

Figure 1. The 60-MHz spectrum of methylenecyclohexane at various temperatures.

below -140° their signals were observed to broaden more rapidly than the peak which corresponds to the TMS internal standard. At -172° , however, the peaks from both the ketone and TMS were extremely broad due to the viscosity of the solution. In neither compound was peak separation observed. The minimum $\nu_{\text{axial}} - \nu_{\text{equatorial}}$ separation which can account for the broadening not attributable to viscosity effects is about 10 Hz. For the deuterated cyclohexanone, the highest temperature at which the spectrum could be at half-maximum separation for this chemical shift difference is -168° . Therefore, the maximum barrier for this process is 5.2 kcal/mole at this temperature. Similar considerations applied to the cyclohexanone spectrum indicate that the maximum ΔF^\ddagger for this process at -170° is 5.1 kcal/mole. The most probable value for these barriers is $\Delta F^\ddagger = 4.9 \pm 0.3$ kcal/mole.

As in the case of cyclohexane, the entropy of activation can very likely be estimated more accurately than it can be measured.^{3,4} The degeneracy for the chair-twist conversion for these compounds is likely two,⁴ which would give an entropy of activation of 1.4 eu. Thus, ΔH^\ddagger differs from ΔF^\ddagger by 1.4 kcal/mole.

The differences in the barriers for methylenecyclohexane and cyclohexanone appear in part to be analogous to those observed in the rotational barriers for propene and acetaldehyde.⁵ This and other contributing factors will be discussed in the full paper.

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The Molecular and Electronic Structure of the Dichlorobis(diarsine)nickel Monocation¹

Sir:

We have begun detailed studies of the spectroscopic and magnetic behavior of several complexes of the ligand *o*-phenylenebisdimethylarsine (diars), in order to elucidate the key features of their electronic structures. In this communication, we report the results of an X-ray structural determination and esr data that lead to an initial formulation of the electronic structure of the spin-doublet complex $[\text{Ni}(\text{diars})_2\text{Cl}_2]\text{Cl}$.

Brown monoclinic crystals of $[\text{Ni}(\text{diars})_2\text{Cl}_2]\text{Cl}^2$ were grown from ethanol solution. Weissenberg photographs indicate the space group $P2_1/c$, with a cell of dimensions $a = 9.33 \pm 0.01 \text{ \AA}$, $b = 9.69 \pm 0.07 \text{ \AA}$, $c = 14.87 \pm 0.02 \text{ \AA}$, and $\beta = 98.6 \pm 0.1^\circ$. The measured density of 1.87 g cm^{-3} is in exact agreement with the density calculated for two cations and two anions per unit cell. In the space group $P2_1/c$, the two nickel atoms and the two chloride ions must occupy special positions on centers of symmetry.

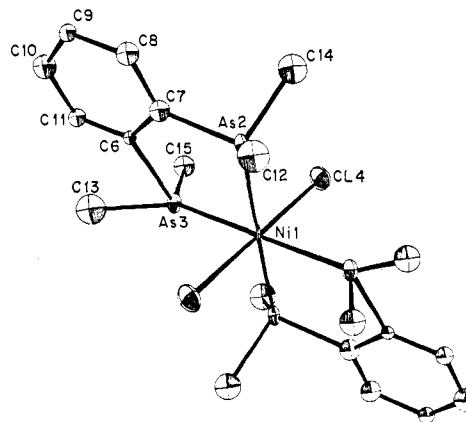


Figure 1. Structure of dichlorobis(diarsine)nickel monocation. The ellipsoids representing the Ni, As, and Cl atoms illustrate the thermal motions implied by the anisotropic temperature factors of these atoms. The carbon atoms are represented by spheres, since their temperature factors were constrained to be isotropic during the refinement of the structure.

All intensity data were collected by the equiinclination Weissenberg method using $\text{Cu K}\alpha$ radiation. Intensities were estimated visually and scaled by standard methods. The atomic form factors for nickel and arsenic were corrected by 3.1 and 1.2 electrons, respectively, for anomalous dispersion. The structure was solved by standard Patterson and Fourier methods and refined by least squares. Eighty parameters were adjusted: coordinates of 13 As, Cl, and C atoms in general positions; anisotropic temperature factors for the Ni, Cl, and As atoms; isotropic temperature factors for the C atoms; and a scale factor. The final R factor is 0.14 for 1366 observed reflections.

The monocation $\text{Ni}(\text{diars})_2\text{Cl}_2^+$ is monomeric and has the structure shown in Figure 1. The four arsenic atoms of two diars ligands surround the nickel atom in

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an approximately square-planar arrangement; the two chlorine atoms complete a slightly elongated octahedral structure. Important bond distances and angles are set out in Table I. The CH₃-As-Ni angles all considerably exceed the tetrahedral angle, probably because of methyl-methyl repulsion between the two diars groups; the other angles about arsenic are less than tetrahedral.

Table I. Principal Intramolecular Distances and Angles^a

| Bond | Bond length, Å | Bond | Bond angle, deg |
|----------------------------------|----------------|---|-----------------|
| Ni-As ₂ | 2.37 | As ₂ -Ni-As ₃ | 86.2 |
| Ni-As ₃ | 2.34 | As ₂ -Ni-Cl ₄ | 92.9 |
| Ni-Cl ₄ | 2.43 | As ₃ -Ni-Cl ₄ | 92.0 |
| As ₂ -C ₇ | 1.92 | C ₇ -As ₂ -Ni | 108.6 |
| As ₂ -C ₁₄ | 1.93 | C ₇ -As ₂ -C ₁₂ | 105.5 |
| As ₂ -C ₁₂ | 1.92 | C ₇ -As ₂ -C ₁₄ | 99.3 |
| As ₃ -C ₆ | 2.01 | C ₁₂ -As ₂ -Ni | 117.6 |
| As ₃ -C ₁₃ | 1.87 | C ₁₂ -As ₂ -C ₁₄ | 104.6 |
| As ₃ -C ₁₅ | 1.97 | C ₁₄ -As ₂ -Ni | 118.4 |
| | | C ₆ -As ₃ -Ni | 108.4 |
| | | C ₆ -As ₃ -C ₁₃ | 102.7 |
| | | C ₆ -As ₃ -C ₁₅ | 101.0 |
| | | C ₁₃ -As ₃ -Ni | 119.9 |
| | | C ₁₃ -As ₃ -C ₁₅ | 100.5 |
| | | C ₁₅ -As ₃ -Ni | 121.3 |

^a The standard deviations (Å) in the distances are about 0.004 for Ni-As, 0.006 for Ni-Cl, and 0.03 for As-C.

We have examined esr spectra of [Ni(diars)₂Cl₂]Cl in the powder form at room temperature and in a frozen ethanol solution at 77°K. In the powder spectrum, three separate *g* values are in evidence; the components of the *g* tensor are *g*₁ = 2.05, *g*₂ = 2.09, *g*₃ = 2.14, Δ*g* = 0.09. In addition, the low-temperature spectrum exhibits hyperfine splitting of approximately 23 gauss which can be assigned to the interaction of the unpaired electron with the four equivalent ⁷⁵As (*I* = 3/2) nuclei. This hyperfine splitting is of considerable interest, because it is the first time arsenic splitting has been observed in a metal complex; it clearly indicates that the unpaired electron is found an appreciable fraction of time on the As donor atoms.

The rhombic *g* tensor and the large total *g* anisotropy are reminiscent of the esr properties of the spin-doublet nickel complexes containing bidentate, sulfur-donor ligands.³ For example, Ni(mnt)₂⁻, whose electronic structure has been the subject of vigorous discussion,³ has a rhombic *g* tensor with Δ*g* = 0.16.⁴ Assuming idealized D_{2h} symmetry, the esr data on Ni(mnt)₂⁻ have been interpreted in terms of a ...[b_{2g}(*xz*)]¹ = ²B_{2g} ground state.⁴ This ²B_{2g} ground state is unlikely for Ni(diars)₂Cl₂⁺, however, because the ligand orbitals which participate in the level of b_{2g} symmetry in Ni(mnt)₂⁻ are unavailable in Ni(diars)₂Cl₂⁺, being strongly involved in σ bonding to the methyl groups of the diars itself. An alternative approach would be to assume a conventional ligand-field model; we would expect the electronic energy levels for an axially elongated, six-coordinate D_{2h} structure to be b_{1g}(*xy*) > a_g(*z*²) >> a_g(*x*² - *y*²) > b_{2g}(*xz*) ~ b_{3g}(*yz*). This would give Ni(diars)₂Cl₂⁺ a [b_{3g}(*yz*)]²[b_{2g}(*xz*)]²[a_g(*x*² - *y*²)]²[a_g(*z*²)]¹ =

(3) (a) F. Lalor, M. F. Hawthorne, A. H. Maki, K. Darlington, A. Davison, H. B. Gray, Z. Dori, and E. I. Steifel, *J. Am. Chem. Soc.*, **89**, 2278 (1967), and references therein. (b) mnt²⁻ = (CN)₂C₂S₂²⁻.

(4) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid.*, **86**, 4850 (1964).

²A_g ground state, if the Ni(III) d⁷ formulation has any merit. A ground state with the unpaired spin in a *z*² level, however, leads to the prediction of a *g* tensor with small anisotropy and approximately axial symmetry, in contrast to what is actually found.

Additional evidence against the Ni(III) ²A_g ground state has been obtained by measuring the esr spectrum of the uncomplexed diars radical cation. Production of the radical cation was achieved by *in situ* uv irradiation (λ > 2200 Å) of a frozen ethanol solution (88°K) of diars. The esr spectrum was recorded during irradiation. The anisotropic pattern (Δ*g* = 0.14) observed for (diars)⁺ is very similar to that of Ni(diars)₂Cl₂⁺, suggesting that the molecular orbital bearing the unpaired electron in the complex is directly derived from that in the radical cation itself. The filled levels of highest energy in diars must involve the lone pairs on the As atoms. These two orbitals give rise to two delocalized molecular orbitals, one symmetric (σ⁺) and one antisymmetric (σ⁻) with respect to rotation about the molecular C₂ axis. The higher energy orbital of the two, σ⁻, must bear the unpaired electron in (diars)⁺; σ⁻, however, is of improper symmetry to combine with the totally symmetric *z*² orbital on the metal. Thus the Ni(III) d⁷ formulation is incompatible with the esr experiments.

A model for the ground state of Ni(diars)₂Cl₂⁺ consistent with the esr data can be built from that proposed for (diars)⁺. The As lone-pair orbitals of the two diars ligands give four symmetry orbitals of relative energies a_g < b_{3u} ~ b_{2u} < b_{1g}. These orbitals may then be combined with the Cl-Ni-Cl unit to give a qualitative overall orbital scheme. The highest filled level of the (diars)₂⁺ combination, b_{1g}(L), is of proper symmetry to combine with the metal b_{1g}(*xy*) orbital. The suggested ground state for Ni(diars)₂Cl₂⁺ is therefore [b_{3g}(*yz*)]²-[b_{2g}(*xz*)]²[a_g(*x*² - *y*²)]²[a_g(*z*²)]²(b_{1g})¹, where b_{1g} is mainly composed of b_{1g}(L) and is σ bonding between Ni and each As.

The unconventional "σ radical" ground-state model proposed here provides an explanation for the fact that the Ni-As bond distances are significantly greater in Ni(diars)₂Cl₂⁺ than in Ni(diars)₂I₂⁵ (2.34-2.37 vs. 2.28-2.30 Å, with standard deviations of less than 0.005 Å in both cases). The increase in bond length on oxidation is the strongest direct evidence in support of the model and is in contrast to the observed slight decrease in Ni-S bond distances in going from Ni(mnt)₂²⁻ to Ni(mnt)₂⁻.⁶

In summary, both esr and direct structural data are in agreement with the formulation of Ni(diars)₂Cl₂⁺ as a metal-stabilized "σ-radical" structure. We are now investigating the single-crystal esr spectrum of [Ni(diars)₂Cl₂]Cl and the isolated (diars)⁺ radical cation in order to add more detail to the present electronic structural model.

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(6) The variation in Ni-S distances indicates that the highest occupied level is [Ni-S] antibonding, as discussed by D. Sartain and M. R. Truter, *J. Chem. Soc., Sect. A*, 1264 (1967).

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