The Structure and Properties of the Diamagnetic Tris(*o*-phenylenebisdimethylarsine)nickel(II) Ion

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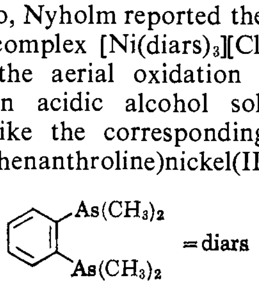
Abstract: A new and convenient method for the preparation in quantity of the diamagnetic complex $[Ni(diars)_3][ClO_4]_2$ is described; its properties have been examined in some detail. A study of the nuclear magnetic resonance spectrum indicates a close similarity with that of $[Co(diars)_3][ClO_4]_3$. This behavior, together with other properties, suggests that the complex cation has a regular octahedral arrangement. Octahedral symmetry would be expected to lead to paramagnetism. A possible explanation for the observed diamagnetism and an interpretation of the electronic spectrum which is consistent with the hypothesis advanced, in essence, requires electrical asymmetry arising from σ and π bonding in a D_3 field.

Some years ago, Nyholm reported the isolation of the red nickel complex $[Ni(diars)_3][ClO_4]_2$ (see I) as a by-product of the aerial oxidation of the complex $[Ni(diars)_2]Cl_2$ in acidic alcohol solution.[1] It was expected that like the corresponding tris(bipyridyl)- and tris(1,10-phenanthroline)nickel(II) cations, this substance would be paramagnetic but it is, in fact, diamagnetic. Considerable theoretical interest attaches to this compound because, unlike the six-coordinate derivatives of the type $[Ni(diars)_2I_2]$, it is not easy to see why a tetragonal distortion, which could explain the diamagnetism, should arise. Work on the properties of this compound has been seriously limited previously because the complex, being a low-yield by-product, was available only in small amounts and so a new method of preparation of $[Ni(diars)_3][ClO_4]_2$ was developed and is reported here. The reaction between nickel chloride hexahydrate and 3 equiv of the ditertiary arsine in cold diethylene glycol leads to the formation of $Ni(diars)_2Cl_2$, the properties of which, in nitromethane solution, are consistent with its formulation as a complex of five-coordinate nickel(II), *viz.*, $[Ni(diars)_2Cl]Cl$.[2] However, if the diethylene glycol solution is heated under reflux for about 1 hr one obtains, in addition to $[Ni(diars)_2Cl]Cl$, which is the main product, some nickel metal and about 10% $[Ni(diars)_3]Cl_2$. This is established from a study of the visible absorption spectrum since the tris(ditertiary arsine) complex has sharp and intense ($\epsilon \sim 1500$ l. mole^{-1} cm^{-1}) absorption bands at 22,985 and 18,870 cm^{-1}. The required complex can be readily isolated from the bis(ditertiary arsine) cation as the insoluble tetraphenylborate which can then be converted into the perchlorate by treatment with perchloric acid. It is noteworthy that, although the $[Ni(diars)_3]^{2+}$ cation, once formed, is very robust, prolonged heating under reflux of a solution of nickel chloride or perchlorate with an excess of the diarsine in several solvents (including ethanol, acetone, dimethyl sulfoxide, dimethylformamide, and the diarsine itself) failed to yield any spectrophotometrically detectable amount of the tris(ditertiary arsine) complex in solution. Some $[Ni(diars)_3]^{2+}$ ion is formed when nickel chloride and diarsine are heated together in ethanol solution (under pressure) for 24 hr at 200°. In neither of these reactions is the yield of $[Ni(diars)_3]^{2+}$ critically dependent upon the ratio of diarsine to nickel chloride; we do not know the mechanism of the formation of the tris(ditertiary arsine) cation but suspect that the reaction proceeds *via* an oxidation–reduction mechanism involving two or more oxidation states of nickel. The fact that the compound is difficult to form but, *once formed*, it is very robust, suggests that the reaction is kinetically, rather than thermodynamically, controlled.



I

Properties of $[Ni(diars)_3][ClO_4]_2$

The complex is sparingly soluble in cold water but dissolves readily in dimethylformamide and in concentrated mineral acids; it is stable for several days when dissolved in hot dilute or cold concentrated mineral acids but is decomposed rapidly by strong alkalis. When an aqueous solution is treated with ceric ammonium sulfate in acid ($HClO_4$ or HNO_3) solution, a transient green color is observed but fades rapidly to form a practically colorless solution. This behavior is in marked contrast to the stability of the $[Ni(diars)_2Cl_2]^+$ ion. However, instability of tris(ditertiary arsine) complexes is not unusual: the $[Fe(diars)_3]^{3+}$ cation has not yet been isolated and the $[Co(diars)_3]^{3+}$ cation is much less stable than the $[Co(diars)_2Cl_2]^+$ ion.

Attempts have been made to prepare a derivative of lower oxidation state. The red $[Ni(diars)_3]^{2+}$ ion reacts readily with sodium borohydride to yield a yellow precipitate which is unstable in air and decomposes even in the absence of oxygen. Ethanolic solutions of this compound decompose rapidly to yield dark brown products which have spectra that are quite different from that of the $[Ni(diars)_3]^{2+}$ ion. All attempts so far to isolate products of oxidation or reduction which show a reproducible composition or reasonable stability have been unsuccessful.

The spectrum of the $[Ni(diars)_3]^{2+}$ ion, Figure 1, is entirely different from those of typically paramagnetic, octahedral, divalent nickel complexes. Two bands are observed in the 350–1200-mμ region, one at 435 mμ and the other at 530 mμ and both of high intensity. A very

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[1] R. S. Nyholm, *J. Chem. Soc.*, 2061 (1950).

[2] C. M. Harris, R. S. Nyholm, and D. J. Phillips, *ibid.*, 4379 (1960).

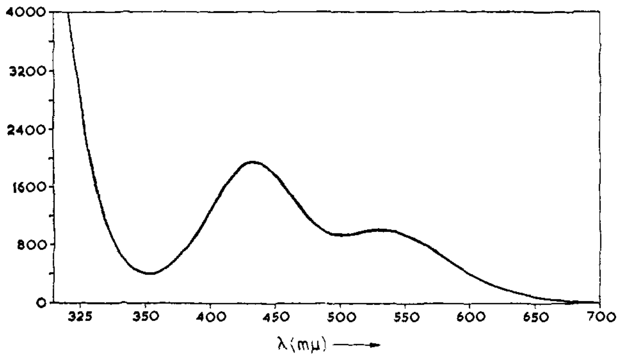

Figure 1. Electronic absorption spectrum of $[Ni(diars)_3][ClO_4]_2$ in aqueous solution.

intense band is observed below 350 mμ, with a maximum at 305 mμ, where the free ligand absorbs, but there is no evidence for any "d–d transitions," other than the two given above.

The magnetic susceptibility per gram of the powdered perchlorate at 20° is -0.34×10^{-6} cgs unit; this gives a corrected molar susceptibility (χ_m') for the metal atom of 146×10^{-6} cgs unit and hence an effective magnetic moment of 0.6 BM, presumably due to temperature-independent paramagnetism.

Discussion of Structure

Attempts to prepare the compounds $[Co(diars)_3][PO_4]$ and $[Ni(diars)_3][SO_4]$, which, it was hoped, would be isomorphous and hence establish the structure of the nickel(II) complex, were not successful.

A study of the nuclear magnetic resonance of the protons of the methyl group of the $[Ni(diars)_3]^{2+}$ cation, in dimethylformamide solution, has been carried out and compared with that of the undoubtedly octahedral $[Co(diars)_3]^{3+}$ cation in D_2O. Both complexes give two sharp symmetrical methyl proton peaks of equal height and area. The resonances occur at τ 7.97 and 8.19 for the nickel complex and at τ 7.63 and 7.93 for the cobalt complex. One could certainly expect that, if the nickel cation was tetragonally distorted, more than two different types of methyl group would be observed. The fact that this does not occur is taken as good evidence for a regular octahedral structure. The narrowness of the nmr lines is consistent with the diamagnetism determined independently on the solid. Narrow resonance lines do not establish diamagnetism unambiguously, since a paramagnetic complex with an extremely short electron relaxation time would also give narrow lines. However, under such circumstances, contact shifts would be observed, and one would not expect to find the resonances in the region usually expected for the methyl group.

A regular octahedral arrangement with D_3 symmetry should give two methyl proton peaks of equal area since each arsenic atom in such a structure contains environmentally nonequivalent methyl groups. However, two other structures were considered: the trigonal prism (D_{3h} symmetry)[3] and a structure based on a trigonal prism where one of the diarsine groups is rotated through 90°, to give a structure of C_{2v} symmetry. In the first of these all the methyl groups would be equivalent; in the second, there would be three nonequivalent groups each containing four methyl groups. Other structures, so far unknown, which might give two methyl proton lines of equal area can be envisaged, but, preferring the simplest interpretation of the results, we conclude that the ion $[Ni(diars)_3]^{2+}$ probably has a regular tris bidentate octahedral geometry. This then leaves us with the problem of explaining the diamagnetism.

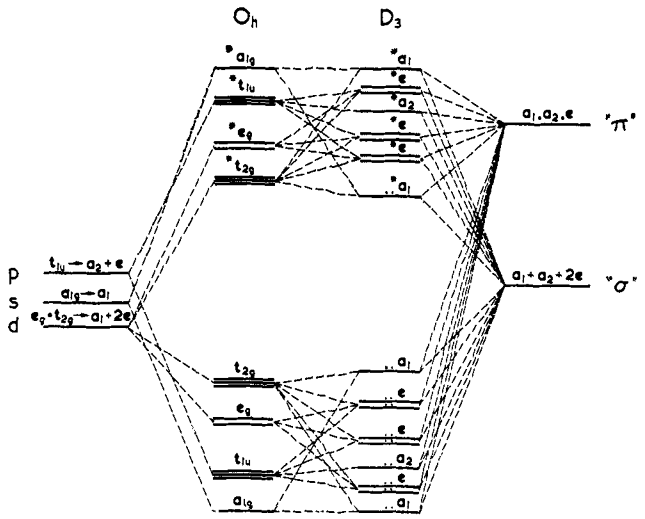

Figure 2. A qualitative molecular orbital diagram of the $[Ni(diars)_3]^{2+}$ ion showing a correlation between the metal and arsenic states and also the relationship between the molecular orbitals of O_h and those of D_3. The relative energies of the states are diagramatic and are not meant, except for the qualification given in the Discussion, to imply any particular energetic relationship.

Taking into account terms arising only from the d-electron set, crystal-field theory indicates that a regular octahedral structure (O_h) should have a $^3A_{2g}$ ground term and that the closest singlet above this term is the ^1E_g term. It is not possible, without contravening Hund's rule (of maximum multiplicity), to allow this singlet term to cross the ground term; there may not be such a restriction if we include singlet terms arising from a coupling scheme involving d, s, and/or p orbitals.[4] However, because of the flexibility of the method and because other formalisms should be ultimately equivalent, we have chosen to interpret the results in terms of a molecular orbital scheme.

The ion $[Ni(diars)_3]^{2+}$ belongs to the point group D_3, and arguments based totally on the symmetry of the complex are consistent with the qualitative molecular orbital diagram shown in Figure 2. In constructing this diagram we have used the 3d, 4s, and 4p orbitals of the metal, six "σ orbitals" originally filled, one from each arsenic, and also included the originally empty 4d "π orbitals" from the arsenics. Accordingly, the d, s, and p orbitals of the metal will transform respectively as $a_1 + 2e$, $a_1 + e$ while both the "σ orbitals" and the "π orbitals" of the arsenic atoms will transform as the species a_1, a_2, and e. It will be noted that, in this field, the distinction between σ and π bonding is lost and, furthermore, states belonging to the same

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[3] R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, 87, 3776 (1965); E. I. Stiefel and H. B. Gray, *ibid.*, 87, 4012 (1965).

[4] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 737.

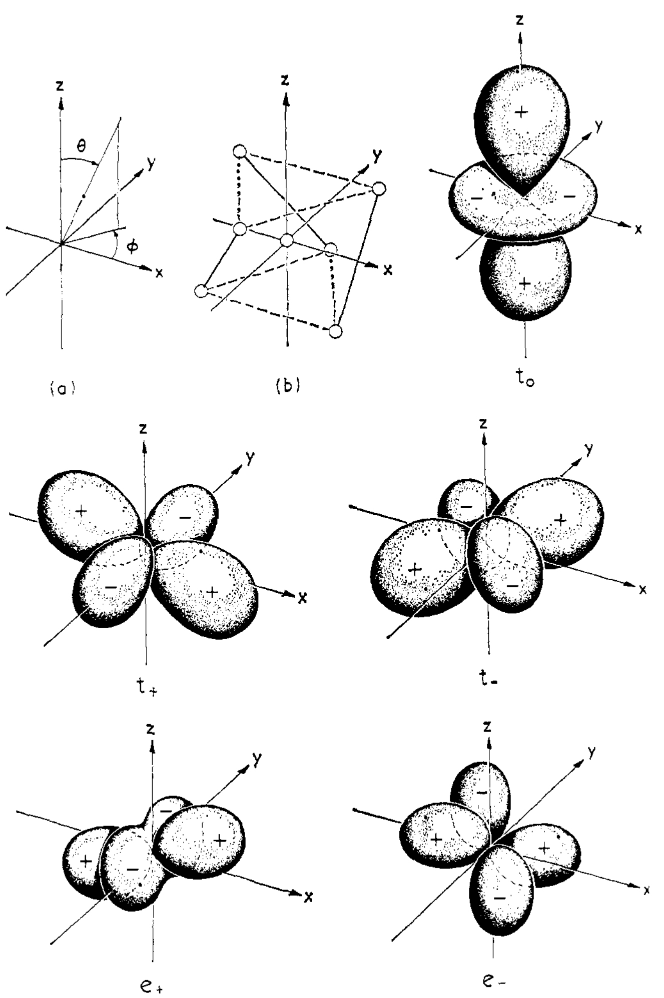

Figure 3. Trigonal d orbitals which form the basis for the irreducible representations of both O_h and D_3. These orbitals refer to the conventions shown in (a) and the coordinate system shown in (b).

symmetry species that are derived from the metal orbitals can become "mixed."

The over-all ordering of the molecular orbitals is unimportant except that the final two electrons must be accommodated in a singly degenerate state lying sufficiently below a doubly degenerate state to cause spin pairing.[5] If our scheme is correct, the two electronic transitions observed (Figure 1) involve the promotion of an electron from the $^*a_1$ orbital to two of the antibonding states lying above it. We do not think that these excitations are to the empty arsenic 4d orbitals since, in other arsine complexes, such transitions do not appear in the visible region. The high intensity of the observed transitions is probably due to the "mixing in" of allowed transitions on the ligand, metal–ligand charge transfer transitions, and the mixing of the d- and p-orbital functions in this field. Although we are uncertain of the precise ordering of the levels, the separation between the ground state and the next-excited state is almost 19,000 cm^{-1} which, although a considerable separation is required for diamagnetism, seems particularly large if we consider that the splitting is due to a trigonal perturbation on an essentially octahedral bonding scheme (Figure 2). We therefore outline a model which might plausibly account for the large splittings.

In discussions of the spectra and magnetism of octahedral metal complexes it is usually a sufficient approximation to consider the donor group microsymmetry of the complex.[6] Thus, for example, $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ ions have very similar magnetic and spectral characteristics, and, although the latter complex belongs strictly to the point group D_3, it is sufficient for most circumstances to consider the effect of the chelate rings in $[Ni(en)_3]^{2+}$ to be a minor perturbation on a set of orbital functions which are quantized along the fourfold axis of O_h. The properties of $[Ni(diars)_3]^{2+}$ indicate that such assumptions are no longer valid even in accounting for the gross characterics of the complex.

We have therefore chosen to investigate the consequences of assuming that the orbital functions, of the central nickel atom of $[Ni(diars)_3]^{2+}$, are best approximated by a set of trigonal functions which arise from quantization along the threefold axis of symmetry. These d orbitals, in real form, are given in Table I,[7]

Table I

$$\left.\begin{aligned}\sqrt{2/3}\,d_{(x^2-y^2)} - \sqrt{1/3}\,d_{(xz)} &\equiv t_+\\ \sqrt{2/3}\,d_{(xy)} + \sqrt{1/3}\,d_{(yz)} &\equiv t_-\end{aligned}\right\}-e$$

$$\left.\begin{aligned}\sqrt{1/3}\,d_{(x^2-y^2)} + \sqrt{2/3}\,d_{(xz)} &\equiv e_+\\ \sqrt{1/3}\,d_{(xy)} - \sqrt{2/3}\,d_{(yz)} &\equiv e_-\end{aligned}\right\}-e$$

$$d_{(z^2)} \equiv t_0 \quad - a_1$$

together with the irreducible representations of D_3 under which they transform.

We have sketched these orbitals in Figure 3 where it must be remembered the z axis is the threefold axis of symmetry and the x axis is a twofold axis of symmetry of the complex. The s orbital will project symmetrically toward the arsenic atoms while, in this field, the p orbitals will be of two types: a degenerate pair ("p_x" and "p_y") which will project in the x,y plane and become mixed with the similar e d orbitals, and the a_2 orbital ("p_z"), which cannot mix with either the d or s orbitals, whose projection is in the z direction.

As has been shown, all these orbitals can become involved in both "σ" and "π bonding" with the arsenic atoms. We have not attempted any numerical calculations because of the gross approximations required to do so, but it is clear from Figure 3 that the four d orbitals comprising the two e symmetry states are directed toward the arsenic atoms much more than the a_1 (d_{z^2} orbital) state. Similarly, the orbitals comprising the e state derived from the metal p orbitals will be directed toward the ligands more than the a_2 state. It seems plausible, therefore, that the e symmetry states will form much stronger bonds than the singly degenerate a_1 and a_2 states, and because the bonding is due to a ligand of high-ligand field strength, it would seem reasonable to expect that the splittings between states will be large. If we assume that the order of the antibonding states will roughly reflect the order of the bonding states (Figure 2), this model might go some

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(5) L. E. Orgel, *J. Chem. Soc.*, 3683 (1961).

(6) *E.g.*, C. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book, Co., Inc., New York, N. Y., 1962.

(7) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

way in explaining the large separation between the ground and first excited state which is observed spectrally and implied magnetically.

Experimental Section

Tris(*o*-phenylenebisdimethylarsine)nickel(II) Perchlorate. Nickel chloride hexahydrate (1.2 g) and *o*-phenylenebisdimethylarsine (3.5 ml, 4.5 g) were mixed in warm diethylene glycol (30 ml). The resulting deep red-brown solution was refluxed for 1 hr, filtered in 100°, and diluted with ethanol (100 ml). Sodium tetraphenylborate (3 g) in acetone (10 ml) was added to the dark brown filtrate; thereupon a pink precipitate was formed. The mixture was warmed and stirred on a steam bath for a few minutes, and the precipitate was filtered and washed with successive portions of hot ethanol (total 500 ml) to remove any of the brown tervalent nickel bis(ditertiary arsine) complex. The solid was recrystallized from acetone–diethyl ether (yield 1.5 g). The tetraphenylborate salt (1.5 g) was taken up in acetone (400 ml) containing dilute perchloric acid (50 ml) and digested on a steam bath for 1 hr. The residue was filtered and dissolved in water (500 ml) and the solution heated for 2 hr. On cooling the solution deposited deep maroon crystals which were filtered and washed with cold water. A further crop of crystals was obtained by evaporating the filtrate to a small volume. Two recrystallizations from hot water containing a few drops of perchloric acid gave the pure salt (1.0 g).

Anal. Calcd for $C_{30}H_{48}O_8Cl_2As_6Ni$: C, 32.3; H, 4.3; Cl, 6.4; As, 40.3. Found: C, 32.4; H, 4.2; Cl, 6.3; As, 39.7.

The nuclear magnetic resonance of the nickel complex was measured by means of a 60-Mc/sec Perkin-Elmer RIO instrument, and that of the cobalt complex was measured with a 100-Mc/sec converted Varian (V-4300B) spectrometer.

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Kinetics and Mechanism of Substitution Reactions of Nitrosyltricarbonylcobalt(0)

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Abstract: Nitrosyltricarbonylcobalt(0) undergoes carbonyl substitution in the presence of phosphines, phosphites, arsines, pyridine and its derivatives, and isonitriles to give the monosubstituted derivatives, $CoNO(CO)_2L$. The preparation and spectra of several mono- and disubstituted derivatives are reported. The rates of these reactions depend on the concentration and nature of the nucleophile. For the phosphines and phosphites the reactions proceed at intermediate to fast rates, and for the arsines and pyridines the rates are slow. These results are in accordance with the substrate being a class b or soft metal. There is little effect on the rates of these reactions with changes in dielectric constant or coordinating ability of the solvent. For nucleophiles with the same ligand atom the rates of the reactions increase with increasing basicity (or polarizability) of the reagents. Triphenylarsine reacts at a rate which is both zero and first order in its concentration. Carbon monoxide exchange experiments indicate that the rate of exchange is independent of the CO concentration. However, the rate of CO substitution by $As(C_6H_5)_3$ at the extrapolated zero concentration of arsine is approximately 50-fold slower than the rate of CO exchange. The results obtained for the substitution reactions support a bimolecular displacement mechanism, and this is discussed in terms of the nature of the chemical bonding in $CoNO(CO)_3$.

Nitrosyltricarbonylcobalt(0) is a member of a family of neutral and anionic compounds which are both isostructural and isoelectronic with tetracarbonylnickel(0). Most of these compounds have been known for quite some time, and all of them form derivatives with appropriate reagents.[2] However, only during the last few years have kinetics studies been made on some of these reactions.[3]

Recently, there has been discussion concerning the anomalous behavior of $Ni(CO)_4$ in CO substitution and CO exchange reactions.[3c] Both reactions are first order in $Ni(CO)_4$ and independent of the concentration of the other reagent. However, the two reactions apparently take place by two different mechanisms since they proceed at different rates and are not competitive.

Heck[3b] has reported briefly on the reaction of $CoNO(CO)_3$ with $P(C_6H_5)_3$ in ether solutions. He found that the rate of reaction was first order in both substrate and nucleophile concentrations. Thus, although this carbonyl is structurally and electronically like $Ni(CO)_4$, the two are dissimilar in their kinetic behavior. Furthermore, the cobalt compound is apparently one of the few simple metal carbonyls that undergoes CO substitution by a process which is dependent upon the nature and concentration of the nucleophile.[3b] Therefore, it offers a unique opportunity to study the properties influencing nucleophilicity toward metals in low oxidation states. This paper reports the kinetic data concerning the first step of CO substitution of $CoNO(CO)_3$

$$CoNO(CO)_3 + L \longrightarrow CoNO(CO)_2L + CO \qquad (1)$$

where L = PR_3, $P(OR)_3$, AsR_3, pyridine and its deriva-

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[1] Taken in part from the Ph.D. Thesis of E. M. T., Northwestern University, 1966.

[2] J. Chatt, P. L. Pauson, and L. M. Venanzi, "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 468.

[3] (a) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961); (b) R. F. Heck, *ibid.*, **85**, 657 (1963); (c) L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *ibid.*, **88**, 2334 (1966).