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Registry No. Ni-I, 56348-41-5; Ni-II, 56348-43-7; Ni-III, 56348-45-9; Ni-IV, 56348-47-1; Fe-I, 55222-32-7; Fe-II, 55190-32-4; Fe-III, 55190-34-6; Fe-IV, 55190-36-8.

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(3) University of Illinois.
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$$^1A_{1g} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^5T_{2g}$$

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Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, British Columbia, V6T 1W5, Canada

Cobalt-59 Nuclear Quadrupole Resonance of Derivatives of Dicobalt Octacarbonyl

LIAN SAI CHIA,[1] WILLIAM R. CULLEN,* MICHAEL C. L. GERRY,* and EDWARD C. LERNER[1]

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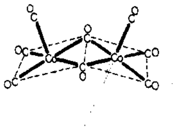
The ^{59}Co nuclear quadrupole resonance spectra of a number of derivatives of dicobalt octacarbonyl are reported. These include the complexes (RC≡CR')$Co_2(CO)_6$ (R = R' = H, CF_3, CH_2OH, C_6H_5; R = H, R' = $C(CH_3)_3$), the norbornadiene derivatives (π-C_7H_8)$Co_2(CO)_6$ and (π-C_7H_8)$_2Co_2(CO)_4$, and the ligand-bridged f$_4$fars$Co_2(CO)_6$ and f$_4$fars(C_6H_5C≡CC_6H_5)$Co_2(CO)_4$. The parameters obtained from the spectra of the alkyne complexes are related to the electronegativities of R and R' with e^2Qq being inversely proportional to η. The data indicate that the sign of e^2Qq is different from that in $Co_2(CO)_8$. The two chemically different cobalt atoms in (π-C_7H_8)$Co_2(CO)_6$ do not have very different NQR parameters. These are similar to those derived for the other complexes with nonplanar $Co_2(CO)_2$ bridging systems but are different from those of (π-C_7H_8)$_2Co_2(CO)_4$ which reinforces the belief that this last complex is planar.

In recent years there has been an increasing interest in the application of nuclear quadrupole resonance (NQR) spectroscopy to structural and bonding problems.[2-4] Although ^{59}Co NQR spectra of a number of compounds have been reported,[4] most of these have been obtained from simple derivatives containing only one cobalt atom per molecule or ion. A notable exception is the NQR spectrum of dicobalt octacarbonyl, A, which has been discussed in detail.[5,6] This carbonyl reacts with group 5 donors and organic π donors with displacement of carbon monoxide.[7] Many of the products are axially symmetric derivatives of the type $LCo(CO)_3$-$Co(CO)_3L$ (e.g., L = $(C_6H_5)_3P$) whose NQR spectra have been described recently.[4,8,9] However other products are often formed and have more complex structures such as B and C, obtained by treating alkynes and norbornadiene with the parent carbonyl A.[10-15] The purpose of the present investigation was to determine the NQR spectra of a variety of derivatives of A to ascertain if the technique would reveal (1) gross differences in structure (e.g., the two inequivalent cobalt atoms in C) and (2) more subtle electronic effects due to, for example, varying the nature of R and R' in B.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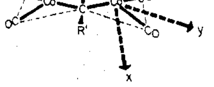
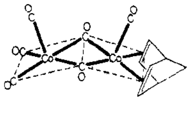


B


C

Experimental Section

All compounds were prepared by methods described in the literature.[12] The NQR spectra were recorded using a Decca instrument with Zeeman modulation. The minimum frequency obtainable was 7 MHz. The resonance frequencies were measured with the aid of the frequency marker on the instrument and checked with a Hewlett-Packard 5246L electronic counter.

Assignment of the Spectra

The ^{59}Co NQR frequencies observed for the compounds investigated are listed in Table I. The spin quantum number I is $^7/_2$ for this nucleus, and the spectra were assigned according to the well-known Hamiltonian[16]

$$\mathcal{H}_Q = \frac{e^2Qq}{4I(2I-1)}[\hat{I}_z{}^2 - \hat{I}^2 + \eta(\hat{I}_x{}^2 - \hat{I}_y{}^2)] \qquad (1)$$

where $\hat{I}$ is the nuclear spin angular momentum operator, having components $\hat{I}_x$, $\hat{I}_y$, and $\hat{I}_z$ along the principal axes of the quadrupole tensor; e^2Qq and η, the quadrupole coupling constant and asymmetry parameter, respectively, are the parameters to be obtained from the spectra. For nuclei of half-integral spin the original $(2I + 1)$-fold nuclear spin degeneracy is partially removed by this Hamiltonian to $(I + {}^1/_2)$ separate levels. Thus for $I = {}^7/_2$ four levels are obtained.

When the nucleus is in an axially symmetric environment, $\eta = 0$ and the quantum number m_I is good; thus each level can be assigned the quantum numbers $\pm m_I$. In an NQR experiment the selection rule is $\Delta m_I = \pm 1$. Thus in this case three strong transitions should be observable. They are equally spaced and occur at frequencies of $^1/_{14}e^2Qq$, $^2/_{14}e^2Qq$, and $^3/_{14}e^3Qq$.

When η is no longer zero, the regularity of the levels and transitions is lost; their relative positions vary according to the value of η. Furthermore, although the number and degeneracy of the levels do not change with η, m_I is no longer a good quantum number. Consequently, besides the three strong transitions described for $\eta = 0$ (but which are now no longer equally spaced), which we designate ν_1, ν_2, and ν_3, further transitions become weakly allowed.[17] These latter occur at sums of the ν's ($f_1 = \nu_1 + \nu_2$ and $f_2 = \nu_2 + \nu_3$) and can be of great assistance in the assignment.

For the complexes studied here the environments at the Co nuclei were far from symmetric. To make the assignments the ratios of the three strong transition frequencies (ν_2/ν_1, ν_3/ν_2) were calculated at intervals of η of 0.0001 and compared with the observed ratios. The calculation was done by constructing the Hamiltonian matrix in the $|I, m_I\rangle$ basis and diagonalizing. If possible the assignments were confirmed by measuring f_1 and f_2. The procedure was particularly useful when lattice effects produced a multiplicity of lines.

$RC{\equiv}CR'Co_2(CO)_6$ Complexes (B). NQR spectra of five complexes having this general formula were obtained. The frequencies are given in Table I. Spectra were measured at more than one temperature for several complexes. Only in one case, noted below, was anything other than the normal behavior of a single phase observed.[2]

For the compound having R = R' = H six strong lines were observed at each of three temperatures. Of these, two were found near 17.6 MHz and four near 11.0 MHz. For such a pattern clearly there must exist Co atoms in two distinct, very asymmetric sites. The closeness of the latter four lines resulted in some ambiguity in their assignments; this was partially resolved by observation of f_1 and f_2, the "forbidden" transitions. Even then the accuracy of the measurements still did not give an unambiguous assignment, and indeed that given in Table I is the best of four possible. However the derived values of e^2Qq and η are independent of the assignment to within experimental uncertainties. The closeness of the two sets of values suggests strongly that the two inequivalent Co nuclei occur in two different lattice sites.

For the *tert*-butyl compound (R = $(CH_3)_3C$; R' = H), a similar situation arose. However, the low-frequency lines were sufficiently separated that the "forbidden" transitions assigned to f_1 removed all ambiguities in assignments. The frequencies were similar to those of the derivative with R = R' = H, though in one case (site II at 0°C) the asymmetry is so high that ν_1 actually exceeds ν_2. The closeness of e^2Qq and η for the two inequivalent nuclei again suggests that they are in inequivalent lattice sites.

At 0°C the compound with R = R' = CH_2OH showed three strong and three weak signals. At 30°C these sets of signals became of equal intensity. This behavior suggests the probable presence of two different phases, denoted α and β in Table I, each with one cobalt site.

The spectrum of the compound having R = R' = CF_3 was measured at 0°C only. Eight lines were observed: two near 13 MHz, four near 10 MHz, and two near 8.3 MHz. Furthermore, the lines near 8.3 and 13 MHz were all rather broad and could reasonably each have been composed of two signals. On this basis, using the frequency ratio chart, the transitions were assigned to four inequivalent sites, for which the asymmetry parameter is rather large (>0.7). In this case the group near 10 MHz is assigned to ν_1. It is interesting that this transition is the most sensitive to slight changes in η,[17] and this results in the resolution of the four transitions. Once again the desired values of e^2Qq and η are very close, consistent with four inequivalent lattice sites. Notably, however, the actual value of e^2Qq is some 20 MHz lower than for the other derivatives.

The situation for the compound having R = R' = C_6H_5 is rather different. Although six transitions were observed, indicating two distinct cobalt sites, the derived values for e^2Qq differed by over 5 MHz. Now the crystal structure for this compound[13] reveals the two cobalt atoms in an individual molecule in considerably different environments; i.e., the molecule is not symmetrical. This asymmetry is seen, in particular, in the benzene rings, whose planes are rotated 62° with respect to each other. It is thus reasonable to suggest that the large differences in coupling constants may result from intramolecular rather than intermolecular effects.

The data in Table I show that both e^2Qq and η for $(RC{\equiv}CR')Co_2(CO)_6$ are sensitive to the nature of R and R'. The similarity of the parameters for the compounds with R = R' = H and with R = $(CH_3)_3C$ and R' = H indicates that the differences are not obviously due to steric effects. In general, e^2Qq decreases with increasing electronegativity of the substituents R and R'. Furthermore, inspection of the data in Table I reveals that in general η and e^2Qq are roughly inversely proportional. A plot of e^2Qq vs. η is given in Figure 1; this is essentially a straight line, as would be expected from the inverse proportionality. It has been shown,[2,4] furthermore, that the coupling constants are dependent almost entirely on the populations of the Co 3d orbitals, as in eq 2 and 3. Here

$$e^2Qq = e^2Qq_{320}[N_{d_{z^2}} + {}^1/_2(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})] \qquad (2)$$

$$\eta = \frac{{}^3/_2[N_{d_{xz}} - N_{d_{yz}}]}{N_{d_{z^2}} + {}^1/_2(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})} \qquad (3)$$

the N's refer to the populations of the appropriate 3d orbitals, and e^2Qq_{320} is the coupling constant for a singly occupied $3d_{z^2}$ orbital. Assuming that the x, y, and z axes change little with R and R', then if $[N_{d_{xz}} - N_{d_{yz}}]$ is constant, e^2Qq and η would indeed be inversely proportional.

To come to a definite conclusion about the bonding we would need to know either the direction of the z principal axis of the quadrupole tensor or the sign of e^2Qq, neither of which is available from the present experiments. However, some useful suggestions consistent with the data can be made. In particular, Sheline et al.[5,6] have shown that the z axis for each Co atom in $Co_2(CO)_8$ is essentially along the Co–CO (axial) direction. Furthermore each molecule has essentially a plane

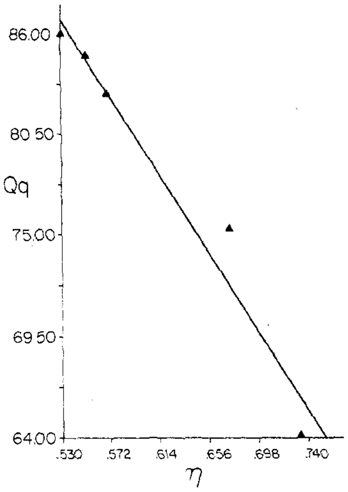
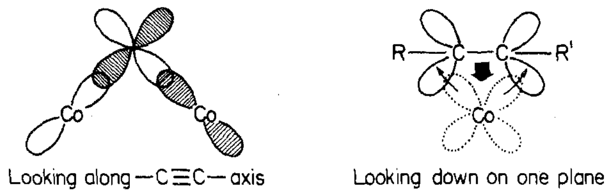


Figure 1. Plot of e^2Qq vs. η for the derivatives $(RC{\equiv}CR')Co_2(CO)_6$. $e^2qQ = (-102.04 \pm 12.30)\eta + (140.99 \pm 7.57)(r = 0.98)$, from linear least-squares analysis.

of symmetry including both Co atoms. Accordingly, a reasonable guess of the principal axes could well be that indicated in B.

The conventional view of the bonding is described diagrammatically in D[12] where views along the C≡C axis and of one CoCC plane are shown. The geometry about each Co atom is essentially trigonal bipyramidal, making its hybridization dsp^3 with one of the hybrid orbitals pointing toward the midpoint of the C≡C bond. This results in two orthogonal bonds from the alkyne, one to each Co atom. This bonding is supplemented by back-bonding in which there is flow of electron density from filled Co d orbitals to π^* antibonding orbitals of the acetylene. In any case all this flow takes place in the xy plane of the quadrupole tensor, implying that $N\mathrm{d}_{z^2}$, $N\mathrm{d}_{xz}$, and $N\mathrm{d}_{yz}$ in eq 2 and 3 are essentially independent of R and R'. This means that $[N\mathrm{d}_{xz} - N\mathrm{d}_{yz}]$ is a constant, and e^2Qq is inversely proportional to η. Furthermore the decrease of e^2Qq with increasing electronegativity of R and R' must result from a decrease in $(N\mathrm{d}_{xy} + N\mathrm{d}_{x^2-y^2})$, so that $[N\mathrm{d}_{z^2} + {}^1/_2(N\mathrm{d}_{xz} + N\mathrm{d}_{yz}) - (N\mathrm{d}_{x^2-y^2} + N\mathrm{d}_{xy})]$ is negative. Since e^2Qq_{320} is also negative,[18] then e^2Qq is positive, in contrast to the sign deduced for $Co_2(CO)_8$.[5] Why this should be so is not clear, though because of the differences in the bonding, the change is not implausible. Nevertheless many assumptions are inherent in this simple scheme and it is noteworthy, for example, that the carbonyl stretching frequencies of $RC{\equiv}CR'Co_2(CO)_6$ increase with increasing electronegativity of R and R',[12] resulting possibly from a decrease in $(N\mathrm{d}_{xz} + N\mathrm{d}_{yz})$, which was considered negligible in our scheme.



D

Other $Co_2(CO)_8$ Derivatives. We have also observed ^{59}Co NQR spectra of four other derivatives.

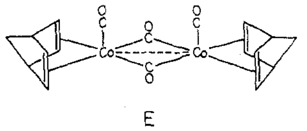
A crystal structure determination[19] of $(CH_3)_2As\overline{C{=}C}$-$\overline{As(CH_3)_2CF_2C}F_2Co_2(CO)_6$ ($f_4farsCo_2(CO)_6$) shows that the basic skeleton is that of $Co_2(CO)_8$, with the As-containing ligand bridging two equatorial positions. The two Co atoms are essentially equivalent in the molecule, so that one might reasonably expect only one set of NQR frequencies. In fact, six lines were observed at both 0 and 30°C, implying the presence of two inequivalent cobalt sites. The two sets of values of e^2Qq and η are reasonably close, suggesting that there are two crystallographically inequivalent Co atoms, in agreement with the solid-state structure.

The derived coupling constants, remarkably, are very close to those of $Co_2(CO)_8$ itself. The reasons for this are unclear, though two possibilities suggest themselves: (i) the π-donating and π-withdrawing powers of the ligand are very close to those of CO itself and (ii) even if these powers are different, the directions of the principal axes change to compensate. A combination of these is also possible. It is notable, however, that this ligand has an almost unique ability to replace CO in metal carbonyls to give stable clusters,[20] so the former suggestion is reasonable.

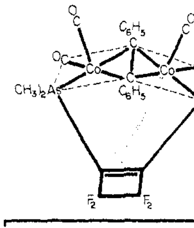
Spectra were also obtained for two complexes in which norbornadiene ligands replaced CO, namely, $(\pi\text{-}C_7H_8)Co_2(CO)_6$ and $(\pi\text{-}C_7H_8)_2Co_2(CO)_4$. The structure of the former has been determined[15] and is shown as C. The basic skeleton is that of $Co_2(CO)_8$, with the diene chelated in the equatorial plane to one Co atom. The Co–C (bridging) distances are also different for the two Co atoms. Thus the two Co atoms are inequivalent, and at least six lines would be expected in the NQR spectrum. Six lines were indeed found, but they have very similar values for e^2Qq and η, so much so as to suggest that the two Co atoms are crystallographically inequivalent, rather than being bonded to two different entities in the molecule. This is a surprising result and difficult to rationalize. Apparently the structure is such that electronic charge can redistribute very easily with changes in ligands.

The doubly substituted complex $(\pi\text{-}C_7H_8)_2Co_2(CO)_4$ is believed to have the norbornadienes chelated to the equatorial positions of the two cobalt atoms,[14] as shown in E. Its infrared spectrum has been interpreted to suggest that the $Co_2(CO)_2$ bridge system is almost planar.[21] Also, although the two Co atoms in the compound could reasonably be expected to be equivalent, two sets of transitions were observed, giving similar coupling constants, thus indicating once more that there are two Co atoms in different crystallographic environments.

The data for $Co_2(CO)_8$, $f_4farsCo_2(CO)_6$, $(\pi\text{-}C_7H_8)Co_2(CO)_6$, and $(\pi\text{-}C_7H_8)_2Co_2(CO)_4$, listed in Table I, show the first three complexes, which have the nonplanar $Co_2(CO)_2$ bridging system, to have tolerably similar values for e^2Qq, and very similar asymmetry parameters. The fourth, on the other hand, has a much lower e^2Qq and a much larger asymmetry parameter and is thus very different. Whether this is a general phenomenon is not clear and requires considerably more experimental data, which we are presently seeking.



E



F

The structure of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2CF_2}$-$Co_2(CO)_4(C_6H_5C{\equiv}CC_6H_5)$ is believed to be as in F.[22] It is thus a composite of the f_4fars and diphenylacetylene complexes described earlier. In view of the similarity of the spectra of $f_4farsCo_2(CO)_6$ and $Co_2(CO)_8$, the present complex might reasonably be expected to have similar coupling constants to $Co_2(CO)_6(C_6H_5C{\equiv}CC_6H_5)$. This, however, is emphatically not so, for both e^2Qq and η are dramatically different in the two complexes. Furthermore, only three lines (implying one lattice site for Co) were observed. Once again the reason for the change is unclear. However, it was for $Co_2(CO)_6(C_6$-

Table I. ^{59}Co NQR Transition Frequencies and Quadrupole Coupling Constants of Derivatives of $Co_2(CO)_8$

Compd	Temp, °C	Site[b]	Freq,[a] MHz	η	e^2Oq, MHz
$(HC\equiv CH)Co_2(CO)_6$	0°	I	17.584 (120) 11.109 (95) 10.530 (100) 28.685 (2) 21.625 (10)	0.543	84.655
		II	17.593 (130) 11.115 (95) 10.757 (100) 28.786 (2) 21.876 (11)	0.559	84.875
	−78°	I	17.754 (220) 11.217 (120) 10.649 (92) 28.956 (4) 21.873 (16)	0.544	85.498
		II	17.788 (230) 11.238 (120) 10.906 (94) 29.006 (4) 22.155 (18)	0.561	85.840
	−196°	I	17.856 (132) 11.281 (88) 10.851 (80) 29.155 (6) 22.170 (11)	0.554	86.098
		II	17.909 (142) 11.319 (86) 11.263 (75) 29.224 (6) 22.612 (12)	0.580	86.685
$(t\text{-}BuC\equiv CH)Co_2(CO)_6$	0°	I	17.165 (220) 10.850 (76) 9.945 (48) 20.795 (4)	0.517	82.377
		II	17.064 (220) 10.805 (72) 11.243 (48) 22.047 (4)	0.620	82.941
	−78°	I	17.922 (106) 11.342 (72) 10.018 (66) 21.353 (1)	0.490	85.780
		II	17.523 (100) 11.088 (60) 10.938 (34) 22.018 (8)	0.576	84.750
$(HOCH_2C\equiv CCH_2OH)Co_2(CO)_6$	30°	α	18.053 (20) 11.421 (17) 10.204 (15)	0.500	86.518
		β	17.699 (19) 11.182 (15) 10.804 (10)	0.559	85.368
	0°	α	18.127 (26) 11.465 (27) 10.220 (30)	0.498	86.856
		β	17.826 (9) 11.263 (18) 10.798 (20)	0.557	86.043
$(CF_3C\equiv CCF_3)Co_2(CO)_6$	0°	I	13.091 (52) 8.396 (40) 10.003 (58)	0.738	64.746
		II	13.091 (52) 8.396 (40) 9.747 (76)	0.722	64.684
		III	12.816 (46) 8.250 (56) 9.757 (76)	0.741	63.523
		IV	12.816 (46) 8.250 (56) 9.605 (52)	2.731	63.485
$(PhC\equiv CPh)Co_2(CO)_6$	0°	I	14.802 (28) 9.429 (20) 10.416 (15)	0.675	72.596
		II	15.936 (24) 10.144 (16) 11.173 (11)	0.671	78.101

Table I (*Continued*)

Compd	Temp, °C	Site[b]	Freq,[a] MHz	η	e^2Qq, MHz
$(PhC{\equiv}CPh)Co_2(CO)_6$ (*continued*)	30°	I	14.786 (20) 9.381 (14) 10.352 (10)	0.673	72.257
		II	15.836 (19) 10.078 (10) 11.152 (7)	0.673	77.618
$f_4fars(PhC{\equiv}CPh)Co_2(CO)_4$	30°	I = II	12.878 (15) 8.480 (10) 10.780 (8)	0.828	64.881
$f_4farsCo_2(CO)_6$	0°	I	18.684 (14) 11.830 (14) 10.114 (9)	0.473	89.097
		II	18.870 (18) 11.940 (12) 10.564 (9)	0.492	90.306
	30°	I	18.668 (16) 11.832 (8) 10.140 (7)	0.470	89.121
		II	18.875 (17) 11.947 (10) 10.552 (8)	0.489	90.324
$(\pi\text{-}C_7H_8)Co_2(CO)_6$	0°	I	17.17 (8) 10.98 (8) 8.125 (3)	0.371	81.14
		II	17.55 (9) 11.31 (8) 7.75 (3)	0.318	82.74
$(\pi\text{-}C_7H_8)_2Co_2(CO)_4$	0°	I	15.172 (21) 9.717 (9) 10.949 (8)	0.700	74.684
		II	14.873 (24) 9.485 (12) 10.793 (7)	0.697	73.212
$Co_2(CO)_8$[c]	−196°	I	19.132 12.334 8.417	0.3149	90.18
		II	18.671 11.818 10.344	0.4837	89.30

[a] Figures in parentheses are signal to noise ratio. Experimental errors: ±~0.050 MHz. All frequencies greater than 20 MHz are f_i's. [b] α = α phase; β = β phase. [c] From ref 5.

$H_5C{\equiv}CC_6H_5$) that two different sites for Co *in the molecule* were observed, because of both an asymmetry of the $Co_2(CO)_2$ bridging system and different torsional angles for C_6H_5. Evidently then the f4fars has removed the asymmetry in the $Co_2(CO)_2$ system. There is probably a steric interference between f4fars and the C_6H_5 group, which would cause differences (especially changes in bond and torsional angles) in this part of the structure between the present complex and $Co_2(CO)_6(C_6H_5C{\equiv}CC_6H_5)$. In view of the large variations in coupling constant in this latter complex this would seem a reasonable explanation. To clarify the situation NQR studies on other related complexes (e.g., $(C_6H_5)_2PC{=}CP(C_6H_5)_2\text{-}CF_2CF_2Co_2(CO)_4C_6H_5C{\equiv}CC_6H_5$) are necessary; unfortunately an attempt to observe a spectrum for this complex was unsucessful.[23]

A final noteworthy point concerning the complex $(f_4fars)(PhC{\equiv}CPh)Co_2(CO)_4$ is that a fairly strong fourth line was observed at 8.92 MHz. It could not be accounted for in terms of a ^{59}Co resonance, though it may have had corresponding lines at frequencies below the lower frequency limit of the spectrometer. An alternative explanation might be that the line is due to an ^{75}As resonance ($I = {}^3/_2$) in a slightly asymmetric environment. ^{75}As resonances are usually found at much higher frequencies,[2] but in the complex this nucleus is in a distorted tetrahedral environment, which would lower its resonance frequency considerably. A search for a similar resonance in $(f_4fars)Co_2(CO)_6$ was unsuccessful, however.

Conclusions

In this work we have measured the variations in nuclear quadrupole coupling constants of several substituted derivatives of dicobalt octacarbonyl. For complexes of general formula $(RC{\equiv}CR')Co_2(CO)_6$ we have been able to detect a dependence on the electronegativities of R and R', and this has enabled reasonable values for the directions of the axes and the sign of e^2Qq to be deduced. We have also found substantial differences in the coupling constants with gross structural variations, though further work is necessary to systematize them.

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Registry No. $(HC{\equiv}CH)Co_2(CO)_6$, 12264-05-0; $(t\text{-}BuC{\equiv}CH)Co_2(CO)_6$, 56792-69-9; $(HOCH_2C{\equiv}CCH_2OH)Co_2(CO)_6$, 55975-76-3; $(CF_3C{\equiv}CCF_3)Co_2(CO)_6$, 37685-63-5; $(PhC{\equiv}CPh)Co_2(CO)_6$, 14515-69-6; $f_4fars(PhC{\equiv}CPh)Co_2(CO)_4$, 55925-89-8; $f_4farsCo_2(CO)_6$, 30171-45-0; $(\pi\text{-}C_7H_8)Co_2(CO)_6$, 56845-88-6; $(\pi\text{-}C_7H_8)_2Co_2(CO)_4$, 50404-93-8; $Co_2(CO)_8$, 10210-68-1.

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Contribution from the Research School of Chemistry,
Australian National University, Canberra, Australia 2600

Dithiocarbamates of Nickel in the Formal Oxidation States I–IV. Electrochemical Study

A. R. HENDRICKSON, R. L. MARTIN,*[1] and N. M. ROHDE

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The electron-transfer properties of 16 nickel(II) dithiocarbamate complexes have been studied in acetone at a platinum electrode. Their oxidation (+0.8 to +1.0 V) is difficult and irreversible with the overall process conforming to the stoichiometry $3Ni(R_2dtc)_2 \rightarrow 2[Ni(R_2dtc)_3]^+ + Ni^{2+} + 4e^-$. The nickel(IV) cation exhibits two successive, relatively facile, reversible reduction steps corresponding to the one-electron-transfer series $[Ni(R_2dtc)_3]^+ \overset{e^-}{\rightleftharpoons} Ni(R_2dtc)_3 \overset{e^-}{\rightleftharpoons} [Ni(R_2dtc)_3]^-$. Both reduction products are unstable according to the equilibria $Ni(R_2dtc)_3 \rightleftharpoons Ni(R_2dtc)_2 + {}^1/_2(R_2tds)$; $[Ni(R_2dtc)_3]^- \rightleftharpoons Ni(R_2dtc)_2 + R_2dtc^-$. Although the formally nickel(III) species could not be prepared and isolated chemically, they are readily formed from $Ni(R_2dtc)_2$ and the electrochemically generated $R_2NCSS\cdot$ radical. The $Ni(R_2dtc)_2$ complexes undergo a one-electron reduction at quite negative potentials (−1.2 to −1.5 V): $Ni(R_2dtc)_2 + e^- \rightleftharpoons [Ni(R_2dtc)_2]^-$. Substituent effects on the redox potentials of nickel dithiocarbamates parallel closely those measured for the oxidation of the free ligand: $[R_2dtc]^- \rightarrow R_2NCSS\cdot + e^-$. Mixed-ligand species have been characterized by voltammetry and unusual reactions of some of the complexes are reported.

Introduction

Electrochemical methods are proving to be invaluable for establishing the electron-transfer relationships between members of the 1,1-dithio chelates of first-row transition metals.[2] In particular, it has been established that both manganese[3] and iron[4] with the dithiocarbamate ligand will support the three-membered electron-transfer series

$$[M(R_2dtc)_3]^+ \overset{e^-}{\rightleftharpoons} M(R_2dtc)_3 \overset{e^-}{\rightleftharpoons} [M(R_2dtc)_3]^- \qquad (1)$$

with the metal ions in formal oxidation states of IV–II. The chemical and electrochemical redox relationships have been analyzed for a variety of substituents (R) using electrochemical techniques such as normal pulse, ac and cyclic voltammetry, coulometry, and spectroelectrolysis, the potentials being found to be dependent upon the electronic properties of R.

The corresponding dithiocarbamate complexes of nickel introduce several new features. The common oxidation state is +2 rather than +3 and $Ni(R_2dtc)_2$ compounds are monomeric, are square planar, and are of a low-spin $3d^8$ electron configuration. Unlike manganese and iron, the corresponding tris-chelated species $Ni(R_2dtc)_3$ and $[Ni(R_2dtc)_3]^-$ have not been isolated. However, oxidation of $Ni(R_2dtc)_2$ with a variety of reagents[5-11] affords the $[Ni(R_2dtc)_3]^+$ cation which has been shown to possess a distorted octahedral geometry in the case of the di-*n*-butyl derivative.[12,13] The isolation of mixed-halo complexes of Ni(III) and Ni(IV)—$Ni((n\text{-}Bu)_2dtc)_2I$ and $Ni(Et_2dtc)_2Br_2$—has also been described,[6,14] although their characterization is incomplete. Oxidation of $Ni(R_2dtc)_2$ with thiuram disulfide (R_2tds) yields ESR spectra consistent with the formation of a low-spin ($S = {}^1/_2$) Ni(III) species.[15]

Spectrophotometric studies have revealed that the dark brown color of the $[Ni((n\text{-}Bu)_2dtc)_3]^+$ cation is photochemically and thermally bleached in CH_3CN and related solvents in a reversible manner.[13] Treatment of $[Ni(R_2dtc)_3]^+$ solutions with isocyanides and phosphines leads to the isolation[16] of a variety of mixed-ligand complexes of nickel(II), $[Ni(R_2dtc)(CNR)_2]^+$, $[Ni(R_2dtc)(PPh_3)_2]^+$, and $[Ni(R_2dtc)(diphos)]^+$, where diphos is the chelating phosphine $Ph_2PCH_2CH_2PPh_2$.

Electrochemical oxidation of $Ni(R_2dtc)_2$ is difficult and irreversible.[2,8,9,17,18] In the present paper, detailed results are presented[18] which establish that nickel dithiocarbamates display a rich and extensive electrochemical behavior which spans the four formal oxidation states Ni(IV), Ni(III), Ni(II), and Ni(I). The two common stereochemistries displayed by nickel (square planar and octahedral) enable two distinct electron-transfer series to be characterized, viz.

$$NiL_3^+ \leftarrow NiL_2 \overset{e^-}{\rightleftharpoons} NiL_2^- \qquad (2)$$

$$NiL_3^+ \overset{e^-}{\rightleftharpoons} NiL_3 \overset{e^-}{\rightleftharpoons} NiL_3^- \qquad (3)$$

The redox interrelationships and coupled chemical reactions are developed fully below. Some substantiating studies with nickel xanthates and mixed-ligand dithiocarbamates are also described.

Experimental Section

Syntheses. General Preparative Method for $Ni(R_2dtc)_2$. An aqueous solution of the sodium or potassium salt of the appropriate dithiocarbamate, prepared by the usual method (KOH, CS_2, HNR_2), was added to a vigorously stirred solution of $NiCl_2\cdot 6H_2O$. The crude green product was filtered, washed with water and ice-cold methanol and