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Solvent Effects on ^{59}Co Chemical Shifts for Tripositive Cobalt(III) Complex Ions

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Interactions of tripositive cobalt(III) complex ions, such as Δ(*lel*$_3$)-[Co(chxn)$_3$]$^{3+}$ (chxn = (*R*,*R*)-1,2-cyclohexanediamine), [Co(oct-en)(2,3,2-tet)]$^{3+}$ (oct-en = *N*-octylethylenediamine, 2,3,2-tet = 3,7-diazanonane-1,9-diamine), [Co(sep)$_3$]$^{3+}$ (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane), and [Co(tn)$_3$]$^{3+}$ (tn = trimethylenediamine), in various solvents were studied using ^{59}Co chemical shifts together with the electronic absorption spectra. The results are discussed in comparison with those of [Co(en)$_3$]$^{3+}$, whose ^{59}Co chemical shift in various solvents had been previously reported to be fairly proportional to the donor numbers. There was a trend that the ^{59}Co chemical shift changes greatly if the acidic NH-hydrogen atoms of the ligands are favorable to form hydrogen bonding with the solvents. The magnitudes of the chemical-shift changes for [Co(tn)$_3$]$^{3+}$ were significantly smaller than those for the en and chxn complexes. This difference can be attributed to the more conformationally labile structure of the tn complex in solution.

^{59}Co NMR spectroscopy is a very useful tool to detect slight changes in the electronic states of the cobalt nucleus; this high sensitivity is applicable to studying the interaction of cobalt(III) complex ions with the secondary coordination sphere.[1)] Mayer and co-workers have found that the ^{59}Co NMR chemical shift for [Co(en)$_3$]$^{3+}$ (en = ethylenediamine) has a very satisfactory linear relationship with the donor numbers of solvents.[2—4)] Their study showed that the ^{59}Co NMR chemical shift changes upfield along with an increase in the donor number. This relation could be explained on the basis of the following two factors: 1) Acceptor properties arising from the acidic NH-hydrogen atoms of the coordinated ethylenediamine ligands. 2) A change in the electron density around the Co-nucleus, which is reflected in a corresponding shift in the resonance frequencies. Factor 1) leads to factor 2).

On the other hand, two of the present authors (M.I. and Y.M.) with their co-workers have measured changes in ^{59}Co NMR chemical shifts for tripositive cobalt(III) complex ions by interactions with multivalent anions or anionic micelles in aqueous solutions.[5—7)] We found that the ^{59}Co NMR peak shifts upfield upon interacting with anions when the interaction is mainly electrostatic, while it shifts downfield relative to the free hydrated state of the cobalt(III) complex cations in a hydrophobic environment.

These solvent and micellar effects could be explained on the basis of the trend that the ^{59}Co NMR signal shifts upfield along with an increase in the electric-field gradient around the cobalt nucleus. In order to systematically understand the effect of the secondary coordination sphere or of the hydrogen-bonding on the electron density around the Co-nucleus, it seems significant to compare the ^{59}Co NMR chemical shifts between a series of cobalt(III) complex ions in various kinds of solvents.

In the present study, we observed ^{59}Co NMR chemical shifts for Δ(*lel*$_3$)-[Co(chxn)$_3$]$^{3+}$, [Co(oct-en)(2,3,2-tet)]$^{3+}$, [Co(sep)$_3$]$^{3+}$, and [Co(tn)$_3$]$^{3+}$ in solvents whose donor numbers ranged from 0 to 39. Tripositive complex ions are convenient for systematic studies on solvation, since the experimentally observed parameters for these complex ions should be governed more by ion–dipole interactions than those for lower-charged ions. The chemical shifts were related to those for the electronic absorption spectra. A comparison of the results concerning the above complexes with those of [Co(en)$_3$]$^{3+}$ is expected to provide useful information concerning the solvation mechanism of the complex ions. The solvent effects can be explained by comparing with the ion-pairing effects on the basis of the donor–acceptor concept.

Experimental

Materials. Complexes of [Co(en)$_3$]Cl$_3$,[8)] Δ(*lel*$_3$)-[Co(chxn)$_3$]Cl$_3$,[9)] [Co(oct-en)(2,3,2-tet)]Cl$_3$,[10,11)] [Co(sep)$_3$]Cl$_3$,[12)] and [Co(tn)$_3$]Cl$_3$[13)] were prepared according to the respective literature methods, and were characterized by their known UV-vis spectra. Since the solubilities of the chlorides in organic solvents were poor, the trifluoromethanesulfonates were obtained for use by the addition of their silver salts to the chlorides of the complexes.

All nonaqueous solvents used were supplied from Wako Pure Chemical Industries, Ltd., except for hexamethylphosphoric triamide (HMPA), which was obtained from Sigma Co. Acetone (AC), 1-propanol (1-PrOH), *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) used were of "infinity pure" grade. Trifluoromethanesulfonic acid (TFS) and acetonitrile (AN) of guaranteed reagents were used without further purification. Nitromethane (NM), methanol (MeOH), ethanol (EtOH), formamide (FA), and HMPA of guaranteed reagents were dried over molecular sieve 3A. For MeOH and EtOH, the dried solvents were furthermore dehydrated using a small amount of metal Na (for MeOH) or a small amount of metal Na together with ethyl phthalate (for EtOH).[14] The solvents treated by desiccating agents were used after distillation. The solvents and their donor numbers are listed in Table 1.

NMR Measurements. The ^{59}Co and ^{23}Na NMR spectra were measured with a JEOL GX-270 FT NMR spectrometer operating at 64.6 and 71.5 MHz, respectively. The temperature of the sample solution was controlled at 27±0.5°C. Since the ^{59}Co chemical shift significantly changes along with a change in the complex concentrations, we determined the chemical shift of each cobalt(III) complex in each solvent by extrapolating the chemical shifts to infinite dilution. The chemical shift for each cobalt(III) complex system is referred to that in the aqueous solution. The experimental errors for the ^{59}Co chemical shifts were 1—4 ppm, whose values depended on the magnitudes of the concentration dependence of the chemical shifts, which are shown in the respective figure captions.

Electronic Absorption Spectra. The electronic absorption spectra were measured with a Shimadzu UV-240 recording spectrometer at ambient temperature and the wavelengths of the first absorption maxima were used for discussion purposes. The errors of the peak wavelengths were within 0.3 nm. All of the measurements were performed for 5×10^{-3} mol dm^{-3} solutions.

Decomposition of Complex Ions by Solvolysis. Some of the complex ions used were not dissolved, or were decomposed in some solvents. We could easily detect the decomposition from its ^{59}Co NMR spectra, since in most cases the peaks disappeared upon decomposition. Furthermore, we performed column chromatography of SP-Sephadex C-25 for cobalt(III) complex solutions after the measurements and the decomposition was confirmed.

In the following systems, the complex ions were decomposed by the solvolysis. [Co(oct-en)(2,3,2-tet)]$^{3+}$: in FA, DMF, DMSO, and HMPA; [Co(sep)$_3$]$^{3+}$: in TFS.

Results and Discussion

Dependence of the ^{59}Co Chemical Shifts on the Complex Concentrations. In some systems the dependence was large; the typical results for the chxn complex are shown in Fig. 1. We obtained the ^{59}Co chemical shift at infinite di-

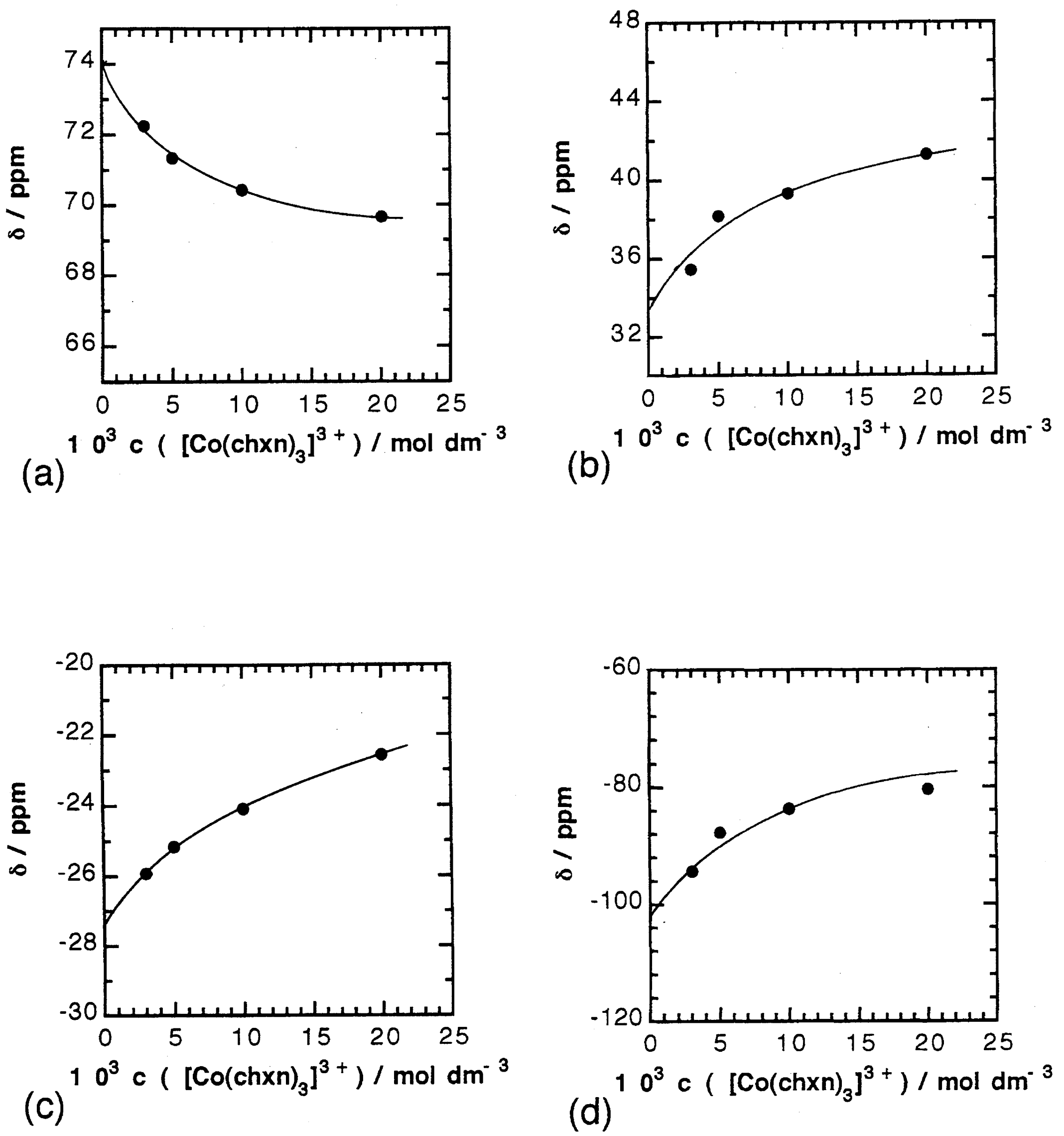

Fig. 1. Typical concentration dependence of ^{59}Co chemical shifts in various solvents. (a) NM, (b) MeOH, (c) DMF, (d) HMPA. The lines are drawn as an aid to the eye.

Table 1. ^{23}NaClO$_4$ and [^{59}Co(en)$_3$](CF$_3$SO$_3$)$_3$ Chemical Shifts Extrapolated to Infinite Dilutions in Various Solvents

No	Solvents	Donor number$^{a)}$	$\delta(^{23}\mathrm{Na})$	$\delta(^{59}\mathrm{Co})$
1	TFS	0	—	184±2
2	NM	2.7	−11.9±0.1	79±2
3	AN	14.1	−6.5±0.1	102±4
4	H_2O	16.4	0	0
5	AC	17.0	−7.1±0.1	50±1
6	MeOH	19.1	−2.7±0.1	30±1
7	1-PrOH	19.6	−1.0±0.2	Insoluble
8	EtOH	20$^{b)}$	−0.2±0.2	Insoluble
9	FA	24.0	−3.4±0.1	−34±1
10	DMF	26.6	−4.1±0.1	−25±1
11	DMSO	29.8	0.3±0.1	−43±1
12	HMPA	38.8	3.8±0.1	−79±2

a) Refs. 2 and 17. b) This value was determined indirectly. (Ref. 17).

lution ($\delta(^{59}\mathrm{Co})$) for each system, and used it for discussion purposes.

^{23}NaClO$_4$ and [^{59}Co(en)$_3$]$^{3+}$. Fairly linear relationships between the chemical shifts and donor numbers of solvents have been reported for ^{23}NaClO$_4$[15,16] and [^{59}Co(en)$_3$](CF$_3$SO$_3$)$_3$ solutions. Their results were reproduced using our reagents. Our results are listed in Table 1 together with the donor numbers of solvents.

[^{59}Co(chxn)$_3$]$^{3+}$ and [^{59}Co(oct-en)(2,3,2-tet)]$^{3+}$. The dependence of the ^{59}Co chemical shift on the solvent donor number (donicity) for the chxn complex was very similar to that for the en complex. Figure 2 is the dependence for the chxn complex. Figure 3 shows a correlation of the $\delta(^{59}\mathrm{Co})$ between the en and chxn complexes. The slope is close to unity (1.1), which means that the hydrogen bonding of the acidic NH-hydrogen atoms with the solvents governs $\delta(^{59}\mathrm{Co})$ of the chxn complex, just as does the en complex. It is noticeable that although the chxn complex (Δ (lel_3) isomer) is conformationally rigid in solution, the difference in the solvation between the chxn and en complexes does not appear to be significant. This is in contrast with our previous result that the interactions of the en and chxn complex ions with the sulfate and phosphate ions (ion-pairings) are effective in a different way on the electric-field gradient around their ^{59}Co nuclei.[6] This means that the difference in the interactions with the second coordination spheres between the en and chxn complexes is enhanced in the dynamic properties of ion-pairings.

Since the chxn complex can be dissolved in more kinds of solvents than the en complex, and the result is very similar, we use the result for the chxn complex as a reference of the ^{59}Co chemical shift hereafter.

Although the oct–en complex was decomposed in some solvents, even the smaller amount of data give significant information. The dependence of the $\delta(^{59}\mathrm{Co})$ of this complex on the donor numbers is smaller than that of the chxn complex (the slope is 0.56), as shown in Fig. 4, which is described as a correlation with the result of the chxn complex. This result means that the solvation through the acidic NH-hydrogen atoms also governs the $\delta(^{59}\mathrm{Co})$ change in this complex.

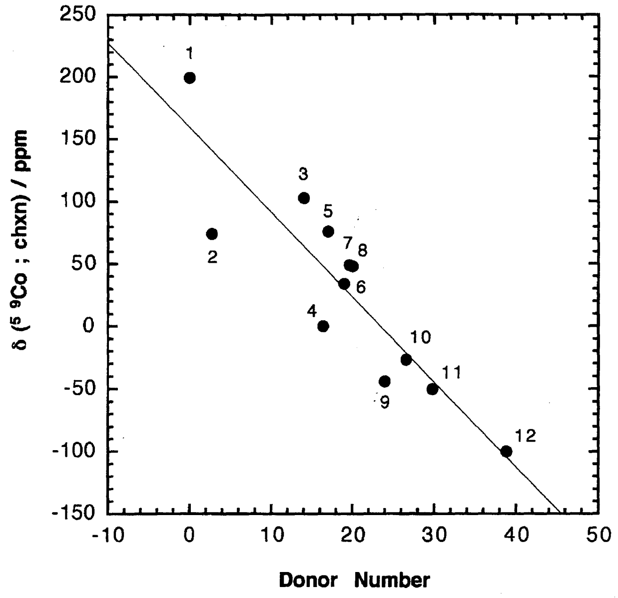

Fig. 2. A correlation between the chemical shifts $\delta(^{59}\mathrm{Co})$ and the solvent donor numbers for the chxn complex. The estimated errors of the chemical shifts are 4 ppm for 12, 2 ppm for 1, 6, and 8, and 1 ppm for the other solvent systems. The correlation coefficient is 0.90.

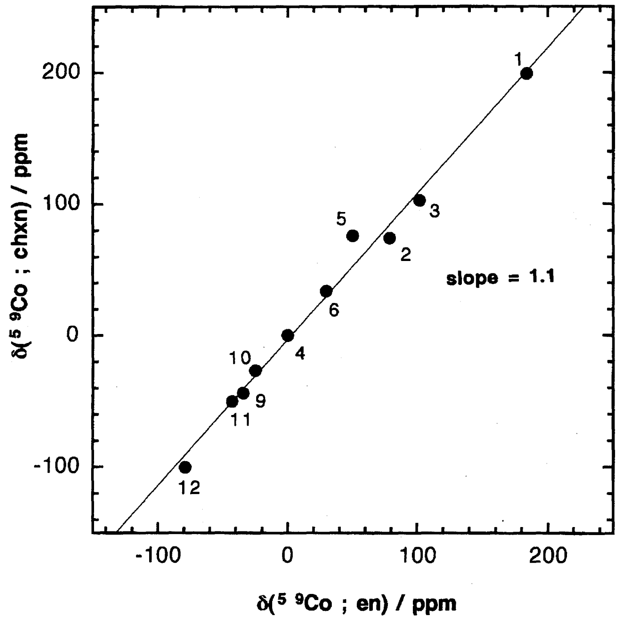

Fig. 3. A correlation of the chemical shift $\delta(^{59}\mathrm{Co})$ between the en and chxn complexes. The correlation coefficient is 0.99.

The change in the $\delta(^{59}\mathrm{Co})$ is closely correlated with the absorption spectra according to the following FMR equation on the basis of the Ramsey equation:[18,19]

$$\delta(^{59}\mathrm{Co}) = -\sigma_{\mathrm{P}} = \frac{kC_{\mathrm{d}}^2}{\langle r^3 \rangle_{\mathrm{d}} \Delta E}, \tag{1}$$

where the symbols are used as ordinary notations.

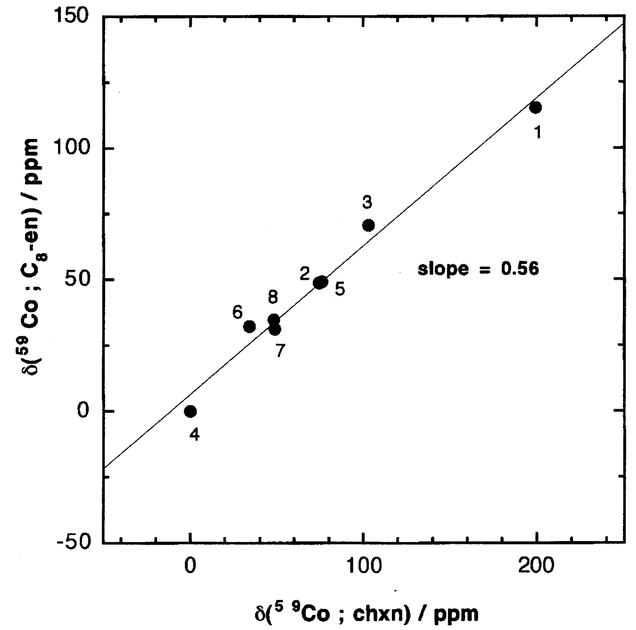

Fig. 4. A correlation of the chemical shift $\delta(^{59}\text{Co})$ between the oct-en and chxn complexes. The correlation coefficient is 0.95. The estimated errors of the chemical shifts for the oct-en complex are around 1 ppm.

In Eq. 1, the effective electronic transition energy (ΔE) is identified with the transition energy, $^1\text{A}_{1\text{g}}\rightarrow{}^1\text{T}_{1\text{g}}$, and is proportional to the reciprocal of the wavelength (λ_1) of the first absorption maxima. If the linearity of $\delta(^{59}\text{Co})$ vs. λ_1 plot (Griffith–Orgel plot) is good,[20] we can say that ΔE governs $\delta(^{59}\text{Co})$. We confirmed that this linearity holds fairly well; Figure 5 shows the results for the chxn and tn complexes. The change in the chemical shift can therefore be attributed to that in the ΔE value.

$[^{59}\text{Co(sep)}_3]^{3+}$. In order to obtain more detailed information concerning the role of the NH-hydrogen bonding of the ligand, we measured $\delta(^{59}\text{Co})$ for $[\text{Co(sep)}_3]^{3+}$, since it has fewer NH-hydrogen atoms. Figure 6 shows the results as functions of the $\delta(^{59}\text{Co})$ of the chxn complex.

The correlation is not good; however, there are two noticeable trends when we look at these figures by dividing the solvents into two groups of larger and smaller donor numbers. One trend is that in the solvents of smaller donor numbers, the magnitudes of the $\delta(^{59}\text{Co})$ changes are appreciably smaller than those for the en and chxn complexes. The slope is 0.25 (from the data in the solvents 2—11 (except for 5, 7, and 8)).[21]

The other trend is that the slope is appreciably larger in the range of the larger donor numbers. In this range, the slope is about 4-times (1.1, using the data for the solvents 4, and 9—12) that in the lower donor number range, and is comparable to those for the en and chxn complexes. The smaller dependence of the $\delta(^{59}\text{Co})$ on the donor numbers suggests a significant role of the acidic NH-hydrogen atoms in the $\delta(^{59}\text{Co})$ changes. It is important that the solvents of larger donor numbers appreciably change the $\delta(^{59}\text{Co})$ for the sep complex. We can say that even for a complex having fewer NH hydrogens, the high donicity of solvents can similarly affect the Co–N bonds.

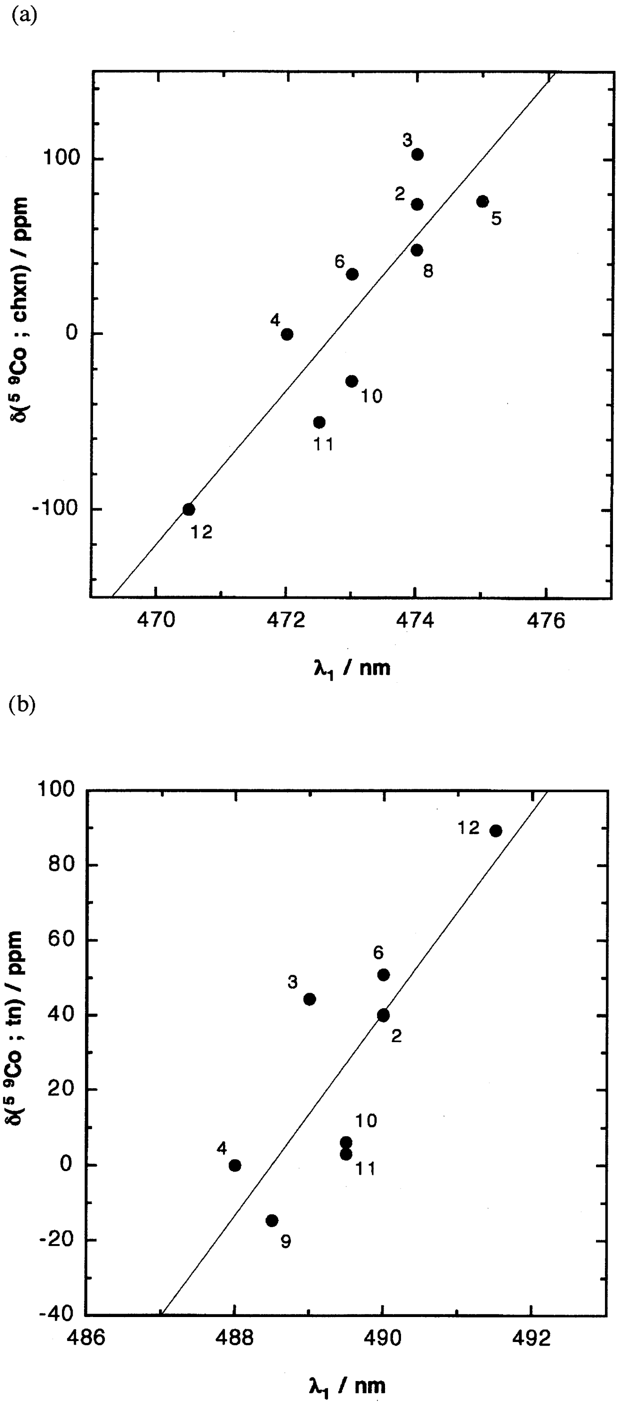

Fig. 5. Correlations between the chemical shifts $\delta(^{59}\text{Co})$ and the wavelengths (λ_1) of the first absorption maxima for the (a) chxn and (b) tn complexes. The correlation coefficients are 0.88 (a) and 0.84 (b).

$[^{59}\text{Co(tn)}_3]^{3+}$. This complex has the same number of acidic NH-hydrogens as that in the en and chxn complexes. However, a plot of the ^{59}Co chemical shifts against those for the chxn complex (Fig. 7) shows two distinguishable features. One is that the slope (0.46, except for 7, 8, and 12) is significantly smaller than unity. The other is that

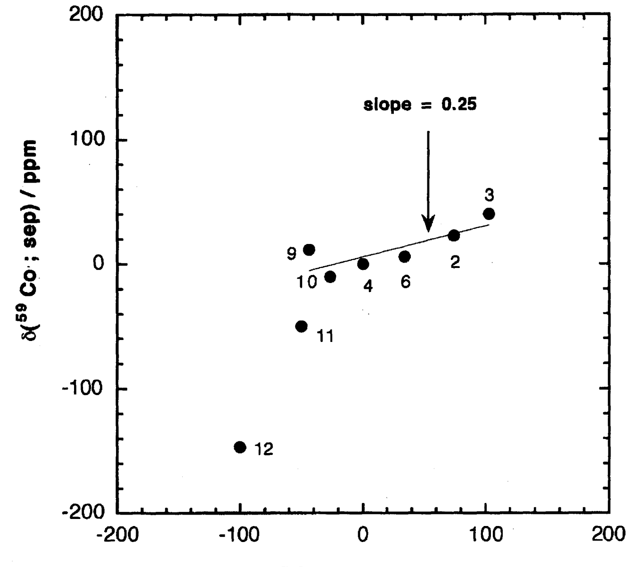

Fig. 6. A correlation of the chemical shifts δ(^{59}Co) between the sep and chxn complexes. The linear least-squares fitting was performed except for the 11 and 12 systems. The correlation coefficient is 0.82. The estimated errors of the chemical shifts for the sep complex are around 1 ppm except for the solvent 3 system (2 ppm).

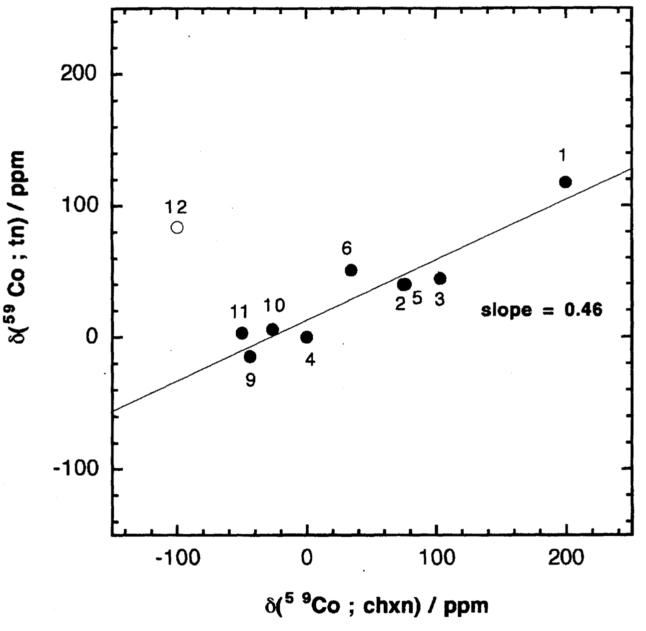

Fig. 7. A correlation of the chemical shifts δ(^{59}Co) between the tn and chxn complexes. The correlation coefficient is 0.93 except for 12. The estimated errors of the chemical shifts for the tn complex are around 1 ppm except for the solvent 12 system (2 ppm).

the donicity of the HMPA is appreciably smaller for the tn complex than those for the en and chxn complexes. We can explain the above two trends by considering the molecular structure of the tn complex in solution. The largest difference in the molecular structure of the tn complex from those of the en and chxn complexes is the conformational lability of the chelate ring in solution.[22] Due to the large lability of this complex, it is unlikely that the solvation through the N–H bonds in the tn complex does not affect the electron density around the Co nucleus compared to the en and chxn complexes. It is characteristic that the slope (0.46) of the δ(^{59}Co) plot for the tn complex is less than or comparable to that (0.56) for the oct-en complex (Fig. 4) in spite of the greater number of NH hydrogen atoms in the former system. This is also reflected in the less-rigid conformation of the tn complex ion; that is, the solvation of this complex does not affect the change in the electron density around the Co nucleus as much as that of the oct-en complex. The larger effect of the conformational lability on the δ(^{59}Co) values in the tn complex is in contrast with the case of the en complex, where even a mixture of the conformational isomers is similarly effective on the δ(^{59}Co) values as the Δ (*lel*$_3$) chxn complex.

Concerning the HMPA solvent, since it is bulky, the steric hindrance is sometimes significantly effective on the solvation of metal ions.[23] The present result also shows that the steric hindrance of the HMPA may become significant in the solvation of the tn complex. Since the solvation of the tn complex is less effective on the Co–N bonds compared to the en and chxn complexes, because of the smaller rigidity of its conformation, the bulky effect of the HMPA on the solvation may be enhanced in this case.

Conclusively, the NH hydrogen of the ligand in the complex cation is effective in the solvation of the en and chxn complexes where a set of the three NH hydrogens is suitable for forming hydrogen bonds with solvents. Even for the sep complex, which has fewer NH hydrogens, the electron density around the Co-nucleus is appreciably affected by the solvation of higher donicity at a site favorable for a donation.

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