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Transition Metal Nuclear Quadrupole Resonance. I. Cobalt-59 Nuclear Quadrupole Resonance in $Cs(1,2\text{-}B_9C_2H_{11})_2Co^{III}$ and the Bonding in Ferrocene

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The pure quadrupole resonance in $Cs(1,2\text{-}B_9C_2H_{11})_2Co^{III}$ has been observed and interpreted. It is shown that one electron of the $1,2\text{-}B_9C_2H_{11}{}^{2-}$ moiety is delocalized on the open face while one electron is delocalized in the boron polyhedral frame. The 1,2 carbons and the 4,7,8 borons are practically identical in their bonding to Co. It has been determined that a cyclopentadienyl moiety donates 0.4 ± 0.1 electron to the metal ϵ_{1g} orbitals and back-accepts 0.5 ± 0.1 electron from the metal ϵ_{2g} orbitals in ferrocene.

Introduction

A large number of carborane transition metal complexes have been synthesized and characterized in recent months.[1,2] One such class of metalocarborane complexes consists of a transition metal completing the icosahedral framework of the $B_9C_2H_{11}{}^{2-}$ anion.[3] These complexes have been formulated as π-bonded complexes structurally analogous to the metalocenes. The chemistry[4] of $B_9C_2H_{11}{}^{2-}$, Cb^{2-}, seems basically to parallel the chemistry of the π-cyclopentadienyl anion, Cp^-. For this reason a study was undertaken to investigate the explicit similarities and differences between a π-cyclopentadienyl–metal and π-carborane–metal bond and to ascertain whether or not there is any preferred bonding to the carbon or boron atoms in the $1,2\text{-}B_9C_2H_9{}^{2-}$ moiety.

In order to accomplish these ends the pure nuclear quadrupole resonance (nqr) spectrum of $Cs(1,2\text{-}B_9C_2H_{11})_2Co^{III}$ was found and compared with the nqr spectrum[5] of $(\pi\text{-}Cp)_2Co^{III}(ClO_4)$.

Experimental Section

The salts $Cs(1,2\text{-}B_9C_2H_{11})_2Co$ and $Cs(1,7\text{-}B_9C_2H_{11})_2Co$ were provided by Professor M. F. Hawthorne of the University of California, Riverside, Calif. A 2.3-g sample of the 1,2 isomer was sealed in a glass vial 15 mm in diameter and 35 mm long. The sample was placed in the radiofrequency coil of a high-power push–pull superregenerative spectrometer.[6] All frequencies in Table I were measured by spectrum-analyzing techniques.[7] The errors, about 30 KHz, were estimated as half the quench frequency. The signal-to-noise ratios given in Table I apply to a sweep rate of 5 MHz/hr and a lock-in time constant of 1 sec.

No signal could be detected in a 1.0-g sample of the 1,7 isomer in the range 10.0–35.0 MHz.

The visible and uv spectra of the 1,2 isomer were obtained on a Cary 14 spectrometer.

Discussion

The absence of any detectable nqr signal in the 1,7 isomer is not surprising in view of the disorder that exists[3] in the solid state. In effect, the statistical disordering of the carborane polyhedra around the Co ion broadens the resonance to such an extent that it is not detectable by conventional techniques. It seems unlikely that the resonance frequency, if detected, would be appreciably different from that of the 1,2 isomer.

The fact that such a strong nqr signal is, however, observed in the 1,2 isomer is reasonable evidence to support the view that it, unlike the 1,7 isomer, is not disordered in the crystalline state.

A comparison of the uv and visible spectra of bis(cyclopentadienyl)cobalt(III) perchlorate[8] and the cesium bis(*o*-carborane)cobaltate(III) (*cf.* Table II) reveals no energy differences greater than 10%. The spectrum suggests that the two compounds are electronically similar to one another.

Interpretation

In nqr[9] one measures the interaction of an electric field gradient, q, with a nuclear quadrupole moment, Q. A nucleus must possess a nuclear spin, I, greater than $^1/_2$ in order that it have a quadrupole moment. In the case of Co^{59}, $I = {}^7/_2$. A finite field gradient around a nucleus requires that the total electronic potential around a nucleus be neither spherically symmetric nor cubic. In effect, one measures the departure from spherical or cubic symmetry. The applicability of nqr to the study of ligand field effects is self-evident. Such studies provide one with a probe capable of sensing both subtle and dramatic changes in the electronic environment around a given transition metal ion. Such changes can be related to bonding in a general way *via* either a valence bond[10] or molecular orbital[11] interpretation.

In the present study the electric field gradient and the asymmetry parameter, η, were determined from

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Table I

Nqr Frequencies in $Cs(1,2\text{-}B_9C_2H_{11})_2Co^{59}$

Co^{59} transitions	Freq, MHz	Signal/noise
$\pm{}^1/_2 \rightarrow \pm{}^3/_2$	11.62	20/1
$\pm{}^3/_2 \rightarrow \pm{}^5/_2$	23.06	35/1
$\pm{}^5/_2 \rightarrow \pm{}^7/_2$	34.62	43/1

Table II

Transition	$(C_5H_5)_2CoClO_4$[a]	$CsCo(1,2\text{-}B_9C_2H_{11})_2$	$(C_5H_5)_2Fe$[b]
ν_1[c]	38,400	35,500	41,700
ν_2	32,700	30,000	30,800
ν_3	24,700	22,300	22,700

[a] Taken from ref 8. [b] Taken from G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, **74,** 2125 (1952). [c] Charge-transfer band.

the data in Table I. Using Cohen's solutions[12] of the secular equation for a nucleus with a spin of $^7/_2$ and the value for the Co^{59} nuclear quadrupole moment,[13] q_{zz} and η defined in terms of its irreducible tensor components (eq 1) can be calculated. The liquid-nitrogen

$$\eta = (q_{xx} - q_{yy})/q_{zz} \qquad (1)$$

and room-temperature values are summarized in Table III for Cp_2CoClO_3 and $Cs(1,2\text{-}B_9C_2H_{11})_2Co$, respectively.

Table III

Field Gradients and Asymmetry Parameters

	$(C_5H_5)_2CoClO_4$[a]	$CsCo(1,2\text{-}B_9C_2H_{11})_2$
q_{zz}, esu/cm^3	5.85×10^{15}	5.51×10^{15}
η	0.0	0.03 ± 0.01

[a] Calculated from data in ref 5.

The direction of the diagonal field gradient tensor in Cp_2Co^+ and $(1,2\text{-}B_9C_2H_{11})_2Co^-$ is primarily determined by the molecular symmetry of the respective ions. In cobalticinium perchlorate the z direction, q_{zz}, is along the fivefold rotation axis. Although the crystal structure of cobalticinium perchlorate has not been reported, it is safe to assume that the point charge sum over the anions and cations in both compounds, *i.e.*, the crystal field contribution, is insufficient to contribute appreciably to either the magnitude or direction of q_{zz}. The very small coupling constants attributable only to the crystal field effects which have been found in $Co(NH_3)_6Cl_3$[14] and $Co(en)_3Cl_3 \cdot 3H_2O$[15] are less than 2% of the coupling constants reported here.

The direction of q_{zz} in the carborane complex is subject to less certainty. It must, however, lie along a plane intersecting the boron at the apex of the polyhedron, the Co, and the center of the C–C bond joining the 1 and 2 positions. This is shown in Figure 1. In all likelihood it is along or only a few degrees off the S_2 axis since the asymmetry parameter, η, is but 0.03.

The molecular electronic interpretation of the electric field gradient is straightforward. In either a valence bond or molecular orbital approach q_{zz} arises from an imbalance of valence electrons. In first-row metalocenes and metalocarboranes there is the possibility of having 3d, 4s, and 4p electrons participating in the metal-to-ligand bond. Since s electrons do not contribute to the field gradient, we need only directly consider 3d and 4p electrons. The indirect effects of 4s populations can safely be ignored since it has been shown that the mixing of the 4s with the $3d_{z^2}$ is less than 1% in vanadocene.[16] It seems generally true that the 4s contribution to bonding in first-row metal complexes is small at best.

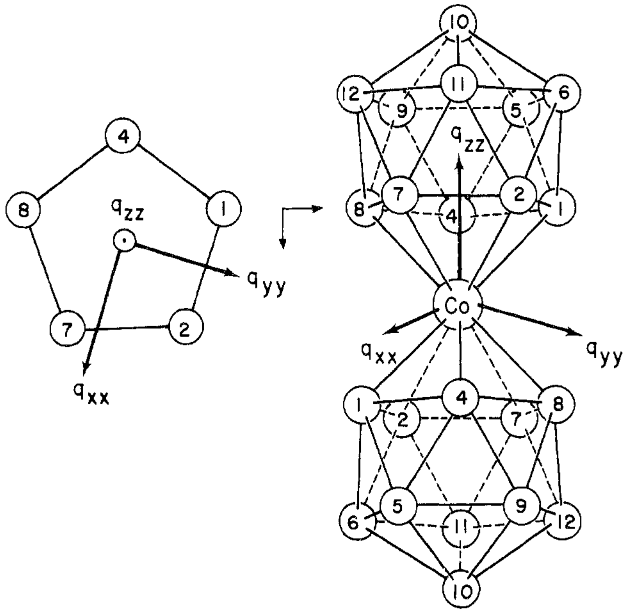

Figure 1.—The relation of the field gradient tensor to the structure of $(1,2\text{-}B_9C_2H_{11})_2Co^-$.

Utilizing the relation of the field gradient to angular momentum,[17] *i.e.*

$$q_{n,l,m} = q_{n,l,0}[1 - (3m^2/l(l+1))] \qquad (2)$$

when n, l, and m are the principal quantum number, angular momentum quantum number, and magnetic quantum number, respectively, one can write an expression for q_{zz} in terms of the various types of d and p electrons

$$q_{zz} = q_{3,2,0}[3d_{z^2} + (3d\epsilon/2) - 3d\delta] + q_{4,1,0}[4p_z - (4p\pi/2)] \qquad (3)$$

where $d\epsilon = d_{xz}, d_{yz}$; $d\delta = d_{x^2-y^2}, d_{xy}$, in the coordinates of Figure 1.

Utilizing equations relating the field gradient to the fine-structure splitting[17] and using Slater's method[18] for determining the Co effective nuclear charge seen by a 3d and 4p electron in the configuration $(Ar)3d^64p^1$, it can be shown that the field gradient arising from one 3d electron is at least 3 times larger than that from a 4p electron. Actual measurements[19] indicate a dif-

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ference of 6.8 times between a Cu 3d and a 4p electron. In all probability the difference in Co would be around 5 ± 1. This can be estimated from differences in the Co and Cu magnetic hyperfine interaction.[19] Recent calculations[20] have estimated the 4p population in octahedral Co(III) complexes at 0.1 electron per 4p orbital. Because of the transformation properties of the 4p and ligand orbitals in D_{5d} this estimate would result in only about 0.1 electron in both the $4p_x$ and $4p_y$ orbitals. Thus, the total contribution to q_{zz} from 4p population would only be 0.02 of that from a $3d_{z^2}$ electron. The molecular field gradient for either complex can thus be written

$$q_{zz} = q_{3,2,0}[3d_{z^2} + (3d\epsilon/2) - d\delta - 0.02] \quad (4)$$

The value for the field gradient contribution of one Co $3d_{z^2}$ electron can be calculated using the quadrupole coupling constant, $B(^4F_{9/2})$, and the magnetic hyperfine interaction obtained from the $^4F_{9/2}$ state measured by Co atomic beam spectroscopy.[13]

In the Fermi hole formalism the $^4F_{9/2}$ state is three 3d positrons in m_l states 2, 1, and 0. Using eq 2 and the measured nuclear quadrupole moment for Co^{59} it can be shown that $q_{zz}(3d_{z^2}) = -9.53 \times 10^{15}$ esu/cm^3. It should be emphasized that this is only a working number. It neglects the Sternheimer correction[21] $(1 - R)$ and a small contribution from spin–orbital coupling.[22] For comparative purposes and for estimating relative electron distribution changes in Co complexes, it is more than adequate. It is immediately obvious from a comparison of q_{zz} for Cp_2Co^- and Cb_2Co^+ and the similarity of their respective visible and uv spectra that the populations of the various 3d orbitals in each compound are virtually identical. This means that the metal-to-ligand bond is identical in both complexes. Since Cp formally has a single negative charge and Cb has a dinegative charge, the data imply that in carborane complexes one charge is delocalized on the open face of the bonds to the Co and the other is delocalized in the boron polyhedron in the 5, 6, 9 , 10, 11, and 12 positions. The second fact that is apparent from the small asymmetry parameter is that the 1,2 carbon positions and the 4,7,8 boron positions are practically identical in both their charge and their ability to donate electrons to the Co. In other words, as far as the electronic environment of Co is concerned, the borons appear as carbons to within 3–4%.

The transition metal to carbon bond lengths in the icosahedral face of $C_5H_5Fe(1,2\text{-}B_9C_2H_{11})$[23] and $Cs(1,2\text{-}B_9C_2H_{11})Re(CO)_3$[24] are, respectively, only 0.05 and 0.03 Å shorter than the transition metal to boron distance. In view of the standard deviations and large thermal motion associated with the bond distances, it is questionable whether any significance can be placed on these values. In any case, real or unreal, the apparent differences are certainly not large enough to indicate any appreciable difference in bonding to the carbons and borons in these molecules.

Using eq 3 one can estimate the effective electron distributions in a series of related metalocenes and carboraneocenes.

Consider first the Co(III) complexes. To a first approximation the compounds can be considered as Co(III) complexes with $3d_{x^2-y^2}{}^2$, $3d_{xy}{}^2(3d\delta^4)$, $3d_{xz}{}^0$, $3d_{yz}{}^0(3d\epsilon^0)$, and $3d_{z^2}{}^2$ electrons. This approximation assumes no metal-to-ligand covalency and is made only to predict the sign of the molecular q_{zz}.

The resulting field gradient, $q_{zz} = +19.06 \times 10^{15}$ esu/cm^3, is positive. This value is 3.45 and 4.46 times too large (in units of q_{zz} measured) assuming q_{zz} measured is positive and negative, respectively. In either case it is clearly necessary to invoke a substantial amount of covalency to account for the observed value. We will assume that the measured values in both Co complexes are positive insofar as the isoelectronic ferrocene q_{zz} has been shown to be positive.[25] In addition, the extent of covalent interaction necessary to account for a positive value is less than that for a negative value.

If we assume that the lattice sum contribution, ~2%, and the errors in the contribution from 4p electron populations in the complexes are additive, which may or may not be true, maximum errors in eq 5 can be

$$3d_{z^2} + (3d\epsilon/2) - 3d\delta = -0.558[Cb_2Co^-] \quad (5a)$$

$$3d_{z^2} + (3d\epsilon/2) - 3d\delta = -0.595[Cp_2Co^+] \quad (5b)$$

estimated as 5–7%. These equations include covalency *via* donation of ligand electrons into the $3d\epsilon$ and back-acceptance of metal $3d\delta$ into the ligand π^*.

Consider now ferrocene and ferrocinium. The field gradient for a 3d electron in iron can be calculated from the ratios of the various $[r^{-3}]$ values.[26] $q_{3,2,0}$ are listed in Table IV for some first-row transition metals for future reference.

Equations similar to (5) can be written for ferrocene and ferrocenium using $q^{Fe}_{3,2,0}$, $Q(Fe^{57m})$, and the quadrupole coupling constants obtained from Mössbauer spectroscopy.[27,28] The mixed cyclopentadienylcarborane complex of Fe(III),[29] $(C_5H_5)Fe(C_2B_9H_{11})$, has to within experimental error the same quadrupole coupling constant as ferrocenium bromide. Although the quadrupole splitting in the Mössbauer spectra of the biscarborane of Fe(III), $[(CH_3)_4N][Fe(C_2B_9H_{11})_2]$, is unresolved,[29] the estimated value is practically the same as for ferrocenium bromide.

The population of the $3d_{z^2}$ orbital can safely be assumed to equal two electrons. Explicit evaluation of the overlap integral[30] between the Fe(II) $3d_{z^2}$ orbital and the a_{1g} orbital of cyclopentadienyl yields a value of only 0.01; thus, the $a_{1g}{}^2$ MO (*cf.* Figure 2) is for all prac-

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TABLE IV

$q_{3,2,0}$ FOR ONE 3d ELECTRON (ESU/CM^3)

Ti^{47}	-3.02×10^{15}
V^{51}	-4.07×10^{15}
Cr^{53}	-5.30×10^{15}
Mn^{55}	-6.65×10^{15}
$^*Fe^{57m}$	-8.08×10^{15}
Co^{59}	-9.53×10^{15}
Ni^{61}	-11.0×10^{15}
Cu^{63}	-13.2×10^{15}

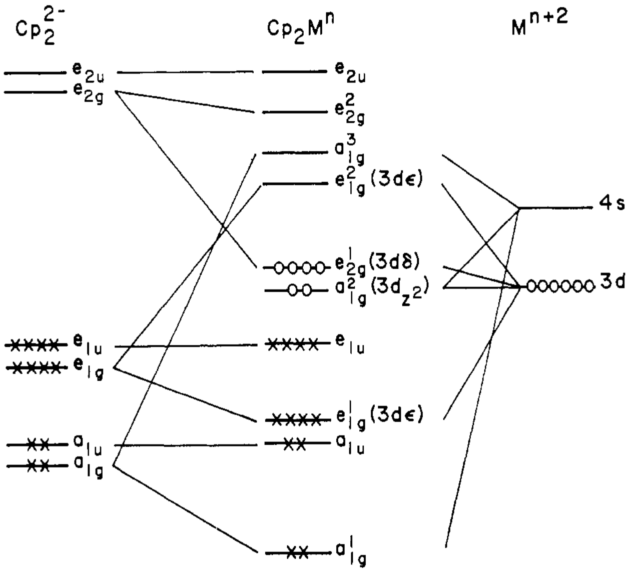

Figure 2.—Qualitative MO diagram of 3d^6 metalocenes.

tical purposes a pure $3d_{z^2}$ wave function. This would naturally be true for Fe(III) and Co(III) orbitals. Therefore, solutions for the observed quadrupole coupling constants can be obtained in terms of only the 3dϵ and 3dδ populations and $Q(Fe^{57m})$ in the case of Fe complexes.

A straightforward interpretation of the quadrupole splitting in the Fe complexes is hampered by the unreliability of the Fe^{57m} nuclear quadrupole moment. Values ranging from 0.1 to 0.46 barn have been recently postulated. There is one redeeming feature common to both Cp_2Fe and Cp_2Co^+ that provides one a very interesting handle on the problem. It is apparent from Table II that the uv and visible spectra of Cp_2Fe and Cp_2Co^+ are sufficiently similar to presuppose that the 3d orbital coefficients are within 5% of each other. A 5% change in a MO coefficient can result in eV changes in the energies of the MO. Furthermore, it is reasonable to assume from a covalency point of view that the Cp–Co(III) and Cp–Fe(II) bonds are within 10% of each other. Finally it will be shown that while assuming equivalent Cp–Co(III) and Cp–Fe(II) bonds one can calculate a Fe^{57m} Q and the 3d orbital coefficients in Cp_2Fe which are in accord with theoretical results. These numbers will, of course, be subjected to about 20 and 10% error, respectively.

Using the available Mössbauer data, eq 6 and 7 in terms of the number of 3dϵ and 3dδ electrons and $Q(Fe^{57m})$ can be arrived at for Cp_2Fe and Cp_2Fe^+, respectively. γ and γ^1 are the quadrupole splittings of

$$(3d\epsilon/2) - 3d\delta_{Cp_2Fe} = -[2\gamma/eq_{3,2,0}^{\overset{Fe}{}}{}^{3d}][Q(Fe^{57m})]^{-1} - 1.98 \quad (6)$$

$$(3d\epsilon/2) - 3d\delta_{Cp_2Fe^+} = +[2\gamma^1/eq_{3,2,0}^{\overset{Fe}{}}{}^{3d}][Q(Fe^{57m})]^{-1} - 1.98 \quad (7)$$

the Mössbauer spectra of Cp_2Fe[27,28] and Cp_2Fe^+.[28] It is necessary to assume that the sign of q_{zz}, thus γ^1, in Cp_2Fe^+ is negative. A positive sign will lead to a negative population of the 3dϵ orbitals. Relating eq 5b to eq 6 and using $q_{3,2,0}$ for an iron d electron, one can estimate the Fe^{57m} nuclear electric quadrupole moment as 0.175 ± 0.02 barn. Much attention has been given to the determination of Q for iron. Most recently the value of 0.2 barn was calculated by Nozik and Kaplan.[31] Earlier values have ranged from a low value of 0.1 barn for iron derived from Fe(II) Mössbauer data to 0.46 barn calculated from Fe(III) Mössbauer data. An upper limit above 0.28 barn is presently accepted while the lower limit of 0.1 barn is in accord with data available. Since the cobalt nuclear moment is known to high accuracy, the error in the 0.175-barn value is due only to differences in 3d populations between cobalticinium and ferrocene. A more extensive discussion of this value will be presented elsewhere.

Subtracting eq 6 from eq 7 one obtains an equation related to the number of 3dδ electrons in the $\epsilon_{2g}{}^1$ MO. Through Mulliken population analyses[32] and an MO interpretation[11] of q_{zz} this can be related in a general way to the 3dδ coefficient, $C(\epsilon_{2g}{}^1)$, in the $\epsilon_{2g}{}^1$ MO, *i.e.*

$$(C(\epsilon_{2g}{}^1))^2 + C(\epsilon_{2g}{}^1)[1 - (C(\epsilon_{2g}{}^1))^2]^{1/2}S_{ij} = 0.75 \quad (8)$$

Using 0.3 for the overlap integral,[33] S_{ij}, between the metal 3dδ and Cp^- orbitals, one obtains

$$C(\epsilon_{2g}{}^1) = 0.78 \quad (9)$$

Similarly the 3dϵ coefficient, $C(\epsilon_{1g}{}^1)$, in the $\epsilon_{1g}{}^1$ MO can be solved

$$(C(\epsilon_{1g}{}^1))^2 + C(\epsilon_{1g}{}^1)[1 - (C(\epsilon_{1g}{}^1))^2]^{1/2}S_{ij} = 0.21 \quad (10)$$

$$C(\epsilon_{1g}{}^1) = 0.34 \quad (11)$$

Table V shows a comparison of the coefficients obtained in this manner with those calculated theoretically.[33,34] In both cases there is good agreement in the ϵ_{1g} MO. However, the values for the ϵ_{2g} MO show some discrepancy.

TABLE V

MO COEFFICIENTS IN $(C_5H_5)_2Fe$

	Metal $\epsilon_{1g}{}^1$	Metal $\epsilon_{2g}{}^1$
Ballhausen	0.450	0.898
Shustorovich and Dyatkina	0.37	0.85
Calculated from nqr results	0.34	0.78

Since the symmetry of the MO's bears a definite relationship to the type of bonding involved, a value for the

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number of electrons participating in each type can be arrived at from the data. The ϵ_{1g} MO represents the donation of ligand electrons to the metal. In these complexes a value of 0.4 ± 0.1 electron is donated by each Cp in the $\pi(\epsilon_{1g})$ MO to the metal $3d\epsilon$. The ϵ_{2g} MO represents the back-acceptance of electrons from the Fe $3d\delta$ into the ligand $\pi^*(\epsilon_{2g})$. A value of 0.5 ± 0.1 electron back-accepted by each Cp is obtained from the data. If we assume that all of the errors in the interpretation are cumulative, an error of ±0.1 electron can be placed on these numbers.

It cannot be said unequivocally at this point that Cb_2Co^- and Cp_2Co^+ are for practical purposes identical with the isoelectronic Cb_2Fe^{2-} and Cp_2Fe. However, it would appear from all available data that they are indeed very similar. Certainly Cb^{2-} and Cp^- are practically indistinguishable in their bonding to Co(III) and Fe(II), respectively.

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CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
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Five-Coordination with "Hybrid" Ligands. III.[1] High- and Low-Spin Five-Coordinate Nickel(II) Complexes with Ligands Containing Oxygen, Sulfur, Nitrogen, Phosphorus, and Arsenic Donor Atoms

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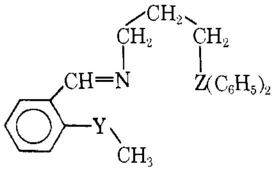
Tridentate Schiff bases formed from *ortho*-substituted benzaldehydes and 3-aminopropyldiphenylphosphine or 3-aminopropyldiphenylarsine (donor sets NNP, ONP, SNP, NNAs, ONAs, SNAs) form with nickel(II) bromide and iodide high- and low-spin complexes with the general formula $NiLX_2$. Their stereochemistry is assigned by spectrophotometric, molecular weight, conductometric, and magnetic susceptibility measurements. Results are discussed mainly in terms of the electronic properties of the donor atoms.

Introduction

Several five-coordinate complexes formed by nickel(II) salts, most often halides, with tridentate ligands, of the general formula $NiLX_2$, have been already described. The first complexes which were isolated were of the low-spin type where the ligands contained the sets of donor atoms AsAsAs, SPS, and PSP.[2–4] Since 1965 high-spin complexes obtained from tridentate ligands with NNN,[5,6] SNN,[7] ONN,[8] NON,[9] and NSN[10] donor sets have been also characterized. The stereochemistry of the complexes so far studied by X-ray analysis has been found to be intermediate between the square pyramid and the trigonal bipyramid. Ligands forming low-spin complexes always contain donor atoms of low electronegativity (P and/or As) and capable of back-bonding; ligands forming high-spin complexes invariably contain highly electronegative donor atoms such as O or N.

In order to study the donor atom influence on the stereochemistry and spin multiplicity of five-coordinate nickel(II) complexes, we have undertaken a thorough investigation systematically varying the donor atoms of tridentate ligands. In previous papers we have reported the results obtained with ligands formed by Schiff bases derived from *ortho*-substituted benzaldehydes and N,N-disubstituted ethylene- and trimethylenediamine (donor sets NNN, SNN, and ONN).[6–8] We wish now to report the results obtained with similar ligands, formed by the reaction of the same aldehydes and 3-aminopropyldiphenylphosphine or 3-aminopropyldiphenylarsine, of the general formula



I, Y = NH, O, S; Z = P, As

The trifunctional ligands formed contain donor atoms that are both high- and low-spin inducing. The

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