# Relation between the Torsion Angles of Acetate Chelate Rings and the Deuteron Nuclear Magnetic Resonance Chemical Shifts for Polyamine-N-carboxylatochromate(III) Complexes

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Deuteron n.m.r. spectra were examined for a series of multidentate polyamine-N-carboxylato complexes with *cis*-$CrN_2O_4$ chromophores in solution. The isotropic contact shifts for the deuteriated acetate methylenes in the paramagnetic chromium(III) complexes were compared with the glycinato chelate ring conformations obtained from *X*-ray structure analyses. There is a fair correlation between the chemical shifts and the torsion angles in the Cr–N–C–C(O) fragment of the acetate(glycinato) rings according to a Karplus-like or $\cos^2\theta$ relation.

There have been a number of conformational analyses of chelate rings by means of n.m.r. spectroscopy.[1] In the case of octahedral bidentate amino acidato complexes, however, few examples have been studied because of their lower extent of puckering or their planarity and/or their conformational interconversion in solution. For the present multidentate polyamino-N-carboxylato chelate system, the somewhat less flexible or rigid ring conformations of the glycinate arms in solution are expected to permit direct application of n.m.r. spectroscopy to conformational analyses or comparison with *X*-ray structural data. Hydrogen-2 n.m.r. spectroscopy of inert paramagnetic chromium(III) complexes is not only useful for the determination of geometrical structures,[2–7] but also can afford stereochemical information on subtle conformational changes through a Karplus-like or $\cos^2\theta$ relation with the contact shifts, in a manner similar to $^1H$ n.m.r. spectroscopy of paramagnetic octahedral nickel(II) complexes which are of limited applicability to stereochemistry because of their lability in solution.[8–10]

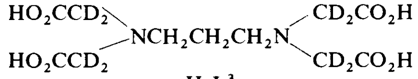
This paper deals with the solution stereochemistry of the chelate rings in ethylenediaminetetra-acetate (edta)-like complexes as determined by $^2H$ n.m.r. spectroscopy and its correlation with structural parameters obtained from *X*-ray structure analyses.

## Experimental

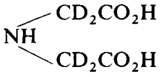
*Deuteriation of the Polyamine-N-carboxylic Acid Ligands.—Iminodiacetic acid with deuteriated acetate methylenes,* ($H_2L^1$). This was prepared by the basic hydrolysis of iminodiacetonitrile in $D_2O$ solution.[11] The extent of deuteriation of the $H_2L^1$ thus obtained was found to be about 46% by measuring proton n.m.r. spectra.

*Ethylenediamine-*N,N′*-diacetic-*N,N′*-dipropionic acid with deuteriated acetate methylenes* ($H_4L^2$) *and propane-*1,3*-diamine-N,N,N′,N′-tetra-acetic acid* ($H_4L^3$) *with deuteriated acetate methylenes.* These ligands were obtained by the method described previously.[7]

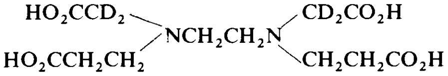
The corresponding complexes were synthesized by the literature methods and identified by their visible absorption spectra.[12,13]



$H_4L^3$



$H_2L^1$



$H_4L^2$

*Measurements.*—Proton n.m.r. spectra were measured on a Hitachi FT-n.m.r. R-600 spectrometer operating at a field of 1.41 T at room temperature. Sodium 4,4-dimethyl-4-silapentanesulphonate was used as an internal reference. Hydrogen-2 n.m.r. spectra were obtained on a Nicolet NT-200 (Washington State University) and/or a JEOL GX-270 spectrometer (Nara Women's University) at ambient temperature in aqueous solution under conditions previously described in detail.[2–6]

## Results and Discussion

A schematic representation of the $^2H$ n.m.r. spectra of the edta-like complexes with deuteriated acetate methylenes is shown in Figure 1. The assignments of the signals were made by comparing the $^2H$ n.m.r. shifts for the $L^3$ and *trans* ($O_5$)-$L^2$ complex with two oxygens ($O_5$) of five-membered N–O rings at the *trans* positions as mentioned previously.[7] A pair of downfield signals are due to methylene deuterons on the in-plane G(Girdling) rings in the $CrO_2N_2$ plane and a pair of upfield ones to those on the out-of-plane R(Relaxed) rings in the $CrO_3N$ plane (Figure 2). These assignments are in agreement with those made by Legg and co-workers.[4,5] As shown in Figure 1, each $^2H$ n.m.r. signal for the G or R rings may be correlated to the vicinal (inequivalent) deuterons A and B of the acetate methylenes (Figures 2 and 3) in the *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetra-acetato($L^4$), edta($L^5$), and propane-1,2-diamine-*N,N,N′,N′*-tetra-acetato($L^6$)chromate(III) complexes for which assignments were made[4,5] in terms of the stereospecific protonation. The separations between the chemical shifts for the vicinal deuterons A and B on each methylene vary from complex to complex as shown in Figure 1. It should be noted that the complexes with similar structure, $[CrL^5]^-$ and $[CrL^4]^-$, give a large difference in chemical shift separation, especially for the R-ring methylene deuterons as shown in Figure 1. This behaviour of the $^2H$ n.m.r. chemical shifts may reflect subtle conformational changes of the glycinate chelates in the edta-like complexes.

Since chromium(III) complexes have the same orbitally non-degenerate ground state ($^4A_2$) as that ($^3A_2$) of octahedral

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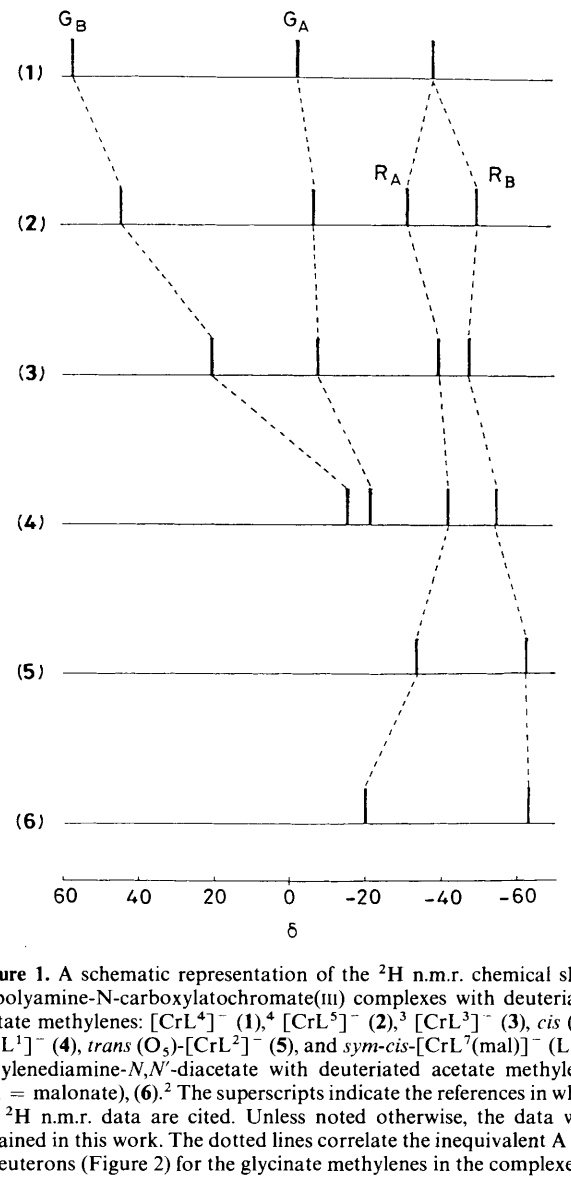

**Figure 1.** A schematic representation of the $^2$H n.m.r. chemical shifts of polyamine-N-carboxylatochromate(III) complexes with deuteriated acetate methylenes: $[\mathrm{CrL^4}]^-$ (**1**),[4] $[\mathrm{CrL^5}]^-$ (**2**),[3] $[\mathrm{CrL^3}]^-$ (**3**), *cis* (N)-$[\mathrm{CrL^1}]^-$ (**4**), *trans* $(\mathrm{O_5})$-$[\mathrm{CrL^2}]^-$ (**5**), and *sym-cis*-$[\mathrm{CrL^7(mal)}]^-$ ($\mathrm{L^7}$ = ethylenediamine-*N,N'*-diacetate with deuteriated acetate methylenes mal = malonate), (**6**).[2] The superscripts indicate the references in which the $^2$H n.m.r. data are cited. Unless noted otherwise, the data were obtained in this work. The dotted lines correlate the inequivalent A and B deuterons (Figure 2) for the glycinate methylenes in the complexes

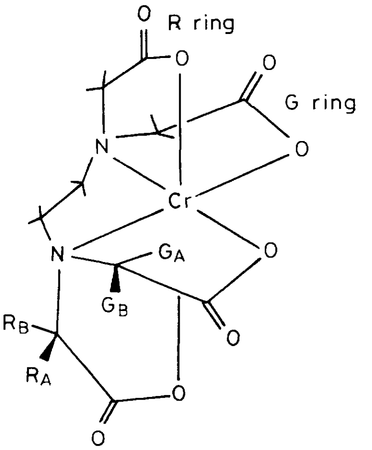

**Figure 2.** Nomenclature for the rings and acetate methylene deuterons in $\Delta(\Lambda\Lambda\Delta)$-$[\mathrm{CrL^5}]^-$. The A(axial) and B(equatorial) deuterons in this complex are substituted by A(equatorial) and B(axial) ones in the $\Lambda(\Delta\Delta\Lambda)$ complex, respectively

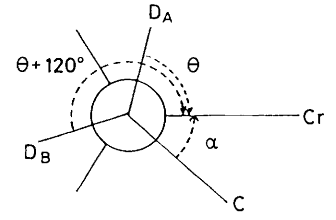

**Figure 3.** Dihedral angles for Cr–N–C–$\mathrm{D_{A(axial)}}$ (θ), Cr–N–C–$\mathrm{D_{B(equatorial)}}$ (θ + 120°), and Cr–N–C–C(O) (α) chains exemplifying the δ conformation with a negative α angle as in Figure 2

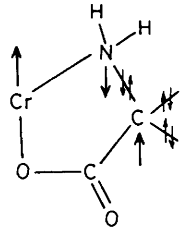

**Figure 4.** A spin polarization mechanism showing alternative positive and negative spin density on ligand atoms in chromium(III) complexes

nickel(II) complexes the $^1$H n.m.r. spectra of which give rise to isotropic contact shifts,[8–10] the $^2$H n.m.r. spectra of the chromium(III) complexes are considered to arise from the same origin as in the case of the nickel(II) complexes.[14] The signs of the contact shifts are interpreted by use of the spin polarization mechanism for the methylene deuterons of the acetates. In contrast to the case of $\mathrm{Ni^{II}}$, chromium(III) complexes may give the spin polarization shown in Figure 4.[14] That is, taking into consideration the correlation between three unpaired $t_{2g}$ electrons and an electron transferred from the highest occupied molecular orbital (h.o.m.o.) on the ligating atoms to the empty $e_g$ metal orbitals, the residual induced electron spin density on the ligating atoms is negative as predicted by Orgel.[14b] In fact, upfield $^2$H n.m.r. shifts are observed for glycinate arms with three intervening bonds between a central chromium(III) ion and the methylene deuterons, downfield ones for the α-methylene deuterons of β-alaninate arms in $[\mathrm{CrL^2}]^-$,[7] in which case four bonds intervene between the central ion and the deuterons. Therefore, the spin polarization mechanism is operative for $^2$H n.m.r. shifts of chromium(III) complexes; as expected, down- and up-field contact shifts correspond to alternative positive and negative spin density for α-methylene deuterons of β-alaninate arms and the acetate methylene deuterons, respectively, though some exceptions for the G-ring acetate methylene deuterons are observed.* This trend in the n.m.r. shifts is opposite to that of nickel(II) complexes,[8–10] but the same as that of low-spin iron(III) complexes.[15]

For the present chromium(III) complexes it is possible to correlate the chelate ring deformation with the isotropic contact shifts through a Karplus-like or $\cos^2\theta$ relation, where the dependence of the contact shifts on the dihedral angle in the D–C–N–Cr fragment is formulated by analogy with that of the vicinal coupling in the diamagnetic H–C–C–H fragment proposed by Karplus,[16] as applied to the $^1$H n.m.r. spectra of nickel(II) complexes.[8–10] Since the variable-temperature n.m.r. shifts of *cis*(N)-$[\mathrm{CrL^1{}_2}]^-$ are found to obey the Curie law, the conformational interconversion for the chelate rings of this type of complexes in solution is slow on the n.m.r. time-scale. This

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* The exceptionally large downfield shifts [$\mathrm{G_B}$ deuterons of complexes (**1**)—(**3**) in Figure 1] may be due to the large contribution from the σ spin delocalization.

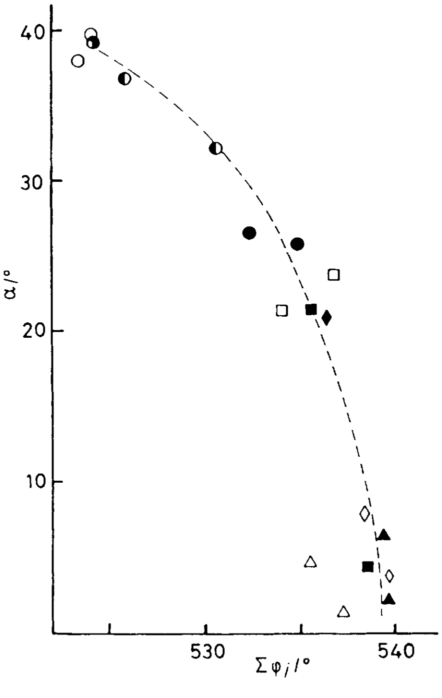

**Figure 5.** Relation between the sum of the five-membered chelate ring internal angles ($\Sigma\varphi_i$) and the torsion angles Cr–N–C–C(O) ($\alpha$): ○, △ Na[Cr(cdta)]·4.5$H_2O$;[18] ○, ◇ Na[Cr(1,3-pdta)]·3$H_2O$ (R. Heral, G. Srdanov, M. I. Djuran, D. J. Radanovic, and M. Bruro, *Inorg. Chim. Acta*, 1984, **83**, 55); ●, ▲ K[Cr(ida)$_2$]·3$H_2O$ (D. Mootz and H. Wunderlich, *Acta Crystallogr., Sect. B*, 1980, **36**, 445); ○, ◆ [Cr($H_2O$)(Hedta)];[20] □, *sym-cis*-[$Cr_2(OH)_2(edda)_2$]·4$H_2O$ (G. Srdanov, R. Heral, D. J. Radanovic, and D. S. Vesellinovic, *Inorg. Chim. Acta*, 1980, **38**, 37); ■, $(-)_{589}$-Li[Cr(eddadp)]·5$H_2O$ (R. T. Helm, W. H. Radanovic, and B. E. Douglas, *Inorg. Chem.*, 1977, **16**, 2351).

The circles refer to the G rings, and the triangles, rhombi, and squares to the R rings. The superscripts indicate the references in which the *X*-ray structural data are cited. Abbreviations: cdta = *trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetra-acetate; 1,3-pdta = propane-1,3-diamine-*N*,*N*,*N*′,*N*′-tetra-acetate; ida = iminodiacetate; edda = ethylenediamine-*N*,*N*′-diacetate; eddadp = ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionate

suggests that the chelate conformation in solution is virtually 'frozen' and comparable with that in crystals. The ring deformation of five-membered amino acidato chelates may be represented by the sum of the internal angles ($\Sigma\varphi_i$) in the rings as postulated previously.[17] Indeed the sum of these angles for the edta-like complexes is related with the torsion angles ($\alpha$) between the Cr–N–C and N–C–C(O) planes in the Cr–N–C–C(O) fragment of the glycinate chelates (Figure 3) as shown in Figure 5. The angles $\alpha$ have not only more direct stereochemical implications than the former ($\Sigma\varphi_i$), but can also be associated with the $^2H$ n.m.r. signals through the $\cos^2\theta$ relation. Therefore, these angles will be used to explore the relationship with the $^2H$ n.m.r. chemical shifts.

Figure 6 illustrates the fair correlation between the $^2H$ n.m.r. signals and the torsion angles for the Cr–N–C–C(O) chains of the glycinate chelates in the present complexes. This tendency is accounted for by the $\cos^2\theta$ relation. Since equatorial methylene deuterons on G-ring chelates for some complexes give exceptional downfield n.m.r. shifts as shown in Figure 1, it is difficult to apply the $\cos^2\theta$ relation directly to the observed chemical shifts. In this case, it is appropriate to relate the difference between the chemical shifts for the vicinal deuteron signals to the structural parameters such as the torsion angles. That is, the $\cos^2\theta$ relation gives equations (1) and (2) for the A (axial) and B (equatorial) vicinal deuterons as shown in Figures 2 and 3, respectively. Thus the difference between their n.m.r. shifts is expressed as in equation (3), where the angles $\alpha$ are previously defined as in Figure 3 (taking a positive sign for clockwise rotation) and *c* is a constant including the spin density.

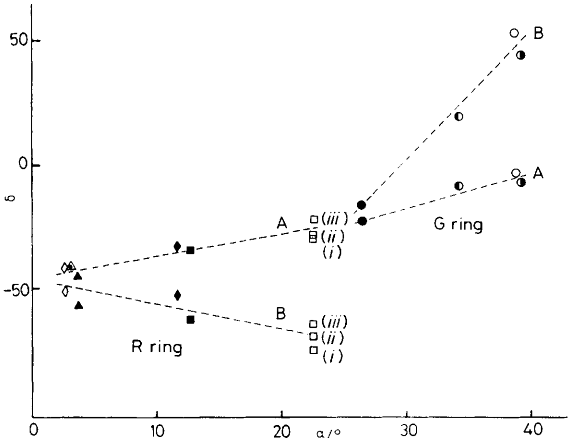

**Figure 6.** Correlation between the torsion angles ($\alpha$) of the glycinate chelate rings in the all protic complexes (average value for two symmetry-equivalent R and/or G rings) and the $^2H$ n.m.r. chemical shifts of the glycinate methylene deuterons: symbols used as in Figure 5; $^2H$ n.m.r. data from ref. 5 are for (*i*) *sym-cis*-[$Cr(H_2O)_2L^7$]$^+$, (*ii*) *sym-cis*-[$CrL^7(ox)$]$^-$ (ox = oxalate) and (*iii*) *sym-cis*-[$CrL^7(mal)$]$^-$

$$\delta_A = C\cos^2\theta \tag{1}$$

$$\delta_B = C\cos^2(\theta + 120°) \tag{2}$$

$$\Delta\delta_{A,B} = \delta_A - \delta_B = -\sqrt{3}/2\, C\sin(2\alpha) \tag{3}$$

The correlation between the shift difference $\Delta\delta_{A,B}$ and the angles $\alpha$ in Figure 6 is in accordance with that expected from equation (3) in both the R- and G-ring cases; $\alpha$ increases with increasing $\Delta\delta_{A,B}$ regardless of the signs. Our recent *X*-ray structure analysis of Na[Cr(*rac*-cdta)]·4.5$H_2O$ (cdta = *trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetra-acetate) reveals an almost planar conformation ($\alpha$ = *ca.* 4°) of the R-ring glycinate chelates.[18] This is consistent with the prediction from an accidentally coincident $^2H$ n.m.r. signal (*i.e.* $\Delta\delta_{A,B} = 0$) of the R-ring methylenes for this complex as in Figure 1. For [$CrL^3$]$^-$ the *trans* ($O_5$) isomer with two glycinate chelates in the R rings gives only one signal for the rings, whereas the *trans* ($O_5O_6$) isomer with one glycinate and one β-alaninate chelate in the R ring exhibits one signal for the G ring and two for the R rings with $\Delta\delta_{A,B}$ *ca.* 17 p.p.m.[7] This n.m.r. behaviour suggests that the R-ring conformation in the *trans* ($O_5$) isomer and the G-ring one in the *trans* ($O_5O_6$) isomer are almost planar, and that the degree of non-planarity or puckering for the R-ring conformation in the *trans* ($O_5O_6$) isomer is similar to that of the R-ring one in [Cr(edta)]$^-$.

Moreover, the signs of the shift difference $\Delta\delta_{A,B}$ may give some information on the ring conformation of the glycinate chelates. The $\Delta\delta_{A,B}$ values for the G- and R-ring methylene deuterons are negative and positive, respectively, according to the n.m.r. signal assignments for the deuterons as shown in Figure 6. Therefore, a negative and positive sign of the torsion angles ($\alpha$) is assumed for the Cr–N–C–D chains in the G- and R-ring methylenes, respectively, from equation (3) with a negative spin density ($C < 0$). This results in δ and λ conformations, as defined for chiral puckered or asymmetric envelope conformations,[19] for the G- and R-ring chelates, respectively, in the

$\Delta(\Delta\Lambda\Delta)$ absolute configuration around a central metal ion, and $\lambda$ and $\delta$ for the G and R rings, respectively, in the $\Lambda(\Lambda\Delta\Lambda)$ configuration. Such conformations are in accord with those obtained for the G ring, but not always for the R ring by *X*-ray structure analyses.[18,20] This fact may reflect the difference in conformational lability of the chelate rings: flexibility for the R-ring chelate and rigidity for the G-ring one, as manifested by the *X*-ray structural studies and conformational analyses.[18,20–22]

It is concluded that the usefulness of $^{2}$H n.m.r. spectroscopy in the study of the solution stereochemistry of various kinds of inert mixed-ligand chromium(III) complexes can be extended to chelate ring conformations other than those studied previously,[2–7] surpassing the utility of $^{1}$H and $^{13}$C n.m.r. spectroscopy for octahedral labile nickel(II) complexes.[8–10,23–25]

## Acknowledgements

We greatly acknowledge Professor J. Ivan Legg of Washington State University, presently of Auburn University (Alabama), for making available the $^{2}$H n.m.r. measurements of a few complexes.

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*Received* 19*th September* 1988; *Paper* 8/03564D