TABLE X

SHIFTS IN ν(XY) (IN cm^{-1}) FOR COMPLEXES OF THE TYPE $(NH_3)_5Ru^{II}X{\equiv}YR$

RY≡X	ν(free ligand)	ν(coord ligand)	$\Delta\nu$	Ref
N_2	2330	2129[a]	−201	*f*
CO	2143	1955[a]	−188	*g*
NO^+	2220	1903[b]	−317	*e, h*
C_6H_5CN	2231	2194[c]	−37	
CH_3CN	2254	2239[c]	−15	
CH_3NC	2166	2095[d]	−71	*i*

[a] I_2 salt. [b] Cl_3 salt. [c] Br_2 salt. [d] $(ClO_4)_2$ salt. [e] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 72. [f] Reference 6. [g] C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. Swanwick, *J. Organometal. Chem.* (Amsterdam), **14**, 349 (1968). [h] Reference 13. [i] Reference 22.

and $[Ru(en)_2(N_2)_2][B(C_6H_5)_4]_2$.[3b] Two bands are observed, both occurring at higher frequency than the ν(CN) of $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$ (Tables III and VI). The spectrum of $[$*trans*-$Ru(NH_3)_4(C_6H_5CN)_2][ClO_4]_2$ showed the expected single ν(CN) higher than the monobenzonitrile complex. This frequency is slightly less than the lower and more intense nitrile band of the *cis*-bis(benzonitrile) complex. The difference is apparently of little significance in terms of the metal–nitrile bond stability since the *trans* salt proved to be the less stable in aqueous methanol solution, presumably because of the competition between the *trans*-nitriles for the same sets of metal π electrons.

The different pathways leading to the formation of 4-cyanobenzoatopentaammineruthenium(III) linkage isomers illustrate basic differences between $Ru(NH_3)_5^{2+}$ and $Ru(NH_3)_5^{3+}$. The reaction of $Ru(NH_3)_5H_2O^{2+}$ [generated by Zn(Hg) reduction of $Ru(NH_3)_5Cl^{2+}$] with 4-cyanobenzoic acid gives exclusively the cyano-coordinated $Ru(NH_3)_5$(4-cyanobenzoic acid)$^{2+}$. This product was anticipated on the basis of the lability of $Ru(NH_3)_5^{2+}$ carboxylate complexes[31] and of the relative inertness of the benzonitrileruthenium(II) species (above). Oxidation to ruthenium(III) apparently does not perturb the coordination sphere as the product showed the increased ν(CN) typical of the ruthenium(III)–nitrile coordination. The carboxylate coordinated isomer is formed by the reaction of $[Ru(NH_3)_5OH][S_2O_6]$ with 4-cyanobenzoic acid in an aqueous slurry. No absorption at 2275 cm^{-1}, characteristic of the nitrile-coordinated isomer, is observed in the ir spectrum of the product, indicating that the reaction is specific for the carboxylate-coordinated isomer. The specificity may be the result either of kinetic (mechanistic) control or of thermodynamic bond stability. Insufficient information is available to discriminate between these possibilities although it is likely that the carboxylate–ruthenium(III) bond is thermodynamically favored over the nitrile–ruthenium(III) linkage owing to the relative "hardness" of Ru(III) and of the $-CO_2^-$ compared to the relative "softness" of RCN. Such a qualitative description is, however, subject to incalculable assumptions as alkylnitriles are known to form quite stable complexes with other tripositive second- and third-row transition metal ions.[32]

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Chancellor's Patent Fund (UCSB) for support of this research.

[31] J. A. Stritar, Ph.D. Thesis, Stanford University, 1967.

[32] (a) B. D. Catsikis and M. L. Good, *Inorg. Chem.*, **8**, 1095 (1969); (b) G. Rouschias and G. Wilkinson, *J. Chem. Soc., A*, 489 (1968).

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Cobalt-59 Nuclear Quadrupole Resonance Spectra of Tetracarbonylcobalt–Tin Compounds[1]

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The ^{59}Co nuclear quadrupole resonance frequencies are reported for compounds of the form $X_nSn[Co(CO)_4]_{4-n}$, where X = Cl, Br, or CH_3, and n = 0, 1, 2, or 3. The nqr frequencies increase with increased halogen substitution and decrease upon methyl substitution. The results support the hypothesis that the populations of the cobalt $3d_{z^2}$ and d_{xz}, d_{yz} orbitals are lower than for the $d_{x^2-y^2}$, d_{xy} orbitals. Cobalt-59 nqr frequencies are reported also for $Cl_2Ge[Co(CO)_4]_2$ and $Hg[Co(CO)_4]_2$.

Studies of the ^{59}Co nqr spectra of tetracarbonylcobalt compounds of the form $Co(CO)_4L$ have shown[3] that the quadrupole resonance frequencies are quite sensitive to the nature of the group L. Analysis of the results was based on the simplifying assumption that the field gradient at cobalt is determined primarily by the 3d orbital populations on the metal, so that q_{zz} is of the form

$$q_{zz} = q_{320}[N_{d_{z^2}} + {}^1/_2(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})] \quad (1)$$

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[2] University of Illinois Fellow, 1965–1968; Standard Oil Co. of California Chevron Fellow, 1968–1969.

[3] T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, **8**, 763 (1969).

where q_{320} represents the field gradient due to a $3d_{z^2}$ electron, and the *N*'s are orbital populations. From a consideration of the 3d orbital populations in $Fe(CO)_5$ and in view of the manner in which q_{zz} varies with change in substituent, it was concluded that the quantity in brackets is negative, *i.e.*, that the d_{xy} and $d_{x^2-y^2}$ orbitals, orthogonal to orbitals of the ligand L, possess a higher overall population than the d_{z^2} and d_{xz}, d_{yz} orbitals (Figure 1). Ligands which are σ donating should then decrease q_{zz}, while those which are π accepting, and thus remove charge from the d_{xz}, d_{yz} set, cause an increase in q_{zz}.

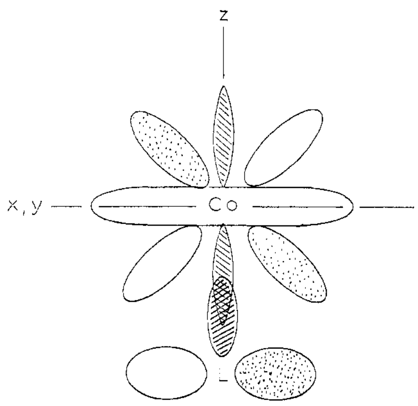

Figure 1.—Schematic representation of the interaction of cobalt 3d orbitals with the ligand L. The d_{xy} and $d_{x^2-y^2}$ orbitals are orthogonal to both the σ and π ligand orbitals. The d_{z^2} orbital is involved in ligand σ bonding, and the d_{xz} and d_{yz} orbitals are involved in π bonding to the ligand.

The cases in which tin is the central atom of the ligand L are particularly interesting, because it would appear that the $-Co(CO)_4$ moiety is capable of a significant degree of π donation into available d orbitals on the tin, as in, for example, $SnCl_3Co(CO)_4$ or $SnBr_3Co(CO)_4$. The present contribution is an attempt to characterize the Sn–Co bond further by examining series of compounds in which chlorine, bromine, or methyl groups on tin are successively substituted by $-Co(CO)_4$. Measurements on $Cl_2Ge[Co(CO)_4]_2$ and $Hg[Co(CO)_4]_2$ are also reported.

Experimental Section

Preparations of Compounds.—All the compounds prepared in this study were synthesized and stored under nitrogen. The reactions were carried out so as to yield 2–4 g of product. All compounds were identified by their infrared spectra; some also were analyzed (Table I). $(CH_3)_3SnCo(CO)_4$,[4] $(CH_3)_2Sn[Co(CO)_4]_2$,[4] $(CH_3)Sn[Co(CO)_4]_3$,[5] $Cl_3SnCo(CO)_4$,[6] and $Br_3SnCo(CO)_4$[6] were all prepared by the methods of Patmore and Graham.

$ClSn[Co(CO)_4]_3$ was prepared as a mixture with $Sn[Co(CO)_4]_4$ when 10 g of $CO_2(CO)_8$ in 50 ml THF was added to 7 ml of $SnCl_4$ in 50 ml of THF. The mixture was stirred until CO evolution ceased, and then the THF was removed. The product was extracted with 500 ml of acetone which was then reduced to approximately 5 ml and filtered to yield the $ClSn[Co(CO)_4]_3$–$Sn[Co(CO)_4]_4$ mixture. Several such mixtures were obtained in the course of the work. The compounds could not be successfully separated by fractional sublimation. The relative intensities of the Co resonances due to the two compounds were seen to change with their relative proportions in the various samples, but no significant variation in the nqr frequencies was noted. $Cl_2Sn[Co(CO)_4]_2$ was prepared by a similar procedure.

A $BrSn[Co(CO)_4]_3$–$Sn[Co(CO)_4]_4$ mixture resulted when $Br_2Sn[Co(CO)_4]_2$ and $Co_2(CO)_8$ were placed in a ratio of 1:1 in THF and stirred until CO evolution ceased. The THF was removed and the product extracted with acetone. The acetone solution was evaporated to approximately 5 ml and was filtered to yield the mixture.

An attempt was made to prepare $ISn[Co(CO)_4]_3$ by combining $I_3SnCo(CO)_4$ and $Co_2(CO)_8$ in a 1:2 ratio in THF. The reaction mixture was stirred until CO evolution ceased. The THF was removed and the product extracted with acetone. The acetone solution was evaporated to about 5 ml and filtered. The infrared spectrum showed a trace of $ISn[Co(CO)_4]_3$ with mostly $Sn[Co(CO)_4]_4$.

The compound $Cl_2SnCo(CO)_{4\,2}$ was examined both as a powder recrystallized from pentane and as a sublimate. As noted in Table II, samples prepared under the two conditions do not yield the same ^{59}Co nqr spectra. The infrared spectrum of the recrystallized powder was in accord with that reported earlier. The infrared spectrum of a solution of the sublimed material was identical with that of the first. Despite variation in chemical analysis, we conclude from the infrared spectra that the same compound exists in two different crystalline modifications. From the rather large difference in ^{59}Co frequencies in these compounds, the cobalt atoms would appear to be in quite different sites; it would be of interest to know the crystal structures of these forms and of the corresponding germanium compound. $Cl_2Ge[Co(CO)_4]_2$ was prepared as described earlier.[4] This reference also contains pertinent infrared spectral data. $Hg[Co(CO)_4]_2$ was prepared by standard methods.[7]

TABLE I

CHEMICAL ANALYSES

Compound	% calcd			% found		
	C	H	X	C	H	X
$Cl_3SnCo(CO)_4$	12.13		26.87	12.27		26.79
$Cl_2Sn[Co(CO)_4]_2$[a]	18.08		13.33	18.27		13.78
$Cl_2Sn[Co(CO)_4]_2$[b]	18.08		13.33	18.66		14.60
$Br_3SnCo(CO)_4$	9.10		45.28	9.57		45.32
$(CH_3)_2Sn[Co(CO)_4]_2$	24.48	1.23		25.32	1.26	
$(CH_3)Sn[Co(CO)_4]_3$	24.15	0.47		24.53	0.67	

[a] Powder from solution. [b] Sublimed.

Quadrupole Resonance Spectra.—The nqr spectra were all obtained at 25°. Some were obtained on a Wilks Model NQR-1A instrument; others, as reported earlier.[3] Frequencies were measured as described earlier[3] and are deemed accurate to about 0.05 MHz. In certain cases it was not found possible to obtain the pure compounds in sufficient quantity to permit determination of the nqr spectra. For example, the compound Sn[Co-

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(4) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

(5) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 2222 (1966).

(6) D. J. Patmore and W. A. G. Graham, *ibid.*, **7**, 771 (1968).

(7) R. B. King, "Organometallic Synthesis," Vol. I, Academic Press, New York, N. Y., 1965, p 101.

TABLE II

^{59}Co NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES FOR $-Co(CO)_4$ COMPOUNDS

Compound	$\nu_3(^{59}Co)$, MHz	$\nu_2(^{59}Co)$, MHz	$\nu_1(^{59}Co)$, MHz	η	eQq_{zz}, MHz
$Cl_3SnCo(CO)_4$[a]	35.02 (10)	23.37 (20)	11.68 (5)	0	163.4
$Br_3SnCo(CO)_4$[a]	34.26 (100)	22.79 (100)	11.65 (4)	0.11	160.0
$Cl_2Sn[Co(CO)_4]_2$[b]	31.94 (60)	21.25 (100)		0.06	149.0
	30.94 (60)	20.48 (100)		0.13	144.6
$Cl_2Sn[Co(CO)_4]_2$[c]	32.49 (45)	21.64 (50)	10.81 (3)	0	151.6
	29.58 (60)	19.58 (50)	10.46 (3)	0.12	138.2
$Br_2Sn[Co(CO)_4]_2$	31.64 (10)	20.98 (7)		0.16	148.0
	31.09 (10)	20.61 (7)		0	145.1
$ClSn[Co(CO)_4]_3$	29.34 (25)	19.48 (25)		0.09	135.9
	28.40 (25)	18.89 (25)		0.06	132.6
$BrSn[Co(CO)_4]_3$	28.47 (25)	18.82 (25)		0.14	133.0
$Sn[Co(CO)_4]_4$	27.69 (85)	18.47 (85)		0	129.2
$CH_3Sn[Co(CO)_4]_3$	26.70 (3)	17.80 (5)		0	124.6
	26.47 (3)	17.56 (5)		0	122.5
	25.77 (8)	17.22 (6)		0	120.2
	25.57 (9)	16.97 (7)		0.10	119.3
	25.34 (9)	16.66 (8)		0.18	118.6
$(CH_3)_2Sn[Co(CO)_4]_2$	22.65 (20)	15.26 (20)	8.15 (7)	0	105.7
$(CH_3)_3SnCo(CO)_4$	20.73 (6)	13.81 (4)		0.03	96.8
	20.47 (6)				
$Cl_3GeCo(CO)_4$[a]	34.62	23.09		0	161.6
	34.15	22.77		0	159.4
$Cl_2Ge[Co(CO)_4]_2$	33.34 (7)	22.20 (3)		0.04	155.6
	30.99 (10)	20.40 (3)		0.17	145.0
$Hg[Co(CO)_4]_2$	24.00 (4)	15.99 (5)		0.05	112.0
	23.75 (4)	15.81 (5)		0	110.8

[a] Reference 3. [b] Powder from solution. Chlorine-35 frequencies for this sample were observed at 17.66 and 17.14 MHz. [c] Sublimed. Chlorine-35 resonances for this sample were observed at 17.78 and 17.08 MHz.

$(CO)_4]_4$ was obtained in three different mixtures, with $BrSn[Co(CO)_4]_3$, $ClSn[Co(CO)_4]_3$, and $ISn[Co(CO)_4]_3$ (in this last case there was very little of the impurity). In all three instances the resonances were observed at the same frequencies. We conclude, therefore, that the presence of impurity in the form of a second cobalt–carbonyl compound is not important in affecting the frequencies observed.

The resonances observed are listed in Table II. Asymmetry parameters and quadrupole coupling constants, eQq_{zz}, were calculated from the observed values for ν_3 and ν_2 as described earlier.[3]

Infrared Spectra.—Except for a few compounds, the frequencies of the highest energy CO stretching mode, corresponding to the A_1^2 normal mode in the localized $-Co(CO)_4$ group, were taken from Graham's work.[4,5] The frequencies for the compounds $Cl_3SnCo(CO)_4$, $Br_3SnCo(CO)_4$, and $Sn[Co(CO)_4]_4$ were measured on hexane solutions using a calibrated Beckman IR-7 infrared spectrophotometer. The highest frequency mode for $Sn[Co(CO)_4]_4$ is of very low intensity, and it was necessary to employ relatively high concentrations of the nearly pure material containing a small amount of $ISn[Co(CO)_4]_3$ as impurity. The highest CO frequencies measured for the three compounds are 2121, 2116, and 2104 cm^{-1}, respectively.

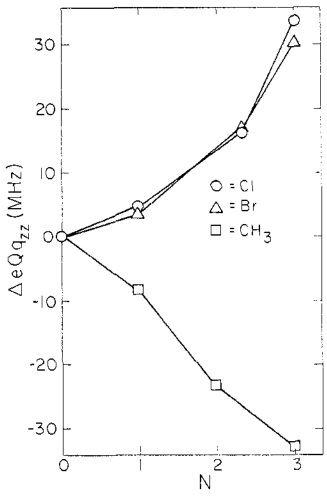

Figure 2.—Variation in the quadrupole coupling constant, eQq_{zz}, at ^{59}Co, measured from $Sn[Co(CO)_4]_4$, as a function of n in $X_nSn[Co(CO)_4]_{4-n}$.

Results and Discussion

The general character of the results in Table II lends further support to the assumption that the sign of the term in brackets in eq 1 is negative. For example, the low value of eQq_{zz} for trimethyltin as ligand demonstrates that relatively strong σ-donor character and poor π-acceptor character lead to a low field gradient at cobalt. It is convenient to think of the halogen-containing series as derived from $Sn[Co(CO)_4]_4$ as a parent compound. Successive replacement of $-Co(CO)_4$ groups by either chlorine or bromine results in successive increases in eQq_{zz} at the remaining cobalt atoms. Thus it may be concluded that such a substitution renders the tin atom a poorer σ donor toward the cobalts, or a better π acceptor, or both. The change in eQq is represented in Figure 2 as a function of the number of replacing halogens. (Where more than one resonance is seen, the average eQq_{zz} is employed.) It is interesting that the change is not linear but is curved upward. This is to be expected, since the number of $-Co(CO)_4$ groups which might absorb each successive change decreases as n increases. It is interesting that the changes are essentially the same for chlorine and bromine substitution. In the absence

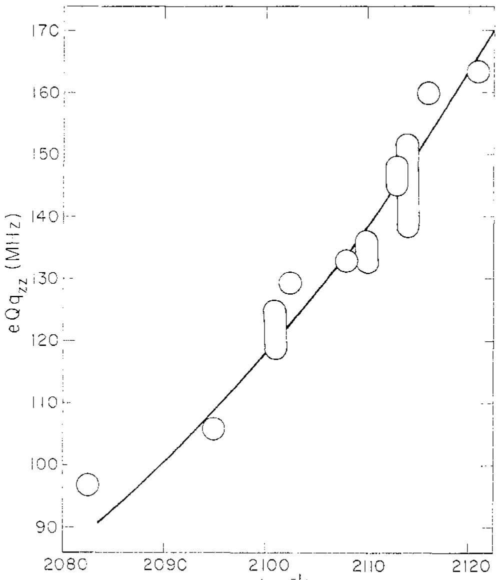

Figure 3.—Variation in the quadrupole coupling constant, eQq_{zz}, at ^{59}Co, as a function of the highest infrared CO stretching frequency measured in hexane solution, for compounds of the form $X_nSn[Co(CO)_4]_{4-n}$ (X = Cl, Br, or CH_3; n = 0, 1, 2, or 3).

of any π-bonding interaction between halogen and tin, this should be difficult to explain. Since bromine is a less electronegative element than chlorine, one would expect the changes upon bromine substitution to be smaller. A π-bonding interaction between chlorine and tin would have the effect of making the tin atom a better σ donor and poorer π acceptor toward the remaining $-Co(CO)_4$ groups.[8] We conclude that chlorine is a relatively stronger π-bonded atom toward tin in these compounds than bromine, thus compensating for its somewhat greater σ-electron withdrawal.

Substitution of CH_3 for $Co(CO)_4$ groups has the effect of lowering eQq_{zz} at the remaining cobalts. This effect is shown also in Figure 2. The $-Co(CO)_4$ group is considerably more electron withdrawing than methyl and is roughly intermediate between methyl and chlorine or bromine in effective electron withdrawal toward the tin atom.

It is of interest to relate observed values of eQq_{zz} at cobalt to properties of the CO groups. The factors which tend to lower eQq_{zz}, *e.g.*, donation from L, should tend also to lower the CO stretching force constants and, *ipso facto*, the CO stretching frequencies. Similarly, π-electron withdrawal from cobalt by L, which raises eQq_{zz}, should also raise the CO force constants and frequencies. The most reliable index of the relative Co–CO interaction obtainable from the vibrational spectrum, short of a detailed vibrational analysis, is the high-frequency, totally symmetric CO stretch. Figure 3 shows a graph of the A_1^2 stretching mode for all of the tin-substituted compounds studied, measured in solution, *vs.* eQq_{zz}. (The range of eQq_{zz} values observed is shown where multiple resonances were observed.) The correlation is reasonably good considering the diverse character of the two observables involved. It suggests that ^{59}Co nqr data on compounds of this type should be of value as a guide to the interpretation of CO vibrational data and that they might serve to test certain conclusions based on simplified force field analyses of the CO stretching modes.

[8] W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

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The Stereoisomers of the Bis(glycinato)-*l*-propylenediamine- and Glycinatobis(*l*-propylenediamine)cobalt(III) Complexes

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The reaction of the *trans*-$CoCl_2(l\text{-pn})_2^+$ complex with glycine in an alkaline solution led to the formation of the $Co(gly)_2(l\text{-pn})^+$ and $Co(gly)(l\text{-pn})_2^{2+}$ complexes. By means of ion-exchange chromatography and solubility difference, a series of geometrical–optical isomers has been separated and characterized by the order of the chromatographic elution, the uv spectra, the CD spectra, and the pmr spectra. The isomers obtained are *trans*(O),*cis*(N)-$\Lambda[Co(gly)_2(l\text{-pn})]Cl \cdot 6H_2O$, *trans*(O),-*cis*(N)-$\Delta[Co(gly)_2(l\text{-pn})]Cl \cdot 2H_2O$, *cis*(O),*cis*(N)-$[Co(gly)_2(l\text{-pn})]Cl \cdot H_2O$ (less soluble), *cis*(O),*cis*(N)-$[Co(gly)_2(l\text{-pn})]Cl$ (more soluble), *cis*(O),*trans*(N)-$\Lambda[Co(gly)_2(l\text{-pn})]Cl \cdot nH_2O$, *cis*(O),*trans*(N)-$\Delta[Co(gly)_2(l\text{-pn})]Cl \cdot 2.5H_2O$, $\Lambda[Co(gly)(l\text{-pn})_2]Cl_2 \cdot 2H_2O$, and $\Delta[Co(gly)(l\text{-pn})_2]Cl \cdot 2H_2O$.

Introduction

Liu and Douglas[1] prepared complexes of the type $Co(aa)(en)_2^{2+}$ (aa = the anion of the optically active alanine, leucine, or phenylalanine) and reported on the circular dichroism spectral characterization of the complexes. Recently, Hall and Douglas[2] extended their study on the same line by using optically active serine, threonine, and proline. In these studies, the complexes have been prepared by the reaction of *trans*-$CoCl_2(en)_2^+$ with the desired amino acids. Matsuoka and her coworkers[3] prepared the complex $Co(gly)_2en^+$ by means of a direct synthesis from the

[1] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[2] S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969).

[3] N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **40**, 1868 (1967).