son, the extent of Pt-C σ interaction should be greatest and accordingly Pt-C bond strengths should be largest in the unsubstituted hexacyanoplatinate(IV).

Similar arguments may be applied to the trends observed in the C-N stretching region. The shift of all C-N stretching modes to lower energies in the order $Cl > Br > I$ is consistent both with σ- and π-bonding arguments. However, the shift of the apical A_1 stretching mode to lower energy than the radial mode (which remains essentially unshifted from the analogous peak of the parent complex) indicates that σ bonding must predominate when one considers the trans influence discussed above for the M-C bonds.

The observations made for the nitroprusside ion are entirely consistent with the above arguments. The apical Fe-C stretching frequency is found at a higher energy than the radial stretching frequency; likewise, the apical C-N stretching frequency appears at a higher energy than the radial C-N frequency.[21] This, of course, is due to the fact that the positively charged nitrosyl ligand, formally designated as NO^+, has a greater capacity for electron withdrawal than the isoelectronic cyanide ion. It exhibits a larger "inductive effect" than the cyanide ion and a greater σ interaction is observed, particularly for the trans cyanide.

An inherent uncertainty is involved in the previous discussions. Strictly speaking, in order to make deductions about bond strengths, stretching force constants rather than stretching frequencies should have been used as the criterion. However, the normal-coordinate analysis has not yet been attempted for the pentacyanohaloplatinates(IV). There may be considerable mode mixing or other interactions which complicate the interpretation of data. Nevertheless, in a series of closely related compounds, these effects will be nearly constant, and the suggested conclusions and trends should be substantially correct even if one argues from frequencies alone. Hopefully, the results of the present work will stimulate further interest in the vibrational spectra of substituted cyanides, particularly in the metal-carbon stretching region.

Summary

Many of the fundamental frequencies have been assigned for the complex ions $Pt(CN)_5Cl^{2-}$, $Pt(CN)_5Br^{2-}$, and $Pt(CN)_5I^{2-}$. The symmetric radial Pt-C and C-N stretching frequencies of these complexes remain essentially unshifted from the unsubstituted complex. However, the apical Pt-C and C-N frequencies are shifted to lower energies in the order $Cl > Br > I$.

Because of the high degree of σ bonding exhibited in these complexes, a number of interesting phenomena are observed: (1) the extent of π bonding, as measured by infrared intensities, is minimal; (2) the positions of C-N absorptions occur at rather high energies; (3) the halide substituents have a greater trans influence than cis influence, though this influence is relatively small in both cases; (4) the trans-influence series is found to be $I > Br > Cl > CN$; (5) by comparison with the effect of halides on the vibrational spectra and bonding in these complexes, intermolecular lattice interactions are sometimes dominant.

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Registry No. $Na_2Pt(CN)_5Cl$, 41523-78-8; $K_2Pt(CN)_5Cl$, 19536-96-0; $Cs_2Pt(CN)_5Cl$, 19536-95-9; $Na_2Pt(CN)_5Br$, 41523-79-9; $K_2Pt(CN)_5Br$, 19536-94-8; $Cs_2Pt(CN)_5Br$, 12071-37-3; $Na_2Pt(CN)_5I$, 41523-81-3; $K_2Pt(CN)_5I$, 18972-63-9; $Cs_2Pt(CN)_5I$, 19537-43-0; $Na_2Pt(CN)_6$, 18988-11-9; $K_2Pt(CN)_6$, 16920-94-8; $Cs_2Pt(CN)_6$, 41523-83-5; *trans*-$K_2Pt(CN)_4Cl_2$, 12072-77-4; *trans*-$K_2Pt(CN)_4Br_2$, 12072-67-2; $K_2Pt(CN)_4$, 562-76-5; $K_2Ni(CN)_4$, 14220-17-8; $K_2Pd(CN)_4$, 14516-46-2.

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Cobalt-59 Nuclear Magnetic Resonance Studies of Stereoisomerism in Tris(bidentate)cobalt(III) Complexes[1]

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Cobalt-59 nmr spectra of stereoisomers of several tris(bidentate)cobalt(III) complexes, where the ligands are (*S*)-1,2-propanediamine and several chiral and achiral β-diketones, have been examined. Chemical shift and line width differences were found among stereoisomers of most of the complexes. Chemical shifts appear to be unrelated in any general way to absolute configuration of the complexes; however, line widths are generally larger for isomers of lower symmetry. Relative chemical shifts and relative energies of the low-energy ligand-field electronic transition, as determined from absorption or circular dichroism spectra, are compared among the different complexes and also among the individual stereoisomers of a given complex. Relative chemical shifts among cobalt(III) complexes of a series of achiral β-diketonate ligands can be explained qualitatively in terms of relative contributions from temperature-independent paramagnetism to the ^{59}Co shielding constant. However, the observed chemical shift differences among diastereomers of complexes having chiral ligands cannot be explained in a similar fashion.

The extremely wide range of chemical shifts occurring in ^{59}Co nmr is well documented; in fact, the ^{59}Co nucleus was one of the first for which the chemical shift phenomenon was observed.[2] Previous work has shown that for a large number of six-coordinate cobalt(III) complexes a fairly linear

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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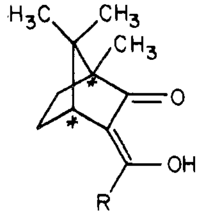
relationship exists between ^{59}Co chemical shifts and the wavelength (nm) of the lowest energy ligand-field absorption band.[3-8] This relationship has been attributed to a magnetic field induced mixing of the $^1T_{1g}$ excited state with the $^1A_{1g}$ ground state in octahedral symmetry, giving rise to a temperature-independent paramagnetic (TIP) contribution to the ^{59}Co shielding constant.[3,4] The magnitude of the TIP term is shown by crystal-field theory to be inversely proportional to the energy separation of the $^1T_{1g}$ and $^1A_{1g}$ states. Thus, for complexes of weak field ligands, TIP is relatively large and results in deshielding of the ^{59}Co nucleus. Deshielding is less pronounced in complexes of strong field ligands, and ^{59}Co resonances of these complexes appear at higher field. Exceptions to the linear chemical shift-wavelength relationship have been noted for a few complexes having sulfur or halide donor atoms.[6-9] These deviations have been attributed to a reduction in TIP due to the nephelauxetic effect.[7,10,11]

Cobalt-59 chemical shifts are extremely sensitive to minor structural alterations in the octahedral coordination sphere. For example, the ^{59}Co nmr signals of $[Co(en)_3]Cl_3$ and $[Co(NH_3)_6]Cl_3$ are separated by more than 1000 ppm,[5] and chemical shift differences of the order of 200 ppm are found between the cis and trans forms of $[Co(en)_2(NH_3)_2]I_3$, $[Co(NH_3)_4(N_3)_2]N_3$, and $[Co(NH_3)_4(NO_2)_2]NO_3$.[5,6] Thus it appeared that ^{59}Co nmr spectroscopy might provide a sensitive probe for investigating stereoisomerism in cobalt(III) complexes. Although the ^{59}Co nucleus has a spin of $^7/_2$ and is subject to quadrupolar relaxation, this disadvantage to nmr studies is offset somewhat by its high isotopic abundance (100%) and relatively high nmr sensitivity.[12]

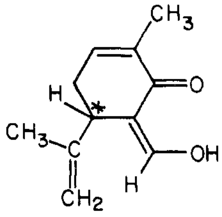
Our interest in the use of ^{59}Co nmr for investigating stereoisomerism results from previous pmr, ORD, and CD studies[13,14] in this laboratory involving chiral β-diketonate complexes of cobalt(III). We were particularly interested in determining whether ^{59}Co chemical shift differences among diastereomeric species could be detected and whether any relationship exists between chemical shifts or line widths and absolute configuration. This paper presents the results of a ^{59}Co nmr study of several tris(bidentate) complexes of cobalt(III) which have separable geometrical or optical isomers. Attempts are made to correlate observed chemical shifts with differences in ligand-field energy levels as determined by absorption or CD spectra.

Experimental Section

Materials. 2,4-Pentanedione (Hacac), 1,1,1-trifluoro-2,4-pentanedione (Htfac), 1,2-ethanediamine (en), and L(+)-1,2-propanediamine [(*S*)-pn)] were purchased respectively from Matheson Coleman and Bell, PCR, Inc., J. T. Baker Chemical Co., and Strem Chemicals, Inc. Standard methods[15] were used to prepare 1-phenyl-1,3-butanedione (Hbzac) and 1-phenyl-1,3-propanedione (Hppd). 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (Htfthbd) was purchased from Matheson Coleman and Bell. (+)-3-Acetylcamphor [(+)-Hatc, I] and (+)- and (−)-hydroxymethylenecarvone [(+)- and (−)-Hhmcar, II] were prepared as previously described.[13,14]



I



II

The cobalt(III) complexes were prepared by methods similar to those described in the literature.[13,14,16] Preparative layer chromatography was used to separate stereoisomers of the β-diketonate complexes. Precoated tlc plates with a 2-mm layer of silica gel F-254 were obtained from Brinkman Instruments, Inc. Each 20 × 20 cm plate could be charged with up to 250 mg of complex. A multiple-development, ascending technique was used; the time required for adequate isomer separation varied from complex to complex. The following solvent systems (by volume) were employed: $Co(tfac)_3$, 30:70 benzene-hexane; $Co(bzac)_3$, 95:5 benzene-ethyl ether; $Co(ppd)_3$, 98:2 benzene-ethyl ether; $Co[(+)\text{-atc}]_3$, 4:1 *n*-hexane-ethyl ether; and Co [(+)- and (−)-hmcar]$_3$, 3:1 *n*-hexane-ethyl ether. Separation attempts for $Co(tfthbd)_3$ proved unsuccessful, and elemental analyses for this complex were only fair. Separation of two diastereomers of $[Co((S)\text{-pn})_3]^{3+}$ was achieved on a cellulose column using the procedure of Dwyer, *et al.*[17]

Physical Measurements. Cobalt-59 spectra were recorded in the absorption mode using a Varian HA-100 spectrometer. A 15.35-MHz radiofrequency unit was employed, and the magnetic field was reduced by about 35% to achieve ^{59}Co resonances at this frequency. All spectra were recorded at ambient probe temperature (32°) unless otherwise indicated. Chloroform and water were used as solvents for the β-diketonate and 1,2-diamine complexes, respectively. Solute concentrations were close to saturation in most cases. Chemical shifts and line widths at half-maximum amplitude were measured by side banding. Values reported in Tables I and II are averages of several

Table I. Data for Cis and Trans Isomers of Cobalt Complexes

Complex[a]	Chemical shift[b, f]	Line width[c, f]	Δ,[d] cm^{-1}
$Co(acac)_3$	0	120 ± 5	16,800
$Co(tfthbd)_3$[e]	−295 ± 1	250 ± 20	16,400
trans-$Co(tfac)_3$	−80 ± 1	190 ± 4	16,700
cis-$Co(tfac)_3$	−76 ± 0.5	160 ± 15	16,700
trans-$Co(bzac)_3$	−12 ± 4	270 ± 7	16,700
cis-$Co(bzac)_3$	−50 ± 1	250 ± 10	16,700
trans-$Co(ppd)_3$	+59 ± 0.5	320 ± 20	16,900
cis-$Co(ppd)_3$	+59 ± 0.5	130 ± 10	16,900

[a] See Experimental Section for ligand abbreviations. [b] In parts per million relative to external $Co(acac)_3$; all measurements made in chloroform solution at 32°. [c] In hertz. [d] Absorption maxima of the low-energy electronic transition measured in chloroform solution at ambient room temperature. [e] Data are reported for the isomeric mixture; result of elemental analysis for carbon was 2% high. [f] Error limits shown are average deviations from the mean of several measurements.

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Table II. Data for Diastereomeric Cobalt Complexes

Complex[a]	Chemical shift[b]	Line width[c]	Δ,[d] cm^{-1}	CD,[e] cm^{-1}	
				$^1A \rightarrow {}^1A$	$^1A \rightarrow {}^1E$
Δ-*cis*-Co[(+)-atc]$_3$	−356 ± 1	220 ± 20	16,400	15,100	16,700
Λ-*cis*-Co[(+)-atc]$_3$	−304 ± 0.5	290 ± 15	16,450	15,100	16,800
Δ-*trans*-Co[(+)-atc]$_3$	−289 ± 1	310 ± 15	16,450	14,800	17,000
Λ-*trans*-Co[(+)-atc]$_3$	−284 ± 0.5	270 ± 10	16,450	15,100	16,900
Δ-*trans*-Co[(−)-hmcar]$_3$ Λ-*trans*-Co[(+)-hmcar]$_3$	+68 ± 2	710 ± 80	16,650	15,100	16,500
Λ-*trans*-Co[(−)-hmcar]$_3$ Δ-*trans*-Co[(+)-hmcar]$_3$	+90 ± 1	730 ± 45	16,650	*f*	16,700
Λ-*cis*-Co[(−)-hmcar]$_3$ Δ-*cis*-Co[(+)-hmcar]$_3$	+99 ± 3	620 ± 30	16,800	14,600	16,600
Δ-*cis*-Co[(−)-hmcar]$_3$ Λ-*cis*-Co[(+)-hmcar]$_3$	+128 ± 1	314 ± 10	16,650	15,100	16,600
[Co(en)$_3$]I$_3$	0[i,j]	110 ± 10	21,320[g,j]	23,360[g,j]	20,280[g,j]
Δ-[Co((*S*)-pn)$_3$]Cl$_3$	−157[i,j] ± 1	310 ± 20	21,370[j]	21,100[h,j]	
Λ-[Co((*S*)-pn)$_3$]Cl$_3$	−93[i,j] ± 1 (trans) −82[i,j] ± 1 (cis)	96 ± 5 110 ± 10		22,780[g,j]	20,280[g,j]

[a] See Experimental Section for ligand abbreviations. [b] In parts per million relative to external Co(acac)$_3$; data from chloroform solution unless otherwise indicated; error limits shown are average deviations from the mean of several measurements. [c] In hertz; error limits shown are average deviations from the mean of several measurements. [d] Absorption maxima of the low-energy electronic transition measured in chloroform solution at ambient room temperature. [e] Values were determined from resolved CD bands. [f] Band not apparent in the CD spectrum. [g] Data from A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965). [h] Value from B. E. Douglas, *Inorg. Chem.*, 4, 1813 (1965). [i] In parts per million relative to external [Co(en)$_3$]I$_3$. [j] Data from aqueous solutions.

determinations. Chemical shift values from spectrum to spectrum of a given complex agreed well, provided the spectra were recorded at the same probe temperature. Slight temperature changes produce significant chemical shift changes (see text). A concentrated solution of Co(acac)$_3$ in chloroform contained in the inner chamber of a coaxial tube system served as the external reference for the β-diketonate complexes. [Co(en)$_3$]I$_3$·H$_2$O was used in the same manner as an external reference for the 1,2-diamine complexes.

CD spectra of the individual diastereomers of Co[(+)-atc]$_3$, Co[(−)-hmcar]$_3$, and Co[(+)-hmcar]$_3$ were recorded in chloroform solution at ambient temperature using a Cary Model 60 spectropolarimeter. The low-energy CD bands of Co[(+)-atc]$_3$ and Co[(+)-hmcar]$_3$ were resolved using a Du Pont Model 310 curve resolver. The optical purity of ligands was checked where necessary on a Perkin-Elmer Model 141 polarimeter. Cis and trans isomers of the complexes were distinguished by pmr spectroscopy using a Varian A-60 instrument. Elemental analyses were performed on an F and M Model 185 C, H, and N analyzer.

Results and Discussion

***cis-* and *trans*-β-Diketonate Complexes.** Cobalt-59 chemical shifts and line widths for cis and trans isomers of several tris(β-diketonate)cobalt(III) complexes are shown in Table I. The fact that larger line widths are observed for the trans isomers is consistent with previous observations on cobalt(III) complexes of other ligands.[6] Cobalt-59 line widths in these diamagnetic complexes are expected to be controlled primarily by quadrupolar relaxation which should be more efficient in the trans isomers on account of their lower symmetry and larger electric field gradients. In an effort to ascertain whether ^{59}Co nmr line widths in these complexes are concentration dependent due to solute-solute interactions or changes in solution viscosity,[18] spectra of *trans*-Co(tfac)$_3$ were recorded over a threefold range of concentrations. The line widths so obtained were identical within experimental error.

Chemical shift values shown in Table I are relative to the resonance of Co(acac)$_3$ set at zero. Negative values imply shifts to low field of Co(acac)$_3$. The overall range of shifts found for the β-diketonate complexes is small relative to the range of nearly 14,000 ppm reported for cobalt(III) complexes in general.[6] As a result of the large line widths and small chemical shift differences, separate signals arising from cis and trans isomers could not be discerned in an isomeric mixture in most cases. It is apparent from the data presented that no general relationship exists between geometrical configuration and relative chemical shifts for the two isomers of a given complex.

Although there have been relatively few ^{59}Co nmr studies of β-diketonate complexes, there is considerable disparity among published chemical shift differences. For example, Yamasaki, *et al.*,[6] report chemical shifts at 23° of +100 and 0 ppm for Co(bzac)$_3$ and Co(tfac)$_3$, respectively, relative to Co(acac)$_3$. Also, the reported chemical shift values of Co(acac)$_3$ relative to K$_3$[Co(CN)$_6$] vary over several hundred parts per million.[4-6,10] The solvents and temperatures employed in these studies vary, and in some cases neither is explicitly mentioned. In view of the known effects of temperature and solvent on ^{59}Co nmr shifts of Co(acac)$_3$,[4] it is likely that the disparity in reported chemical shifts of cobalt(III) β-diketonate complexes arises from use of different solvents and temperatures. Clearly, these conditions must be stated when reporting ^{59}Co chemical shift values.

Using a crystal-field approach, Griffith and Orgel[3] and Freeman, *et al.*,[4] showed that temperature-independent paramagnetism in octahedral cobalt(III) complexes arises from mixing of the $^1A_{1g}$ ground state with the singlet excited state of lowest energy, $^1T_{1g}$, in the presence of a magnetic field. The extent of mixing is inversely proportional to the energy separation, Δ, of the two states, which in turn is determined by the strength of the crystal field. The linear relationship between ^{59}Co chemical shifts and 1/Δ found for a large number of octahedral cobalt(III) complexes is thus attributed to TIP contributions to the ^{59}Co shielding constant, σ. Freeman, *et al.*,[4] give an expression for σ as

$$\sigma_j = A - B_0 / \Delta_j \tag{1}$$

where A and B_0 are assumed constant.

Among the series of β-diketonate complexes in Table I, differences in Δ are small relative to values usually reported in experimental verifications of eq 1. However, the relation between chemical shift and Δ is followed qualitatively. The ligand-field splitting for Co(ppd)$_3$ is slightly greater than that of Co(acac)$_3$; thus the TIP is expected to be slightly less for Co(ppd)$_3$. The positive chemical shift observed for Co(ppd)$_3$

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(18) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).

is consistent with this expectation. The other complexes in Table I have smaller Δ values than the $Co(acac)_3$ reference. Larger TIP contributions are expected for these, resulting in negative chemical shifts as observed. Note that the most negative chemical shift is found for $Co(tfthbd)_3$, the complex having the smallest value of Δ. A plot of chemical shifts *vs.* $1/\Delta$ is roughly linear. Thus it appears that for this series of complexes ^{59}Co chemical shifts may be explained qualitatively by TIP contributions to the ^{59}Co shielding constants, using absorption maxima as a rough measure of TIP. A more quantitative fit cannot be expected in view of the fact that differences in Δ approach the limits of error ($\pm 100\ cm^{-1}$).

Diastereomeric β-Diketonate Complexes. Cobalt-59 chemical shifts and line widths for complexes having several diastereomeric forms are presented in Table II. Absolute configurations are known for the diastereomers of $Co[(+)\text{-atc}]_3$ through a combination of pmr, CD, and X-ray diffraction experiments described in detail earlier.[14,19] Configurational assignments for the diastereomers of $Co[(+)\text{-hmcar}]_3$ and $Co[(-)\text{-hmcar}]_3$ are based on pmr spectra and on the similarity of their CD spectra with those of the $Co[(+)\text{-atc}]_3$ diastereomers. The negative chemical shifts observed for the four diastereomers of $Co[(+)\text{-atc}]_3$ are consistent with the fact that their low-energy, ligand-field absorption maxima fall to the low-energy side of the absorption maximum of $Co(acac)_3$. Negative chemical shifts are also expected for the diastereomers of $Co[(+)\text{-hmcar}]_3$ and $Co[(-)\text{-hmcar}]_3$ using eq 1 and the observed absorption maxima. This is in contrast to what is found, and the discrepancy cannot be explained by error in either Δ or chemical shift values. It appears for this complex that either the absorption maxima are not good measures of TIP relative to that of $Co(acac)_3$ or factors other than TIP make a measurable contribution to the ^{59}Co chemical shift.

It is clear from the data presented in Table II that observable ^{59}Co chemical shift differences occur among diastereomers of the cobalt(III) complexes investigated. However, there is no obvious correlation between absolute configuration and relative chemical shifts among a set of diastereomers. Line widths for the trans diastereomers of complexes listed in Table II are larger than those of the cis diastereomers in most cases, as is expected from simple symmetry considerations. Isotropic absorption spectra of diastereomers of a given complex generally reveal no significant differences in energy of the low-energy, ligand-field transition, thus precluding a ready explanation of their relative chemical shifts in terms of eq 1. In all these complexes the $^1T_{1g}$ excited state in octahedral symmetry is split into two components, ^1A and ^1E, upon lowering the symmetry to C_3.[20] This splitting is not apparent in the absorption spectra, but it is readily seen in the circular dichroism spectra of all the complexes since the $^1A \rightarrow {}^1A$ and $^1A \rightarrow {}^1E$ transitions have opposite Cotton effects. Experimentally, small differences in energy of the CD maxima attributed to the $^1A \rightarrow {}^1A$ and/or $^1A \rightarrow {}^1E$ transitions are found among the four diastereomers of a given complex (Table II). These differences can arise from a number of factors including small differences in energy of the transitions and variations in the relative signs and magnitudes of configurational and vicinal contributions to the net CD.

Chemical shifts for the diastereomers of $Co[(+)\text{-atc}]_3$, $Co[(-)\text{-hmcar}]_3$, and $Co[(+)\text{-hmcar}]_3$ in chloroform solution are compared in Table II with energies of the $^1A \rightarrow {}^1A$ and $^1A \rightarrow {}^1E$ CD maxima in chloroform solution. The latter values were corrected for the effects of band overlap by means of a curve resolver. Four enantiomeric pairs, *e.g.*, Δ-*trans*-$Co[(+)\text{-hmcar}]_3$ and Λ-*trans*-$Co[(-)\text{-hmcar}]_3$, exist among the eight diastereomers possible for tris(hydroxymethylenecarvonato)cobalt(III); these are grouped together in the table. Chemical shift values and electronic absorption energies agree within experimental error for the components of each enantiomeric pair. There is rough trend toward more positive chemical shifts with increasing energy of the $^1A \rightarrow {}^1E$ CD band for the diastereomers of $Co[(+)\text{-atc}]_3$. This would be expected from eq 1 if it could be assumed that the observed differences in CD maxima arise primarily from energy differences in the $^1A \rightarrow {}^1E$ transition. However, this trend is likely fortuitous in view of the facts that differences among these CD bands approach the limits of error and that a satisfactory trend of this sort is not found for the $^1A \rightarrow {}^1A$ band of $Co[(+)\text{-atc}]_3$ or for either CD band of the tris(hydroxymethylenecarvonato)cobalt(III) diastereomers. The results imply that the above assumption is invalid and that relative TIP contributions (if they are in fact primarily responsible for chemical shift differences here) are not accurately measured by CD maxima.

The effects of temperature and concentration changes on the ^{59}Co nmr spectrum of Λ-*trans*-$Co[(+)\text{-atc}]_3$ were examined. Although a threefold change in concentration has no noticeable effect on the spectrum, both chemical shifts and line widths show a marked temperature dependence. Increasing the temperature results in an upfield shift of the resonance signal with a temperature coefficient of ~1 ppm per degree and a reduction in line width of approximately 3 Hz per degree. Griffith and Orgel[3] attributed the temperature dependence of ^{59}Co chemical shifts to increased occupation of higher vibrational modes at higher temperatures. This is expected to decrease Δ and shift ^{59}Co resonances to higher frequency (lower field). Shifts in the expected direction were observed by Freeman, *et al.*,[4] for $Co(acac)_3$ using $K_3[Co(CN)_6]$ as a reference; however, the ^{59}Co signal of Λ-*trans*-$Co[(+)\text{atc}]_3$ referenced to $Co(acac)_3$ shows a temperature dependence of opposite sign. The most likely explanation for the latter observation is that the temperature coefficients of Λ-*trans*-$Co[(+)\text{-atc}]_3$ and $Co(acac)_3$ differ in magnitude but not in sign, thus causing an *apparent* upfield shift with increasing temperature for Λ-*trans*-$Co[(+)\text{atc}]_3$. The rate of quadrupolar relaxation (and hence nmr line widths) of quadrupolar nuclei is proportional to both the quadrupole coupling constant and the rotational correlation time of the molecule. The observed decrease in line width with increasing temperature for Λ-*trans*-$Co[(+)\text{-atc}]_3$ is qualitatively consistent with the expected decrease in rotational correlation time with increasing temperature.

Δ and Λ diastereomers of $[Co((S)\text{-pn})_3]Cl_3$ were isolated by the method of Dwyer, *et al.*,[17] and examined by ^{59}Co nmr using an aqueous solution of $[Co(en)_3]I_3$ as the external reference. Data are presented in Table II. Λ-(+)-$[Co((S)\text{-pn})_3]Cl_3$ is contained in the first and more predominant band to be eluted from the cellulose column. The configuration of the cation is assigned on the basis of an X-ray study[21] of its enantiomer, Δ-(−)-$[Co((R)\text{-pn})_3]^{3+}$, which is the predominant diastereomer formed using the *R* ligand.[17] The abso-

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[19] W. DeW. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Amer. Chem. Soc.*, 92, 7620 (1970).

[20] Actually, only the cis diastereomers have a threefold symmetry axis; the trans isomers have no symmetry. However, from the close similarity of the CD spectra of cis and trans forms of a given complex having identical helical configurations, it is apparent that all the diastereomers have *effective* C_3 symmetry.

[21] H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Jap.*, 39, 92 (1966).

lute configuration of Δ-(−)-$[Co((S)\text{-pn})_3]^{3+}$ has been determined by X-ray methods.[22]

The most striking feature of the ^{59}Co nmr spectra is the appearance of two resonances of relative area 1.6:1.0 for Λ-$[Co((S)\text{-pn})_3]Cl_3$. Although four diastereomers exist in principle for $[Co((S)\text{-pn})_3]^{3+}$, usually only two isomers, differing in helicity, are isolated. These "isomers" may each contain cis and trans species, and indeed MacDermott[23] succeeded in separating the cis and trans forms of Δ-$[Co((R)\text{-pn})_3]Br_3$. Thus, we tentatively assign the two signals observed for Λ-$[Co((S)\text{-pn})_3]Cl_3$ to cis and trans forms of this complex. Line widths of the two signals are not sufficiently different to justify detailed assignments; however, it would seem reasonable on statistical grounds to assign the predominant signal to the trans isomer. The Δ isomer exhibits an unusually broad signal, and the existence of two resonances for this isomer is not firmly established. Λ-$[Co((S)\text{-pn})_3]Cl_3$ is stable at elevated temperatures. However, when solvent is removed from the Δ isomer by gentle heating[24] and the sample is later redissolved, ^{59}Co nmr of the new solution reveals three signals. One of these has a chemical shift very close to that of the Δ isomer before heating, and chemical shifts of the other two are within error of the values found for the Λ isomer. Apparently Δ-$[Co((S)\text{-pn})_3]Cl_3$ partially isomerizes to the more stable Λ isomers during the above process.

The absorption maxima of $[Co(en)_3]^{3+}$ and $[Co((S)\text{-pn})_3]^{3+}$ are within the limits of error of each other, and only small chemical shift differences are expected using eq 1. Since the observed chemical shift differences are appreciable, it is clear that eq 1 is not followed here. Only one CD band is observed for the Δ isomer;[25] this has a maximum near the weighted average of the two maxima for Λ-$[Co((S)\text{-pn}_3]^{3+}$. Thus the relative chemical shifts of these Δ and Λ diastereomers are not simply related to their relative CD maxima.

Attempts were made to examine ^{59}Co nmr spectra of several other diastereomeric cobalt(III) complexes having mixed O and N donor atoms. However, the spectra of these complexes could not be obtained on our instrument, presumably as a result of efficient quadrupole relaxation. Mixed-donor complexes of cobalt(III) have quadrupole coupling constants at least an order of magnitude larger than those having identical donor elements,[26] and this is expected to lead to larger line widths by a factor of at least 100 for the mixed-donor complexes.

Registry No. $Co(acac)_3$, 21679-46-9; $Co(tfthbd)_3$, 41875-84-7; *trans*-$Co(tfac)_3$, 41768-43-8; *cis*-$Co(tfac)_3$, 41768-44-9; *trans*-$Co(bzac)_3$, 33990-23-7; *cis*-$Co(bzac)_3$, 33990-24-8; *trans*-$Co(ppd)_3$, 41768-47-2; *cis*-$Co(ppd)_3$, 41765-60-0; Δ-*cis*-$Co[(+)\text{-atc}]_3$, 32490-75-8; Λ-*cis*-$Co[(+)\text{-atc}]_3$, 32592-77-1; Δ-*trans*-$Co[(+)\text{-atc}]_3$, 32490-74-7; Λ-*trans*-$Co[(+)\text{-atc}]_3$, 32490-73-6; Δ-*trans*-$Co[(-)\text{-hmcar}]_3$, 25797-15-3; Λ-*trans*-$Co[(-)\text{-hmcar}]_3$, 25797-14-2; Δ-*trans*-$Co[(+)\text{-hmcar}]_3$, 41875-82-5; Λ-*trans*-$Co[(+)\text{-hmcar}]_3$, 41765-61-1; Δ-*cis*-$Co[(-)\text{-hmcar}]_3$, 26582-20-7; Λ-*cis*-$Co[(-)\text{-hmcar}]_3$, 25797-16-4; Δ-*cis*-$Co[(+)\text{-hmcar}]_3$, 41765-62-2; Λ-*cis*-$Co[(+)\text{-hmcar}]_3$, 41875-83-6; $[Co(en)_3]I_3$, 15375-81-2; Δ-$[Co((S)\text{-pn})_3]Cl_3$, 14516-62-2; Λ-*cis*-$[Co((S)\text{-pn})_3]Cl_3$, 20470-19-3; Λ-*trans*-$[Co((S)\text{-pn})_3]Cl_3$, 41765-65-5;, Co, 7440-48-4.

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[22] Y. Saito, *Pure Appl. Chem.*, 17, 21 (1968).

[23] T. E. MacDermott, *Inorg. Chim. Acta*, 2, 81 (1968).

[24] At this point a greenish color is noticeable; however, the original orange color of the complex returns upon dissolving the greenish product in water.

[25] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

[26] W. van Bronswyk, *Struct. Bonding*, 7, 87 (1970).

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Heats of Reaction of Pyridine, Triphenylphosphine, and Triphenyl Phosphite with the Chloro-, Bromo-, and Iodo-1,5-cyclooctadienerhodium(I) Dimers and Dichlorobis(benzonitrile)palladium(II)

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The heats for the following reactions in dichloromethane are reported: $[RhX(COD)]_2 + 2B \rightarrow 2[RhX(COD)(B)]$; $[RhX(P(OC_6H_5)_3)_2]_2 + 2P(OC_6H_5)_3 \rightarrow 2[RhX(P(OC_6H_5)_3)_3]$; $[RhX(COD)_2] + 2P(OC_6H_5)_3 \rightarrow [Rh_2X_2(COD)(P(OC_6H_5)_3)_2] + COD$; $[Rh_2X_2(COD)(P(OC_6H_5)_3)_2] + 2P(OC_6H_5)_3 \rightarrow [RhX(P(OC_6H_5)_3)_2]_2 + COD$; $[PdCl_2(C_6H_5CN)_2] + 2B \rightarrow [PdCl_2B_2] + 2C_6H_5CN$; and $[PdCl_2(COD)] + 2P(OC_6H_5)_3 \rightarrow [PdCl_2(P(OC_6H_5)_3)_2] + COD$ (B = pyridine, triphenylphosphine; X = Cl, Br, I; COD = 1,5-cyclooctadiene). Relative displacement energies are for the rhodium compounds, triphenyl phosphite >> 1,5-cyclooctadiene and triphenylphosphine > pyridine, and for the palladium compounds, triphenylphosphine > triphenyl phosphite > pyridine >> cyclooctadiene. Arguments are given that solvent–solute enthalpic contributions are not predominant in the displacement energies. For a given reaction, the effect of varying the halogens upon the observed enthalpies is very small or nonexistent. Equilibrium constants for the first reaction are too high to measure when B = triphenylphosphine and are approximately 5×10^4 when B = pyridine.

Introduction

We have been obtaining enthalpic and kinetic data for metal-olefin compounds[1-3] in order to gain insight into the nature of the metal–olefin bond and its relation to the rates at which these compounds react. We have obtained a large amount of auxiliary enthalpic data on a number of well-known reactions, some of which we wish to report here.

There is an enormous amount of stability constant and enthalpic data[4,5] pertaining to metal–ligand displacement re-

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[1] W. Partenheimer, *Inorg. Chem.*, 11, 743 (1972).

[2] W. Partenheimer and E. F. Hoy, *J. Amer. Chem. Soc.*, 95, 2840 (1973).

[3] W. Partenheimer and E. H. Johnson, *Inorg. Chem.*, 12, 1274 (1973).

[4] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Burlington House, London, 1964.