiourea than bromide or iodide in the spectrochemical series,¹² the tetragonal component of the field in the Br⁻ and I⁻ complexes is larger than in the Cl⁻ compound, which accords with the observed magnetic behavior.

An expression has been derived⁷ for the temperature dependence of magnetic susceptibility of tetragonal Ni(II) complexes where the separation, ΔE , between the ¹A ground state and the ³B state is small. We assume the magnetic moment of the fully paramagnetic [Ni(detu)₄Cl₂] to be 3.2 B.M.,¹³ and have calculated ΔE as a function of temperature. The calculations (Table I) indicate a decrease in tetragonality with increasing temperature, consistent with in-plane vibrational motions, but because of the approximations in the derivation of the equation used, no further significance can be attached to this behavior.

The equilibrium constant, K , for the reaction



may be calculated from a knowledge of the mole fractions, N_1 and N_3 , of the individual singlet and triplet species. A plot of $\ln K$ vs. $1/T$ has a slight curvature, confirming the variation of ΔE with temperature, and from the slope at 25° we calculate $\Delta \bar{H}_{298} = 4$ kcal./mole, $\Delta F = 0.9$ kcal./mole, and $\Delta S = 10$ e.u. The fact that ΔH is larger than ΔE , and that ΔS is larger than $R \ln 3$, suggests that the reaction being considered involves not only the uncoupling of spins, but also a loosening up of the lattice. X-Ray powder patterns have been obtained at both 77 and 300°K., and these show that the gross crystal structure does not change with temperature; there is no evidence of any lines splitting.

A second important observation on this system is recorded in Fig. 1, where it will be noted that the intensity of the absorption band at 4900 Å. increases markedly with temperature. We believe that this band may be assigned to a transition from the ³B excited state to a higher energy level. This result accords nicely with the magnetic results.¹⁴

(12) R. L. Carlin and S. L. Holt, Jr., *Inorg. Chem.*, **2**, 849 (1963).

(13) The moment of [Ni(etu)₄Cl₂] is 3.29 B.M. ($\theta = -15^\circ$), of [Ni(etu)₆(ClO₄)₂] is 3.22 B.M., and of [Ni(detu)₆(ClO₄)₂] is 3.17 B.M.

(14) A referee has suggested that these results may alternately be ascribed to the effects of antiferromagnetism. We believe that this is unlikely for the following reasons. The shortest Ni-Ni distance¹⁰ in [Ni(tu)₄Cl₂]

Acknowledgment.—This research has been supported by a grant from the National Science Foundation, and by the ARPA program at Brown. We thank Professor A. Wold for arranging the measurement of the powder patterns at Lincoln Laboratory.

is over 8 Å., and we assume that it is at least as large in $[\text{Ni}(\text{detu})_2\text{Cl}_2]$. Metal-metal bonding is therefore not evident, nor is a path for superexchange interaction apparent in the structure¹⁰ of $[\text{Ni}(\text{tu})_4\text{Cl}_2]$. We also assume its absence here. Furthermore the spectra (Fig. 1) are similar to other compounds with a tetragonal field,¹¹ such as $[\text{Ni}(\text{etu})_4](\text{ClO}_4)_2$. Lastly, the effects of magnetic coupling on spectra are not well known, but appear to be small.¹² The temperature dependence of the spectrum therefore does not appear to be due to exchange effects.

(15) J. W. Stout, *J. Chem. Phys.*, **31**, 709 (1959); D. S. McClure, *ibid.*, **38**, 2289 (1963).

METCALF CHEMICAL LABORATORIES
BROWN UNIVERSITY
PROVIDENCE 12, RHODE ISLAND

S. L. HOLT, JR.
R. J. BOUCHARD
R. L. CARLIN

RECEIVED OCTOBER 30, 1963

Orbital Degeneracy and the Electron Spin Resonance Spectrum of the Benzene-1-*d* Negative Ion¹

Sir:

In recent years there has been considerable interest in the Jahn-Teller theorem² and in the simpler molecules such as the negative ion radical of benzene to which it is applicable.^{3,4} The ground electronic state of this radical is doubly degenerate, but the substitution of a methyl group as in the toluene and *p*-xylene anions has a large enough effect to remove the degeneracy.^{4,5} Although the substitution of deuterium for hydrogen in a free radical normally has a negligible effect on the spin-density distribution, it is possible that the degeneracy of the benzene anion would be lifted by deuterium substitution, and we consequently have investigated the electron spin resonance spectrum of the negative ion of benzene-1-*d*.

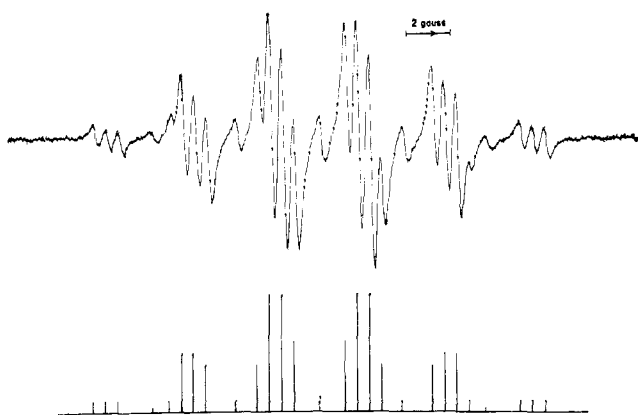


Fig. 1.—First derivative of the e.s.r. spectrum of the benzene-1-*d* anion. The reconstruction includes dotted lines corresponding to a 4% impurity of C_6H_6^- .

The e.s.r. spectrum of the benzene-1-*d* anion is shown in Fig. 1. Benzene-1-*d*, which was prepared by the

(1) Supported in part by the National Science Foundation through Grant NSF-GP-1370.

(2) H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)*, **A161**, 220 (1937); H. A. Jahn, *ibid.*, **A164**, 117 (1937).

(3) W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.*, **33**, 1695 (1960); H. M. McConnell and A. D. McLachlan, *ibid.*, **34**, 1 (1961); H. M. McConnell, *ibid.*, **34**, 13 (1961).

(4) T. R. Tuttle, Jr., and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).

(5) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961); T. R. Tuttle, Jr., *J. Am. Chem. Soc.*, **84**, 1492 (1962); V. V. Voevodskii, S. P. Solodovnikov, and V. M. Chibrikov, *Dokl. Akad. Nauk SSSR*, **129**, 1982 (1959).

(6) L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, 235 (1946).

method of Weldon and Wilson,⁶ was dissolved in a 1,2-dimethoxyethane-tetrahydrofuran mixture and reduced to the anion radical with a sodium-potassium alloy using the procedure of Bolton.⁷ An X-band superheterodyne spectrometer⁸ was employed with a sample temperature of -100° . The spectrum is readily interpreted as arising from $\text{C}_6\text{H}_5\text{D}^-$ with about a 4% impurity of C_6H_6^- . The latter serves as a convenient internal standard, and the hyperfine splittings relative to benzene, $r^{\text{X}_i} = a^{\text{X}_i}(\text{C}_6\text{H}_5\text{D})/a^{\text{H}}(\text{C}_6\text{H}_6)$, are: $r^{\text{H}_2} = r^{\text{H}_3} = r^{\text{H}_5} = r^{\text{H}_6} = 1.046 \pm 0.002$, $r^{\text{H}_4} = 0.908 \pm 0.005$, and $r^{\text{D}_1} = 0.148 \pm 0.002$. Using $a^{\text{H}}(\text{C}_6\text{H}_6) = 3.75$ gauss^{4,7} gives (in gauss): $a^{\text{H}_2} = 3.92 \pm 0.01$, $a^{\text{H}_4} = 3.41 \pm 0.01$, and $a^{\text{D}_1} = 0.55 \pm 0.01$. The widths of both the deuterated and undeuterated benzene anion absorption lines were the same within experimental error and had the value 0.3 gauss between points of extreme slope. The symmetry of the $\text{C}_6\text{H}_5\text{D}^-$ spectrum about the central line of the C_6H_6^- spectrum implies an equality of the *g*-values of the two radicals to within three parts in 10^6 .

The spectrum of the monodeuteriobenzene anion thus shows that the twofold degeneracy of the ground electronic state of the benzene negative ion is lifted on deuterium substitution. The increase relative to the benzene negative ion of the spin densities from positions 2, 3, 5, and 6, and the decrease at the other positions, indicates that the orbital which is antisymmetric with respect to reflection in the plane through the 1 and 4 positions makes a greater contribution than the symmetric orbital. The antisymmetric orbital is also predominant, and to a much larger extent, in the toluene and *p*-xylene anions.⁵ The direction of the changes that we have found on deuterium substitution is consistent with the secondary isotope effects observed on rates and equilibria.⁹ In the methyl-substituted anions, the stabilization of the antisymmetric orbital is thought to arise from the electron-repelling effect of the methyl groups,^{5,10} but the importance of vibronic interactions is not fully understood. The role of these interactions in the deuteriobenzene anions is currently under investigation.

Adding together the hyperfine splittings in the monodeuteriobenzene anion gives $(1/6)(4r^{\text{H}_2} + 2r^{\text{H}_4}) = 1.000 \pm 0.001$, so that a constant value of $Q_{\text{CH}^{\text{H}}}$ in McConnell's¹¹ relation $a^{\text{H}_i} = Q_{\text{CH}^{\text{H}_i}}^{\text{H}}$ for C_6H_6^- and $\text{C}_6\text{H}_5\text{D}^-$ implies the equality of the spin densities at the 1- and 4-positions in the deuterated radical. There is thus a small but significant isotope effect since $a^{\text{H}_4}/a^{\text{D}_1} = 6.15 \pm 0.11$ while the value of 6.514 is expected if the difference in proton and deuterium splittings is caused only by the magnetic properties of the two isotopes.¹²

The anion of benzene-1,4-*d*₂ has also been observed, but the sample was contaminated with an appreciable amount of benzene-1-*d*. Preliminary studies indicate the spectrum is consistent with predictions based on the spectrum of the benzene-1-*d* anion. Further aspects of the effect of deuterium substitution on the benzene anion spectrum are being actively investigated.

(7) J. R. Bolton, *Mol. Phys.*, **6**, 219 (1963).

(8) J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955); J. W. H. Schreurs and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 756 (1961).

(9) E. A. Halevi in "Progress in Physical Organic Chemistry," Vol. 1 Interscience Publishers, Inc., New York, N. Y., 1963.

(10) T. H. Brown, M. Karplus, and J. C. Schug, *J. Chem. Phys.*, **38**, 1749 (1963); T. H. Brown and M. Karplus, *ibid.*, **39**, 1115 (1963).

(11) H. M. McConnell, *ibid.*, **24**, 633, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(12) B. Venkataraman and G. K. Fraenkel, *ibid.*, **33**, 588 (1965).