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TRANSITION METAL NUCLEAR QUADRUPOLE RESONANCE I. Co59 NQR IN Cs(I,2-B9C2H11)2Co(III) AND THE BONDING IN FERROCENE.

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TRANSITION METAL NUCLEAR QUADRUPOLE RESONANCE

I. Co^{59} NQR IN $\text{Cs}(\text{1,2-B}_{92}\text{C}_{112}\text{H}_{12})\text{Co}(\text{III})$

AND THE BONDING IN FERROCENE

Charles B. Harris

February 1968

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Transition Metal Nuclear Quadrupole Resonance

I. Co^{59} NQR in $\text{Cs}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co(III)}$

and the Bonding in Ferrocene

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Abstract

The pure quadrupole resonance in $\text{Cs}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co(III)}$ has been observed and interpreted. It is shown that one electron of the $(1,2\text{-B}_9\text{C}_2\text{H}_{11})^{2-}$ 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 electrons to the metal ϵ_{1g} orbitals and back accepts 0.5 ± 0.1 electrons 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

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- (1) M. F. Hawthorne, D. C. Young, and P. A. Wagner, J. Am. Chem. Soc., 87, 1818 (1965); M. F. Hawthorne and T. D. Andrews, *ibid.*, 87, 2496 (1965); M. F. Hawthorne and R. L. Pilling, *ibid.*, 87, 3987 (1965).
- (2) M. F. Hawthorne and T. D. Andrews, Chem. Commun., 19, 443 (1965).

metallocarboranes complexes consists of a transition metal completing icosahedral framework of the $B_9C_2H_{11}^{2-}$ anion.³ These complexes have

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- (3) A. Zalkin, T. E. Hopkins, and D. H. Templeton, Inorg. Chem., 6, 1911 (1967).

been formulated as Π -bonded complexes structurally analogous to the metallocenes. The chemistry⁴ of $B_9C_2H_{11}^{2-}$, Cb^{2-} , seems to basically

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- (4) M. F. Hawthorne and P. A. Wagner, J. Am. Chem. Soc., 87, 4392 (1965).

parallel the chemistry of the Π -cyclopentadienyl, Cp^{1-} . 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 $1,2-B_9C_2H_9^{2-}$ moiety.

In order to accomplish these ends the pure nuclear quadrupole resonance (nqr) spectrum of $\text{Cs}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co(III)}$ was found and compared with the nqr spectrum⁵ of $(\pi\text{-Cp})_2\text{Co(III)(ClO}_4)$.

(5) J. Voitländer, H. Klucke, R. Longino, and H. Thieme, *Naturwiss.*, 49, 491 (1962).

Experimental Section

The salts $\text{Cs}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}$ and $\text{Cs}(1,7\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}$ were provided by Professor M. F. Hawthorne at the University of California, Riverside. 2.3 grams of the 1,2 isomer were sealed in a glass vial 15 mm in diameter and 35 mm long. The sample was placed in the rf coil of a high power push-pull superregenerative spectrometer.⁶ All frequencies in Table I

(6) C. B. Harris, unpublished results; G. E. Peterson, private communication.

were measured by spectrum analyzing techniques.⁷ The errors given in

(7) G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instr.*, 37, 1081 (1966).

brackets were estimated as one-half the quench frequency. The signal-to-noise ratios given in Table I apply to a sweep rate of 5 megahertz per hour and a lock-in time constant of one second.

No signal could be detected in a 1.0 gram sample of the 1,7 isomer in the range 10.0 to 35.0 megahertz.

The visible and uv spectrum of the 1,2 isomer was 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 exists³ in the solid state. In effect, the statistical disordering of the carborane polyhedral 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 than 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 spectrum of bis-cyclopentadienyl cobalt(III) perchlorate⁸ and the cesium bis-ortho-carborane cobaltate(III)

(8) G. Wilkinson, J. Am. Chem. Soc., 74, 6148 (1952).

(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 nqr⁹ one measures the interaction of an electric field gradient, q ,

(9) T. P. Das and E. L. Hahn, Solid State Phys., Suppl. 1, (1958).

with a nuclear quadrupole moment, Q . A nucleus must possess a nuclear spin, I , greater than one-half 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 bond¹⁰ or molecular orbital¹¹ interpretation.

(10) C. H. Townes and B. P. Dailey, J. Chem. Phys., 17, 782 (1949).

(11) F. A. Cotton and C. B. Harris, Proc. Natl. Acad. Sci. U.S., 56,
12 (1966).

In the present study the electric field gradient and the asymmetry parameter, η , were determined from the data in Table I. Using Cohen's

solutions¹² of the secular equation for a nucleus with a spin of 7/2 and

(12) M. H. Cohen, Phys. Rev., 96, 1278 (1954).

the value for the Co⁵⁹ nuclear quadrupole moment,¹³ q_{zz} and η defined

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \quad (1)$$

(13) D. v. Ehrenstein, H. Kopfermann and S. Penselin, Z. Physik, 159, 230 (1960).

in terms of its irreducible tensor components can be calculated. The liquid nitrogen and room temperature values are summarized in Table III for $\text{Cp}_2\text{CoClO}_3$ and $\text{Cs}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}$, respectively.

The direction of the diagonal field gradient tensor in the $\text{Cp}_2\text{Co}^{1+}$ and $(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^{1-}$ is primarily determined by the molecular symmetry of the respective ions. In cobalticinium perchlorate the z direction, q_{zz} , is along the 5-fold rotation axis. Although the crystal structure of the 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 crystalline field effects which have been found in $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ ¹⁴ and $\text{Coen}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ¹⁵ are less than 2 per cent

(14) T. Sugawara, J. Phys. Soc. Japan, 14, 858 (1959).

(15) B. A. Scott and R. A. Bernheim, J. Chem. Phys., 44, 2004 (1966).

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 bisecting the boron at the apex of the polyhedron, the Co, and the center of the C-C bond in 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 metallocenes and metallocarboranes 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

(16) E. M. McConnell, W. W. Porterfield, and R. E. Robertson, J. Chem. Phys., 30, 442 (1959).

It seems generally true that the 4s contribution to bonding in first row metal complexes is small at best.

Utilizing the relation of the field gradient to angular momentum,¹⁷

-
- (17) C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, N.Y., N.Y., 1955.
-

i.e.

$$a_{n,l,m} = a_{n,l,0} \left[1 - \frac{3m^2}{l(l+1)} \right] \quad (2)$$

when n , l , and m are the principle quantum number, angular momentum quantum number, and magnetic quantum number, respectively, one can write down (cf. Eq. 3) an expression for a_{zz} in terms of the various types of d and p electrons;

$$a_{zz} = a_{3,2,0} [\# 3d_{z^2} + \# 3d_{\epsilon/2} - \# 3d_{\delta}] + a_{4,1,0} [\# 4p_z - \# 4p_{\pi/2}] \quad (3)$$

($d_{\epsilon} = d_{xz}$, 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 splitting¹⁷ and using Slater's method¹⁸ for determining the Co effective

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- (18) J. C. Slater, Phys. Rev., 36, 57 (1930).
-

nuclear charge seen by a 3d and 4p electron in the configuration $(Ar)3d^6 4p^1$ it can be shown that the field gradient arising from one 4p electron is at least 3 times smaller than that from a 3d electron. Actual measurements¹⁹

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- (19) V. S. Korol'kov and A. G. Makhanev, Optika i Spektroskopiya, 12, 87 (1962).
-

indicate a difference of 6.8 times between a Cu 3d and 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 calculations²⁰ have estimated the 4p population

(20) H. Basch, A. Viste, and H. B. Gray, J. Chem. Phys., 44, 10 (1966).

in octahedral Co(III) complexes at 0.1 of an 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 of an 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 Equation (2) and the measured nuclear quadrupole moment for Co⁵⁹ it can be shown that $q_{zz} 3d_{z^2} = -9.53 \times 10^{15}$ esu/cm². It should be emphasized that this is only a working number. It neglects the Sternheimer correction²¹ $(1-\gamma_{\infty})$ and a small contribution

(21) R. M. Sternheimer, Phys. Rev., 84, 244 (1951); 86, 316 (1952); 95, 736 (1954).

from spin-orbital coupling.²² For comparative purposes and for estimating

(22) R. Ingalls, Phys. Rev., 133, A787 (1964).

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 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 implies 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, and 8 boron positions are practically identical both in their charge and 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% or visa versa.

The transition metal to carbon bond lengths in the icosahedral face of $C_5H_5Fe(1,2-B_9C_2H_{11})$ ²³ and $Cs(1,2-B_9C_2H_{11})Re(CO)_3$ ²⁴ are respectively

(23) A. Zalkin, D. H. Templeton, T. E. Hopkins, J. Am. Chem. Soc., 87, 3988 (1965).

(24) A. Zalkin, T. E. Hopkins and D. H. Templeton, Inorg. Chem., 5, 1189 (1966).

only 0.05 Å 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 Equation (3) one can estimate the effective electron distributions in a series of related metallocenes and carboraneocenes.

Consider first the Co(III) complexes. In 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/cm², is positive. This value is 3.45 and 4.46 times too large 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

(25) R. L. Collins, J. Chem. Phys., 42, 1072 (1965).

necessary to account for a positive value is less than that for a negative value.

If we assume that the lattice sum contribution, $\sim 2\%$, and the contribution from 4p electron populations in the complexes are additive,

which may or may not be true, the following equations which are accurate to 5-7% can be written.

$$\#_{3d_{z^2}} + \#_{3d_{\epsilon}/2} - 3d_{\delta} = -0.558 [\text{Co}_2\text{Co}^-] \quad (5a)$$

$$\#_{3d_{z^2}} + \#_{3d_{\epsilon}/2} - 3d_{\delta} = -0.595 [\text{Cp}_2\text{Co}^+] \quad (5b)$$

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 ferrocenium. The field gradient for a $3d$ electron in iron can be calculated from the ratios of the various $[\gamma^{-3}]$ values.²⁶ $q_{3,2,0}$ are listed in Table IV for some first row transition

(26) J. Fidone, Nuovo Cimento, 11, 736 (1959).

metals for future reference.

Equations similar to (5) can be written for ferrocene and ferrocenium using $q_{3,2,0}$, Q Fe^{57m} , and the quadrupole coupling constants obtained from Mössbauer spectroscopy.^{28,29} The mixed cyclopentadienyl-carborane

(28) G. K. Wertheim and R. H. Herber, J. Chem. Phys., 38, 2106 (1963).

(29) U. Zahn, P. Kienle and H. Eicher, Z. Physik, 166, 220 (1962).

complex of Fe(III),³⁰ $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})$, has to within experimental

(30) R. H. Herber, private communication.

error the same quadrupole coupling constant as ferrocenium bromide. Although the quadrupole splitting in the Mössbauer spectra of the bis-carborane of Fe(III), $[(CH_3)_4N][Fe(C_2B_9H_{11})_2]$, is unresolved,³⁰ the estimated value is practically the same as ferrocenium bromide.

The population of the $3d_{z^2}$ orbital can safely be assumed to equal two electrons. Explicit evaluation of the overlap integral³¹ between

(31) J. D. Dunitz and L. E. Orgel, J. Chem. Phys., 23, 954 (1955).

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 practical 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 $3d_e$ and $3d_o$ populations and $Q_{Fe^{57m}}$ in the case of Fe complexes. These are shown graphically in Figure 3.

It is apparent that there are many possible solutions only one of which is correct.

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 b to 0.46 b have been recently postulated. There is one redeeming feature common to both Cp_2Fe and $CpCo^+$ that provides one a very interesting handle on the problem. It is apparent from Table II that the uv and visible spectrum 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 uv 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 subject to about 20% and 10% error, respectively.

Using the available Mössbauer data the following equations in terms of the number of 3d ϵ and 3d δ electrons and $Q Fe^{57m}$ can be arrived at for Cp_2Fe and $CpFe^+$, respectively.

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

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

r and r^1 are the quadrupole splittings of the Mössbauer spectra of Cp_2Fe ^{28,29} and Cp_2Fe^+ ²⁹. It is necessary to assume that the sign of q_{zz} , thus r^1 , in Cp_2Fe^+ is negative. A positive sign will lead to a negative population of the 3d ϵ orbitals. Relating Equation (5b) to Equation (6) and using $q_{3,2,0}$ for an iron one can estimate the Fe^{57m} nuclear electric quadrupole moment as 0.175 ± 0.02 . Much attention has been given to the determination of Q for iron. Most recently the value of 0.2 barns was calculated by Nozik and Kaplan.³² Earlier values have ranged from a low

(32) A. J. Nozik and M. Kaplan, Phys. Rev., 159, 273 (1967).

value of 0.1 barns for iron derived from Fe(II) Mössbauer data to 0.46 barns calculated from Fe(III) Mössbauer data. An upper limit of above 0.28 is presently accepted while the lower limit of 0.1 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 Equation (6) from Equation (7) one obtains an equation related to the number of 3d δ electrons in the ϵ_{2g}^1 MO. Through Mulliken population analysis³³ and an MO interpretation¹¹ of q_{zz} this can be related

(33) R. S. Mulliken, J. Chem. Phys., 23, 1841 (1955); 23, 1833 (1955).

in a general way to the 3d δ coefficient, $C\epsilon_{2g}^1$, in the ϵ_{2g}^1 MO:

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

Using 0.3 for the overlap integral,³⁴ S_{ij} , between the metal 3d δ and Cp⁻

(34) J. P. Dahl and C. F. Ballhausen, Mat. Fys. Medd. Dan. Vid. Selsk. 33, No. 5 (1961).

orbitals one obtains,

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

Similarly the 3de coefficient, $C\epsilon_{1g}^1$, in the ϵ_{1g}^1 MO can be solved:

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

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

Table V shows a comparison of the coefficients obtained in this manner with those calculated theoretically.^{34,35} In both cases there is good

(35) E. M. Shustorovich and M. E. Dyatkina, Dokl. Akad. Nauk. SSSR, 128, 1234 (1959).

agreement in the ϵ_{1g} MO. However, the values for the ϵ_{2g} MO show some discrepancy.

Since the symmetry of the MO's bears a definite relationship to the type of bonding involved, a value for the 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 electrons is donated from the ligand $\Pi(\epsilon_{2g})$ to the metal 3de. The ϵ_{2g} MO represents the back acceptance of electrons from the Fe 3d₀ into the ligand $\Pi^*(\epsilon_{2g})$. A value of 0.5 ± 0.1 electrons is obtained from the data. If we assume that all the errors in the interpretation are cumulative, an error of ± 0.1 electrons 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 to 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.

Acknowledgement

The Cs(1,2-B₉C₂H₁₁)Co salts were generously supplied by Professor M. F. Hawthorne, University of California, Riverside. This work was supported by the Inorganic Materials Research Division, Lawrence Radiation Laboratory under the auspices of the United States Atomic Energy Commission.

Table I.

NQR Frequencies in $\text{Cs}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^{59}$

Transition	Frequency (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.

Visible and UV Spectra

Transition	$(C_5H_5)_2CoClO_4$ ^a	$CsCo(1,2-B_9C_2H_{11})_2$	$(C_5H_5)_2Fe$ ^b
γ_1 ^c (cm ⁻¹)	38,400	35,500	41,700
γ_2 (cm ⁻¹)	32,700	30,000	30,800
γ_3 (cm ⁻¹)	24,700	22,300	22,700

(a) Taken from Reference 8.

(b) Taken from Reference 36.

(c) Charge transfer band.

(36) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward,
J. Am. Chem. Soc., 74, 2125 (1952).

Table III.

Field Gradients and Asymmetry Parameters.

$(C_5H_5)_2CoClO_4^a$	$CsCo(1,2-B_9C_2H_{11})_2$
$q_{zz} = 5.85 \times 10^{15} \text{ esu/cm}^3$	$q_{zz} = 5.51 \times 10^{15} \text{ esu/cm}^3$
$\eta = 0.0$	$\eta = 0.03 \pm 0.01$

(a) Calculated from data in Reference 5.

Table IV.

$q_{3,2,0}$ for one 3d Electron in 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}

Table V.

MO Coefficients in $(C_5H_5)_2Fe$

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

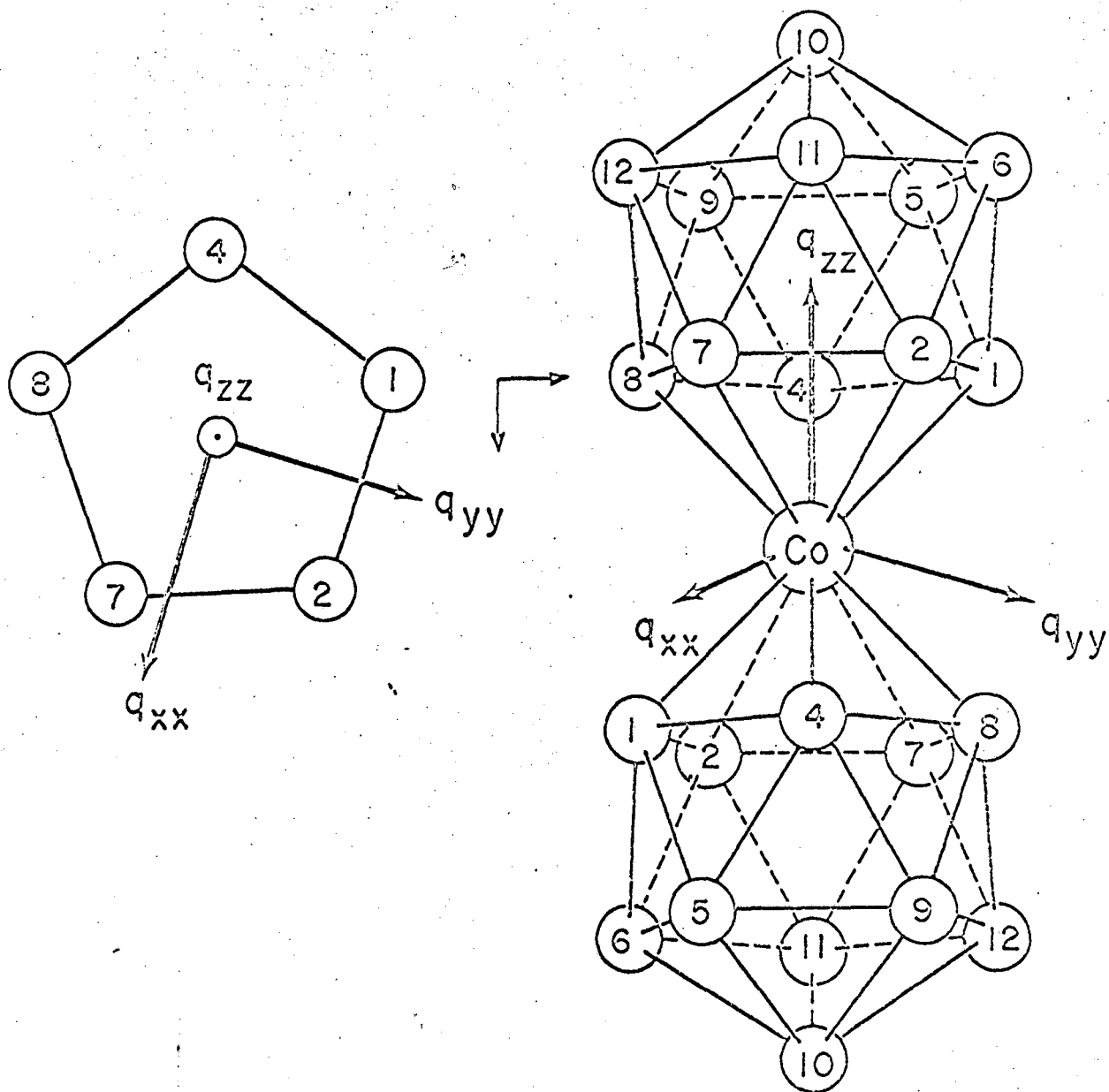


Figure 1. The relation of the field gradient tensor to the structure of $(1,2-B_9C_2H_{11})_2Co^{-1}$.

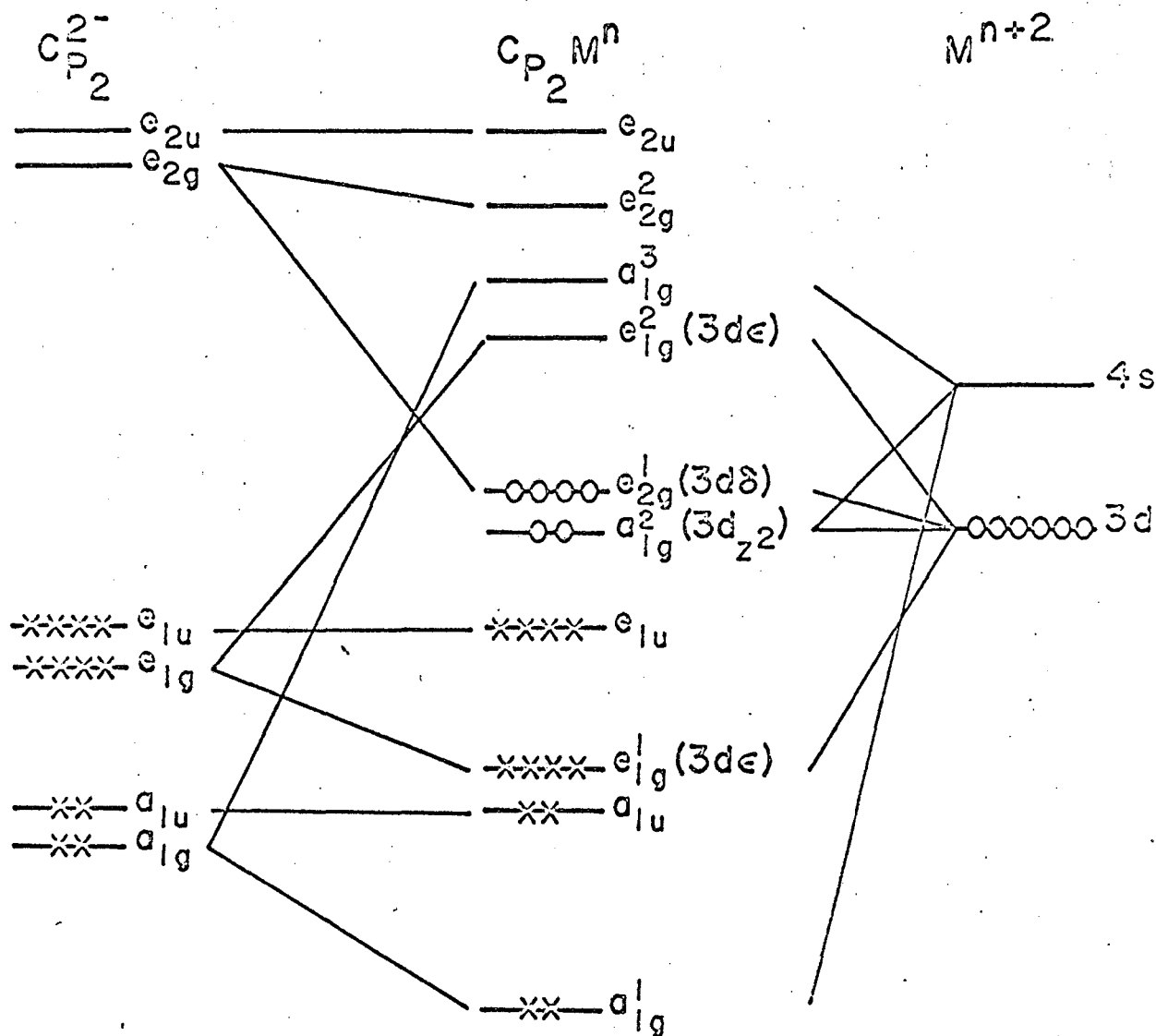


Figure 2. Qualitative MO diagram of $3d^6$ metallocenes.

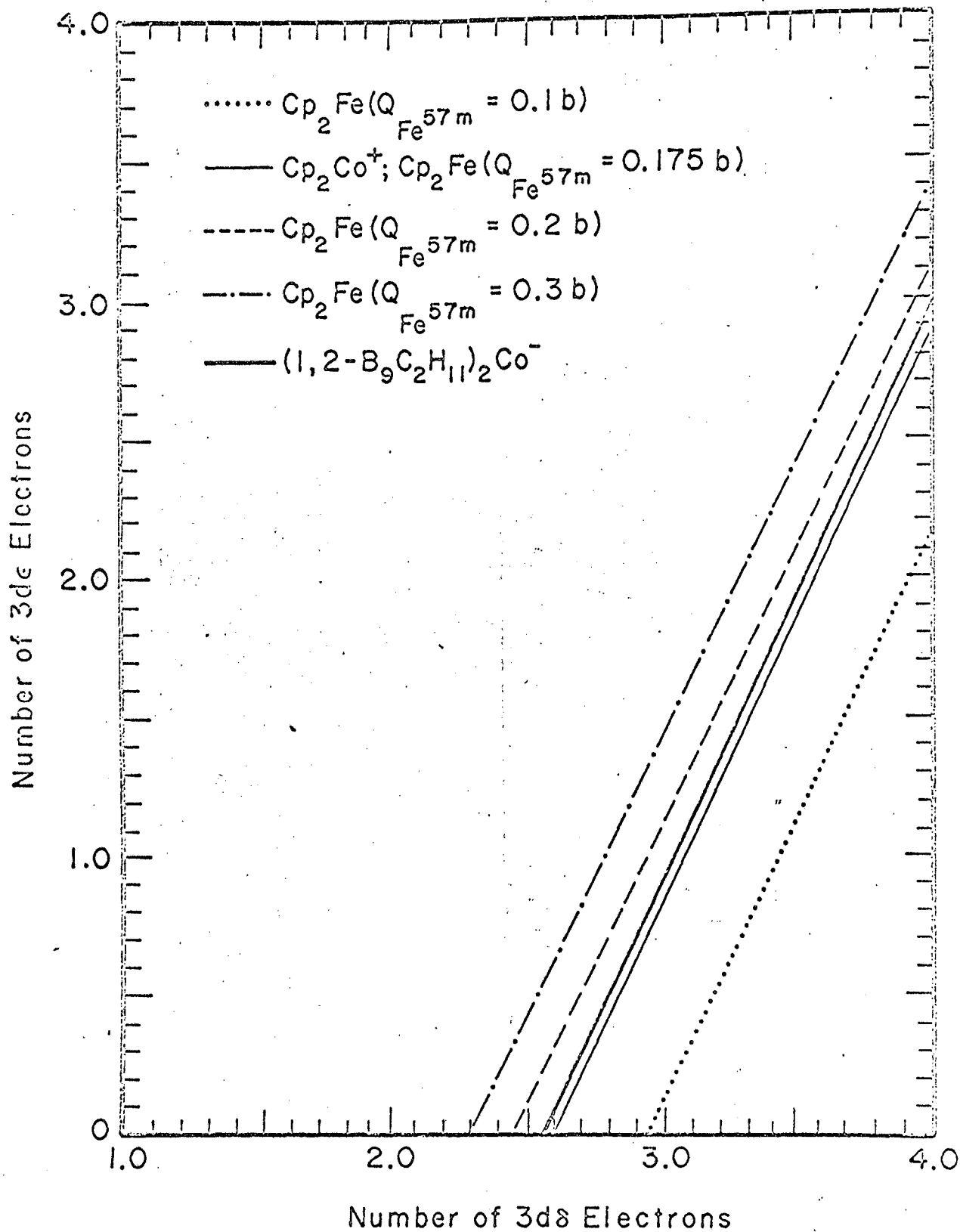


Figure 3. Graphic solution of the quadrupole coupling constants in some $3d^6$ metallocene and carborane complexes.

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