The Electronic Ground State of Bis(maleonitriledithiolene)nickel Monoanion. Sulfur-33 Hyperfine Interaction

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Abstract: We have observed satellites due to hyperfine coupling of the electron spin with naturally abundant ^{33}S in the epr spectra of bis(maleonitriledithiolene)nickel monoanion and several related nickel dithiolene monoanion complexes. We have analyzed the hyperfine tensor of ^{33}S in a single crystal of $(n\text{-}Bu_4N)[CuS_4C_4(CN)_4]$ containing approximately 1% of the nickel complex as a substituent. The hyperfine tensor has axial symmetry within experimental error, and the unique axis is found to lie along the normal to the plane of the complex. The ^{33}S tensor is thus not consistent with an ^2A_g ground state but rather supports a $^2B_{3g}$ ground state in which the half-filled out-of-plane π molecular orbital is extensively delocalized over the ligands. The result is consistent with earlier conclusions from paramagnetic resonance where these were based only on ^{61}Ni hyperfine structure and the *g* tensor.

Delocalization of the unpaired electrons of paramagnetic transition metal complexes over ligand orbitals frequently results in the appearance of ligand hyperfine structure in the electron paramagnetic resonance (epr) spectrum. The ligand hyperfine structure provides direct information about the nature of the electronic ground state of the complex and the extent of electron spin delocalization over ligand orbitals. We have observed hyperfine satellites in the epr spectra of several monoanion bis(dithiolene)nickel complexes which are due to ^{33}S in natural abundance (0.74%, $I = {}^3/_2$). We have examined in detail the ^{33}S hyperfine tensor of bis(maleonitriledithiolene)nickel anion ($Ni(mnt)_2^-$) at 1% concentration in a single crystal of diamagnetic, isomorphous, $(n\text{-}Bu_4N)[CuS_4C_4(CN)_4]$. ^{33}S satellites were also observed in the low-temperature glass epr spectra of this and several other bis(dithiolene)nickel monoanion complexes.

Two ground-state configurations have been proposed for $Ni(mnt)_2^-$ ($S' = {}^1/_2$). The first of these was proposed by Gray, *et al.*,[2,3] and is $(\ldots 4b_{2g}{}^2 4a_g{}^1)$. The half-filled $4a_g$ molecular orbital was calculated[2] to be a linear combination of $d_{x^2-y^2}$ on the metal and in-plane $3p_{y'}$ orbitals on the four sulfur atoms. The prime refers to a local sulfur atom coordinate system. We are using the coordinate system given in Figure 1. The important feature to be noted about this configuration is that near the sulfur atom the electron density is contained in a p-type orbital directed *in the molecular plane.*[4]

The second configuration for the ground state was obtained from single-crystal paramagnetic resonance measurements[5] and is $(\ldots a_g{}^2 b_{3g}{}^1)$. This configuration was also found for the similar ion $NiS_4C_4H_4^-$ by independent molecular orbital calculations of Schrauzer and Mayweg.[6,7] The b_{3g} (or $3b_{2g}$) orbital has been found to be largely delocalized over the ligands. The molecular orbital calculation for $NiS_4C_4H_4^-$ found it to be 18% d_{yz} (Figure 1) on the metal atom,[6] while analysis of the *g* tensor and ^{61}Ni hyperfine tensor[5] of $Ni(mnt)_2^-$ yielded 25–50% d_{yz}. In this case, however, the electron density near the sulfur atoms is contained in *out-of-plane* $3p_{z'}$ orbitals ($z = z'$, see Figure 1).

We shall use the properties of the ^{33}S hyperfine tensor to estimate the extent of electron delocalization in the half-filled molecular orbital and to show that it agrees only with the $^2B_{3g}$ ground state of the two possibilities mentioned above.

Ligand Atom Hyperfine Interaction

The interaction between the magnetic moment of a nucleus and the magnetic field set up by the spin moments of the electron can be described by the Hamiltonian in eq 1.

$$\mathcal{H}_{hf} = 2\gamma_n\beta_0\sum_k\{r_k{}^{-5}[3(\mathbf{r}_k\cdot\mathbf{s}_k)(\mathbf{r}_k\cdot\mathbf{I}) - r_k{}^2(\mathbf{s}_k\cdot\mathbf{I})] + [8\pi\delta(r_k)/3]\mathbf{s}_k\cdot\mathbf{I}\} \quad (1)$$

The coupling of electronic orbital momentum with the nuclear spin will be neglected since, for complexes whose *g* values do not differ greatly from 2, this will yield a negligible contribution to the hyperfine Hamiltonian.[8] In eq 1, γ_n is the nuclear magnetogyric ratio, β_0 is the Bohr magneton, $\mathbf{r}_k$ is the electron–nucleus vector, $\mathbf{s}_k$ the spin momentum operator of the *k*th electron, $\delta(r_k)$ its δ function at the nucleus in question, and $\mathbf{I}$ is the spin momentum operator of the nucleus. Evaluation of the matrix elements of $\mathcal{H}_{hf}$ for a ligand atom is not quite straightforward since the operators must be re-

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[1] National Aeronautics and Space Administration Predoctoral Fellow.

[2] S. I. Shupack, E. Billig, R. F. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

[3] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966).

[4] Actually, in D_{2h} symmetry $3p_{y'}$ and $3p_{x'}$ as well as 3s orbitals can mix. Although no such mixing is indicated in the published[2] mo eigenvectors of $Ni(mnt)_2^-$, a small admixture of $3p_{x'}$ into the $4a_g$ orbital would merely rotate the principal axis of the local spin distribution slightly away from y', but it will remain in the plane of the molecule. For the purposes of further discussion, we will assume that the $4a_g$ orbital is made up of only a $3p_{y'}$ p-orbital contribution near sulfur.

[5] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

[6] G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 3585 (1965).

[7] The out-of-plane π antibonding orbital which has its lobes directed toward the ligands is labeled $4b_{2g}$, $3b_{2g}$, and b_{3g} in ref 2, 6, and 5, respectively. References 2 and 6 label the axis bisecting both ligands *x*, while in ref 5 and this current work it is labeled *y*. We will refer to the orbital as b_{2g} when discussing ref 2 and 6 with the understanding that, whether labeling the orbital b_{2g} or b_{3g}, we refer to the orbital which reduces to a d_{yz} orbital on the metal atom in Figure 1.

[8] W. Marshall, "Paramagnetic Resonance," Vol. I, Academic Press Inc., New York, N. Y., 1963, p 347.

ferred to a coordinate system centered on the ligand nucleus. If we assume that the principal axis system for $^{33}S_I$ is as shown in Figure 1, the spin Hamiltonian for its hyperfine interaction is given in the $x'y'z$ coordinate system by eq 2, where $A_{x'x'}$, $A_{y'y'}$, and A_{zz} are the

$$\mathcal{H}_S' = A_{x'x'}I_{x'}S_{x'} + A_{y'y'}I_{y'}S_{y'} + A_{zz}I_zS_z \qquad (2)$$

elements of the diagonal hyperfine tensor. We can now express (2) in the molecule-fixed xyz coordinate system centered on $^{33}S_I$ by a suitable coordinate transformation. We obtain eq 3. The spin Hamiltonian (eq 3) gives the correct hyperfine interaction when the

$$\mathcal{H}_S = A_{zz}I_zS_z + {}^1/_4(A_{x'x'} + A_{y'y'})(I_+S_- + I_-S_+) + (i/4)(A_{x'x'} - A_{y'y'})(I_-S_- - I_+S_+) \qquad (3)$$

basis set is a set of eigenfunctions of S_z' where S' is the fictitious spin[9] ($S' = {}^1/_2$ in this case). In the presence of spin–orbit coupling, the actual spin, S, is not a good quantum number, since configurations with $m_S = \pm{}^1/_2$ are admixed. The actual Hamiltonian (eq 1) gives the correct hyperfine interaction within the framework of perturbation theory when the basis set is that obtained by applying the spin–orbit coupling as a perturbation. If we represent the ground-state Kramers' doublet obtained by this procedure[5] as $\Psi_+{}^{m_I},\Psi_-{}^{m_I}$, where the m_I superscript refers to the nuclear spin quantum number of ^{33}S, and the eigenfunctions of S_z' as $|{}^1/_2,m_I)$, $|-{}^1/_2,m_I)$, we can obtain the principal hyperfine tensor values by a comparison of matrix elements. McGarvey discusses this procedure in

$$A_{zz}({}^1/_2,m_I|I_zS_z|{}^1/_2,m_I) = (\Psi_+{}^{m_I}|\mathcal{H}_{hf}|\Psi_+{}^{m_I}) \qquad (4)$$

$$(A_{x'x'} + A_{y'y'})(-{}^1/_2,m_I + 1|I_+S_-|{}^1/_2,m_I) = 4(\Psi_-{}^{m_I+1}|\mathcal{H}_{hf}|\Psi_+{}^{m_I}) \qquad (5)$$

$$-(A_{x'x'} - A_{y'y'})(-{}^1/_2,m_I - 1|I_-S_-|{}^1/_2,m_I) = 4i(\Psi_-{}^{m_I-1}|\mathcal{H}_{hf}|\Psi_+{}^{m_I}) \qquad (6)$$

detail.[10] Spin–orbit effects are not very large in Ni(mnt)$_2^-$ type ions since the g values are all within 8% of the free spin value of 2.0023. In the approximation of neglecting spin–orbit coupling for the calculation of the hyperfine tensor of ^{33}S, the fictitious spin becomes the same as S, and eq 4, 5, and 6 become much simplified. It is readily verified that

$$A_{zz} = 4\gamma_n\beta_0(\Psi_+|s_z[(8\pi\delta(r)/3) + r^{-3}(3\cos^2\theta - 1)]|\Psi_+) \qquad (7)$$

$$A_{x'x'} = 4\gamma_n\beta_0(\Psi_-|s_-[(4\pi\delta(r)/3 + ({}^1/_4)r^{-3}(1 - 3\cos^2\theta + 3\sin^2\theta\sin 2\phi)]|\Psi_+) \qquad (8)$$

$$A_{y'y'} = 4\gamma_n\beta_0(\Psi_-|s_-[(4\pi\delta(r)/3) + {}^1/_4r^{-3}(1 - 3\cos^2\theta - 3\sin^2\theta\sin 2\phi)]|\Psi_+) \qquad (9)$$

The first term in each matrix element represents the Fermi contact interaction which is proportional to $|\Psi_\pm(0)|^2$ at the $^{33}S_I$ nucleus. This term is particularly sensitive to sulfur s orbitals present in the half-filled molecular orbital. The second term in each matrix element disappears for s orbitals but contributes to the principal tensor values for 3p orbitals on sulfur. Each term in the matrix elements has either a δ function or

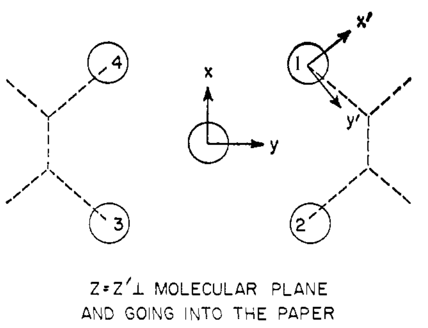

Figure 1. Coordinate system for $NiS_4C_4(CN)_4^-$ ion.

inverse cube dependence on the distance of the electron from the sulfur nucleus. The limits of integration for obtaining the matrix elements can thus be set near the sulfur atom without incurring unreasonable error. We will adopt the convention, within a linear combination of atomic orbitals–molecular orbital framework, of integrating over only the atomic orbitals centered on sulfur.[11]

Equations 7–9 are readily evaluated in terms of the normalized coefficients, C_s and C_p, of sulfur 3s and 3p orbital contributions to the half-filled molecular orbital. We will distinguish two possibilities, namely, that (a) the half-filled orbital is of b_{3g} symmetry in which the sulfur p orbital which is admixed is $3p_z$, and (b) the half-filled orbital is of a_g symmetry in which the sulfur p orbital which is admixed is primarily $3p_{y'}$. The principal tensor values then obtained are given in Table I.

Table I. Principal Tensor Elements of ^{33}S Hyperfine Interaction in Ni(mnt)$_2^-$ [a]

	Symmetry of half-filled mo	
	b_{3g} (yz)	a_g ($x^2 - y^2$, mostly)
$A_{x'x'}$	$\langle a\rangle^b - b^c$	$\langle a\rangle - b$
$A_{y'y'}$	$\langle a\rangle - b$	$\langle a\rangle + 2b$
A_{zz}	$\langle a\rangle + 2b$	$\langle a\rangle - b$

[a] Coordinate system is shown in Figure 1. [b] $\langle a\rangle = (16\pi\gamma_n\beta_0/3)\cdot C_s^2|\Psi_{3s}(0)|^2$. [c] $b = (4\gamma_n\beta_0/5)C_p^2\langle r^{-3}\rangle_{3p}$.

The hyperfine tensor is predicted to be axially symmetric for either half-filled molecular orbital, but the unique axis is the z axis for the $^2B_{3g}$ ground state and the y' axis for the ^2A_g ground state.

Experimental Section

Single crystals containing approximately 1 mol % (n-Bu$_4$N)-NiS$_4$C$_4$(CN)$_4$ in the isomorphous diamagnetic copper complex were grown by solvent evaporation from CH_2Cl_2–$CHCl_3$ solutions. A suitable crystal was aligned by X-ray techniques using a Buerger precession camera. The complete structure of (n-Bu$_4$N)CuS$_4$C$_4$-

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[9] M. H. L. Pryce, *Proc. Phys. Soc.* (London), **A63**, 25 (1950).

[10] B. R. McGarvey, "Transition Metal Chemistry," Vol. III, Marcel-Dekker, New York, N. Y., 1966, p 89.

[11] A referee has suggested that eq 7–9 should be extended to include the direct dipole–dipole interaction between the ^{33}S nucleus and the electron spin in orbitals centered on the metal atom. This consideration certainly is required when evaluating the hyperfine tensor of ligand atoms in "normal" complexes in which the delocalization of the half-filled molecular orbital over ligand atoms is not extensive. In these "normal" complexes, the larger distance of the metal orbital from the ligand nucleus is compensated by a metal atom spin density which is frequently one to two orders of magnitude larger than the spin density in ligand orbitals due to delocalization. In the dithiolene complexes which we are considering here the magnitude of the traceless part of the ^{33}S hyperfine tensor is at least two orders greater than that predicted for a molecular orbital *which is 100% localized on the metal atom.* Thus, it is clear that the "direct" interaction can be neglected.

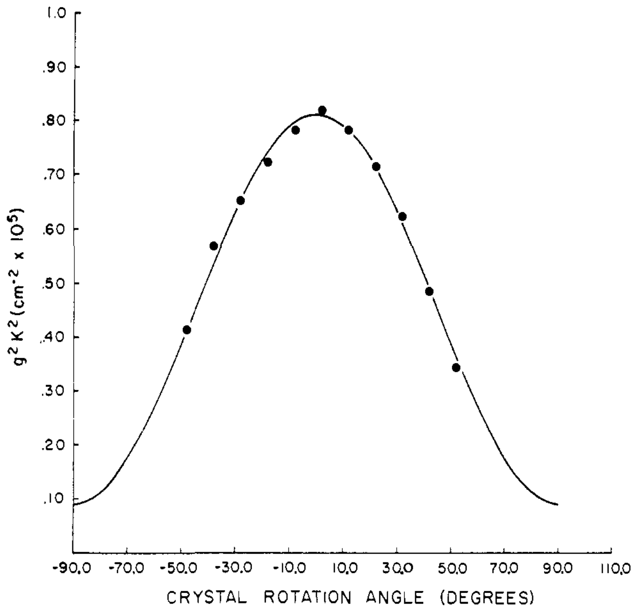

Figure 2. g^2K^2 as a function of crystal rotation angle for rotation about the *b* crystal axis. The solid curve is a theoretically calculated least-squares line giving the values of $A_\parallel$ and $A_\perp$ listed in Table II. The circles are experimentally determined points. The standard deviation in g^2K^2 is 1.5×10^{-7} cm^{-2}. The crystallographic *a* axis occurs at a crystal rotation angle of 22°.

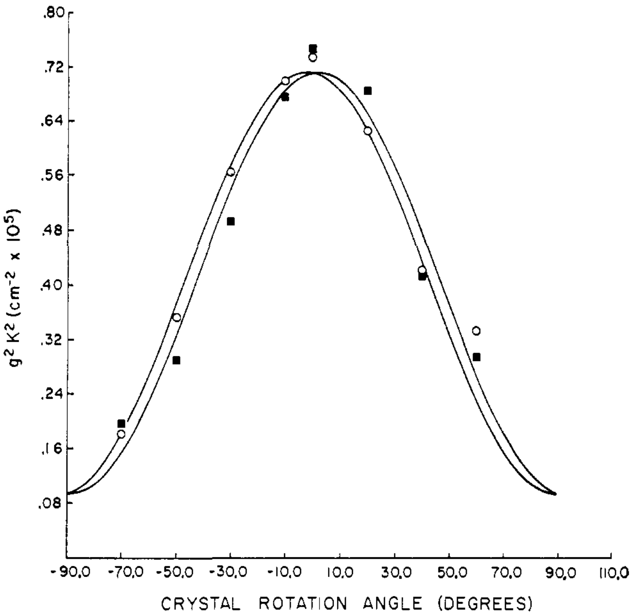

Figure 3. g^2K^2 as a function of crystal rotation angle for rotation about the c' crystal axis. The solid curve is theoretically calculated using values of $A_\parallel$ and $A_\perp$ obtained from the *b*-axis rotation and the previously determined *g* tensor. The squares and circles are experimentally determined points for the two magnetically nonequivalent molecules, the squares corresponding to the curve that peaks to the right. The standard deviation in g^2K^2 is 4.0×10^{-7} cm^{-2}. The crystallographic *a* axis occurs at a crystal rotation angle of 0°.

$(CN)_4$ has been determined by X-ray diffraction.[12] Paramagnetic resonance measurements were made at room temperature on an ordinary X-band epr spectrometer using a 100-kHz field modulation. The crystals were mounted on a polystyrene post with an indicator that could be rotated against a fixed angular scale. By this means the crystal was rotated inside the cavity about the *b* crystal axis, remounted, and rotated about the c' axis, with the rotation axis maintained perpendicular to the magnetic field. Measurements were made every 10 or 20°.

Satellites from $NiS_4C_4(CN)_4^-$ ions containing one ^{33}S nucleus could be observed in natural abundance. The width of the epr lines was 2.5 G peak to peak at 1% dilution, and ^{33}S satellites could be detected provided the outer lines of the satellite quartet were split out from the ^{32}S line by ±7 G or more. ^{33}S satellites could be distinguished from other weak lines in the spectrum by the lack of Ni concentration dependence of their intensity relative to the central line. The other weak lines are caused by Ni-Ni pairs whose magnetic resonance is split by electron dipole-dipole coupling. All glass spectra were obtained at −170° using chloroform-dimethylformamide as solvent. The magnetic field was monitored with a proton resonance gaussmeter whose frequency was measured by means of a Hewlett-Packard Model 5245L frequency counter.

Analysis of Data

$(n\text{-}Bu_4N)CuS_4C_4(CN)_4$ has a monoclinic unit cell containing two structural units which are magnetically equivalent in the *b*-axis rotation but whose resonances split out in the c'-axis rotation.[12] In the *b*-axis rotation, the molecular *z* axis comes within 2° of being coincident with the magnetic field direction. The maximum splitting of the extreme ^{33}S satellite lines was found to occur with *z* parallel to the applied field. Furthermore, the ^{33}S satellites could only be observed within angles of ±50° about the *z* axis, since the splitting becomes too small for orientations in which the magnetic field is closer to the molecular plane. In the rotation about the *b* axis, the intersection of the magnetic field with the molecular plane makes an angle of 10° with the x' and x''' axes (S_1 and S_3) and 80° with the x'' and x'''' axes (S_2 and S_4). If there were a sizable difference between $A_{x'x'}$ and $A_{y'y'}$ we would expect to observe a splitting of each satellite into two lines, one due to $^{33}S_1$ and $^{33}S_3$ and the other to $^{33}S_2$ and $^{33}S_4$. Only one set of satellites was ever observed in the *b*-axis rotation, and the satellite widths were not noticeably greater at angles of ±50° with respect to the *z* axis than they were with the field parallel to *z*.

Within experimental error, therefore, the ^{33}S hyperfine tensor is axially symmetric, with the unique axis normal to the molecular plane. The ^{33}S hyperfine coupling constant, *K*, should follow an equation of the form of (10), where α, β, and γ are the direction cosines

$$g^2K^2 = (\alpha^2 g_{xx}^2 + \beta^2 g_{yy}^2)A_\perp^2 + \gamma^2 g_{zz}^2 A_\parallel^2 \quad (10)$$

of the magnetic field in the molecule axis system (Figure 1), and $A_\parallel$ and $A_\perp$ are the principal ^{33}S tensor values along the normal to the molecular plane and in the molecular plane, respectively. We have fit the experimental data for the *b*-axis rotation by least squares to eq 10. The *g* tensor and direction cosines for each crystal setting were obtained from previous work.[5,12] The calculated least-squares plot of g^2K^2 *vs.* rotation angle, along with the experimental points, are shown in Figure 2. Finally, to verify these values, we have calculated ^{33}S hyperfine splittings for both magnetically nonequivalent molecules in the c'-axis rotation using values of $A_\parallel$ and $A_\perp$ obtained from the rotation about the *b* axis. The calculated curves and experimental points for the c' axis rotation are shown in Figure 3. The agreement between experimental points and calculated curves can be improved considerably by assuming that the c' axis was aligned about 2° from the rotation axis. Considering the possibility of alignment error and the weakness of the satellite resonances (half

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[12] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 3, 1507 (1964).

as intense as those in Figure 2), the agreement with the calculated curves must be considered satisfactory. The values of $A_{\parallel}$ and $A_{\perp}$ obtained from the *b*-axis rotation are given in Table II. We know only absolute values of these quantities.

Table II. Principal Values of *g* Tensor and ^{33}S Hyperfine Tensor in $NiS_4C_4R_4^-$ Ions

R	g_1	g_2	g_3	$\lvert A_{zz}\rvert = \lvert A_{\parallel}\rvert$, cm^{-1} × 10$^{4\ a}$	$\lvert A_{x'x'}\rvert = \lvert A_{y'y'}\rvert = \lvert A_{\perp}\rvert$, cm^{-1} × 10$^{4\ a}$
CN^b	2.160	2.042	1.998	14.27	4.55
CN^c				14.9	*d*
CF_3^{c,e}	2.137	2.044	1.996	14.5	*d*
H^{c,f}	2.126	2.039	1.996	13.9	*d*
CH_3^{c,g}	2.119	2.040	2.001	13.7	*d*
C_6H_5^{c,g}	2.122	2.041	1.999	13.7	*d*
tdt^{c,h}	2.183	2.048	2.016	13.3	*d*

[a] Axis system is that of Figure 1. [b] Data from single-crystal measurements as described in the text, g_1, g_2, and g_3 are g_{xx}, g_{yy}, and g_{zz}, respectively, of Figure 1. See ref 5. [c] Measurements made on chloroform–dimethylformamide glass at 100°K. Satellites occur on the high-field (g_3) peak and are thus interpreted as A_{zz} of the ^{33}S tensor. [d] Splittings on low (g_1) and medium (g_2) field peaks of glass spectrum are too small to be observed. [e] *g*-tensor values from A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964). [f] *g*-tensor values from ref 6. Solvent was a pyridine–chloroform glass. [g] *g*-tensor values from this work. [h] Complex is bis(toluene-3,4-dithiolene)nickel anion. *g*-tensor values are from ref 3.

In the frozen-glass epr spectra of several analogous (bisdithiolene)nickel monoanion complexes, lines due to ^{33}S hyperfine structure could be seen *only as satellites of the high field* (lowest *g* value) *peak*. Each of the complexes investigated has a rhombic *g* tensor with principal *g* values similar to those of $Ni(mnt)_2^-$. Since $Ni(mnt)_2^-$ has the axis of minimum *g* value as well as the unique axis of the axial ^{33}S hyperfine tensor normal to the molecular plane,[4] we assume that the other nickel complexes do as well. The appearance of ^{33}S satellites with closely the same splitting only on the high-field line in the glass spectra of each of these complexes is additional evidence that the electronic structures are similar, even to the immediate environment of the sulfur. The small differences in $A_{\parallel}$ given in Table II are probably a reflection of a slightly different weighting of metal and ligand orbitals in the b_{3g} molecular orbital.

Discussion

Since we have found that the ^{33}S hyperfine tensor is axial, as nearly as we can determine with its axis along the molecular *z* axis, we conclude that the half-filled molecular orbital has b_{3g} symmetry rather than a_g symmetry. The a_g choice, according to Table I, would have required the unique axis to be oriented in the molecular plane, along the *y′* axis.[13,14] In order to estimate the sulfur 3s and $3p_z$ contributions to the half-filled orbital, we must know the relative signs of $A_{\parallel}$ and $A_{\perp}$. This could be obtained from measurements in solution where the observed splitting would be given by $^1/_3(A_{\parallel} + 2A_{\perp}) = \langle a\rangle$. Attempts to resolve ^{33}S hyperfine lines in solution were unsuccessful. The narrowest peak-to-peak line width which we were able to obtain at X-band frequencies was 5.5 G. Either an isotopically enriched sample must be used or measurements should be made at lower microwave frequencies where narrower lines would be expected.[15,16] With a 5.5-G line width, we estimate that the smallest splitting we could resolve corresponds to $|\langle a\rangle| \sim 10$ G. Unfortunately, this is larger than the predicted isotropic splitting based either on $A_{\parallel}$ and $A_{\perp}$ having the same, or opposite, signs (*vide infra*), so that we cannot use the solution measurements to assign relative signs to the two principal values. The best we can do is to calculate the 3s and $3p_z$ spin populations based on both possibilities.

The estimation of 3s and $3p_z$ spin populations on the sulfur atoms poses severe problems in itself. The isotropic term $\langle a\rangle$ and the anisotropic term *b* may be obtained from eq 7, 8, and 9. They are found to be

$$\langle a\rangle = (16\pi\gamma_n\beta_0/3)C_s^2|\Psi_{3s}(0)|^2 \qquad (11)$$

and

$$b = (4\gamma_n\beta_0/5)C_p^2\langle r^{-3}\rangle_{3p} \qquad (12)$$

in terms of the spin populations C_s^2 and C_p^2, which may be taken as the coefficients squared of the sulfur 3s and $3p_z$ orbitals in the half-filled molecular orbital. Of course, if the complex is rigorously planar, $C_s^2 = 0$. The quantities $|\Psi_{3s}(0)|^2$ and $\langle r^{-3}\rangle_{3p}$ are abstract quantities, being properties of the atomic orbitals used as basis functions for the molecular orbital calculation. In free radicals, such quantities are usually approximated by those calculated from SCF wave functions *of the free atom.* Several sets of SCF wave functions are available for sulfur which can be used to obtain estimates of these quantities. Morton,[17] using SCF wave functions of Watson and Freeman,[18] has obtained values of 4.85 and 7.92 au for $\langle r^{-3}\rangle_{3p}$ and $|\Psi_{3s}(0)|^2$, respectively. Hurd and Coodin,[19] using the Herman and Skillman SCF functions,[20] have obtained 6.14 au and 10.0 au, respectively. Also, Malli and Fraga,[21] using wave functions of Clementi[22] and Malli,[23] obtain $\langle r^{-3}\rangle_{3p} = 4.85$ au for the neutral sulfur atom but find that this value is reduced to 4.04 au for the sulfur monoanion. This calculation reflects the extreme sensitivity of quantities such as $\langle r^{-3}\rangle$ to the atomic charge. The effect of charge on atomic parameters should be

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[13] We have just learned (H. B. Gray, private communication) that recent molecular orbital calculations by M. J. Baker-Hawkes[14] on square-planar nickel dithiolene anion complexes now predict that the half-filled molecular orbital is of b_{2g} symmetry, rather than the previously obtained a_g symmetry. Thus a rather serious discrepancy between theory and experiment now has been removed.

[14] M. J. Baker-Hawkes, Ph.D. Thesis, Columbia University, 1967.

[15] In these complexes, the limiting contribution to the line width in solution at *x*-band frequencies results from the *g* anisotropy. At small η/T (where η is the solvent viscosity), the spin–rotational interaction causes an increase in line width with increasing *T*.[16] At large η/T, the lack of averaging of the *g* anisotropy causes the line width to increase as *T* is lowered. The low-temperature line-width mechanism is proportional to the applied magnetic field in the experiment whereas the high-temperature mechanism is independent of field. Thus, the minimum line width obtainable should decrease at a lower microwave frequency.

[16] R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).

[17] J. R. Morton, *Chem. Rev.*, 64, 454 (1964).

[18] R. E. Watson and A. J. Freeman, *Phys. Rev.*, **123**, 521 (1961).

[19] C. M. Hurd and P. Coodin, *J. Phys. Chem. Solids*, **28**, 523 (1967).

[20] F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall Inc., Englewood Cliffs, N. J., 1963.

[21] G. Malli and S. Fraga, *Theoret. Chim. Acta* (Berlin), 7, 75 (1967).

[22] E. Clementi, "Tables of Atomic Functions," International Business Machines Corp., Yorktown Heights, N. Y., 1965.

[23] G. Malli, *Can. J. Phys.*, **44**, 3121 (1966).

considered particularly in ions where local charge densities near atoms are likely to differ considerably from zero. The agreement between the calculations of Morton[17] and of Malli and Fraga,[21] which are based upon different analytic wave functions, have encouraged us to accept the value of 4.85 au for $\langle r^{-3}\rangle_{3p}$ of the *neutral* sulfur atom rather than the larger value obtained by Hurd and Coodin.[19] Also $\langle r^{-3}\rangle$ calculated by Malli and Fraga for other atoms gives good agreement with experimental magnetic dipole hyperfine structure constants. Our conclusions are rather insensitive to the choice of a value for $|\Psi_{3s}(0)|^2$, and in any case it is unlikely that direct 3s electron involvement is the principal mechanism contributing to the Fermi contact hyperfine interaction. For the sake of consistency, we shall use Morton's value of 7.92 au. We have used the molecular orbital configuration of Shupack, *et al.*[2] (corrected for the ordering of the $4a_g$ and $4b_{2g}$ orbitals), to estimate the local charge density of sulfur in the monoanion complex. A charge density of approximately -0.3 per sulfur atom is consistent with the ground-state configuration. A "best" value for the quantity $\langle r^{-3}\rangle_{3p}$ may be found, then, by linear interpolation between the calculated values[21] for the sulfur atom and monoanion. This gives a value of $\langle r^{-3}\rangle_{3p} = 4.61$ au, which we shall use for the sulfur atom in the complex. In Table III we list the results of the calculations of atomic orbital spin populations by means of eq 11 and 12, using each possibility for the relative signs of $A_{\parallel}$ and $A_{\perp}$. Also given are the total ligand spin densities based upon the ligand symmetry orbitals and group overlap integrals of Shupack, *et al.*,[2] and of Schrauzer and Mayweg.[6] It is difficult to estimate the reliability of these spin distributions. They rely heavily on the choice of an effective value for $\langle r^{-3}\rangle_{3p}$. With the choice that we have made, taking opposite signs for $A_{\parallel}$ and $A_{\perp}$, we predict a half-filled molecular orbital which is entirely ligand in character and must be considered unreasonable in light of the ^{61}Ni hyperfine tensor and the considerable anisotropy of the *g* tensor reported earlier.[5] If $A_{\parallel}$ and $A_{\perp}$ have the same sign, the b_{3g} molecular orbital is found to be roughly 50% delocalized over the ligands, a result in accord with the earlier work.[5]

Table III. Spin Populations of ^{33}S Orbitals of $Ni(mnt)_2^-$ Obtained from the Possible Principal Hyperfine Tensor Values

	Signs of $A_{\parallel}$ and $A_{\perp}$	
	Same	Opposite
$A_{\parallel} = 2b + \langle a\rangle$, $cm^{-1} \times 10^4$	14.27	14.27
$A_{\perp} = -b + \langle a\rangle$, $cm^{-1} \times 10^4$	4.55	−4.55
$\langle a\rangle$, $cm^{-1} \times 10^4$	7.79	1.72
b, $cm^{-1} \times 10^4$	3.24	6.28
C_p^2 [a]	0.128	0.249
C_s^2 [b]	0.0086	0.0019
Total ligand spin density	0.52[c] 0.58[d]	1.04[c] 1.17[d]

[a] Calculated from eq 12, with $\langle r^{-3}\rangle_{3p} = 4.61$ au. [b] Calculated from eq 11, with $|\Psi_{3s}(0)|^2 = 7.92$ au. [c] Calculated using an eigenvector of 0.490 for sulfur $3p_z$ in the $4b_{2g}$ ligand orbital and a group overlap integral of 0.058.[2] (The $4b_{2g}$ orbital of ref 2 is the same as the b_{3g} orbital of ref 5.) [d] Calculated using an eigenvector of 0.462 for sulfur $3p_z$ in the ligand $3b_{2g}$ orbital and a group overlap integral of 0.077.[6] (The $3b_{2g}$ orbital of ref 6 is the same as the b_{3g} orbital of ref 5.)

It should be pointed out that the choice of a larger value of $\langle r^{-3}\rangle_{3p}$ for the complex, such as that of Hurd and Coodin,[19] results in the prediction of less ligand contribution for either choice for signs of $A_{\parallel}$ and $A_{\perp}$. Choice of opposite signs in this case leads to a molecular orbital which is approximately 80% ligand in character and which *can* be reconciled with the g tensor and ^{61}Ni hyperfine tensor.[5] Also it would be in better agreement with the composition of the b_{3g} orbital as determined by the molecular orbital calculations.[2,6] Knowledge of the relative signs of $A_{\parallel}$ and $A_{\perp}$ would resolve this ambiguity.

The small isotropic coupling of ^{33}S cannot arise from a large contribution of 3s character to the wave function near the sulfur atom, as can be seen from Table III. This result is consistent with a rigorously planar ion which would not allow the mixing of s and p_z orbitals of sulfur from symmetry considerations. The isotropic coupling, $\langle a\rangle$, probably arises from polarization of the spins in σ orbitals of sulfur by the spin in the b_{3g} orbital by a mechanism similar to that giving rise to proton and heteroatom isotropic coupling in aromatic free radicals.[24] This is a reasonable mechanism in this case since the $3p_z$ spin population of the sulfur atom is high.[25]

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(24) H. M. McConnell, *J. Chem. Phys.*, 24, 764 (1956).

(25) NOTE ADDED IN PROOF. We have been informed by Professor G. N. Schrauzer that he has made a recent calculation of the ground-state configuration of $NiS_4C_4H_4^-$ using the extended ω-technique developed by Nakajima,[26] which produces self-consistent molecular orbitals. This treatment[26] produces a singly occupied $3b_{2g}$ molecular orbital[6] having 51% metal and 49% ligand character, a significant increase in metal character over the original calculation.[6] This distribution is in excellent agreement with our estimates of this molecular orbital from the ^{33}S hyperfine tensor based upon the same signs for $A_{\parallel}$ and $A_{\perp}$ (Table III). We thank Professor Schrauzer for informing us of these new results.

(26) T. Nakajima and S. Katagiri, *Mol. Phys.*, 7, 149 (1963).