downfield.[19,38] Thus, the isotropic hyperfine shift induced by a downfield SR will add to the susceptibility shift in such a case.

The observation of the shift of the $^{25}Mg^{2+}$ resonance is important for possible studies of the physiological divalent cations. The binding of these cations to the shift reagent anion or to the shift reagent ligand could be strong. At higher pH values, precipitation can be observed in $Dy(CA)_3^{6-}$ solutions containing Mg^{2+}. Considerably more precipitation is observed when $Dy(CA)_3^{6-}$ and Ca^{2+} are mixed (likewise with $Dy(DPA)_3^{3-}$). We have observed a shift of the $^{43}Ca^{2+}$ resonance of greater than 40 ppm upfield (ca. 60-Hz line width) induced by $Dy(NTA)_2^{3-}$ (50 mM $CaCl_2$, 75 mM $Li_3Dy(NTA)_2$). However, since this isotope is so rare,[33] many NMR studies of Ca^{2+} biochemistry may be made with $^{113}Cd^{2+}$ as a surrogate.[39] We have observed a downfield shift of over 20 ppm in the $^{113}Cd^{2+}$ resonance induced by $Dy(NTA)_2^{3-}$ (300 mM $CdSO_4$, 100 mM $Na_3Dy(NTA)_2$),[43] although at higher concentrations of Cd^{2+} (as the sulfate) some precipitation is noted. Perhaps SR with smaller charges will be more useful for studies of the divalent cations.

The interactions of shift reagents with alkaline-earth-metal cations are also important in considerations of studies of alkali-metal cations in the presence of divalent cations, often the physiological situation. The divalent ions interfere in two different ways: (1) by very effectively competing with the monovalent cation for the SR and (2) by competing with the lanthanide ion for the SR ligand (we have demonstrated behavior of this type with Lu^{3+} [1]). Neutral products of this latter reaction or hydrolysis of positive products to form neutral compounds most likely accounts for the precipitations we have noted in some mixtures. Monoligand SR anions may be more immune to this reaction than bis or tris complexes. In both cases, the SR is effectively inactivated.[1,3]

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Registry No. $Li_6Dy(CA)_3$, 86260-93-7; $Li_6Tm(CA)_3$, 86260-94-8; H_3CA, 138-60-3; $DyCl_3$, 10025-74-8; $TmCl_3$, 13537-18-3; LiOH, 1310-65-2; $^{25}Mg^{2+}$, 66650-06-4; $^{39}K^+$, 16686-67-2; $^{87}Rb^+$, 51377-95-8; $^{23}Na^+$, 17341-25-2; nitrogen, 7727-37-9.

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(43) Chu, S., unpublished results.

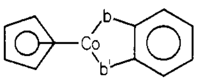
Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

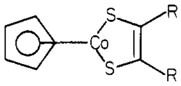
The Metal Atom's View of the Bonding in *o*-Benzoquinone, *o*-Dithiobenzoquinone, and *o*-Benzoquinone Diimine Metallacycles of $(\eta^5\text{-}C_5H_5)Co$. A ^{59}Co NQR Study of the *cis*-a_3b_2 Ligand Geometry

EDWARD J. MILLER and THOMAS B. BRILL*

Received December 10, 1982

Bidentate *o*-quinone ligands, $bb'C_6H_4$, where b, b' = O, S, NR (R = H, CH_3, C_6H_5), and 1,2-dithiolenes form complexes with $(\eta^5\text{-}C_5H_5)Co$ containing a five-membered metallacycle ring:

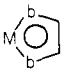




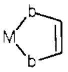
The ^{59}Co nuclear quadrupole resonance spectra show that the ground-state electron distribution of the cobalt atom is directly controlled by the electronegativity of b, b'. Substitution of the metallacycle at the α and β positions only minimally perturbs the electron distribution on the cobalt atom. From the point of view of cobalt, the Co–b interaction is mostly a σ-bond that responds to the push–pull exertion on the electrons by b alone. Co–b π-bonding is not strikingly evident in the NQR spectra. However, the apparent effects of π-bonding on Co were detected in noncyclic $(\eta^5\text{-}C_5H_5)Co(b)b'$ complexes where b, b' = CO, $P(OR)_3$, PR_3. Comparison of the NQR data for the metallacycles, where the formal oxidation state of cobalt is uncertain, with the noncyclic complexes containing Co(I) suggests that the metallacycles also are best thought of as Co(I) complexes. The reactions of the metallacycle complexes with Lewis acids and bases could be sensitive to the electron distribution on Co. Preliminary results of several such reactions are reported.

Introduction

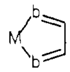
The bonding in unsaturated five-membered metallacycle rings, formulated as I–III, has attracted considerable attention.



I



II



III

The well-known dithiolene complexes, where b = S, have been widely investigated.[1,2] *o*-Benzoquinones,[3] where b = O, *o*-benzoquinone diimines,[4-6] where b = N, and the metallacyclopentadienes,[7] where b = C, are less thoroughly studied but have attracted increasing attention recently. Throughout many of these investigations, the degree of π-electron delo-

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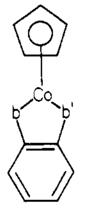
calization is a major theme. It is generally thought that significant delocalization, I, occurs in d^6 and d^8 complexes when b = N and S,[1,2,4–6] but less or no delocalization takes place when b = O[3] and C.[7] When b = S, the extent of π-electron delocalization could be rather variable.[1,2] Overall, the matter of π-delocalization in metallacycles of this type has not reached a satisfactory resolution.[1]

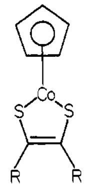
The spectroscopic methods used to characterize the bonding in these complexes usually probe the non-metal portion of the metallacycle ring or, in the case of electronic spectroscopy, give a composite picture of the ground and excited electronic states. For instance, despite possible differences in the electron delocalization over the metallacycle, most of the compounds have intense colors. When M is the (η^5-C_5H_5)Co fragment and b = O, N, and S, the complexes are deep purple, green, and bronze. The bond distances are frequently used as evidence of a particular formulation, I, II, or III.[4–6,8–10] Because the metal must play a vital role in the π-electron delocalization through the full metallacycle, it would be useful to probe the ground-state electron distribution on the metal in a range of metallacycles and structurally related complexes of types IV–VI. We are not aware of spectroscopic studies of a specific metal atom in a range of metallacycles as a function of b from which the electronic structure might be learned. One technique able to detect relative changes in the electron distribution with the requisite sensitivity is ^{59}Co nuclear quadrupole resonance (NQR) spectroscopy.[11,12]



IV

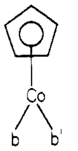
b, b′ = O, S, NR

(R = H, CH_3, C_6H_5)



V

R = H, CN, CF_3



VI

b, b′ = CO, $P(OCH_3)_3$,

$P(C_2H_5)_3$, $P(C_6H_5)_3$

With the results of an NQR study, a number of questions about the bonding in the metallacycle appear in better light. For instance, (1) how extensive is π-bonding between Co and b from the point of view of the cobalt atom? An answer to this question would help clarify the importance of π-electron delocalization over the entire metallacycle. (2) Although not of fundamental significance because of electroneutrality, are these compounds best described as having the Co(I) or Co(III) formal oxidation state? (3) To what ground-state electronic properties of the ligands is the cobalt atom sensitive? This paper describes the variations in the electron density at the cobalt atom in the metallacycles IV and V and several noncyclic complexes, VI. The cobalt atom's view of the bonding can be seen in perspective.

Experimental Section

Ligands. *o*-Anisidine (Aldrich), azobenzene (Eastman), and *o*-aminothiophenol (Aldrich) were used as received. *o*-Phenylenediamine (Eastman) was purified by the standard procedure,[13] and catechol (Eastman) was sublimed. 5-Methyl-2-aminophenol,[14] *N*-methyl-2-aminophenol,[15] dithiocatechol,[16] *N*-methyl-*o*-anisidine,[17] and $NaS_2CCN\cdot 3DMF$[18] were prepared by published procedures. *N*-methyl-*o*-phenylenediamine was obtained from *N*-methyl-2-nitroaniline by reduction.[17,19] Perchlorothiocatechol was prepared from $[Fe(S_2C_6Cl_4)_2]_n$.[20]

Metal Complexes. Most of the complexes were prepared from (η^5-C_5H_5)CoI_2(CO).[21] (η^5-C_5H_5)$CoO_2C_6H_4$, (η^5-C_5H_5)Co$(NH)_2C_6H_4$, (η^5-C_5H_5)Co(NH)SC_6H_4, and (η^5-C_5H_5)$CoS_2C_6H_4$ were synthesized by the method of Heck.[22] (η^5-C_5H_5)Co(NC_6H_5)-NHC_6H_4,[23] (η^5-C_5H_5)$CoS_2C_4N_2$,[24] and (η^5-C_5H_5)$CoS_2C_2H_2$[25] were prepared by other published procedures. (η^5-C_5H_5)$Co(CO)_2$ (Pressure Chemical) was used as received. From this complex, (η^5-C_5H_5)Co-$[S_2C_2(CF_3)_2]$[26] and (η^5-C_5H_5)$CoN_4(C_6H_5)_2$[27] were prepared.

(η^5-C_5H_5)Co(CO)$[P(C_6H_5)_3]$[28] and (η^5-C_5H_5)Co$[P(C_6H_5)_3]_2$[29] were obtained as previously reported. We thank Dr. Ron McKinney (Du Pont) for a sample of (η^5-C_5H_5)Co$[P(OCH_3)_3]_2$ and Shayne Landon (University of Delaware) and Dr. Steve Ittel (Du Pont) for the preparation of (η^5-C_5H_5)Co$[P(C_2H_5)_3]_2$ by metal vapor methods.

These known complexes were identified by the accurate matching of their melting points, physical properties, and spectra to those in the original syntheses. The ^{1}H NMR spectra showed all of the proper features.

(η^5-C_5H_5)Co(NH)(NCH_3)C_6H_4. (η^5-C_5H_2)CoI_2(CO) (2.5 g, 6.1 mmol) was added to *N*-methyl-*o*-phenylenediamine (0.75 g, 6.1 mmol) in 15 mL of diethyl ether. The resulting brown solution was stirred with 20 mL of aqueous NaOH (20%) for 2 h. The color of the solution changed from brown to purple, and gas was evolved. The mixture was extracted with 75 mL of ether. The aqueous layer was washed with diethyl ether (2 × 50 mL). The combined ether layers were dried with anhydrous $MgSO_4$ and filtered. Evaporation yielded a green oil, which was dissolved in a minimum amount of benzene and chromatographed on alumina. The mobile red band was collected and evaporated to dryness, yielding a green crystalline product. Recrystallization from hexane gave pure material: 0.45 g (30% yield); mp 115–117 °C. Molecular weight: found, 244.038 ± 0.003; theoretical, 244.041. ^{1}H NMR ($CDCl_3$): 6.95 (m, C_6H_4, 4), 4.02 (s, C_5H_5, 5), 3.40 ppm (s, NCH_3, 3).

(η^5-C_5H_5)Co(NH)OC_6H_3(CH_3). (η^5-C_5H_5)CoI_2(CO) (1.50 g, 3.70 mmol) and 5-methyl-2-aminophenol (0.704 g, 5.72 mmol) were dissolved in 50 mL of CH_2Cl_2. Aqueous sodium acetate (10 g/75 mL) was added and the mixture vigorously stirred for 1 h. The solution, initially purple, turned blue within minutes. The two layers separated, and the aqueous layer was washed with CH_2Cl_2 (2 × 50 mL). The combined washings were dried with anhydrous $MgSO_4$ and filtered. Upon evaporation, bronze-colored crystals (0.55 g, 60% yield) were obtained. Decomposition without melting was noted above 200 °C. Molecular weight: found, 245.025 ± 0.003; theoretical, 245.025. ^{1}H NMR ($CDCl_3$): 6.75 (m, C_6H_3, 3) 5.05 (s, C_5H_5, 5), 1.55 ppm (s, CH_3, 3).

(η^5-C_5H_5)Co(NCH_3)OC_6H_4. This complex was prepared in the same manner as (η^5-C_5H_5)Co(NH)OC_6H_3(CH_3), except that *N*-methyl-*o*-aminophenol was used as the ligand. The purple crystals (81% yield) decomposed above 240 °C without melting. Molecular weight: found, 245.025 ± 0.003; theoretical, 245.025. ^{1}H NMR ($CDCl_3$): 7.2 (m, C_6H_4, s), 5.20 (s, C_5H_5, 5), 3.25 ppm (s, CH_3, 3).

(η^5-C_5H_5)Co($S_2C_6Cl_4$). This complex was prepared in the same manner as (η^5-C_5H_5)Co(NH)OC_6H_3(CH_3) except that perchlorodithiocatechol was used as the ligand. The purple crystals (71% yield) decomposed above 180 °C. Molecular weight: found, 401.791 ± 0.003; theoretical, 401.789. ^{1}H NMR ($CDCl_3$): 5.6 ppm (s, C_5H_5).

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Spectra. The ^{59}Co NQR spectra were recorded on a Wilks NQR-IA superregenerative oscillator spectrometer at room temperature. The frequencies are accurate to ±0.005 MHz. The ^{1}H NMR spectra were recorded on a Perkin-Elmer R-12B relative to internal $Si(CH_3)_4$. Melting points were measured in open capillary tubes and are uncorrected. Exact masses were obtained on a Du Pont 492B mass spectrometer. The resolution was at least one part in 3300 at 5% valley.

Results

^{59}Co NQR spectra on these diamagnetic $(\eta^5\text{-}C_5H_5)Co(b)_2$ complexes are the first for this class of compounds, although spectra for $(\eta^5\text{-}C_5H_5)$Co(diolefin) complexes have been reported.[30] NQR studies of metallacycles have not appeared. It is interesting to note as a sidelight that the coupling constant for $(\eta^5\text{-}C_5H_5)Co[P(C_6H_5)_3]_2$ had the highest value reported to date for cobalt.

Because NQR spectroscopy is a solid-state technique, the spectra contain a small crystal-lattice electric field gradient (EFG) superimposed upon the vastly dominant intramolecular EFG.[31] Because these complexes are neutral and the Co atom is protected from the crystal lattice to some extent by the ligands, the crystal-lattice contribution is probably no more than a few percent of the overall effect. In several of the complexes two sets of closely spaced ^{59}Co NQR signals appear, which indicates that two cobalt atoms are present in the asymmetric unit of the cell. The crystal structures of $(\eta^5\text{-}C_5H_5)Co(NH)_2C_6H_4$[32] and $(\eta^5\text{-}C_5H_5)CoS_2C_6H_4$[33] have subsequently confirmed this observation. There could be other complexes where crystallographically different Co atoms exists, but the spacing of the signals may be indistinguishably small.

For reasons that may result from lattice disorder, no NQR signals were obtained from $(\eta^5\text{-}C_5H_5)Co(NH)OC_6H_4$. This problem was overcome without altering the Co center by preparing a slightly more asymmetric molecule. The NQR spectrum for this metallacycle was obtained when a CH_3 group was placed para to the imine.

A previously unrecognized solid-state reaction was discovered during the NQR study of $(\eta^5\text{-}C_5H_5)CoS_2C_6H_4$. This compound has been formulated as a monomer, IV.[22] Immediately following its preparation or recrystallization from CH_2Cl_2, the structure was a monomer. However, after several weeks the NQR spectrum of the solid changed drastically. The new complex was identified as the dimer of IV, containing additional Co–S bonds. A structural, thermochemical, kinetic, and spectroscopic characterization of this unusual reversible solid-phase interconversion will appear elsewhere.[33]

The Relationship of Bonding to the NQR Spectra. NQR spectroscopy provides a very sensitive probe of the ground-state electron distribution in the orbitals of an atom containing a quadrupolar nucleus.[31] While an experimental measurement of the absolute electron density is difficult in a complex molecule, the NQR experiment can be used to advantage for relative comparisons among a series of compounds. ^{59}Co, having a nuclear spin of $I = {}^7/_2$, provides three resonances: ν_1 ($\Delta m_I^2 = \pm{}^1/_2 \leftrightarrow \pm{}^3/_2$), ν_2 ($\Delta m_I^2 = \pm{}^3/_2 \leftrightarrow \pm{}^5/_2$), ν_3 ($\Delta m_I^2 = \pm{}^5/_2 \leftrightarrow \pm{}^7/_2$). Frequently only ν_2 and ν_3 are observed because the intensity of ν_1 is usually weaker than that of ν_2 or ν_3. However, with two assigned resonances, it is straightforward[31] to calculate the ^{59}Co coupling constant, e^2Qq/h, and the asymmetry parameter, η. e^2Qq/h measures the largest component of the EFG along the z principal axis by convention. η measures the deviation of the EFG from axial symmetry about the z axis. The values of η can range from 0 to 1. The broad features of the electric field gradient at cobalt can be constructed from the coordination-sphere model[34] for a *cis*-a_3b_2 arrangement of ligands about Co. The cyclopentadienyl ring is considered in the usual manner as a tridentate ligand (a_3) occupying a facial position of the trigonal bipyramid. The two remaining ligands, b_2, are cis. Electrostatic charges arranged in this geometry help explain several aspects of the EFG at the cobalt atom. The model is, of course, only a qualitative guide.

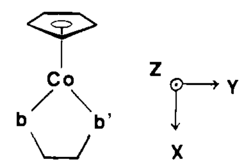

Figure 1. Probable orientation of the principal axes of the EFG tensor at the cobalt atom.

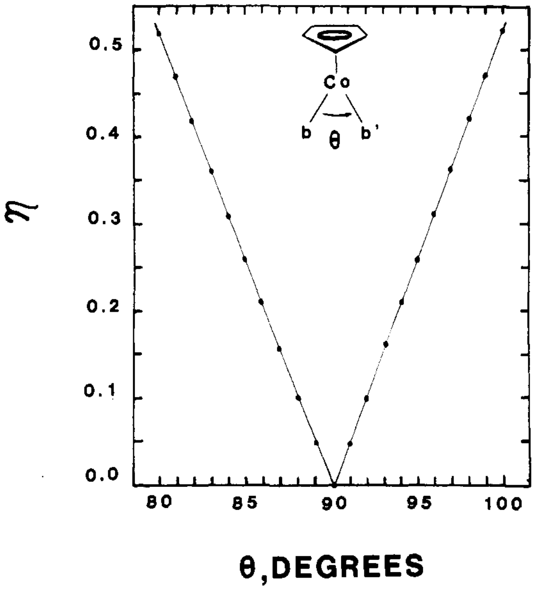

Figure 2. Variation in η as a function of the b–Co–b angle, excluding the contribution from the cyclopentadienyl ring.

The principal axes of the EFG can be oriented in several ways. However, the position that places the z axis perpendicular to the $Co(b)_2$ plane (Figure 1) is most consistent with the experimental data and is also the projection that follows from an angular arrangement of atoms in other systems.[35] The components of the EFG tensor at Co were calculated for the *cis*-a_3b_2 trigonal bipyramid of atoms and yield the tensor components given as

$$q = e\begin{bmatrix} B - {}^3/_4A & -{}^3/_4A & 0 \\ -{}^3/_4A & B - {}^3/_4A & 0 \\ 0 & 0 & -2B + {}^3/_2A \end{bmatrix} \tag{1}$$

The largest component (the z direction) has

$$q \propto |2B - {}^3/_2A| \tag{2}$$

where A is the EFG from one site of the cyclopentadienyl ligand, a_3, and B is the EFG from the b or b′ ligand. A and B can be thought of simply as the "bonding characteristics" that produce an EFG at cobalt. They would usually be σ- and/or π-bonding in the M–b,b′ bond. The EFG from η^5-C_5H_5 is essentially constant through IV, V, and VI. Consequently, the EFG at cobalt will be controlled mostly by the

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Table I. ^{59}Co NQR Spectra for the $(\eta^5\text{-}C_5H_5)Co(b)b'$ Complexes IV Where b, b′ = N, O, S[a]

b	b′	freq, MHz ν_3	freq, MHz ν_2	e^2Qq/h, MHz	η
O	O	36.162 (4)	23.037 (4)	171.71	0.409
NH	O[b]	35.140 (2)	23.019 (3)	164.71	0.209
NCH_3	O	34.974 (3)	23.100 (5)	163.56	0.147
NC_6H_5	NC_6H_5 (N_2)[c]	34.206 (4)	22.153 (3)	160.97	0.287
NC_6H_5	NH	34.109 (3)	22.457 (3)	159.65	0.173
NH	NH	33.795 (8)	22.197 (2)	158.10	0.156
		34.097 (10)	22.269 (10)	159.97	0.230
				159.03 (av)	0.193 (av)
NCH_3	NH	33.089 (3)	21.363 (2)	155.93	0.307
NH	S	32.646 (7)	20.793 (6)	155.04	0.411
S	S	31.618 (4)	19.979 (6)	152.10	0.531
		31.445 (4)	19.878 (6)	150.89	0.514
				151.49 (av)	0.522 (av)
S	S (Cl_4)[d]	31.350 (5)	19.901 (10)	149.36	0.446

[a] All spectra were taken at room temperature; parenthetical numbers are signal-to-noise ratios. [b] A CH_3 group is para to the oxygen atom. [c] bb′ = diphenyltetraazadiene (in VII). [d] Perchloro-*o*-dithioquinone.

bonding characteristics of the b ligands, which are being varied in this study. Diagonalization of eq 1 when the b–Co–b angle is 90° yields an asymmetry parameter, η, given by eq 3. The

$$\eta = \left|\frac{{}^3/_2 A}{2B - {}^3/_2 A}\right| \tag{3}$$

variation of η as a function of the b–Co angle excluding, for clarity, the cyclopentadienyl contribution is shown in Figure 2. η is delicately sensitive to this angle. Changes of 0.5 unit occur with 10° excursions from the idealized 90° angle. Therefore, without supporting structural data, one must be careful about using η as a measure of bonding alone. η contains both structural and bonding information.

The coordination-sphere model qualitatively simulates the EFG effects and gives the most plausible orientation of the principal axes. Ultimately, the bonding orbitals must be related to the EFG to develop an understanding of the electron distribution. In a slightly more detailed description, information about the Co–b bond is transmitted to the cobalt nucleus via the electron populations, N_{d_i}, of its d orbitals. Equation 4 relates e^2Qq/h to these populations. $(e^2Qq/h)_0$

$$e^2Qq/h = (e^2Qq/h)_0\left[N_{d_{z^2}} + \frac{N_{d_{xz}} + N_{d_{yz}}}{2} - N_{d_{x^2-y^2}} - N_{d_{xy}}\right] \tag{4}$$

is the EFG produced by a single d electron on Co. The z axis of the EFG tensor and the axis of the d_{z^2} orbital are positioned to coincide with one another. If relative trends through a series of compounds are sought, then e^2Qq/h is simply proportional to the magnitude of the bracketed quantity. Knowing the relative magnitude of the sum of the positive terms compared to the negative terms helps determine how different types of metal–ligand bonds will affect the EFG at Co (vide infra).

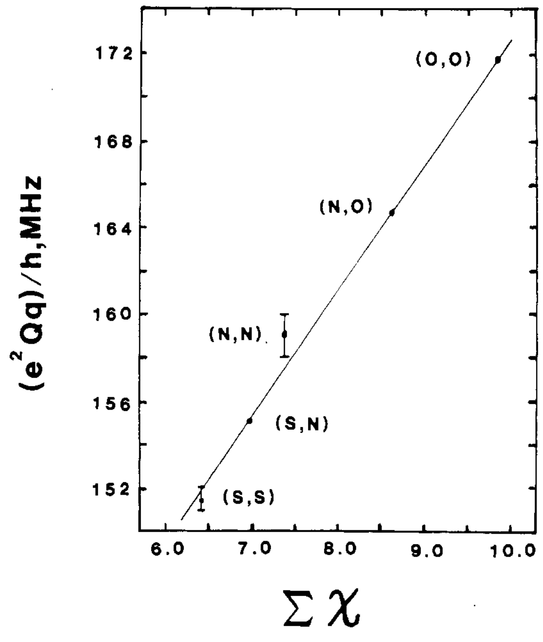


Figure 3. Correlation between the ^{59}Co coupling constant and the sum of the electronegativities for the b, b′ atoms shown.

The asymmetry parameter, η, is controlled mostly by the difference in the population of the d_{xz} and d_{yz} orbitals according to eq 5.

$$\eta = \frac{{}^3/_2|N_{d_{xz}} - N_{d_{yz}}|}{e^2Qq/h} \tag{5}$$

The recent Xα calculation by Gross, Trogler, and Ibers[4] for $(\eta^5\text{-}C_5H_5)CoN_4H_4$ specifies the d orbitals participating in the σ- and π-bonding with the metallacycle. They employed the same axis system as is adopted by the EFG tensor. The d_{xy} orbital is predominantly σ-bonding. d_{yz} and d_{xz} have important coefficients in the π orbitals of the metallacycle. The d_{z^2} and $d_{x^2-y^2}$ orbitals are nominally filled and nonbonding.

The Cobalt Atom's View of the Metallacycle. The quadrupole coupling constants for the $(\eta^5\text{-}C_5H_5)Co$ fragment involved in various metallacycles, IV and V, are given in Tables I and II. From the results three implications about the ground-state electron distribution in the Co–b bond can be obtained.

First, e^2Qq/h (Table I) for $(\eta^5\text{-}C_5H_5)Co(b)b'$ metallacycles (b, b′ = O, N, S) correlates directly with the sum of the Mulliken–Jaffe electronegativities[36] for the b, b′ atoms. The

Table II. ^{59}Co NQR Data for the R-Substituted $(\eta^5\text{-}C_5H_5)Co(1,2\text{-dithiolene})$ Complexes V[a]

R	freq, MHz ν_3	freq, MHz ν_2	freq, MHz ν_1	e^2Qq/h, MHz	η
phenylene (in IV)	31.618 (4)	19.979 (6)		152.10	0.531
	31.445 (4)	19.878 (6)		150.89	0.514
				151.49 (av)	0.522 (av)
perchlorophenylene (in IV)	31.350 (5)	19.901 (10)		149.36	0.446
CF_3	31.184 (9)	19.732 (6)	17.470 (2)	149.27	0.492
CN	30.665 (15)	19.376 (20)	18.185 (3)	147.48	0.534
H	31.187 (4)	19.882 (3)		148.00	0.403
	30.860 (5)	19.725 (4)		146.18	0.381
				147.09 (av)	0.392 (av)

[a] At room temperature; parenthetical numbers are signal-to-noise ratios.

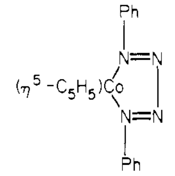
Table III. ^{59}Co NQR Data for the Noncyclic $(\eta^5\text{-}C_5H_5)Co(b)b'$ Complexes VI[a]

b	b′	freq, MHz ν_3	freq, MHz ν_2	freq, MHz ν_1	e^2Qq/h, MHz	η
CO	CO	33.419	21.632		157.29[b] (154.41)[c]	0.289
CO	$P(C_6H_5)_3$	33.729	21.879	14.141	158.64	0.277
$P(OCH_3)_3$	$P(OCH_3)_3$	34.469	22.857	11.981	161.02	0.108
$P(C_2H_5)_3$	$P(C_2H_5)_3$	35.922	23.904	12.218	167.7	0.063
$P(C_6H_5)_3$	$P(C_6H_5)_3$	37.624	25.057		175.61	0.047

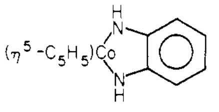
[a] At room temperature except for the $(\eta^5\text{-}C_5H_5)Co(CO)_2$ spectrum; parenthetical numbers are signal-to-noise ratios. [b] At 77 K. [c] Extrapolated to RT room temperature from the coupling constants measured at 77, 143, 195, and 210 K.

tight interrelationship is shown graphically in Figure 3. The smallest EFG is produced by the least electronegative b, b′ atom combination, while the largest value arises from the most electronegative b, b′ combination. The variation in the cobalt EFG is, therefore, governed by the electron density in the Co–b bond, as mandated by the electronegativity concept.

Second, the electron distribution on the cobalt atom is rather insensitive to substitution of the metallacycle ring. The effect of substituents on the EFG at a metal has served as a useful probe of the metal–ligand bond in the past.[11,12,37] α-Substitution of the ring was accomplished by functionalizing the nitrogen atom in the *o*-phenylenediamine and *o*-aminophenol complexes. The effect of β-substitution was analyzed with the help of the 1,2-dithiolene complexes (Table II). The 1,4-diphenyltetraazadiene and *o*-phenylenediamine complexes, VII and VIII, represent yet another type of alteration of the five-membered ring at a site remote from the cobalt atom. The most notable feature of these data is the relative insensitivity of the ground-state electronic structure of the cobalt atom to the pendant groups of the b, b′ atoms.



VII



VIII

Third, the electron distributions of I, II, and III assign different formal oxidation states to the metal. An indication of the most appropriate formal oxidation state for the cobalt atom is obtained by comparing the values of e^2Qq/h in Tables I and II to those in Table III. The complexes in Table III are undeniably Co(I) by the usual method of electron counting. The magnitudes and ranges of e^2Qq/h for all of the complexes in Tables I–III are observed to be about the same. Differences in η exist but the ranges overlap. Recall that η is sensitive to small structural changes. On the basis of the generally similar NQR data in Tables I–III the compounds in Tables I and II appear to have electron distributions characteristic of Co(I). In this vein, Trogler et al.[5] concluded that $(\eta^5\text{-}C_5H_5)Co(\alpha\text{-diimine})$ complexes are Co(I). Of course, the formal oxidation state of the metal in these complexes is probably not fundamentally significant, because it is unlikely that high positive charge can reside on the cobalt atom, given the nature of the ligands present.

With these three experimental findings and the Xα calculations of Gross et al.[4] in mind, the sign of the bracketed quantity in eq 4 can be determined. $N_{d_{x^2-y^2}}$ and $N_{d_{z^2}}$ are essentially equal and cancel one another.[4] Hence, the sign will be determined by the relative occupations of the orbitals of π-symmetry ($N_{d_{xz}}$, $N_{d_{yz}}$) compared to the σ-symmetry orbital ($N_{d_{xy}}$). As b becomes more electronegative (Figure 3), $N_{d_{xy}}$ must decrease because the Co–b bond is more ligand centered. A decrease in $N_{d_{xy}}$ will increase e^2Qq/h only if the total magnitude of the positive terms of eq 4 exceeds the negative terms; i.e., the bracketed quantity is positive. The d_{xz} and d_{yz} orbitals (π-symmetry) must retain considerable electron density in order for $N_{d_{xz}}$ and $N_{d_{yz}}$ to outweigh $N_{d_{xy}}$, which suggests that the Co–b bond is still predominantly a σ-bond. While some Co → b π-delocalization may exist in these complexes, the ground-state populations of the cobalt orbitals of π-symmetry remain quite large.

Table IV. Comparison of N–Co–N Bond Angles in *o*-Quinone Diimine Complexes of Cobalt

complex type	compd	N–Co–N angle, deg
IV	$(\eta^5\text{-}C_5H_5)Co(NH)_2C_6H_4$	84.0[a]
		84.1
IV	$(\eta^5\text{-}C_5H_5)Co(NH)(NC_6F_5)C_6F_4$	83.4[b]
VII	$(\eta^5\text{-}C_5H_5)Co[N(C_6F_5)_2]_2N_2$	79.0[c]

[a] Reference 32. [b] Reference 5. [c] Reference 6.

Table V. Comparison of S–Co–S Bond Angles in 1,2-Dithiolene Complexes of Cobalt

complex type	compd	S–Co–S angle, deg
V	$(\eta^5\text{-}C_5H_5)CoS_2C_2(CF_3)_2$	92.2[a]
V	$(\eta^5\text{-}C_5H_5)CoS_2C_2(CN)_2$	93.2[b]
IV	$(\eta^5\text{-}C_5H_5)CoS_2C_6H_4$	92.6[c]
		91.9

[a] Baird, H. W.; White, B. M. *J. Am. Chem. Soc.* 1966, *88*, 4744–45. [b] Reference 8. [c] Reference 33.

It is informative to probe the effect of Co–b π-bonding on the EFG of the cobalt atom. To this end the complexes in Table III were investigated. Strong π-acceptor ligands, such as CO, produce the lowest EFG while ligands with less π-acidity raise the EFG at cobalt. This trend probably results from differences in the magnitude of $N_{d_{xz}}$ and $N_{d_{yz}}$ through the series. Representing one extreme, $(\eta^5\text{-}C_5H_5)Co(CO)_2$ has a smaller overall magnitude of the bracketed quantity in eq 4 because d → π^* migration reduces $N_{d_{xz}}$ and $N_{d_{yz}}$ of cobalt. The reverse is true at the other extreme where, for $(\eta^5\text{-}C_5H_5)Co[P(C_6H_5)_3]_2$, less Co → b π-electron migration is expected. The trend in π-acidity,[38] CO > $P(OCH_3)_3$ > PR_3, is mimicked by the EFG. The values of η are also consistent with this interpretation of the bonding. η has the largest value when the Co → b π-bonding is the largest owing to a significant difference between $N_{d_{xz}}$ and $N_{d_{yz}}$ (eq 5). As the π-bonding diminishes, so does η because $N_{d_{xz}}$ and $N_{d_{yz}}$ become more similar.

The asymmetry parameters for the metallacycles compiled in Tables I and II when plotted against the sum of the electronegativities of b (Figure 4) may not be random. A base-line value of η exists according to the coordination-sphere model. Superimposed upon this value is a structural contribution due to differences in the $Co(b)_2$ angle (Figure 2). We stress that Figure 2 should be used for qualitative guidance rather than prediction. Tables IV and V list the N–Co–N and S–Co–S angles for several $(\eta^5\text{-}C_5H_5)Co$ complexes. The 8–10° difference in these angles between $\overset{\frown}{S\,S}$ and $\overset{\frown}{N\,N}$ ligands can account for the observed range of η values. No conclusion

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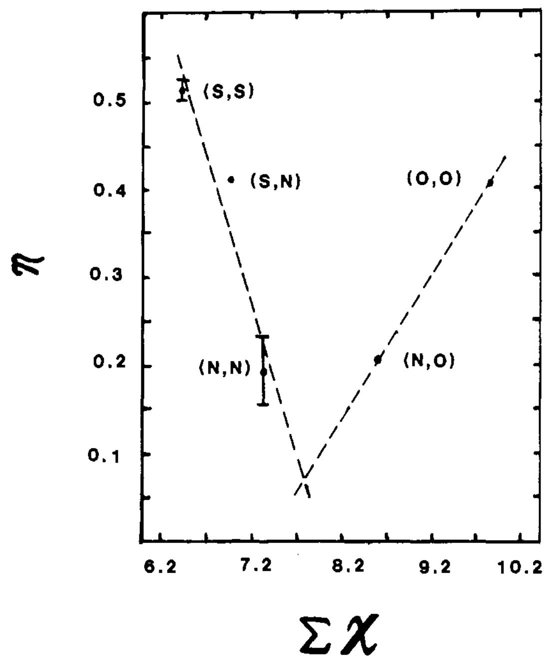

Figure 4. Variation in the EFG asymmetry parameter of ^{59}Co with the sum of the electronegativities of the b, b′ atoms shown.

about the CoO_2 bond angle can be drawn because the structure of *o*-quinones of comparable organometallic complexes have not been determined. The angles in inorganic *o*-quinone complexes of Cr, Fe, and Co are found to range 79–91°.[39]

Metallacycle ring substitution provides an additional probe of the bonding within the metallacycle. σ-Induction and π-resonance/polarization by the substitutent might be observed at the cobalt atom. For instance, ring substituents have a pronounced effect on the ^{14}N NQR spectra of substituted nitrogen heterocycles.[40] Substitution of the α and β positions with respect to cobalt was investigated. α-Substitution is respesented by b = NH, NC_6H_5, and NCH_3 (Table I). H and C_6H_5 have similar inductive and resonance substituent constants[41] and, as expected, generate about the same EFG at cobalt. CH_3 is electron releasing, which makes the nitrogen atom less electronegative.[41] By the arguments presented above, methyl substitution should and does decrease the EFG at the cobalt atom.

The tetraazadiene, VII, and the *o*-phenylenediamine, VIII, represent both α-substitution and a change in the metallacycle backbone. The EFG at cobalt is virtually the same for both, which indicates that, from the prospective of the Co atom, their ground-state electronic structures are essentially the same. A similar conclusion has been reached from the bond distances and electronic spectra of the two complexes.[6]

The dithiolene complexes in Table II involve various β-substituents. When a neutral substituent, H, is replaced by the electron-withdrawing groups, CN and CF_3, the effect on the EFG at cobalt is very small. The electronegativity of H = 2.1, while CN and CF_3 = 2.8.[42] A significant alteration in the π-electron density of the metallacycle might be produced by the *o*-dithioquinone ligand because the phenyl ring and the metallacycle complete for the π-electrons. The EFG at cobalt is still minimally perturbed, however. Note that in accordance with the expected trend in polarization of the ring, e^2Qq/h follows the order R = H ≤ CN < CF_3 < phenylene, although the difference through the series is very small. When combined with the fact that perchloro-*o*-dithioquinone (which should be the most electron withdrawing of all) generates an intermediate value of e^2Qq/h, the correlation becomes quite tenuous. We conclude that β-substitution of the metallacycle hardly affects the ground-state electron distribution on the metal atom.

The overall insensitivity of the ground-state electronic structure of Co to any type of metallacycle ring substitution is evidence that the heteroatoms b, b′, insulate the cobalt atom from the remainder of the ring. This result is an experimental confirmation of Gordon and Fenske's MO calculations,[43] which show that the electron density on the metal atom is relatively insensitive to the overall charge on chromium complexes of *o*-quinones. We observe that the distribution of electron density on the cobalt atom is mostly controlled by the donor atoms, b, b′, rather than by the extended metallacycle. The σ-bond electron density, combined perhaps with some π-electron density, rises and falls in tandem with the electronegativities of b, b′.

Trogler and co-workers[4–6,44–47] have documented a contrasting interpretation of metal tetraazadiene complexes, VII, which suggests that strong metal-to-ring π-delocalization takes place. It is plausible that the discrepancy between their model and the view presented here involving somewhat less π-delocalization arises from disproportionate effects of π-bonding on the chemical reactivity vs. the orbital population trends extracted from the NQR spectra. With the caveat that the σ and π electrons are essentially only heuristically separable, the ^{59}Co NQR spectra for a series of electronically dissimilar b ligands (O, N, S) consistently point toward the σ-bond as the major (but not necessarily the only) Co–b interaction.

Some Reactions of the Metallacycles Related to the Electron Distribution. The reactions of complexes with Lewis acids and bases should be sensitive to the metal electron density. For instance, the (pentamethylcyclopentadienyl)rhodium (catechol) complex, which Espinet et al.[48] proposed to contain Rh(III), functions as a weak Lewis acid toward triphenylphosphine. (η^5-C_5H_5)$CoS_2C_2R_2$ complexes react with phosphines and phosphites to produce addition products.[49] The coordination number of the metal increases from 5 to 6. Heck mentioned[22] that the cobalt complexes of IV did not react with Lewis bases but did not specify the bases. If complexes IV are 18-e Co(I) complexes, they might prefer to react instead with Lewis acids. The energy released in the acid–base complexation would have to be large enough to overcome the entropy term and the molecular distortion energy. Only a few points will be mentioned here as more work is planned.

The Lewis basicity of the complexes toward $HgBr_2$ was tested. (η^5-C_5H_5)Co(1,2-dithioquinone) and (η^5-C_5H_5)Co(*o*-phenylenediamine) react in acetone with $HgBr_2$. The imine produces an insoluble brown product, (η^5-C_5H_5)Co-$(NH)_2C_6H_4 \cdot HgBr_2$, which is difficult to characterize. The complex dissociates in solvents in which it is soluble. However, the envelope of the N–H stretching modes of the solid adduct is about 100 cm^{-1} lower than that of the pure cobalt complex.

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We theorize that the N and S atoms, rather than Co, function as the base site toward the Hg atom. A chainlike structure in which the mercury atom has a coordination number of at least 4 could form. It is well-known[2] that the atoms of 1,2-dithiolenes are able to act as nucleophilic sites. Some Lewis acid behavior is exhibited by the catechol complex of IV, which reacts with $NH_2CH_2C_6H_5$ in hexane to produce a brown solid. Again, dissociation to the reactants occurs in solvents that dissolve the complex. None of the other complexes in Table I react with benzylamine. Apparently, the oxygen atoms of $(\eta^5\text{-}C_5H_5)CoO_2C_6H_4$ withdraw enough electron density from the cobalt center to allow for weak coordination by the amine.

Registry No. IV (b = b′ = O), 33195-38-9; IV (b = NCH_3, b′ = O), 86409-54-3; IV (b = NC_6H_5, b′ = NH), 12133-03-8; IV (b = NCH_3, b′ = NH), 86409-55-4; IV (b = NH, b′ = S), 33154-55-1; IV (b = b′ = S), 86409-56-5; V (R = CF_3), 12128-51-7; V (R = CN), 12082-04-1; V (R = H), 12306-74-0; VI (b = b′ = CO), 12078-25-0; VI (b = CO, b′ = $P(C_6H_5)_3$), 12203-85-9; VI (b = b′ = $P(OCH_3)_3$), 32677-72-8; VI (b = b′ = $P(C_2H_5)_3$), 79639-49-9; VI (b = b′ = $P(C_6H_5)_3$), 32993-07-0; VII, 76418-81-0; VIII, 12133-01-6; $(\eta^5\text{-}C_5H_5)Co(NH)OC_6H_3(CH_3)$, 86409-53-2; $(\eta^5\text{-}C_5H_5)Co(S_2C_6Cl_4)$, 86409-57-6; $(\eta^5\text{-}C_5H_5)CoI_2(CO)$, 12012-77-0; $NH_2CH_2C_6H_5$, 100-46-9; *N*-methyl-*o*-phenylenediamine, 4760-34-3; 5-methyl-2-aminophenol, 2835-98-5; *N*-methyl-*o*-aminophenol, 611-24-5; perchlorodithiocatechol, 86392-80-5.

Contribution from the Departamento de Quimica-Fisica, Facultat de Quimica, Universitat de Barcelona, Tarragona, Spain, and Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

Polymeric One-Dimensional $[CoXL_2]_n$ vs. Dimeric $[CoXL_2]_2$. Theoretical Analysis of the Factors Favoring Each Form

E. CANADELL*[†] and O. EISENSTEIN*[‡]

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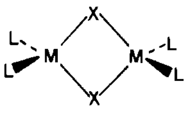
The polymeric one-dimensional structure of $[CoI(NO)_2]_n$ and dimeric structure of $[CoCl(NO_2)]_2$ are analyzed by band structure and extended Hückel calculations, and the factors favoring the dimer vs. the polymer are discussed. It is shown that d^{10} metal atoms that are linked by an electropositive atom and carry strong π-acceptor groups will prefer a polymeric over a dimeric structure.

Electronic factors favoring polymeric over dimeric structures in oligomeric systems are not well-known. This dichotomy between dimers and polymers is commonly found in inorganic systems. Molecular orbital and band structure calculations are attempted to clarify this problem for the first time.

Numerous tetrahedral M_2L_6 transition-metal dimers are known. While most dimers with d^{10} metal centers have the general edge-sharing tetrahedral structure of type **1**, a few exist as polymeric one-dimensional chain structures of type **2**. This is the case for $[CoX(NO)_2]_n$ with X = I[1] or Br.[2] The structure is made up of a zigzag chain of CoX in which the cobalt atom is tetrahedrally coordinated and no Co–Co bond is present as evidenced by the long Co–Co distance (3.86 Å, X = I). The polymer of type **2** does not exist for X = Cl. On the other hand, the dimer $[CoCl(NO)_2]_2$ of type **1** is well characterized.[3] To our knowledge, no polymer of type **2** is known for a transition-metal center with an incompletely filled d shell. In this paper, we present an analysis of the electronic structures of dimer **1** and polymer **2** and describe the conditions that favor one form over the other.



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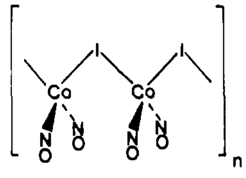

2

Theoretical Procedure

The tight-binding method[4] of band structure calculation obtained by the extended Hückel method has been used. Given a set of basis atomic orbitals $\{\chi_\mu\}$ for the atoms of a unit cell, the set of the Bloch basis orbitals $\{b_\mu(\mathbf{k})\}$ are formed as

$$b_\mu(\mathbf{k}) = N^{-1/2}\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}\chi_\mu(r - \mathbf{R}_l) \qquad (1)$$

where $\mathbf{k}$ is the wave vector and $\mathbf{R}_l = l\cdot\mathbf{d}$, with $\mathbf{d}$ being the primitive vector. With these Bloch basis orbitals the extended Hückel method leads to the eigenvalue equation

$$H(\mathbf{k})\ C(\mathbf{k}) = S(\mathbf{k})\ C(\mathbf{k})\ e(\mathbf{k}) \qquad (2)$$

where $H_{\mu\nu}(\mathbf{k}) = \langle b_\mu(\mathbf{k})|H_{\text{eff}}|b_\nu(\mathbf{k})\rangle$ and $S_{\mu\nu} = \langle b_\mu(\mathbf{k})|b_\nu(\mathbf{k})\rangle$. The solution of this eigenvalue problem results in LCAO crystal orbitals $\psi_n(\mathbf{k})$

$$\psi_n(\mathbf{k}) = \sum_\mu C_{n\mu}(\mathbf{k})\ b_\mu(\mathbf{k}) \qquad (3)$$

and eigenvalues $\epsilon_n(\mathbf{k})$. The band structure is then determined by performing the above calculation for various values of $\mathbf{k}$ (usually within the first Brillouin zone; $-0.5\mathbf{K} \le \mathbf{k} \le 0.5\mathbf{K}$ where $\mathbf{K} = 2\pi/\mathbf{d}$). The parameters of the extended Hückel calculation and geometries are given in the Appendix.

A unit cell of **2** contains one $CoI(NO)_2$ unit. In our calculations, lattice sums were carried out to the third nearest neighbors (i.e., l = −3, −2, −1, 0, 1, 2, 3 in eq 1) and eq 2 was solved at $\mathbf{k}$ = 0.0**K**, 0.1**K**, 0.2**K**, 0.3**K**, 0.4**K**, and 0.5**K**.

Results and Discussion

The energy of the unit cell $CoI(NO)_2$ within polymer **2** can be compared to the energy of the same chemical fragment within the dimer of type **1**. The $CoI(NO)_2$ fragment is found to be 4.4 kcal/mol more stable inside the polymer than inside the dimer. The opposite is true for the $CoCl(NO)_2$ fragment,

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[†] Universitat de Barcelona.

[‡] University of Michigan.

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