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Nuclear Magnetic Resonance Studies on Cobalt Complexes. I. Cobalt-59 Nuclear Magnetic Resonance Spectra of Cobalt(III) Complexes.

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Cobalt-59 NMR spectra were recorded for forty tervalent diamagnetic cobalt complexes. The chemical shift and line width were briefly discussed using Ramsey's expression and assuming quadrupolar interaction. The chemical shift is correlated with the total electronegativity of all ligand atoms and radial factors. As to chemical shift data, Ramsey's formula can be applied when proper consideration of the radial factor is given. Comments are given on earlier chemical shift data.

Introduction

Measurements of chemical shifts and line widths in nuclear magnetic resonance (NMR) spectra of cobalt-59 for several complex compounds have been carried out and the results are interpreted in terms of the chemical bonding of cobalt to ligands. Since Proctor and Yu,[1] several studies have been carried out concerning the NMR of this nucleus, which revealed that it has relatively large chemical shifts, and large temperature dependences. Griffith and Orgel[2] reported that the chemical shift is related to Dq values, or the wavenumber of the first absorption maximum of the electronic spectra of the compounds investigated. This interpretation is based on the expectation that the chemical shift could be interpreted according to the general theory on chemical shifts which was developed by Ramsey,[3] taking account of the two terms of first and second order perturbations on the molecular electronic orbitals. Freeman, Murray and Richards[4] also extended the measurement and interpretation of cobalt-59 NMR according to Griffith and Orgel.[2] Several Indian scientists[5,6,7] also reported the relatively large chemical shift of this nucleus. Recently, Lucken, Noack and Williams[8] investigated the chemical shift and line width of several organocobaltic complexes, such as cobalticenium, and several carbonyl derivatives. They also explained the chemical shift using a molecular orbital treatment. These situations seem to require further investigation. Ramsey's theory has so far been well applied to the simple system of hydrogen, however, it is not certain whether it can be applied to cobalt-59 NMR, as was done by Griffith and Orgel.

We have been studying cobalt-59 NMR in an effort to determine whether the relation proposed by Griffith and Orgel holds for all cobalt compounds. In this report we present chemical shift data for about forty cobalt(III) complexes which do not simply obey the aforementioned relationship, but which can be expressed as a simple function of the electronegativities of the atoms of the ligands which are directly bonded to the central cobalt atom.

Experimental Section

Materials. All cobalt(III) complexes examined were synthesized in this laboratory by standard methods. The purities of prepared complexes were determined by titration with EDTA after decomposition with caustic alkalies, etc., and the ammonia contents of ammine complexes was determined by the Kjeldahl method. All compounds were nearly 100% pure, except for the nitropentacyanocobaltate(III) complex, which unavoidably contained small amount of hexacyanocobaltate(III) as a by-product.

Apparatus. A 6.1403 Mc nuclear magnetic resonance spectrometer equipped with a bridge-type detector was constructed in this laboratory and used for measurement. All spectral measurements were carried out at room temperature (23°C). Water-soluble complexes were put into aqueous solution, and sealed in small glass tubes 8.9 mm in diameter. Several nonelectrolytic complexes, such as tris(acetylacetonato)cobalt(III), were dissolved in proper organic solvents, such as chloroform, benzene, or acetone, and sealed in the above glass tubes. Potassium hexacyanocobaltate(III) was used as the external standard ($\sigma=0$), and tris(acetylacetonato)cobalt(III) was used as the secondary standard ($\sigma=12{,}500$ ppm). The resonant fields for these reference compounds were exactly determined through measurement of the proton NMR frequency using an autodyne oscillator. The chemical shift of each sample was determined by interpolation, or extrapolation from these two standards.

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(1) W. G. Proctor and F. C. Yu, *Phys. Rev.*, *81*, 20 (1951).

(2) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 53, 601 (1957).

(3) N. F. Ramsey, *Phys. Rev.*, *78*, 699 (1950).

(4) R. Freeman, G. R. Murray, and R. E. Richards, *Proc. Roy. Soc.*, *A242*, 455 (1957).

(5) S. S. Dharmatti and C. R. Kanekar, *J. Chem. Phys.*, *31*, 1436 (1960).

(6) N. S. Biradar and M. A. Pujar, *Current Sci.* (India), 35, 385 (1966). *Chem. Abstr.*, 65, 13047c (1966).

(7) C. R. Kanekar, M. M. Dhingra, V. R. Marathe and R. Nagarajan, *J. Chem. Phys.*, *46*, 2009 (1967).

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

The line widths of the cobalt-59 NMR spectra were measured as the peak-to-peak intervals of their first derivatives, except for several narrow line spectra, such as those of hexacyanocobaltate(III). The line widths of the latter were measured by side-band detection using a modulation frequency of 1 Kc. The magnetic field inhomogeneity produced minimum line widths of about 0.05 gauss (=50 c/s).

Results

The results of the measurement of chemical shifts and line widths are summarized in Table I. Besides these complexes, NMR spectra could not be observed in about fifty complexes because of their low solubility or because the limitation of our spectrometer with respect to large line widths. The resonant fields of all complexes observed are located lower than hexacyanocobaltate(III). The largest chemical shift from hexacyanocobaltate(III) was observed for the tricarbonatocobaltate(III) complex. This compound is erroneously referred to as "carbonatocobalt(III) nitrate" by Freeman and others.[4] Trioxalato-, and tris(acetylacetonato)complexes also show remarkably large shift, being slightly smaller than that of tricarbonato complex. Other complexes are situated between hexacyano- and tricarbonato complexes.

Table I. Chemical Shift and Line Width Data of Cobalt-59 NMR Spectra

Complexes No.	Chemical Shift (ppm)	Line Width (gauss)
1. $K_3[Co(CN)_6]$	0 [a]	$\underline{0.05}$
2. $K_3[Co(CN)_5NO_2]$	1,400	10
3. $[Co(C_2H_5CSS)_3]$	6,360	0.3
4. $[Co(i\text{-}C_3H_7CSS)_3]$	6,360	0.5
5. $[Co((C_2H_5)_2NCSS)_3]$	6,450	0.3
6. $[Co(NH_2OH)_6]Cl_3$	6,500	0.21
7. $Li[Co(NH_3)_2(NO_2)_4]$	6,860	1
8. $[Co(phen)_3]Cl_3$	7,080	0.8
9. *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$	7,080	0.5
10. *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$	7,080	0.5
11. peripheral-$[Co(NH_3)_3(NO_2)_3]$	7,200	0.5
12. *cis*-$[Co(en)_2(NH_3)_2]I_3$	7,300	0.2
13. $[Co(en)_3]Cl_3$		$\underline{0.12}$
14. $Na_3[Co(NO_2)_6]$	7,440	$\underline{0.10}$
» (unknown impurity)	(8.160)	0.4
15. $[Co(NH_3)_5NO_2]Cl_2$	7,440	0.3
16. *trans*-$[Co(en)_2(NH_3)_2]I_3$	7,510	0.4
17. $[Co(NH_3)_6]Cl_3$	8,100	$\underline{0.22}$
18. $[Co(en)_2C_2O_4]Cl$	8,960	3
19. $[Co(NH_3)_5N_3](N_3)_2$	9,100	0.3
20. $[Co(NH_3)_5OH_2]Cl_3$	9,170	3
21. *trans*-$[Co(NH_3)_4(N_3)_2]N_3$	9,170	0.5
22. $[Co(en)_2CO_3]Cl$	9,180	3
23. *cis*-$[Co(NH_3)_4(N_3)_2]N_3$	9,400	0.3
24. $[Co(NH_3)_4CO_3]_2SO_4$	9,680	3
25. *cis*-$[Co(NH_3)_4(OH_2)_2]Cl_3$	9,820	3
26. $K[Co(edta)]$	10,300	4
27. facial-$[Co(NH_3)_3(OH_2)_3](NO_3)_3$	10,500	0.20
28. $K[Co(NH_3)_2(CO_3)_2]$	11,500	3
29. $[Co(bzac)_3]$	12,400	0.5
30. $[Co(dbzm)_3]$	12,400	0.5
31. $[Co(acac)_3]$	12,500 [a]	$\underline{0.11}$
32. $[Co(tfac)_3]$	12,500	0.16
33. $[Co(acac\text{-}Br)_3]$	12,500	0.5
34. $K_3[Co(C_2O_4)_3]$	13,000	0.25
35. $K_3[Co(CO_3)_3]$	13,900	0.25

[a] For these complexes, resonant field was exactly determined by the use of autodyne apparatus with proton, and used for standards. Underlined line width data was obtained by side-band detection method. Others are peak-to-peak values. Abbreviations: en, ethylenediamine; phen, o-phenanthroline; edta, ethylenediaminetetraacetate; bzac, benzoylacetonate; dbzm, dibenzoylmethanate; acac, acetylacetonate; tfac, trifluoroacetylacetonate; acac-Br, 3-bromoacetylacetonate.

Line width varies sizably among these complexes. Octahedrally symmetric complexes, such as hexacyano-, hexammine, and tris(ethylenediamine) complexes, always show very narrow spectra (0.1-0.3 gauss line widths). CoO_6 and CoS_6 type complexes also show sharper line widths, where O and S refer oxygen or sulphur atoms in ligands, respectively, which are bonded to cobalt. Other complexes show relatively broad spectra except several CoN_6 type complexes, such as azidopentamminecobalt(III).

The line width data in Table I includes the contributions of the inhomogeneity of magnetic field and modulation broadening. The latter is especially large in the case of low solubility complexes, because large amplitude of modulation was necessary for the measurements of these samples. Hence, the real line width should be smaller than the values listed in the Table, in principle, however, those contributions are negligible and the values in the Table can be safely taken as those of the real values.

Discussion

Chemical Shift. According to Ramsey,[3] the chemical shift can be expressed as the sum of two terms, σ_d and σ_p, given in the following expression :

$$\sigma = \sigma_d + \sigma_p$$

$$\sigma_p = -2\beta^2 \sum_{n\neq o} (E_n - E_o)^{-1} \left[\langle \psi_o | \sum_i L_i | \psi_n \rangle \langle \psi_n | \sum_k r_k^{-3} L_k | \psi_o \rangle + \langle \psi_n | \sum_i L_i | \psi_o \rangle \langle \psi_o | \sum_k r_k^{-3} L_k | \psi_n \rangle \right]$$

The symbols ψ_o, ψ_n represent the wave function of the ground and excited states of energy E_o and E_n, respectively, L_i is the angular momentum operator for electron i, r is its distance from the nucleus under study, and β is the Bohr magneton.

As mentioned above, Griffith and Orgel[2] treated the data with crystal field theory, and introduced a simple relation for chemical shift. Their treatment implies that the only contribution to the second paramagnetic term is due to the first d-d transition. Freeman, Murray, and Richards extended their theory, and concluded the presence of good correlation between the chemical shift and wavelengths of the first absorption maxima (or reciprocals of Dq).[4]

In the course of our investigation, however, several CoS_6 type complexes showed that their chemical shift values do not obey the correlation rule given above, where S refers to a sulphur atom on the ligand which is bonded to cobalt. Tris(ethylxanthato)cobalt(III), and other CoS_6 type complexes have the same magnitude of Dq as tricarbonatocobaltate(III); however, the observed chemical shifts are much smaller than that expected from Griffith and Orgel's treatment.*

(*) Kanekar and others[7] recently reported the chemical shift values of these compounds which do not coincide with those of the present results of our measurements. However we carry out our discussion on the basis of our measurements because the latter results are based on the repeated measurements for the compounds cautiously synthesized.

Moreover, for several pentammine-type complexes, the magnitude of chemical shift do not change according to the spectrochemical series. Azidopentammine complex has the Dq value of 1.94 kK, and aquopentammine complex has 2.06 kK. If the Griffith-Orgel correlation holds, the chemical shift of aquopentammine complex should be much smaller than that of azidopentammine complex. Figure 1a shows the Griffith-Orgel correlation for about forty complexes, including CoS_6 type ones which do not obey the linear relation.

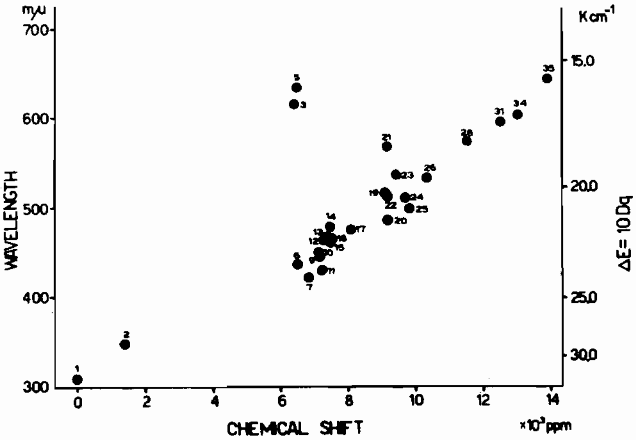

Figure 1a. The relation between chemical shift and the wavelength of the first absorption maxima.

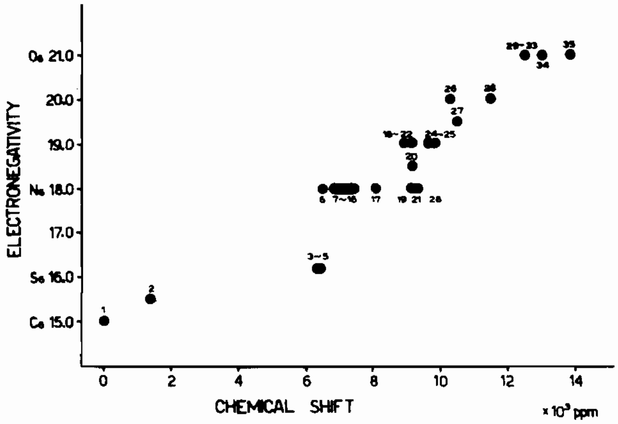

Figure 1b. Classification of chemical shift data by the total electronegativity of six ligand atoms.
The number in these figures corresponds to that in the Table I.

In order to elucidate this difficulty, we tried to investigate other trend of chemical shifts of those compounds. As a trial, we arranged the chemical shift data against the total electronegativity of the six ligand atoms which are directly bonded to cobalt. The result of the investigation is shown in Figure 1b. As may be seen, the chemical shift increases linearly with x in the sequences CoO_xN_{6-x} and CoN_xC_{6-x}, where O, N and C refer to oxygen, nitrogen and carbon atoms which are bonded to cobalt, respectively. On the other hand, the chemical shift changes according to the values of Dq under a definite ligand atom combination. For instance, chemical shift increases according to the following sequence of CoN_6 type: $[Co(NH_2OH)_6]^{3+}$, $[Co(NH_3)_3(NO_2)_3]$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5N_3]^{2+}$, which corresponds to a decrease in the Dq values. For other ligand atom combinations, similar trends are obtained.

When Griffith and Orgel related chemical shift values to Dq, they assumed that the radial parameter of the molecular orbital electron, which may be related to chemical shift and Dq, can be taken as constant. Since the relation does not hold, as shown above, the assumption of the constancy of the radial factor has to be withdrawn. In order to have a rough estimation of the relative magnitude of electron cloud, "nephelauxetic series" will be considered. It has been established that the order of this series is determined by the kind of ligand atom which is directly bound to the central metal ion. For example, NH_3, en, NCS^-, N_3^-, NO, etc., which are all nitrogen-coordinative ligands, occupy nearly the same sites in the nephelauxetic series. This is assumed to infer than the radial parameter of the molecular orbital electron, $\langle r^{-3} \rangle$, is not much changed among the ligands cited above.

Line Width. Four factors are counted which determine NMR line widths, *i.e.*, dipolar, quadrupolar, and scalar coupling, and exchange interactions. Generally speaking, cobalt(III) complexes, which are typical "inert" complexes, are not assumed to show line widths dominantly determined by electronic exchange interactions. Dipolar interaction also cannot be dominant because of the low concentration of the sample. As a consequence, scalar coupling and quadrupolar interaction (relaxation) are taken as the important factors which determine the line width.

For scalar coupling, Lauterbur,[9] and Loewenstein[10] investigated hexacyanocobaltate(III) using enriched carbon-13 cyanide ligands. They observed a coupling constant between Co-59 and C-13 of about 100 c/s. Lucken, Noack and Williams also observed scalar coupling between Co-59 and P-31, and F-19 in $HCo(PF_3)_4$.[8] A similar interaction is likely to exist in CoN_6 type complexes, or in other nitrogen-coordinated complexes. However, we could not observe any hyperfine splitting in the NMR spectra of cobalt-59 for these complexes. In fact, the line widths of $[Co(NH_3)_5]^{3+}$, $[Co(en)_3]^{3+}$, etc., are apparently broader than the line width of hexacyanocobaltate(III) and tris(acetylacetonato)cobalt(III) complexes. This may be due to the effect of scalar coupling between Co-59 and N-14.

Quadrupolar relaxation is expected to be the most dominant source of line width. For the binary complexes, CoA_xB_{6-x}, the field gradient at the central cobalt nucleus (which affects the quadrupolar relaxation of the central nucleus) is calculated for a point-charge, or point-dipole model (see Table II). From the result of this calculation, it is apparent that the *cis*-*cis*(facial) configuration produces a zero field gradient as well as the octahedrally symmetric complexes, CoA_6 and CoB_6. For CoA_4B_2 type (as well as for reversely coordinated CoA_2B_4 type) complexes, the field gradient of the *trans*-isomer is twice as large as that for the *cis*-isomer.

(9) P. C. Lauterbur, *J. Chem. Phys.*, *42*, 799 (1965).
(10) A. Loewenstein and M. Shporer, *Mol. Phys.*, *9*, 293 (1965).

Table II. Electric Field Gradient at the Central Cobalt Nucleus in a Series of CoA_xB_{6-x} ($x=0\sim6$) Complexes. (Relative Value)[a]

Octahedral	*cis*	Peripheral	*trans*
CoA_6, CoB_6	CoA_4B_2, CoA_2B_4	CoA_3B_3	CoA_4B_2, CoA_2B_4
Facial			
CoA_3B_3	CoA_5B, $CoAB_5$		
0	2	3	4

[a] Calculated using point-charge model. (See Figure 2).

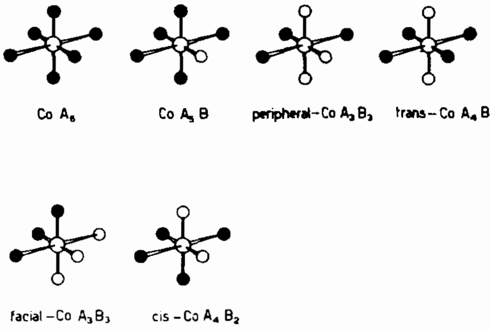

Figure 2. Point-charge model of a series of CoA_xB_{6-x} complexes.

This qualitative evaluation accounts well for the experimental line width. The triaquotriamminecobalt(III) complex, which is prepared by the aquation of trinitratotriamminecobalt(III), and has been assigned a facial configuration, shows a much narrower line width than the diaquotetrammine, or dicarbonatodiammine complexes. Another triaquotriamminecobalt(III) complex, which is derived from the dichrochloride, and assigned a *cis-trans* (peripheral) configuration, shows much broader spectra, which cannot be easily observed. After aging for several hours, it can be observed as a narrow spectrum, which suggests gradual transformation to the facial triaquotriammine complex. As for the *cis-trans* isomer pairs, the *trans* isomer shows broader spectra than the *cis* isomer in almost all cases. For dinitrotetrammine- (croceo and flavo), diazidotetrammine-, and diamminebis(ethylenediamine)-complexes, the *trans* isomers usually show slightly (but not negligible) broader spectra than the *cis* isomers.

Consequently, it can be safely concluded that the most important source of the line width of cobalt-59 NMR spectra is quadrupolar relaxation. It is also necessary to consider the scalar coupling of ligand atoms if they have non-zero nuclear spins, but it is not so dominant and important as quadrupolar relaxation.

During the course of this investigation, a few points of interest were found, which will be noted in the following. It is well known that the hexanitrocobaltate(III) complex shows a doublet in its cobalt-59 NMR spectrum. Gasser and Richards[11] investigated this complex and stated that the isomeric mixture gives such a doublet spectrum. However, it is not expected that the isomeric (presumably nitrito- complex) complexes show chemical shifts of this magnitude (if hexanitrito-complex is formed, its chemical shift will become much larger). We measured the NMR spectrum of sodium hexanitrocobaltate(III) samples of five different origins, and found that the freshly recrystallized complex do not give the lower field spectra in the fresh solution. Both aged crystals and aged solutions showed similar doublet spectrum. Therefore, the lower field spectrum is assigned to the complexes which must be the product of decomposition. The latter is probably nitrogen-hexacoordinated, *e.g.*, nitroso-nitro mixed complexes.

We could not observe the NMR spectra of monochloropentammine, and *trans*-dichlorobis(ethylenediamine) cobalt(III) complexes, which should have the largest field gradients among the complexes which were synthesized in this experiment. For *trans*-dichlorobis(ethylenediamine) cobalt(III) chloride, nuclear quadrupole resonance studies have been carried out by Hartmann, Fleissner and Sillescu[12] and Watanabe and Yamagata.[13] The line width of cobalt-59 NMR in aqueous solution can be estimated to be almost 100 gauss, according to their data and the Debye approximation. This is too broad to be observed with the usual NMR spectrometer. Consequently, the report of observation of spectra for these compounds could be attributed to impurities in the samples. Tris(ethylenediamine)cobalt(III) complex may be the acontaminant in dichlorobis(ethylenediamine)-, and carbonatobis(ethylenediamine)cobalt(III) complexes, which can show the cobalt-59 NMR spectrum at the position which was reported as above two complexes by Freeman and others.

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(12) H. Hartmann, M. Fleissner, and H. Sillescu, *Theor. Chim. Acta*, 2, 63 (1964).
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