predicted Ce–C bond length of 2.75 Å compares very well with the observed value of 2.742 (8) Å.

The one distinct difference of this structure from the ones previously reported which contain COT^{2-} is the large thermal motion of the COT^{2-} ring 2 coordinated to both the Ce and K ions. In this case the dianion is sandwiched between two positive charges and might be expected to be somewhat less tightly coordinated to the cerium. However, the equal average Ce–C bond lengths for rings 1 and 2 evidence that this is not the case.

In summary, the molecular symmetry of $[Ce(C_8H_8)]^{2-}$ anion is D_{8d}. Although the rings are staggered instead of eclipsed, the coordination geometry is substantially identical with that for the actinide compounds, $U(C_8H_8)_2$ and $Th(C_8H_8)_2$.[2] In both the $[Ce(C_8H_8)_2]^-$ and $U(C_8H_4(CH_3)_4)_2$[20] complexes the characterization of rotameric configurations different from the eclipsed geometry demonstrates that the barrier to rotation is very low and that the most stable geometry in the solid state may be largely determined by intermolecular rather than intramolecular interactions.

Acknowledgment.—We thank Professor A. Streitwieser, Jr., for his helpful discussion and interest in this work, and Mr. K. Hershon who assisted in the early stages of structure solution. We gratefully acknowledge the financial support of the National Science Foundation through Grants GP-13278 and GP-29764 and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Professor Seaborg and the U. S. Atomic Energy Commission for providing computer time at the Lawrence Berkeley Laboratory.

(20) K. O. Hodgson and K. N. Raymond, *Inorg., Chem.*, in press.

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Electron Spin Resonance Studies of $Ni(diars)_2Cl_2^+$

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Electron spin resonance studies have been carried out on the spin-doublet complexes $[Ni(diars)_2Cl_2]Y$ ($Y^- = Cl^-, ClO_4^-$). The esr parameters measured on samples diluted in a diamagnetic host crystal $[Co(diars)_2Cl_2]ClO_4$ are as follows: $g_{\parallel} = 2.008$, $g_{\perp} = 2.142$; $A_\sigma^{As} = -8.5$, $A_\pi^{As} = -6.9$, $A_z^{As} = -32$, $A_x^{Cl} = -32$, $A_y^{Cl} = -50$, $A_z^{Cl} = -29$ G. From these studies it is suggested that the energy-level ordering of 3d orbitals in $Ni(diars)_2Cl_2^+$ is $a_g(x^2 - y^2) < b_{2g}(xz) \approx b_{3g}(yz) < a_g(z^2) < b_{1g}(xy)$, and that in the ground state the unpaired electron occupies the $a_g(z^2)$ molecular orbital which is strongly delocalized over the metal and all six ligand donor atoms. In a concentrated powder of $[Ni(diars)_2Cl_2]Cl$, a rhombic g tensor is observed ($g_1 = 2.054$, $g_2 = 2.091$, $g_3 = 2.142$). Admixture of Ni $3d_{xz}$ in the $a_g(z^2)$ molecular orbital as a result of a change in axial (Ni–Cl) interaction in the concentrated powder is suggested as the probable explanation of this observation.

Introduction

The electronic structure of the six-coordinate paramagnetic species $[Ni(diars)_2X_2]Y$ (diars = *o*-phenylenebisdimethylarsine; $X^- = Cl^-, Br^-, SCN^-$; $Y^- = Cl^-, Br^-, SCN^-, ClO_4^-$) has been the subject of two recent electron spin resonance studies. Rogers and Manoharan,[1] on the basis of the observed halide superhyperfine splittings, proposed that the unpaired electron is in the metal d_{z^2} orbital. However, we had pointed out in an earlier communication[2] that a $^2A_g(d_{z^2})$ ground state is not consistent with the highly anisotropic three-g-value powder spectrum exhibited by $[Ni(diars)_2Cl_2]Cl$. As an alternative we proposed a model in which the unpaired electron is delocalized primarily over the ligands in an orbital of xy symmetry.

Comparison of our powder data and the solution results of Rogers and Manoharan[1] suggests that the g values of the $Ni(diars)_2X_2^+$ system are extremely sensitive to environmental effects. Thus we have investigated single-crystal and dilute-powder esr spectra of the $Ni(diars)_2Cl_2^+$ cation in several hosts. In this paper we report an analysis of the new esr data and discuss the probable electronic ground state of the $[Ni(diars)_2X_2]Y$ complexes.

Experimental Section

Preparation of Compounds.—$[Ni(diars)_2Cl_2]Cl$,[3] $[Co(diars)_2Cl_2]Cl$,[4] $[Ni(diars)_2Cl_2]ClO_4$,[3] $[Co(diars)_2Cl_2]ClO_4$,[4] and $[Rh(diars)_2Cl_2]Cl$[5] were prepared according to literature methods. Crystals for esr spectra were grown from ethanol solution. These crystals contained 1–3% $Ni(diars)_2Cl_2^+$ doped into the two cobalt salts. Powders were prepared by grinding crystals of $[Ni(diars)_2Cl_2]Cl$ in $[Co(diars)_2Cl_2]Cl$ and $[Ni(diars)_2Cl_2]Cl$ in $[Rh(diars)_2Cl_2]Cl$ which contained approximately 75, 50, 25, 10, and 3 mol % Ni.

Instrumental Procedure.—Esr spectra were taken using both a Varian V-4502 X-band spectrometer with a V-4532 dual sample cavity and a Varian V-4500 K-band spectrometer. In the X-band experiments the field was calibrated using a standard solid sample of DPPH. In the K-band experiments an Alpha Model 675 nmr gaussmeter was used for field calibration. All low-temperature experiments were done using a Varian V-4540 variable temperature apparatus.

Single-Crystal Measurements.—Single-crystal measurements on the X-band spectrometer were made using a Magna Devices M-10 rotating sample holder. Spectra were taken on doped crystals of $[Ni(diars)_2Cl_2]Cl$ in $[Co(diars)_2Cl_2]Cl$ and $[Ni(diars)_2Cl_2]ClO_4$ in $[Co(diars)_2Cl_2]ClO_4$. The crystal structures of both

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(1) P. T. Manoharan and M. Rogers, *J. Chem. Phys.*, **53**, 1682 (1970).

(2) P. Kreisman, R. E. Marsh, J. Preer, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 1067 (1968).

(3) R. S. Nyholm, *J. Chem. Soc.*, 2061 (1950).

(4) R. S. Nyholm, *ibid.*, 2071 (1950).

(5) R. S. Nyholm, *ibid.*, 857 (1950).

these salts are known. The isomorphous compounds [M(diars)$_2$Cl$_2$]Cl (M = Ni, Co) crystallize in the monoclinic space group $P2_1/_c$.[6a] The relationships between crystal and molecular axes in these compounds are complicated.[6b] The [Co(diars)$_2$Cl$_2$]ClO$_4$ salt, on the other hand, crystallizes in space group $C2$, with the advantage of much simpler relationships between crystal and molecular axes.[7] In this crystal the $\vec{b}$ axis is perpendicular to the nickel–arsenic plane (*i.e.*, parallel to the molecular $\vec{z}$ axis) and the $\vec{a}$ axis makes a 29° angle with the molecular $\vec{x}$ axis. All magnetic ions in this host are identically oriented with respect to the crystal-axis system. In each experiment, the doped crystal was rotated in turn about $\vec{a}$, $\vec{b}$, and $\vec{c}$ axes, and spectra were recorded at 5° intervals.

Some data were also taken at K-band frequencies on [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl. The crystal was placed in a 2 mm wide quartz capillary tube with a flat bottom so that the $\vec{a}^*$ axis of the crystal was parallel to the tube axis. The magnet was rotated about the cavity and spectra taken every 5°.

Magnetic-Susceptibility Measurements.—Magnetic-susceptibility measurements were made on a solid sample of [Ni(diars)$_2$Cl$_2$]Cl using a Princeton Applied Research FM-1 vibrating sample magnetometer and an Andonian Associates liquid helium dewar. Two variable temperature runs were made, one using liquid nitrogen coolant from room temperature to 75°K and a second using liquid helium coolant from 192 to 15°K. The data were corrected for the diamagnetism of the holder and calibrated at room temperature with HgCo(SCN)$_4$.

Results and Discussion

Figure 1 shows a plot of $1/\chi$ *vs.* T for [Ni(diars)$_2$Cl$_2$]Cl from 190 to 15°K. The susceptibility follows the Curie–Weiss law with a Weiss constant $\Theta = 10$°K. The room temperature magnetic moment is 1.756 BM, in good agreement with the value reported originally by Nyholm.[3] Esr spectra were taken of powdered [Ni(diars)$_2$Cl$_2$]Cl at X- and K-band frequencies. Three g values are observed

$$g_1 = 2.0539 \pm 0.0005$$

$$g_2 = 2.0913 \pm 0.0005$$

$$g_3 = 2.1421 \pm 0.0005$$

The esr spectrum of [Ni(diars)$_2$Cl$_2$]ClO$_4$ has been studied by other workers[8] and is identical with that of the trichloride.

A powder spectrum of 3% [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl at K band is illustrated in Figure 2a. Instead of the three-g-value pattern seen in the concentrated powder, a two-g-value spectrum results, with $g_{\parallel} = 2.008$ and $g_{\perp} = 2.142$. We have studied the concentration dependence of the g values of Ni(diars)$_2$Cl$_2^+$ in three different hosts. Doped powders were prepared in [Co(diars)$_2$Cl$_2$]Cl, [Co(diars)$_2$Cl$_2$]ClO$_4$, and [Rh(diars)$_2$Cl$_2$]Cl, varying the initial concentration of nickel in solution from 75% down to 3%. All three matrices showed essentially the same kind of concentration dependence. A three-g-value pattern is evident in powders obtained from solutions in which the initial nickel concentration is above 50%. When the solution contains 25% nickel there is a marked increase in the intensity of the peak at $g = 2.14$ and decreases of intensity at $g = 2.09$ and 2.05. By the time the nickel concentration has been reduced to 10%, the two latter bands have completely disappeared and a weak band at $g = 2.00$ can be detected. Figure 2b illustrates the spectrum of a [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl powder obtained from a solution initially 25% Ni.

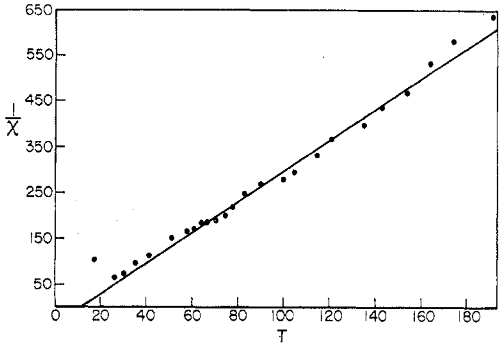

Figure 1.—Reciprocal susceptibility ($1/\chi$) *vs.* temperature for [Ni(diars)$_2$Cl$_2$]Cl from 190 to 15°K using liquid helium coolant.

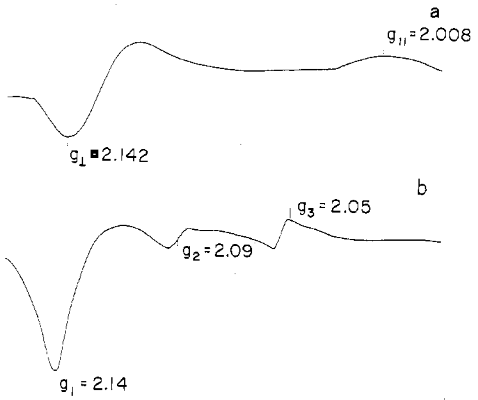

Figure 2—K-Band spectra of [Ni(diars)$_2$Cl$_2$]Cl doped into [Co(diars)$_2$Cl$_2$]Cl: (a) approximately 3% [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl, (b) approximately 25% [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl.

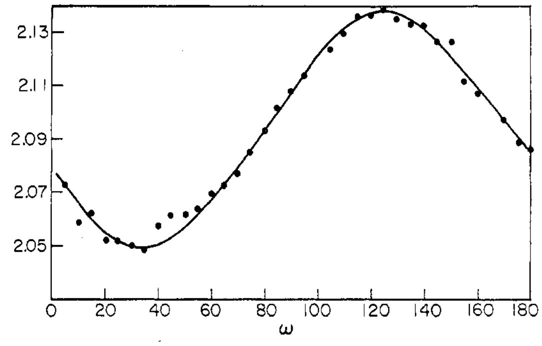

Figure 3.—The angular variation of the g value of a dilute single crystal of 3% [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl mounted on the $\vec{b}$ axis. The solid line is a theoretical curve calculated assuming $g_{\parallel} = 2.00$ and $g_{\perp} = 2.14$.

The effective g value *vs.* angle was measured for a single crystal of 3% [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl mounted on both the $\vec{a}$ and $\vec{b}$ axes. Figure 3 shows the data points for the $\vec{b}$ axis spectra. The single-crystal data are in excellent agreement with the principal g values measured in the dilute-powder spec-

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(6) (a) P. K. Bernstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, **11**, 3040 (1972). (b) The relationships between crystal and molecular axes are as follows: $\vec{x} = 0.8284\vec{a} + 0.1004\vec{b} - 0.5510\vec{c}^*$, $\vec{y} = 0.2712\vec{a} + 0.8021\vec{b} + 0.5317\vec{c}^*$, $\vec{z} = 0.4952\vec{a} - 0.5901\vec{b} + 0.6372\vec{c}^*$. Here, x is the axis which bisects the two arsenics and passes through the benzene rings. The y axis also bisects the arsenics and the z axis completes the orthogonal set. $g_{\parallel}$ is in the z direction and $g_{\perp}$ is in the plane defined by the x and y axes.

(7) P. J. Pauling, D. W. Porter, and G. B. Robertson, *J. Chem. Soc. A*, 2728 (1970).

(8) C. Corvaja and P. L. Nordio, *Ric. Sci.*, **38**, 44 (1968).

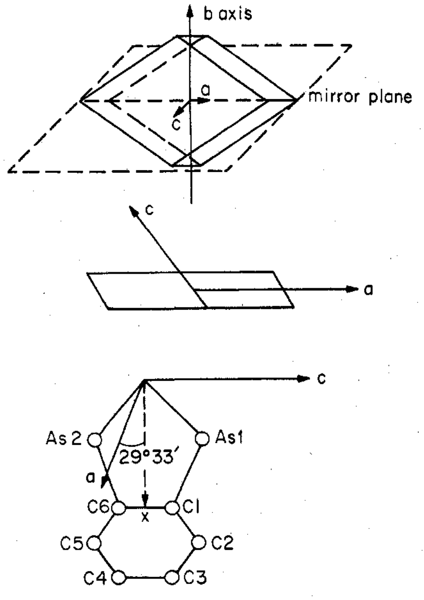

Figure 4.—The external morphology and crystal structure of [Co(diars)$_2$Cl$_2$]ClO$_4$.

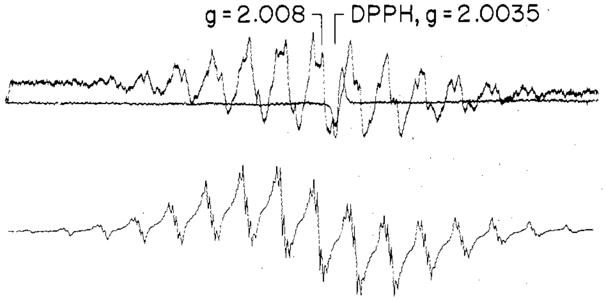

Figure 5.—The experimental (top) and simulated (bottom) X-band spectra of dilute [Ni(diars)$_2$Cl$_2$]ClO$_4$ in [Co(diars)$_2$Cl$_2$]ClO$_4$ mounted on the $\vec{a}$ axis with H || $\vec{b}$. A DPPH standard was used.

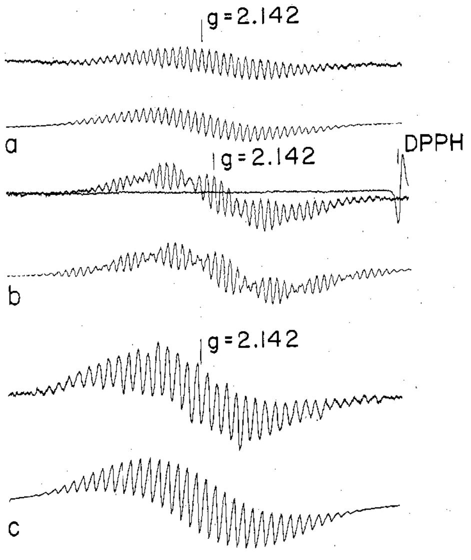

Figure 6.—Experimental (top) and simulated (bottom) X-band spectra: (a) dilute [Ni(diars)$_2$Cl$_2$]ClO$_4$ in [Co(diars)$_2$Cl$_2$]ClO$_4$ mounted on the $\vec{b}$ axis with H || $\vec{a}$, (b) dilute [Ni(diars)$_2$Cl$_2$]ClO$_4$ in [Co(diars)$_2$Cl$_2$]ClO$_4$ mounted on $\vec{b}$ with H 9° from the molecular $\vec{y}$, (c) dilute [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl mounted on the $\vec{b}$ axis with H || to the molecular $\vec{x}$ axis.

trum except for two points at ω = 40 and 45°. At these orientations, the complexity of the hyperfine pattern created difficulties in determining the precise centerpoint of the spectrum.

Single-Crystal Spectra of [Ni(diars)$_2$Cl$_2$]ClO$_4$ in [Co(diars)$_2$Cl$_2$]ClO$_4$.—Because of the difficulties inherent in working with [Co(diars)$_2$Cl$_2$]Cl, we changed to the host [Co(diars)$_2$Cl$_2$]ClO$_4$. The relationships of crystal and molecular axes in this salt are shown in Figure 4.

Spectra were taken of a doped single crystal of 3% [Ni(diars)$_2$Cl$_2$]ClO$_4$ in [Co(diars)$_2$Cl$_2$]ClO$_4$ at 5° intervals about each of the three principal crystallographic axes. The best of these spectra were computer simulated using a modified version of a computer program written by Gladney and Swalen.[9] The original and simulated spectra were compared visually and the best match of positions and intensities was chosen in each case. Figure 5 shows the experimental and simulated spectra of the crystal mounted on the $\vec{a}$ axis with the magnetic field parallel to the $\vec{b}$ axis. Other representative simulated spectra are shown in Figure 6.

Analysis of the spectra gives the following principal values for the ligand superhyperfine tensor elements: $A_x^{\mathrm{Cl}} = \pm 32$; $A_y^{\mathrm{Cl}} = \pm 50$; $A_z^{\mathrm{Cl}} = \pm 29$; $A_\sigma^{\mathrm{As}} = \pm 8.5$; $A_\pi^{\mathrm{As}} = \pm 6.9$; $A_z^{\mathrm{As}} = \pm 32$ G. Details are given in Appendix I. Theoretical considerations dictate that the sign of the dipole term in the z direction should be positive for chlorine and negative for arsenic. This choice of signs eliminates all possibilities except four in which the contact terms are negative.

Ground State of Ni(diars)$_2$Cl$_2$$^+$.—An idealized representation of the molecular structure of Ni(diars)$_2$Cl$_2$$^+$ is shown in a reference coordinate system in Figure 7. Because both benzene rings are tipped and the axial ligands are distorted by 2° from octahedral positions, the correct molecular symmetry is C_i. We shall ignore the slight axial distortion, however, and analyze the molecular orbital problem in C_{2h} symmetry. The g-value pattern and the observed chlorine superhyperfine tensor elements for dilute [Ni(diars)$_2$Cl$_2$]ClO$_4$ in [Co(diars)$_2$Cl$_2$]ClO$_4$ are consistent with the d-level ordering $\mathrm{a_g}(x^2 - y^2) < \mathrm{b_{2g}}(xz) \approx \mathrm{b_{3g}}(yz) < \mathrm{a_g}(z^2) < \mathrm{b_{1g}}(xy)$, and a $^2\mathrm{A_g}(z^2)$ ground state. The expression for the highest occupied orbital is

$$\mathrm{a_g}(z^2) = \mathrm{a_1 d_{z^2}} + \mathrm{a_2}\phi_{\mathrm{p_zCl}}(\mathrm{a_g}) + \mathrm{a_3}\phi_{\mathrm{sAs}}(\mathrm{a_g}) - \mathrm{a_4}\phi_{\mathrm{p_xAs}}(\mathrm{a_g}) - \mathrm{a_5}\phi_{\mathrm{p_yAs}}(\mathrm{a_g}) - \mathrm{a_6}\phi_{\mathrm{sCl}}(\mathrm{a_g}) - \mathrm{a_7}\phi_{\mathrm{p_xCl}}(\mathrm{a_g})$$

where

$$\phi_{\mathrm{sCl}}(\mathrm{a_g}) = \frac{1}{\sqrt{2}}(\mathrm{s_5} + \mathrm{s_6});\ \phi_{\mathrm{p_zCl}}(\mathrm{a_g}) = \frac{1}{\sqrt{2}}(\mathrm{p}_{z_5} - \mathrm{p}_{z_6});$$

$$\phi_{\mathrm{p_xCl}}(\mathrm{a_g}) = \frac{1}{\sqrt{2}}(\mathrm{p}_{x_5} - \mathrm{p}_{x_6});$$

$$\phi_{\mathrm{sAs}}(\mathrm{a_g}) = \frac{1}{2}(\mathrm{s_1} + \mathrm{s_2} + \mathrm{s_3} + \mathrm{s_4});$$

$$\phi_{\mathrm{p_xAs}}(\mathrm{a_g}) = \frac{1}{2}(\mathrm{p}_{x_1} - \mathrm{p}_{x_2} - \mathrm{p}_{x_3} - \mathrm{p}_{x_4});$$

$$\phi_{\mathrm{p_yAs}}(\mathrm{a_g}) = \frac{1}{2}(\mathrm{p}_{y_1} - \mathrm{p}_{y_2} - \mathrm{p}_{y_3} - \mathrm{p}_{y_4})$$

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(9) H. M. Gladney and J. D. Swalen, IBM Research Laboratories, San Jose, California.

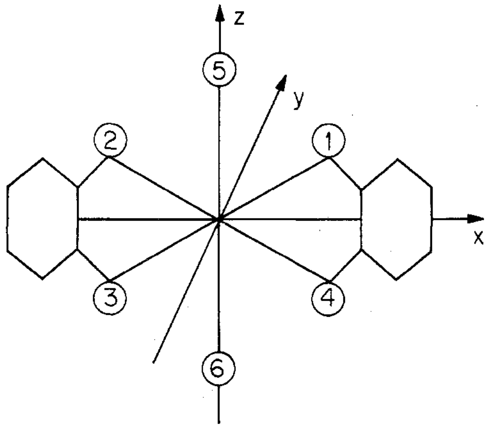

Figure 7.—The reference coordinate system used in constructing molecular orbitals for $Ni(diars)_2Cl_2^+$.

We note especially that C_{2h} symmetry permits the Cl $3p_x$ orbital to be mixed in $a_g(z^2)$, which provides an explanation for the fact that the chlorine superhyperfine tensor is not axially symmetric.

We turn now to an evaluation of the coefficients of the basis orbitals which make up $a_g(z^2)$. In view of the negative contact terms it is reasonable that neither chlorine 3s nor arsenic 4s orbitals contribute appreciably to the ground state. Thus we take $a_3 = a_6 = 0$. Further, we expect from the molecular geometry that $As(p_x)$ mixing should be about the same as $As(p_y)$ mixing, and we have set $a_4 = a_5$. Then from three linearly independent dipole equations given in Appendix II, plus the normalization equation, we can solve for the four remaining independent coefficients in the $a_g(z^2)$ orbital. There are four possible combinations of signs for the chlorine and arsenic constants which predict the correct signs for the dipole terms. We have solved the four simultaneous linear equations for each possibility. Three solutions predict extremely low values for a_1^2 and are not compatible with the observed g values.[10] The fourth solution, however, is quite reasonable and we have selected it as the most appropriate one. The results are as follows: $A_x^{Cl} = -32$, $A_y^{Cl} = -50$, $A_z^{Cl} = -29$, $A_{iso}^{Cl} = -37$, $A_\sigma^{As} = -8.5$, $A_\pi^{As} = -6.9$, $A_z^{As} = -32$, $A_{iso}^{As} = -15.8$ G, $a_1^2 = 0.4345$, $a_2^2 = 0.1335$, $a_4^2 = a_5^2 = 0.1584$, $a_7^2 = 0.1151$. The principal conclusion from this analysis is that the unpaired electron in $a_g(z^2)$ is thoroughly delocalized over the $[NiAs_4Cl_2]^+$ system. The stability of $Ni(diars)_2Cl_2^+$ is probably due in large part to this delocalization.

The observation that the concentrated powder spectrum of $Ni(diars)_2Cl_2^+$ shows a rhombic g tensor cannot be accommodated in terms of a ^2A_g ground state with only a metal $3d_{z^2}$ contribution. The possibility that the different g pattern arises from spin–spin interactions can be ruled out on the basis of the magnetic susceptibility data. Chemical substitution of another ligand for chloride has also been ruled out as a candidate explanation.[10]

We can account for the change in g values by postulating that $3d_{xz}$ is mixed with $3d_{z^2}$ in the $a_g(z^2)$ orbital of the molecular cation in the concentrated powder. Admixture of Ni $3d_{xz}$ into the $a_g(z^2)$ molecular orbital is permitted in C_{2h} symmetry, and only a small $3d_{xz}$ contribution is needed to result in $g_y > g_x$ and a larger value for g_z, as is observed. The Ni–Cl bond distance is longer in the pure $[Ni(diars)_2Cl_2]Y$ compounds than it is expected to be when the complex cation is diluted into $[Co(diars)_2Cl_2]ClO_4$, and the Ni-orbital makeup of $a_g(z^2)$ appears to be quite sensitive to the nature of this Ni–Cl interaction. Another example of this sensitivity is provided by a comparison of dilute single crystal and solution contact terms. In the single crystal $A_{Cl} = -37$, $A_{As} = -15.8$ G whereas in solution the observed values are $A_{Cl} = \pm 17$ and $A_{As} = \pm 24$ G.[1]

Acknowledgments.—The authors would like to thank Drs. Gordon Rodley and Fred Tsay for helpful discussions and Dr. Jerry Swalen for sending us a copy of his spectral simulation program. We thank the National Science Foundation for support of this research.

Appendix I

Treatment of Data.—The constants which best fit the four spectra shown in Figures 5 and 6 are as follows

Figure	Orientations	Constants, Gauss
5	H || to $\vec{b} = \vec{z}$	29, 32, 32
6a	H || to $\vec{a}$	37.5, 7.5, 7.5
6b	H 9° from $\vec{y}$	50, 7.5, 8
6c	H || to $\vec{x}$	32, 8, 8

It was necessary to determine which constant belongs to which ligand and also whether the crystal was mounted along the $+b$ or $-b$ axis.

There is a relationship between the two pairs of arsenic atoms. If

$$\Delta E_1 = A + 2B \sin\theta \cos\theta$$

then

$$\Delta E_2 = A - 2B \sin\theta \cos\theta$$

where A is the diagonal element of the superhyperfine matrix in the xy coordinate system and B is the off-diagonal element. If, for the unambiguous orientation H || to $\vec{a}$, we assume both possibilities for the arsenic splitting constants and diagonalize the hyperfine matrix, we find that the combination 37.5, 7.5 results in an imaginary principal value for the hyperfine tensor. Thus, 7.5, 7.5 are the correct arsenic splitting constants. For the orientation H || to $\vec{b}$ all four arsenic atoms are equivalent and therefore the arsenic constant is ±32 G and the chloride constant is ±29 G. We determined the exact orientation by solving for the chloride hyperfine tensor assuming each possibility in turn. The principal values thus obtained were used to predict the chloride splitting at other orientations. An excellent fit was obtained assuming that the crystal was mounted on the $+b$ axis.

Appendix II

Calculation of the Superhyperfine Tensor Elements of the Chlorine and Arsenic Ligands.—The (electron spin)–(nuclear spin) interaction which gives rise to the experimentally observed hyperfine splitting may be expressed as follows

$$\mathcal{H}_{SI} = g_e g_n \beta_e \beta_n \left(\frac{8\pi}{3} \sum_{i,k} \delta(r_{ik}) I_i \cdot S_k - \sum_{i,k} [r_{ik}^2 (S_k \cdot I_i) - 3(S_k \cdot r_{ik})(I_i \cdot r_{ik})] r_{ik}^{-5} \right)$$

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[10] P. Bernstein, Ph.D. Thesis, California Institute of Technology, 1970.

Here g_e is the free electron g value, g_n the nuclear g value for the ligand in question, β_e the Bohr magneton, β_n the nuclear magneton, and I_i the nuclear spin vector for nucleus i. S is the electron spin vector for the one unpaired electron in this system. Using spherical polar coordinates and the coordinate system shown in Figure 8, we can expand $\mathcal{H}_{SI}$ into a form more useful for calculations. The expressions for the superhyperfine tensor follow (all calculations use the treatment and formalism of McGarvey[11])

Chlorine $\quad P' = g_e g_{Cl} \beta_e \beta_n$

$$\mathcal{H}_{SI} = P'\left[\frac{8\pi}{3}\delta(r)S_z + \frac{(3\cos^2\theta - 1)}{r^3}S_z + \frac{3}{2}\frac{\sin\theta\cos\theta}{r^3}(e^{-i\phi s+} + e^{i\phi s-})\right]I_z + P'\left[\frac{8\pi}{3}\delta(r)S_x + \frac{(3\sin^2\theta\cos^2\phi - 1)}{r^3}S_x + \frac{3\sin^2\theta\sin\phi\cos\phi}{r^3}S_y + \frac{3\sin\theta\cos\theta\cos\phi}{r^3}S_z\right]I_x + P'\left[\frac{8\pi}{3}\delta(r)S_y + \frac{(3\sin^2\theta\sin^2\phi - 1)}{r^3}S_y + \frac{3\sin^2\theta\sin\phi\cos\phi}{r^3}S_x - \frac{3\sin\theta\cos\theta\sin\phi}{r^3}S_z\right]I_y$$

Arsenic $\quad P' = g_e g_{As} \beta_e \beta_n$

$$\mathcal{H}_{SI} = P'\left[\frac{8\pi}{3}\delta(r)S_z + \frac{(3\cos^2\theta - 1)}{r^3}S_z + \frac{3}{2}\frac{\sin\theta\cos\theta}{r^3}(e^{-i\phi s+} + e^{i\phi s-})\right]I_z + P'\left[\frac{4\pi}{3}\delta(r)(S+ + iS-) + \frac{1}{4}\frac{(1 - 3\cos^2\theta)}{r^3}(S+ + iS-) + \frac{3}{4}\frac{\sin^2\theta}{r^3}(e^{2i\phi s-} + ie^{-2i\phi s+}) + \frac{3}{2}(1 + i)\frac{\sin\theta\cos\theta}{r^3}(\cos\phi + \sin\phi)S_z\right]I_\sigma + P'\left[\frac{4\pi}{3}\delta(r)(S+ - iS-) + \frac{1}{4}\frac{(1 - 3\cos^2\theta)}{r^3}(S+ - iS-) + \frac{3}{4}\frac{\sin^2\theta}{r^3}(e^{2i\phi s-} - ie^{-2i\phi s+}) + \frac{3}{2}(1 - i)\frac{\sin\theta\cos\theta}{r^3}(\cos\phi - \sin\phi)S_z\right]I_\pi$$

Alternatively, we can express this same Hamiltonian as

$$\mathcal{H}' = \sum_{i=1}^{4} A_{zi}I_{zi}S_z + A_{\sigma i}I_{\sigma i}S_\sigma + A_{\pi i}I_{\pi i}S_\pi + \sum_{j=1}^{2} A'_{zj}I_{zj}S_z + A'_{xj}I_{xj}S_x + A'_{yj}I_{yj}S_y$$

Here $A'_x A'_y A'_z$ are the principal elements of the chlorine superhyperfine tensor and $A_\sigma A_\pi A_z$ are the arsenic hyperfine constants. We calculated the principal superhyperfine tensor elements by setting the matrix elements of $\mathcal{H}_{SL}$ equal to the corresponding matrix elements of $\mathcal{H}'$.

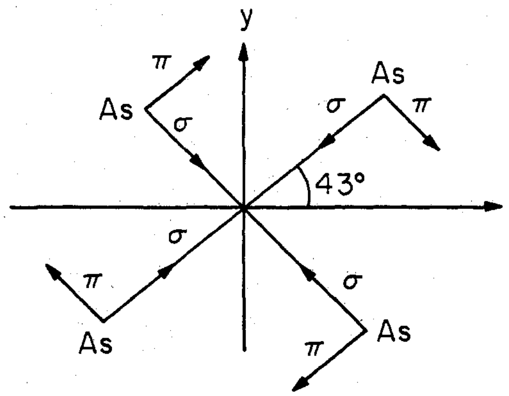

Figure 8.—The principal coordinate systems for the g tensor and the A tensors.

Because of the difficulties involved[12] we have not attempted to calculate the contact term. The expressions for the dipole terms to first order follow. For chlorine

$$A^{Cl}{}_{z\ \mathrm{dipole}} = \frac{P'a_1^2}{R^3} + \frac{4}{5}P'a_2^2\left\langle\frac{1}{r^3}\right\rangle_{3p} - \frac{2}{5}P'a_7^2\left\langle\frac{1}{r^3}\right\rangle_{3p}$$

$$A^{Cl}{}_{x\ \mathrm{dipole}} = \frac{-P'a_1^2}{2R^3} - \frac{2}{5}P'a_2^2\left\langle\frac{1}{r^3}\right\rangle_{3p} + \frac{4}{5}P'a_7^2\left\langle\frac{1}{r^3}\right\rangle_{3p}$$

$$A^{Cl}{}_{y\ \mathrm{dipole}} = \frac{-P'a_1^2}{2R^3} - \frac{2}{5}P'a_2^2\left\langle\frac{1}{r^3}\right\rangle_{3p} - \frac{2}{5}P'a_7^2\left\langle\frac{1}{r^3}\right\rangle_{3p}$$

$$P'/\hbar = 0.06646 \times 10^{-16}$$

$$\frac{1}{R^3} = 0.0714 \times 10^{24}\ 1/\mathrm{cm}^3\ (R \text{ is the Ni-Cl distance})$$

$$\left\langle\frac{1}{r^3}\right\rangle_{3p} = 55 \times 10^{24} \text{ electrons/cm}^3$$

The dipole terms for arsenic are

$$A^{As}{}_{z\ \mathrm{dipole}} = \frac{P'a_1^2}{R^3} - \frac{2}{5}P'(a_4^2 + a_5^2)\left\langle\frac{1}{r^3}\right\rangle_{4p}$$

$$A^{As}{}_{\sigma,\pi\ \mathrm{dipole}} = \frac{-P'a_1^2}{2R^3} + \frac{P'}{5}(a_4^2 + a_5^2)\left\langle\frac{1}{r^3}\right\rangle_{4p}$$

$$P'/\hbar = 0.07745 \times 10^{-16}$$

$$\frac{1}{R^3} = 0.0790 \times 10^{24}\ 1/\mathrm{cm}^3\ (R \text{ is the Ni–As distance})$$

$$\left\langle\frac{1}{r^3}\right\rangle_{4p} = 46.8 \times 10^{24} \text{ electrons/cm}^3$$

The $\langle 1/r^3\rangle$ integrals over the ligand were calculated using a computer program written by Dr. T. Dunning. The metal integrals were calculated by the method of Helmholz.[13] Clementi radial wave functions were used for chlorine 3p[14] and Watson–Freeman functions for As 4p.[15]

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