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^{59}Co NMR Study of the Metal–Ligand Bond Covalency in Cobalt(III) Complexes

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The effect of the metal–ligand bond covalency on the magnetic shielding of the cobalt nucleus in cobalt(III) complexes of octahedral ligand field symmetry has been examined by ^{59}Co nuclear magnetic resonance spectroscopy. The paramagnetic circulation, arising from the $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition, deshields the cobalt nucleus less effectively in complexes with a more covalent metal–ligand bond, because the circulation is driven away from the metal ion by the action of ligands. This circulation-removing ability of ligands, expressed by the *circulation-removing ratio*, is presented for 38 complexes of the type CoO_6, CoN_6, CoC_6, CoS_6, $CoSe_6$, CoP_6, and $CoAs_6$. The circulation-removing ratio is mainly influenced by the electronegativity of the ligand atom directly bonded to cobalt(III), and a linear relationship between the ratios and metal–ligand bond ionicities exists. Calculation of the circulation-removing ratio in the molecular orbital scheme and its comparison with the experimental data are also presented. The results obtained show that the NMR spectroscopy of metal ions may be generally used for examination of the metal–ligand bond properties in spin-paired d^6 transition-metal complexes.

Introduction

Second-order paramagnetism in spin-paired d^6 transition-metal complexes attracts considerable attention, since it contains information about electron charge distributions in complexes. Central-ion nuclear magnetic resonance spectroscopy is a very convenient technique for the study of this paramagnetism through the central-ion magnetic shielding. Thus, for the cobalt nucleus in cobalt(III) complexes, variations of diamagnetic shielding from complex to complex are expected to be so small in comparison with variations of paramagnetic shielding that the ^{59}Co NMR chemical shifts can be discussed in terms of variations in paramagnetic shielding only. Another favorable circumstance is that the paramagnetic shielding of the cobalt nucleus arises from the distribution of electrons in the orbitals that are predominantly cobalt 3d orbitals. Hence, the results of ligand field theory are readily applicable when calculating the paramagnetic shielding. As a consequence, the ^{59}Co magnetogyric ratios are directly related to the $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition energies by[1]

$$\gamma = \gamma_0(1 - \sigma^d) + \gamma_0 \frac{B}{\Delta E(^1T_{1g} \leftarrow {}^1A_{1g})} \tag{1}$$

The term denoted by B is a function of the electron charge distribution in the molecular orbitals involved in the paramagnetic circulation and of particular interest in the study of the metal–ligand bond covalency.

Freeman, Murray, and Richardson[1] were the first to observe the linear relationship between the ^{59}Co NMR frequencies and the wavelengths of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition, which suggests that both the diamagnetic shielding term σ^d and the paramagnetic circulation term B are slightly influenced by ligands. However, deviations from the Freeman–Murray–Richardson (FMR) linear relationship were subsequently observed and attributed to the influence of the metal–ligand bond covalency on the term B.[2-9]

For a study of the bond covalency through change of the paramagnetic circulation term B as it is registered in the ^{59}Co NMR chemical shifts it is essential to know the exact value of the ^{59}Co magnetogyric ratio of the bare cobalt nucleus (γ_0). In previous considerations of the bond covalency influence on cobalt nuclear shielding, the extrapolated FMR value was used,[3-7] although it has been in poor agreement with two other studies directed at evaluating the ^{59}Co magnetogyric ratio γ_0.[10,11] Recently the validity of FMR extrapolation has been questioned.[7,8] In our most recent study,[12] an improved value of γ_0 was determined by investigating the temperature dependence of ^{59}Co chemical shifts and electronic transition wavelengths. The obtained value is in close agreement with the value obtained from a ^{59}Co NMR study of intermetallic cobalt compounds[10] and differs greatly from the FMR value. Therefore we undertook to reexamine the effect of metal–ligand bond covalency on the magnetic shielding of the cobalt nucleus in cobalt(III) complexes.

Results and Discussion

Effect of the Metal–Ligand Bond Covalency on Paramagnetic Circulation. The ^{59}Co magnetogyric ratios and $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition wavelengths for 38 cobalt(III) complexes of CoO_6, CoN_6, CoS_6, $CoSe_6$, CoC_6, CoP_6, and $CoAs_6$ types are presented in Table I. Only seven complexes have

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Table I. ^{59}Co NMR Chemical Shifts (δ), ^{59}Co Magnetogyric Ratios (γ, MHz T^{-1}), Wavelengths of the $^1T_{1g} \leftarrow {}^1A_{1g}$ Electronic Transition ($1/\Delta E$, nm), Circulation Removing Ratios ($\eta_{\sigma\pi}$) and Nephelauxetic Ratios (β_{35}) for Cobalt(III) Complexes of Octahedral Ligand Field Symmetry

complex[a]	δ[b]	γ[c]	$1/\Delta E$	$\eta_{\sigma\pi}$	β_{35}	ref[d]
CoO$_6$ Type						
$[Co(H_2O)_6]^{3+}$	15100	10.258	606	0.58	0.61	13, 14
$[Co(OH)_6(NH_3)_{12}]^{6+}$[e]	14850	10.256	625	0.55	(0.62)	15, 16
$[Co(CO_3)_3]^{3-}$	13900	10.246	645	0.51	0.49	3, 1
$[Co(C_2O_4)_3]^{3-}$	13000	10.237	605	0.52	0.49	3, 1
$[Co(tfthbd)_3]$	12800	10.235	609	0.51		17, 17
$[Co(2,4\text{-}ptdn)_3]$	12500	10.232	597	0.52		3, 1
$[Co(ppd)_3]$	12440	10.231	592	0.52		17, 17
CoN$_6$ Type						
$[Co(NH_2(CH_2)_4NH_2)_3]^{3+}$	8670	10.193	501	0.49	0.54	(18)
$[Co(NH_2(CH_2)_3NH_2)_3]^{3+}$	8350	10.190	488	0.49	0.52	19, 20
$[Co(NH_3)_6]^{3+}$	8170	10.188	475	0.50	0.55	6, 6
$[Co(NO_2)_6]^{3-}$	7440	10.181	480	0.47		6, 6
$[Co(pn)_3]^{3+}$	7290	10.179	470	0.47	0.53	1, 1
$[Co(NH_2(CH_2)_2NH_2)_3]^{3+}$	7130	10.178	468	0.47	0.53	1, 1
$[Co(o\text{-}phen)_3]^{3+}$	7080	10.177	470	0.47		3, 21
$[Co(bpy)_3]^{3+}$	6620	10.173	450	0.47		22, 21
$[Co(NH_2OH)_6]^{3+}$	6500	10.171	440	0.48	0.56	3, 23
$[Co(dmg)_3]$	4880	10.155	365	0.50		(24)
CoS$_6$, CoSe$_6$, CoC$_6$ Types						
$[Co(S_2P(OC_2H_5)_2)_3]$	8980	10.196	740	0.34	0.36	6, 25
$[Co(S_2CNH_2)_3]$	7230	10.179	650	0.34	0.33	12, 12
$[Co(S_2CN(CH_2)_4)_3]$	7070	10.177	655	0.34		6, 6
$[Co(S_2CN(CH_3)_2)_3]$	6700	10.173	654	0.33		6, 6
$[Co(S_2CN(C_2H_5)_2)_3]$	6450	10.171	650	0.32	0.34	3, 25
$[Co(S_2CN(C_3H_7)_2)_3]$	6320	10.170	633	0.33		6, 6
$[Co(S_2CSC_2H_5)_3]$	6460	10.171	625	0.34		22, 22
$[Co(S_2CS)_3]^{3-}$	6390	10.170	625	0.34		(26)
$[Co(S_2COCH_3)_3]$	6250	10.169	625	0.33	0.30	(27)
$[Co(S_2COC_2H_5)_3]$	6250	10.169	625	0.33	0.30	12, 12
$[Co(S_2CCH_2C_6H_5)_3]$	5830	10.165	590	0.34		(28)
$[Co(Se_2CN(CH_3)_2)_3]$	6760	10.174	667	0.32	0.30	6, 25
$[Co(CNO)_6]^{3-}$	1300	10.119	400	0.32	0.41	(29)
$[Co(CN)_6]^{3-}$	0	10.1057	311	0.34	0.42	1, 1
CoP$_6$, CoAs$_6$ Types						
$[Co(P(OCH_3)_3)_6]^{3+}$	−305	10.103	350	0.29	(0.22)	7, 31
$[Co(phosphite\text{-}I)_6]^{3+}$	−307	10.103	341	0.29		7, 7
$[Co(phosphite\text{-}II)_6]^{3+}$	−360	10.102	339	0.29		7, 7
$[Co(CH_3OP(OCH_2)_2)_6]^{3+}$	−1190	10.094	317	0.27		7, 7
$[Co(P(OCH_2)_3CCH_3)_6]^{3+}$	−1240	10.093	300	0.28	(0.29)	7, 31
$[Co(triars)_3]^{3+}$	4900	10.152	658	0.27		6, 6
$[Co(diars)_3]^{3+}$	−100	10.105	430	0.25		(30)

[a] Abbreviations: Htfthbd = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadiene; Hppd = 1-phenyl-1,3-propadiene; ptdn = 2,4-pentanedionato; pn = 1,2-propanediamine; *o*-phen = *o*-phenanthroline; bpy = 2,2′-bipyridyl; dmg = dimethylglyoximato; phosphite-I = $(CH_3O)_{ax}\overbracket{POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O}$; phosphite-II = $(CH_3O)_{eq}\overbracket{POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O}$; diars = *o*-phenylenebis(dimethylarsine). [b] Although ^{59}Co chemical shifts of symmetric complexes may be determined with a precision of a few ppm, a comparison of the results reported by different authors shows that listed values may have an error of ±50 ppm. [c] Magnetogyric ratios were calculated from chemical shifts with use of the relation $\gamma = \gamma_S(1 + \delta)$. The standard magnetogyric ratio is that of the hexacyanocobaltate(III) ion, $\gamma_S = 10.1057$ MHz T^{-1}.[1,6] The estimated error in magnetogyric ratios amounts to ±50 ppm of the listed values. [d] The first reference refers to the NMR data and the second to the optical data. The references for synthesis of the complexes measured in this work are given in parentheses. [e] Data are given for the central cobalt ion, which occupies an octahedral environment of six bridging OH$^-$ ions.

been studied for the first time, but data for most of these complexes are of crucial importance. Thus the hexakis(fulminato) complex is the second example of a CoC$_6$ chromophore, and tris(*o*-phenylenebis(dimethylarsine))cobalt(III) is the second example of a CoAs$_6$ chromophore that has been studied by ^{59}Co NMR spectroscopy. Data for tris(1,4-butanediamine)cobalt(III) and tris(dimethylglyoximato)cobalt(III) expand, by more than a factor of 2, the known range of cobalt shielding in CoN$_6$ complexes. Similarly, tris(dithiophenylacetato)cobalt(III) expands the shielding range in CoS$_6$ complexes.

For the complexes in Table I, the correlation between the ^{59}Co magnetogyric ratios and the $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition wavelengths is presented in Figure 1. With use of the intercept value $\gamma_0(1 - \sigma^d) = 10.04$ MHz T^{-1} determined in our previous work,[12] the data for complexes studied may be correlated by four lines, each line corresponding to complexes having the same electronegativity of the atoms directly bonded to cobalt(III). The slope of the line and consequently the value of the term B in eq 1 are smaller for the less electronegative ligands, that is, for ligands that would be expected to form a more covalent bond with cobalt(III). The variation of the term B is connected with the changes of paramagnetic current distribution in the complexes. The paramagnetic circulation close to the cobalt nucleus deshields the nucleus much more efficiently than one induced further away. Therefore, it may be concluded that less electronegative ligands

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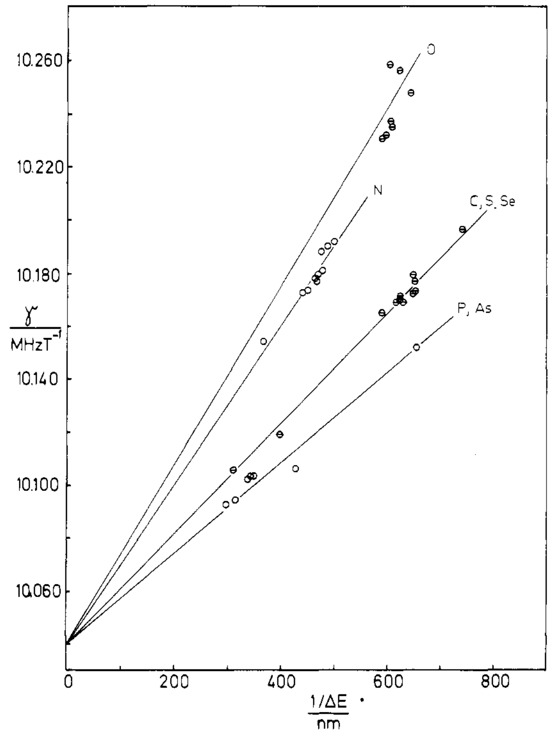

Figure 1. Correlation between ^{59}Co magnetogyric ratios and $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition wavelengths. The lines are drawn for the complexes of the same electronegativity of the ligating atoms (correlation coefficients, as one goes from the line for oxygen to the line for arsenic, are 0.61, 0.95, 0.99, and 0.98).

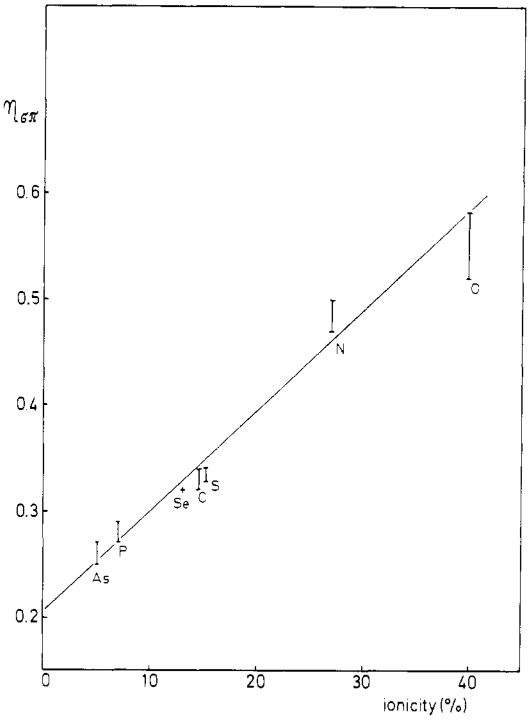

Figure 2. Correlation between the circulation-removing ratios and the ionicities of the metal–ligand bond. The bond ionicities, given by the expression $16(X_L - X_{Co}) + 3.5(X_L - X_{Co})^2$, were calculated by using Pauling values for the electronegativities[32] of ligating atoms (X_L), while for cobalt the electronegativity of Allred and Rochow[33] was used.

act to remove parmagnetic circulation from the cobalt nucleus.

In the framework of molecular orbital theory the term B has the form

$$B = 4\mu_B{}^2[\langle\psi_{t_{2g}}|l_z|\psi_{e_g}\rangle\langle\psi_{e_g}|l_z/r^3|\psi_{t_{2g}}\rangle + \mathrm{cc}] \qquad (2)$$

(where μ_B is the Bohr magneton, r is the distance from the cobalt nucleus, l_z is the orbital angular momentum operator, and cc stands for complex conjugated). B reaches a maximum for the free Co^{3+} ion, when t_{2g} and e_g molecular orbitals are reduced to the pure cobalt d orbitals, and the term is readily evaluated, giving $B_0 = 32\mu_B{}^2\langle r^{-3}\rangle_d$. Using B_0 as the reference value, we may quantify the circulation-removing ability of ligands by introducing the circulation-removing ratio:

$$\eta_{\sigma\pi} = \frac{B}{B_0} = \frac{\gamma - \gamma_0(1 - \sigma^d)}{32\gamma_0\mu_B{}^2\langle r^{-3}\rangle_d}\Delta E(^1T_{1g} \leftarrow {}^1A_{1g}) \qquad (3)$$

With use of the numerical values $\gamma_0(1 - \sigma^d) = 10.04$ MHz T^{-1} and $32\gamma_0\mu_B{}^2\langle r^{-3}\rangle_d = 6240$ MHz T^{-1} cm^{-1},[12] $\eta_{\sigma\pi}$ was calculated for all the complexes studied (Table I). As is seen from Table I, the circulation-removing ratio is primarily sensitive to the electronegativities of the atoms directly bonded to cobalt. For the CoO_6 chromophore it has values in the range 0.51–0.58, for CoN_6 the range is 0.47–0.50, for CoC_6, CoS_6, and $CoSe_6$ the range is 0.32–0.34, and finally for the CoP_6 and $CoAs_6$ chromophores the range is 0.25–0.29. There is no overlap among the regions quoted, which suggests that the circulation-removing ratio could be used for the determination of the complex chromophore. The circulation-removing ratios are in an almost linear relationship with the bond ionicities, as presented in Figure 2. In this context, the small variations among the circulation-removing ratios of the complexes of the same chromophore may be reflecting the actual electronegativity of the ligating atom in different ligands.

Circulation-Removing Ratio in a MO Scheme. The circulation-removing ratio, although not explicitly defined, has been used in the form $k'^2\langle r^{-3}\rangle_{\bar{d}}/\langle r^3\rangle_d$ as a measure of the covalency of metal–ligand bonding in cobalt(III) complexes.[5,8,12] Namely, the term B was evaluated by approximating e_g and t_{2g} molecular orbitals with deformed d orbitals, which gives $B = 32\mu_B{}^2k'^2\langle r^{-3}\rangle_{\bar{d}}$. The orbital angular momentum reduction factor k' has been introduced[32] as a measure of electron delocalization effects or the "symmetry-restricted covalency". The mean reciprocal cube distance of the d electron from the cobalt nucleus, $\langle r^{-3}\rangle_{\bar{d}}$, is expected to be reduced in comparison to the free-ion value, $\langle r^{-3}\rangle_d$, due to the "central field covalency", which refers to the transfer of negative charge from the ligand to the metal ion, resulting in an expansion of d orbitals. However, for a more detailed investigation of the covalency influence the molecular t_{2g} and e_g orbitals must be expressed as a linear combination of the corresponding atomic orbitals. In this case B is no longer given by $32\mu_B{}^2k'^2\langle r^{-3}\rangle_{\bar{d}}$ because the LCAO is not separable into radial and angular parts. This was not always recognized, and the LCAO expression for k' was introduced in the consideration of the effect of symmetry-restricted covalency on B.[4] Such an approach overestimates the impact of electron delocalization on the term $\langle\psi_{e_g}|l_z/r^3|\psi_{t_{2g}}\rangle$. Therefore, we shall start from the expression (see eq 2 and 3)

$$\eta_{\sigma\pi} = \frac{1}{8\langle r^{-3}\rangle_d}[\langle\psi_{t_{2g}}|l_z|\psi_{e_g}\rangle\langle\psi_{e_g}|l_z/r^3|\psi_{t_{2g}}\rangle + \mathrm{cc}] \qquad (4)$$

and proceed to the evaluation of the circulation-removing ratio with use of LCAO molecular orbitals

$$\psi_{e_g} = a_\sigma d_\sigma + b_\sigma\phi_\sigma \qquad \psi_{t_{2g}} = a_\pi d_\pi + b_\pi\phi_\pi \qquad (5)$$

where $\phi = \sum_i c_i\lambda_i$ is the appropriate symmetry-adapated combination of ligand orbitals. In the calculation of the matrix elements of eq 4 we adopted the approximate procedure

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Table II. Explicit Form of the LCAO Coefficients a and b Relevant to the Expressions for the Circulation-Removing Ratios[a]

	a_σ	b_σ	a_π	b_π
$\eta_{\sigma^*\pi^*}$	$\dfrac{\beta_\sigma + \alpha_\sigma G_\sigma}{\sqrt{1 - G_\sigma^2}}$	$-\dfrac{\alpha_\sigma + \beta_\sigma G_\sigma}{\sqrt{1 - G_\sigma^2}}$	$\dfrac{\beta_\pi + \alpha_\pi G_\pi}{\sqrt{1 - G_\pi^2}}$	$\dfrac{\alpha_\pi + \beta_\pi G_\pi}{\sqrt{1 - G_\pi^2}}$
$\eta_{\sigma^*\pi}$	-//-	-//-	α_π	β_π
η_{σ^*0}	-//-	-//-	1	0

[a] α and β are LCAO coefficients of the metal d orbitals and ligand symmetry-adapted combinations of atomic orbitals in the e_g and t_{2g} bonding MO.

suggested by Cornwell.[35] Thus, for the operator l_z/r^3 one may drop all the terms except those on cobalt, which gives

$$\langle \psi_{e_g}|l_z/r^3|\psi_{t_{2g}}\rangle = -2i\langle r^{-3}\rangle_{\bar{d}} a_\sigma a_\pi \tag{6}$$

For the operator l_z it is necessary to keep the terms on all atoms, which gives

$$\langle \psi_{t_{2g}}|l_z|\psi_{e_g}\rangle = a_\sigma a_\pi\langle d_\pi|l_z|d_\sigma\rangle + a_\pi b_\sigma\langle d_\pi|l_z|\phi_\sigma\rangle + a_\sigma b_\pi\langle \phi_\pi|l_z|d_\sigma\rangle + b_\sigma b_\pi\langle \phi_\sigma|l_z|\phi_\pi\rangle \tag{7}$$

The first three terms are readily evaluated. In the evaluation of the last term we shall neglect overlap effects so that the local origins are properly used for l_z. After this, it follows that

$$\langle \psi_{t_{2g}}|l_z|\psi_{e_g}\rangle = 2i(a_\sigma a_\pi + a_\pi b_\sigma G_\sigma + a_\sigma b_\pi G_\pi - \tfrac{1}{2} b_\sigma b_\pi) \tag{8}$$

where G_i is the metal–ligand group overlap integral. If eq 4, 6, and 8 are combined, the circulation-removing ratio is given by

$$\eta_{\sigma\pi} = a_\sigma a_\pi(a_\sigma a_\pi + a_\pi b_\sigma G_\sigma + a_\sigma b_\pi G_\pi - \tfrac{1}{2} b_\sigma b_\pi)\frac{\langle r^{-3}\rangle_{\bar{d}}}{\langle r^{-3}\rangle_{d}} \tag{9}$$

Now, we may distinguish three cases: $\eta_{\sigma^*\pi^*}$ (involving a transition between antibonding orbitals $\psi^*_{t_{2g}} \rightarrow \psi^*_{e_g}$), $\eta_{\sigma^*\pi}$ (involving a bonding–antibonding transition), and η_{σ^*0} (involving a nonbonding–antibonding transition). The difference in eq 9 comes through the explicit form of the coefficients a and b in each case, as is presented in Table II.

The derived expression was applied to the complex ions $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$, for which the theoretical calculations of electron charge distribution have been reported.[34,35] The calculations show that for $[Co(NH_3)_6]^{3+}$ practically all the metal–ligand bond covalency is due to σ bonding, hence η_{σ^*0} should be applied. In $[Co(CN)_6]^{3-}$ π back-donation takes place and $\eta_{\sigma^*\pi}$ is appropriate. The coefficients a and b were calculated by using the reported values of orbital populations and metal–ligand bond overlaps.[34,35] The ratio $\langle r^{-3}\rangle_{\bar{d}}/\langle r^{-3}\rangle_d$ was estimated with reliance on the reported cobalt ion formal charge in the complexes and with the approximate d-orbital radial functions of the cobalt ions given by Richardson and collaborators.[36] Thus we obtained $\eta_{\sigma^*0} = 0.57$ for $[Co(NH_3)_6]^{3+}$ and $\eta_{\sigma^*\pi} = 0.37$ for $[Co(CN)_6]^{3-}$, which is in reasonable agreement with the experimental values 0.50 and 0.34. An analysis shows that in the case of $[Co(NH_3)_6]^{3+}$ about 10% of the circulation-removing ratio reduction is due to the d-orbital expansion, i.e., to the central field covalency, while 30% of the ratio reduction is a consequence of the electron delocalization or the symmetry-restricted covalency. For $[Co(CN)_6]^{3-}$ about 20% of the ratio reduction is caused by the central field covalency, while 40% of the reduction is due to the symmetry-restricted covalency. Therefore, the change of the symmetry-restricted covalency seems to be the major cause of the variations of the circulation-removing ratio from complex to complex.

Circulation-Removing Ratio and Nephelauxetic Ratio. In our previous study[12] we observed the close correspondence between the nephelauxetic and the circulation-removing ratios. For the majority of cases given in Table I the difference between the two ratios is less than 10%.

According Jørgensen[25] the nephelauxetic ratio β_{35} may be approximated as $\beta_{35} = a_\sigma^2 a_\pi^2 \cdot f(Z)$. Here, $f(Z)$ is a function of the effective nuclear charge (due allowance for the central field covalency being implied in Z). On the basis of expression 9, the circulation-removing ratio may be roughly approximated as $\eta_{\sigma\pi} = a_\sigma^2 a_\pi^2 \langle r^{-3}\rangle_{\bar{d}}/\langle r^{-3}\rangle_d$. Therefore, the symmetry-restricted covalency should have a similar impact on both ratios through the value of $a_\sigma^2 a_\pi^2$. In contrast, the central field covalency may be expected to affect the ratios unequally. Thus, $f(Z)$ is more sensitive to covalency than $\langle r^{-3}\rangle_d$, since the major contribution to the interelectronic repulsion parameters comes from the region further from the cobalt nucleus.[39] The close correspondence of the two ratios may be taken as another proof that the symmetry-restricted covalency has the dominant impact on the ratios.

In a few cases a pronounced difference between the ratios is observable. For the hexacyanocobaltate(III) ion β_{35} is 20% greater than $\eta_{\sigma\pi}$ (Table I). However, the nephelauxetic ratios given in Table I are calculated in the usual way by taking the Racah parameters $C/B = 4$, which may not be appropriate for the hexacyanocobaltate(III) ion.[40] In general, the circulation-removing ratio is in a better linear relationship with bond ionicities than is the nephelauxetic ratio.

When the ratios are compared, it should be noted that the circulation-removing ratio has been obtained for a number of cobalt(III) complexes for which the nephelauxetic ratio cannot be determined, since the $^1T_{2g} \leftarrow {}^1A_{1g}$ electronic transition overlaps with intense metal–ligand charge-transfer bands.

Conclusion

With a general insight having been given herein into the effect of metal–ligand bond covalency on the paramagnetic shielding of the central ion in cobalt(III) complexes, certain disputes concerning the correlation between ^{59}Co chemical shifts and electronic transition wavelengths appear to be resolved.

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The effect of the metal–ligand bond covalency on the paramagnetic shielding has been quantified by introducing the circulation-removing ratio. This ratio for a series of ligands follows closely the electronegativities of the ligating atoms. The circulation-removing ratio has nearly constant value for a given chromophore, irrespective of the ligand field splitting magnitude. It may be added that it is surprising how independent the ratio is of the value of ligand field splitting, when both parameters reflect properties of the same metal–ligand bond.

As a measure of metal–ligand bond covalency in spin-paired d^6 transition-metal complexes, the circulation-removing ratio $\eta_{\sigma\pi}$ seems supplementary to the nephelauxetic ratio. However, the former ratio has some distinct advantages. Unlike the nephelauxetic ratio, $\eta_{\sigma\pi}$ may be related to the metal–ligand bond properties by a simple theoretical calculation, and it may be determined in complexes for which only the first spin-allowed d–d transition is discernible.

The results obtained suggest that central-ion NMR spectroscopy can be used as a powerful new means of examinning metal–ligand bond covalency in spin-paired d^6 transition-metal complexes.

Experimental Section

The ^{59}Co magnetogyric ratios of the examined complexes were determined with a Bruker SXP-100 pulse Fourier transform NMR spectrometer operating at 21.5 MHz. Absorption spectra were taken by a Varian Super Scan 3 spectrophotometer. All measurements were performed at room temperature (~25 °C).

For measurements we used aqueous solutions of the tris(1,4-butanediamine)cobalt(III) complex and of the hexakis(fulminato) complex, while tris(*o*-phenylenebis(dimethylarsine)cobalt(III), tris(dimethylglyoximato)cobalt(III), and tris(trithiocarbonato)cobalt(III) complexes were dissolved in Me_2SO. Tris(dithiophenylacetato)cobalt(III) was dissolved in chloroform. Concentrations of ~0.2 M for NMR spectra and ~10^{-2} M for spectrophotometric measurements were used.

All the complexes were synthesized by the reported procedures (for references see Table I).

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Registry No. $[Co(CNO)_6]^{3-}$, 45225-00-1; $[Co(diars)_3]^{3+}$, 47778-65-4; $[Co(NH_2(CH_2)_4NH_2)_3]^{3+}$, 83897-72-7; $Co(dmg)_3$, 14877-98-6; $Co(S_2CCH_2C_6H_5)_3$, 20963-66-0; $[Co(S_2CS)_3]^{3-}$, 51475-74-2; Co, 7440-48-4.

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Aluminum-27 Nuclear Magnetic Resonance Study of Aluminum(III) Interactions with Carboxylate Ligands

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Aluminum-27 NMR in high field has been employed in aqueous solution, at 10 mM concentration, for the study of the interactions of Al(III) with citrate, lactate, and ethylenediaminetetraacetate (EDTA). In the reaction with lactate, slow-exchange phenomena make possible the observation of distinct peaks for hydrated Al(III), 1:1 and 1:3 Al–lactate complexes, as well as mixed aquo–lactato and hydroxo–lactato complexes. Increasing pH leads to substitution of water in the Al(III) coordination sphere by lactate and eventually to substitution of lactate by hydroxide. A 1:3 Al(III)–lactate complex produced in the presence of excess lactate remains in a metastable condition and does not readily dissociate when more Al(III) is added. Increased pH has similar effects on the reaction of Al(III) with citrate, but the reaction with EDTA leads to only one peak that corresponds to a very stable complex; apparently no mixed aquo–EDTA or hydroxo–EDTA complexes can be observed.

Introduction

Our interest in the interactions of aluminum with various ligands in aqueous solution originates in the recent observations of increased aluminum concentrations in two human pathological conditions. Specific increased aluminum levels have been detected in Alzheimer's disease,[2-4] the prevalent form of senile dementia, and dialysis encephalopathy[5-7] resulting from renal dialysis. Furthermore, aluminum may play a key role in the toxic processes associated with acidification of the environment by pollutants.[8,9]

The present series of experiments was carried out to determine the suitability of ^{27}Al NMR as a probe for Al(III) complexation in dilute aqueous solution. Most of the previous studies employing ^{27}Al NMR have been performed in organic solvents at 0.1 M concentration or greater.[10-12] The hydrolysis of Al(III)[13-18] and chelation by a variety of ligands[19,20] has

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