# $^2$H NMR spectra for mixed ligand chromium(III) complexes with deuteriated malonato and acetylacetonato ligands

Sumio Kaizaki*
*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560 (Japan)*

Naoko Hirota, Chikage Tanaka, Junko Tano
*Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630 (Japan)*

Liu Xi Lan
*Department of Chemistry, Sichuan Teachers College, Nanchog 637002 (China)*

and J. Ivan Legg**
*Department of Chemistry, Washington State University, Pullman, WA, 99164-4630 (USA)*

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**Abstract**

$^2$H NMR chemical (isotropic contact) shifts of various kinds of mixed ligand paramagnetic chromium(III) complexes with deuteriated malonato and/or acetylacetonato ligands were measured and discussed in relation to the relative positions of the deuterons in ligands with respect to the remaining coordination atoms. The contact shifts of methylene deuterons of the malonato ligands were found to be remarkably sensitive to ligating atoms located at the coordination site perpendicular to the malonato chelate plane, depending on the kind of ligating atoms, i.e. oxygen or nitrogen, and moreover on subtle differences of identical ligating atoms, e.g. primary or secondary amines. On the other hand, the contact shifts of the methyl deuterons of the acetylacetonato ligand are susceptible to the change of the ligating atoms at the coordination site coplanar with the acetylacetonato chelate plane.

## Introduction

Since the first demonstration of the routine utility of $^2$H NMR spectra for determining the solution structure of chromium(III) complexes in 1982 [1], a number of applications of $^2$H NMR spectra to the stereochemical and electronic properties of Cr(III) complexes have been made [1–14]. $^2$H NMR spectra for chromium(III) complexes with the orbitally non-degenerate electronic ground state have been found to be due to the isotropic contact shifts as in the case of octahedral Ni(II) complexes [12–15]. Moreover, the $^2$H NMR signals exhibit significant line narrowing by a factor of about 40. Accordingly, an enhancement in total resolution of about 6.5 is a big advantage in favor of using $^2$H NMR spectra compared with $^1$H NMR [1]. However, there has been no systematic study to indicate the more general usefulness of $^2$H NMR contact shifts as related to the electronic effects of the ligating atoms in mixed ligand chromium(III) complexes, other than the solvent and axial-ligand dependence of $^2$H NMR shifts for *trans*-$[CrX_2(N)_4]$ type complexes [14].

This paper deals with the positional dependence of $^2$H NMR isotropic contact shifts of the malonato methylene and acetylacetonato methyl deuterons in various kinds of mixed ligand chromium(III) complexes. On these experimental bases, the origin of the contact shifts will also be examined.

## Experimental

### *Materials*

The ligands are abbreviated as follows: mal = malonate; ox = oxalate; nta = nitrilotriacetate; $\beta$-alada = $\beta$-alanine-*N*,*N*-diacetate($^-$OOCCH$_2$CH$_2$N(CH$_2$CO-O$^-$)$_2$); acacBr = 3-bromoacetylacetonate; acaNO$_2$ = 3-nitroacetylacetonate; tfa = trifluoroacetylacetonate; Hmalon = malonaldehyde (1,3-propanedial); 3,2,3-

*Author to whom correspondence should be addressed.
**Present address: Auburn University, Auburn, AL, USA.

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tet = 1,4,7,10-tetraazadecane ($NH_2CH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2NH_2$); 2,3,2-tet = 1,4,8,11-tetraazaundecane ($NH_2CH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2NH_2$); amp = 2-aminomethylpyridine; edda = ethylenediamine-*N*,*N*′-diacetate ($^-OOCCH_2NHCH_2CH_2NHCH_2COO^-$); 1,3-pdda = 1,3-propanediamine-*N*,*N*′-diacetate ($^-OOCCH_2NHCH_2CH_2CH_2NHCH_2COO^-$). Other ligands are abbreviated according to ref. 16.

The following complexes were prepared by the literature methods; $K_3[Cr(mal)_3]\cdot 3H_2O$ [17], *cis*-, *trans*-$K[Cr(mal)_2(H_2O)_2]\cdot 3H_2O$ [17], $Na[Cr(mal)_2(en)]\cdot 0.5H_2O$ [18], *trans*-$Na[Cr(mal)_2(py)_2]\cdot 2H_2O$ [19], *cis*-$Li[Cr(mal)_2(py)_2]\cdot 3.5H_2O$ [19], $Na[Cr(mal)_2(N,N\text{-}Me_2\text{-}en)]\cdot 2.5H_2O$ [19], $Na[Cr(mal)_2(amp)]\cdot 2.25H_2O$ [19], $Ca[Cr(mal)_2(gly)]\cdot 0.15CaBr_2\cdot 0.5CH_3OH\cdot 4H_2O$ [19], $K_3[Cr(mal)_2(ox)]\cdot 3H_2O$ [19], $Na_2[Cr(mal)_2(acac)]\cdot 2.5H_2O$ [19], $[Cr(mal)(en)_2]Cl$ [20], $[Cr(acac)_3]$ [21], $[Cr(acaBr)_3]$ [22], $[Cr(acaNO_2)_3]$ [23], $K_2[Cr(acac)(nta)]$ [9], $[Cr(acac)_2(en)]Cl$ [24], $[Cr(acac)(en)_2]Cl_2$ [24], $[Cr(acaBr)(en)_2]Cl_2$ [24], $[Cr(malon)_3]$ [25], $[Cr(acac)_2(bpy)]Cl$ [26]. These complexes were identified by means of absorption spectra. Two isomers have been found for some *cis*-bis(malonato) complexes [19], but the NMR data for only one of them (*cis*-I isomer) are presented here.

The corresponding deuteriated malonato complexes were obtained by deuteriating the protic ones in weakly basic $D_2O$ solutions around pH 8. Deuteriated acetylacetone was prepared by the method of Egan *et al.* [27]. Partially deuteriated $[Cr(acac\text{-}d_7)_3]$ and $[Cr(tfa\text{-}d_4)_3]$ were obtained by the direct preparative method of Sharma and Bhasin for $[Cr(acac)_3]$ with use of potassium dichromate in $D_2O$ instead of $H_2O$ [28]. $^2H$ NMR spectra showed the partial incorporation of $^2H$ into the methyl groups as well as the 3-methine of the acac and tfa ligands. Partial deuteriation of Hmalon (1,3-propanedial) was performed by using $D_2O$ for the reaction of tetraethoxypropane with $H_2O$ [25].

*Preparation of $Na[Cr(mal)_2(bpy)]\cdot 2.5H_2O$*

One gram of $[CrCl_3(dmf)(bpy)]$ was dissolved in 10 $cm^3$ of a $H_2O$–dmf (1:1) mixture containing 0.54 g of malonic acid and 0.54 g of sodium carbonate by heating on a hot plate. For a while, the reaction mixture changed to red solution. This was filtered off. After the filtrate was allowed to stand in a refrigerator overnight, red crystals were obtained. These were dissolved in methanol and filtered off to remove a violet compound. Ether was added to the filtrate and a red precipitate was obtained. This was recrystallized from water and ethanol. *Anal.* Calc. for $Na[Cr(mal)_2(bpy)]\cdot 2.5H_2O$, $CrNaC_{16}H_{17}O_{10.5}N_2$: C, 40.01; N, 3.57; H, 5.83. Found: C, 40.14; H, 3.50; N, 5.73%.

*Preparation of $[Cr(mal)(3,2,3\text{-tet})]Cl\cdot 1.5H_2O\cdot 0.3KCl$*

A mixture of *trans*-$[CrCl_2(3,2,3\text{-tet})]Cl\cdot H_2O$ (1.6 g), malonic acid (0.6 g) and KOH (0.6 g) in 150 $cm^3$ of $H_2O$ was heated on a water bath for about 6 h, and was condensed to about 10 $cm^3$. The addition of acetone to this solution gave an oily substance. This was extracted with methanol to give a red–violet solution. After filtration, 100 $cm^3$ of acetone was added to the filtrate. This procedure was repeated twice. Finally, the methanol extract was condensed to dryness. The precipitate was recrystallized from water and acetone. *Anal.* Calc. for $[Cr(mal)(3,2,3\text{-tet})]Cl\cdot 0.3KCl\cdot 1.5H_2O$, $CrK_{0.3}Cl_{1.3}C_{11}H_{27}O_{5.5}N_4$: C, 31.98; H, 6.59; N, 13.56. Found: C, 31.57; H, 6.66; 13.65%.

*Preparation of $[Cr(mal)(2,3,2\text{-tet})]Cl\cdot 2.5H_2O$*

This was prepared from *cis*-$[CrCl_2(2,3,2\text{-tet})]Cl\cdot H_2O$ by a method similar to that for the corresponding 3,2,3-tet complex. *Anal.* Calc. for $[Cr(mal)(2,3,2\text{-tet})]Cl\cdot 2.5H_2O$, $CrClC_{10}H_{27}O_{6.5}N_4$: C, 30.40; H, 6.84; N, 14.18. Found: C, 30.93 H, 6.80; N, 14.11%.

*Preparation of $Ba[Cr(mal)_2(tfa)]\cdot 2.5H_2O$*

This was prepared by a method similar to that for $Na_2[Cr(mal)_2(acac)]$ as described previously [19]. *Anal.* Calc. for $Ba[Cr(mal)_2(tfac)]\cdot 2.5H_2O$, $CrBaF_3C_{11}H_{13}O_{12.5}$: C, 22.34; H, 2.22. Found: C, 22.76; H, 2.21%.

*Preparation of $[Cr(acac)_2(gly)]$*

To an aqueous solution of *trans*-$[Cr(acac)_2(H_2O)_2]ClO_4\cdot 2H_2O$ (0.1 g, 0.0024 mol $dm^{-3}$) was added an equimolar amount of glycine and sodium hydroxide. The mixture was warmed at 50 °C for 0.5 h. The color of the solution changed from brown to red–violet. An SP-Sephadex column chromatography for the reaction solution by eluting with water was performed in order to remove the starting cationic complex. The red eluate of $[Cr(acac)_2(gly)]$ was condensed almost to dryness by a vacuum rotary evaporator. Recrystallization was carried out with methanol and ether. *Anal.* Calc. for $[Cr(acac)_2(gly)]$, $CrC_{12}H_{18}O_6N$: C, 44.45; H, 5.59; N, 4.32. Found: C, 43.62; H, 5.58; N, 4.40%.

*Measurements*

The absorption spectra were recorded in aqueous solution with a Shimadzu UV-240 spectrophotometer. The $^2H$ NMR spectra were measured at ambient temperature as previously described in detail [3] with a Nicolet NT-200WB at Washington State University and/or a Jeol 270 GX spectrometer at Nara Women's University and a Jeol 270 GSX or 400 GSX spectrometer at Osaka University. The spectra were reported relative to $CDCl_3$ at +7.26 ppm (by sample replacement). The samples (*c.* 0.05 mol $dm^{-3}$) were dissolved in

0.0005–0.001 mol $dm^{-3}$ $HClO_4$ solution for the malonate complexes and in aqueous solution for the acetylacetonato mixed ligand complexes except for the tris(acac) type complexes for which chloroform was used. For the malonato complexes, data were collected within several minutes in order to avoid protonation of the malonate methylene deuterons.

X-ray powder patterns were obtained by the X-ray powder diffraction method (Rigaku RAD-ROC, Cu K$\alpha$) at the X-ray Diffraction Service of the Department of Chemistry of Osaka University.

## Results and discussion

### *$^2$H NMR spectra of malonato complexes*

In Table 1 are collected the $^2$H NMR chemical shifts together with the degeneracy of the deuteriated malonato complexes numbered with arabic numerals. Only one NMR signal is observed for *trans*-$[Cr(mal\text{-}d_2)_2(H_2O)_2]^-$ (**2**) and *trans*-$[Cr(mal\text{-}d_2)_2(py)_2]^-$ (**3**). The former one (**2**) is close to that for $[Cr(mal\text{-}d_2)_3]^{3-}$ (**1**), whereas the latter one (**3**) is shifted to higher field as shown in Table 1. This suggests that the NMR shifts depend mainly on the axial aqua oxygen and pyridine nitrogen ligating atoms, not on the basal malonato oxygen atoms. $[Cr(mal\text{-}d_2)_2(en)_2]^-$ (**4**) and *sym-cis*-[Cr(mal)-(3,2,3-tet)]$^+$ (**5**) complexes with $C_2$ symmetry give one NMR signal near 40 ppm, whereas two signals are observed for the unsym-*cis*-[Cr(mal)(2,3,2)-tet]$^+$ complex (**6**) with $C_1$ symmetry as shown in Fig. 1. This indicates that the $^2$H NMR signals for two deuterons of the malonato methylene are so sensitive as to be discriminated with respect to a subtle difference in the primary and secondary amines of the 2,3,2-tet ligand as shown in Fig. 2(a). Two inequivalent deuterons in the malonato methylene may be affected by the primary and secondary amines at the coordination site perpendicular (out-of-plane) to, but not coplanar (in-plane) with, the malonato chelate plane, because the distances from each of the outer-of-plane amines to two deuterons are inequal in contrast to the equal distance from the in-plane amines to the two deuterons as shown in Fig. 2(a).

A similar situation is encountered with *trans*(O)-$[Cr(mal\text{-}d_2)(O)_2(L)_2]$ type complexes. Among them, $^2$H NMR signals of the edda and nta type complexes substantiate the dominant influence of the out-of-plane ligating atoms. That is, unsym-$[Cr(mal\text{-}d_2)(\beta\text{-alada})]^{2-}$ (**10**) gives two well split signals with a small interval, whereas only one signal is observed for sym-*cis*-$[Cr(mal\text{-}d_2)(edda)]^-$ (**7**), $[Cr(mal\text{-}d_2)(nta)]^{2-}$ (**8**) and sym-$[Cr(mal\text{-}d_2)(\beta\text{-alada})]^{2-}$ (**9**) as shown in Table 1. Therefore, it can be seen that the NMR shifts of the unsym-($\beta$-alada) complex (**10**) are influenced predominantly by both the ligating oxygen atoms of the out-of-plane five-membered acetate and six-membered propionate chelates as shown for $O_5$ and $O_6$ of (b) in Fig. 2, but not by the in-plane N and O ones. This behavior also manifests the high sensitivity to the subtle difference

TABLE 1. $^2$H NMR chemical shifts of the malonato Cr(III) complexes

| No. | Complex | Chemical shifts (ppm) (degeneracy) | | | |
|---|---|---|---|---|---|
| **1** | $[Cr(mal\text{-}d_2)_3]^{3-}$ [a] | | 29.0(6) | | |
| **2** | *trans*-$[Cr(mal\text{-}d_2)_2(H_2O)_2]^-$ | | 30.4(4) | | |
| **3** | *trans*-$[Cr(mal\text{-}d_2)_2(py)_2]^-$ [a] | | 21.0(4) | | |
| **4** | $[Cr(mal\text{-}d_2)(en)_2]^+$ | | 37.0(2) | | |
| **5** | sym-*cis*-$[Cr(mal\text{-}d_2)(3,2,3\text{-tet})]^+$ | | 38.3(2) | | |
| **6** | unsym-*cis*-$[Cr(mal\text{-}d_2)(2,3,2\text{-tet})]^+$ | | 41.1(1) | 34.7(1) | |
| **7** | sym-*cis*-$[Cr(mal\text{-}d_2)(edda)]^-$ [a] | | 30.0(2) | | |
| **8** | $[Cr(mal\text{-}d_2)(nta)]^{2-}$ [b] | | 31.0(2) | | |
| **9** | sym-$[Cr(mal\text{-}d_2)(\beta\text{-alada})]^{2-}$ [b] | | 29.0(2) | | |
| **10** | unsym-$[Cr(mal\text{-}d_2)(\beta\text{-alada})]^{2-}$ [b] | | 35.0(1) | 29.0(1) | |
| **11** | *cis*-$[Cr(mal\text{-}d_2)_2(H_2O)_2]^-$ | | 51.2(2) | 31.9(2) | |
| **12** | $[Cr(mal\text{-}d_2)_2(ox)]^{3-}$ | | 29.7(2) | 20.3(2) | |
| **13** | $[Cr(mal\text{-}d_2)_2(acac)]^{2-}$ | | 35.2(2) | 21.4(2) | |
| **14** | $[Cr(mal\text{-}d_2)_2(tfa)]^{2-}$ | 52.9(1) | 35.6(1) | 28.9(1) | 18.7(1) |
| **15** | $[Cr(mal\text{-}d_2)_2(en)]^-$ | 52.5(2) | | | −1.3(2) |
| **16** | $[Cr(mal\text{-}d_2)_2(bpy)]^-$ [a] | 57.0(2) | | | −4.0(2) |
| **17** | *cis*-$[Cr(mal\text{-}d_2)_2(py)_2]^-$ | 56.5(2) | | | −2.0(2) |
| **18** | unsym-*cis*-$[Cr(mal\text{-}d_2)(1,3\text{-pdda})]^-$ [c] | 56.0(1) | | | −1.0(1) |
| **19** | $[Cr(mal\text{-}d_2)_2(N,N\text{-}Me_2\text{-en})]^-$ | 61.6(2) | | 3.0(1) | −2.6(1) |
| **20** | $[Cr(mal\text{-}d_2)_2(amp)]^-$ | 54.2(1) | 51.1(1) | 3.2(1) | 1.2(1) |
| **21** | $[Cr(mal\text{-}d_2)_2(gly)]^{2-}$ | 52.5(1) | 38.9(1) | 23.4(1) | 4.8(1) |
| **22** | $[Cr(mal\text{-}d_2)(acac)_2]^-$ | | 27.8(2) | | |

Data taken from [a]ref. 1; [b]ref. 9; [c]ref. 6.

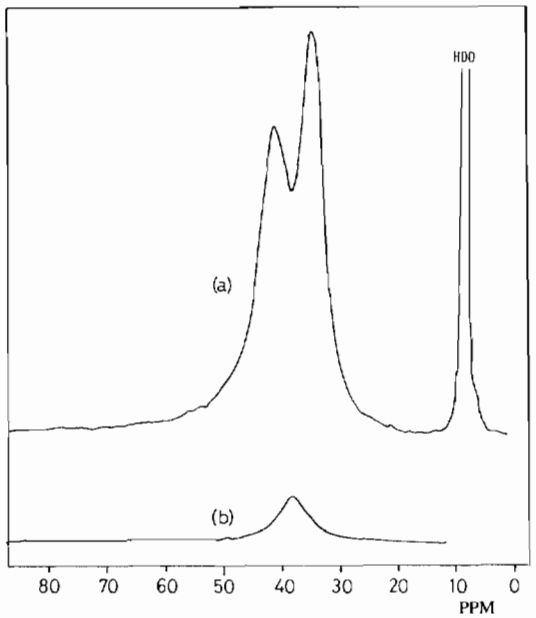


Fig. 1. $^2$H NMR spectra of unsym-*cis*-[Cr(mal-$d_2$)(2,3,2-tet)]$^+$ (**6**) (a) and sym-*cis*-[Cr(mal-$d_2$)(3,2,3-tet)]$^+$ (**5**) (b).

in the ligating carboxylate oxygens between the five- and six-membered N–O chelates at the out-of-plane coordination sites of the malonato chelate.

The *cis*-[Cr(mal-$d_2$)$_2$($O_2$)] type complexes are also expected to exhibit the discrimination in the ligating oxygens between the malonato and other ligands, since *cis*-[Cr(mal-$d_2$)$_2$($H_2O$)$_2$]$^-$ (**11**), [Cr(mal-$d_2$)$_2$(ox)]$^-$ (**12**) and [Cr(mal-$d_2$)$_2$(acac)]$^-$ (**13**) complexes have two inequivalent deuterons; one is located on the side of another malonato ligand and the other is close to the oxalato, aqua, or acac ligating oxygen *cis* to one malonato ligating oxygen under consideration as shown in Fig. 2(c). In these cases, the chemical shift differences are larger than that for unsym-[Cr(mal-$d_2$)($\beta$-alada)]$^{2-}$ (**10**) (Table 1 and Fig. 3(a)). This fact suggests that the differences in the Cr–O bond properties between the malonato ligating oxygen and the oxalato, aqua or acaç ones differ largely from those between the ligating carboxylate oxygens of the five-membered acetato and six-membered propionato chelates in the $\beta$-alada complex (**10**); the former being larger than the latter. As shown in Fig. 4(a), the bis(malonato)trifluoroacetylacetonato complex (**14**) gives four NMR signals, which correspond to four inequivalent malonato methylene deuterons. The chemical shifts range widely from 20 to 55 ppm irrespective of the $Cr(O)_6$ chromophore. This may indicate that the differences in Cr–O bonds between two inequivalent oxygen ligators of the trifluoroacetylacetonato ligand are larger than those between carboxylato oxygen ligators such as mal and ox.

Two large split signals near +55 and 0 ppm are observed for [Cr(mal-$d_2$)$_2$(en)]$^-$ (**15**), the corresponding

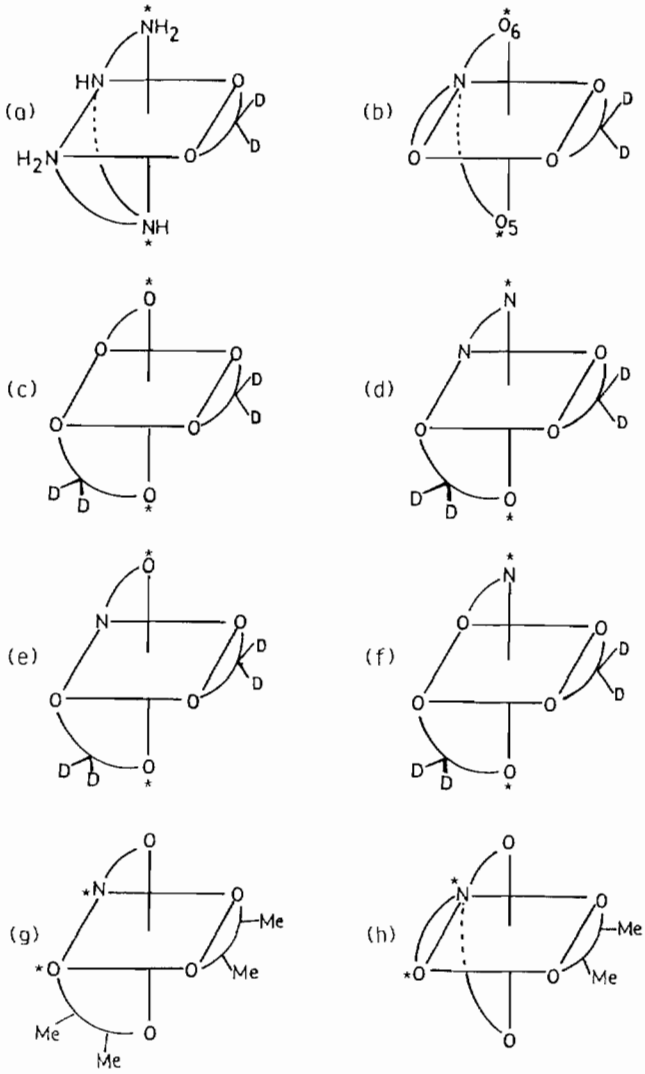


Fig. 2. Schematic structures showing the discriminations of deuterons by the out-of-plane and in-plane ligators (asterisked atoms) for the malonato complexes ((a)–(f): $O_5$ and $O_6$ in (b) refer to the five- and six-membered N–O chelates; (e) and (f) are from the different views for the same gly complex) and the acac complexes, respectively (see text).

2,2′-bipyridine (**16**) and *cis*-bis(pyridine) (**17**) complexes, and usym-*cis*-[Cr(mal-$d_2$)(1,3-pdda)]$^-$ (**18**) as shown in Table 1 and Fig. 3(c). Such remarkable differences may arise from the different influence to two inequivalent malonato deuterons from the amine nitrogen (en, bpy, py or 1,3-pdda) and another malonato or 1,3-pdda oxygen ligators both of which are located at the coordination site perpendicular to the malonato chelate in question as shown in Fig. 2(d). For the complex with two inequivalent nitrogen ligators such as [Cr(mal-$d_2$)$_2$(*N*,*N*-$Me_2$-en)]$^-$ (**19**) and [Cr(mal-$d_2$)$_2$(amp)]$^-$ (**20**) three or four signals are observed as shown in Table 1 and Fig. 4(b) and (c); each splitting observed around +55 and 0 ppm. These facts also manifest the high

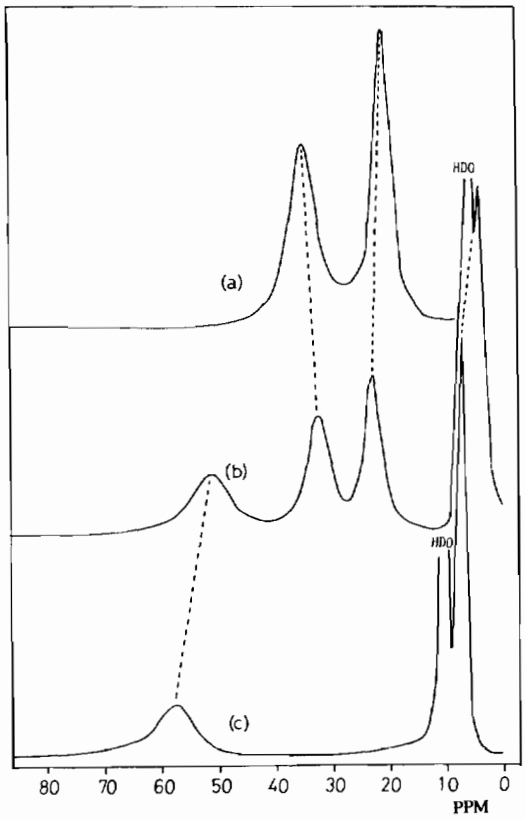


Fig. 3. $^2$H NMR signals for $[Cr(mal\text{-}d_2)_2(ox)]^{3-}$ (**12**) (a), $[Cr(mal\text{-}d_2)_2(gly)]^{2-}$ (**21**) (b), $[Cr(mal\text{-}d_2)_2(en)]^{-}$ (**15**) (c). The dotted lines indicate the connections according to the tentative assignments for the signals (see text).

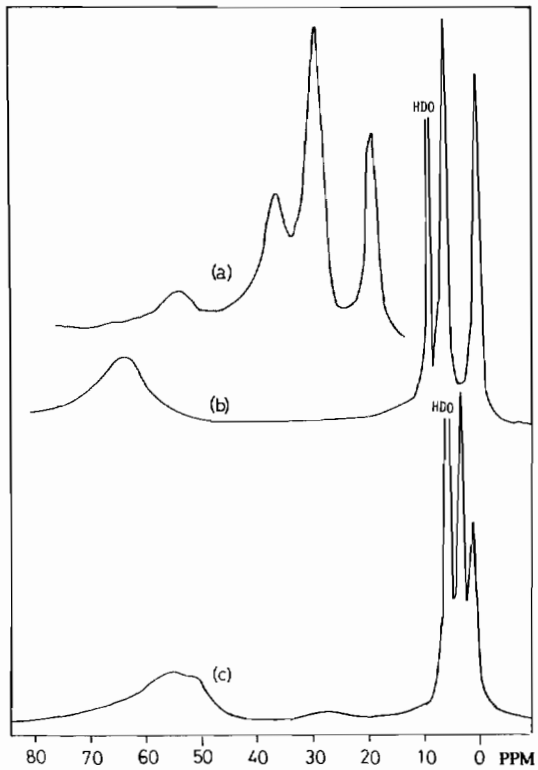


Fig. 4. $^2$H NMR spectra of $[Cr(mal\text{-}d_2)_2(tfa)]^{2-}$ (**14**) (a), $[Cr(mal\text{-}d_2)_2(N,N\text{-}Me_2\text{-}en)]^{-}$ (**19**) (b), and $[Cr(mal\text{-}d_2)_2(amp)]^{-}$ (**20**) (c).

sensitivity of the $^2$H NMR signals to subtle differences in nitrogen ligators.

$[Cr(mal\text{-}d_2)_2(gly)]^{2-}$ (**21**) with four inequivalent deuterons of the two malonato ligands is anticipated to give four NMR signals, because two of each malonato ligands ((e) and (f) in Fig. 2) are situated in the same circumstances as those for the bis(malonato)oxalato complex (**12**) and the bis(malonato)ethylenediamine complex (**15**) ((c) and (d) in Fig. 2), respectively. In fact, the observed NMR spectrum shows four signals as in Fig. 3(b). Each signal can correspond to those for the oxalato (**12**) and ethylenediamine (**15**) complexes as connected by the dotted lines in Fig. 3(a)–(c). Accordingly, the $^2$H NMR spectrum of this complex is considered to be the one superimposed between that of the oxalato and ethylenediamine complexes. In view of such superposition or additivity between the $^2$H NMR signals as well as the large difference in influence of the NMR signals from the out-of-plane ligators for *trans*-(N,O)-$[Cr(mal\text{-}d_2)(O)_2(N)_2]$ type complexes, the chemical shifts of $[Cr(mal\text{-}d_2)(O)_4]$ type complexes are predicted to differ significantly from those of $[Cr(mal\text{-}d_2)(N)_4]$ ones. This is not the finding shown in Table 1. Therefore, the imbalance in interaction between the metal ion and the out-of-plane ligators in a complex may result in the NMR shift differences.

From this evidence, the dependence of the $^2$H NMR shifts of the malonato deuterons on the out-of-plane ligators may be tentatively elucidated through the $\pi$ symmetry interaction with d orbitals of the Cr(III) ion according to the following consideration. A set of two C–H $\sigma$ bonds for the malonato methylene fragment forms a $b_1$ orbital when the malonato chelate is taken as the molecular ($yz$) plane in $C_{2v}$ point group. This orbital has $\pi$ bond type symmetry which can interact with the $d_\pi(b_1)$ orbital of the Cr(III) ion. Thus, it is likely that the chemical shift difference for the methylene deuterons results from the difference in the $\pi(b_1)$ type interactions between the $d_\pi$ orbitals and the out-of-plane ligators; e.g. for $[Cr(mal\text{-}d_2)_2(en)]^{-}$ (**15**) and related complexes showing large shift difference, no $\pi$ and $\pi$ acceptor interaction for Cr–N bonds in en and bpy or py, respectively, and $\pi$ donor one for Cr–carboxylato oxygen bonds are inferred on the basis of the angular overlap model (AOM) parameter values (expressed as $e_\pi(N)=0$ or $<0$ and $e_\pi(O)>0$) [29]. On the other hand, the small shift difference found for unsym-*cis*-$[Cr(mal\text{-}d_2)(2,3,2\text{-tet})]^{+}$ (**6**) and unsym-$[Cr(mal\text{-}d_2)(\beta\text{-alada})]^{2-}$ (**10**) may be due to the different geometrical distortions, probably leading to subtle dif-

ference in overlaps between the metal $d_\pi$ orbitals and the $\sigma$ and/or $\pi$ ones of out-of-plane ligators.

*Assignment of $^2H$ NMR signals*

Two large split $^2H$ NMR signals of $[Cr(mal\text{-}d_2)_2(en)]^-$ (**15**) exhibit the selective protonation of malonato methylene deuterons in aqueous solution. The lower field signal near +50 ppm disappears faster than the higher field one. From $^1H$ NMR spectra of cobalt(III) complexes, it is assumed in terms of the selective deuteriation that the faster deuteriated hydrogen of malonato methylenes in some $[Co(mal)_2(L)]$ type complexes, where L is ethylenediamine or *N,N*-dimethylethylenediamine, is the one which is closer to the chelate L [30]. On this basis, the faster disappearing (protonated) NMR signal of the malonato methylenes near +50 ppm in $[Cr(mal\text{-}d_2)_2(en)]^-$ (**15**) and the analogous complexes correspond to the deuterons closer to the ethylenediamine chelate, whereas the remaining signals around 0 ppm are due to those remote to the diamine chelates.

*$^2H$ NMR spectra of the acetylacetonato complexes*

$^2H$ NMR chemical shifts and the degeneracy for the deuteriated acetylacetonato complexes numbered with roman numerals are given in Table 2. The $^2H$ NMR spectra for methyl deuterons of the acetylacetonato ligands in the tris(acac-$d_6$) chromium(III) complex (**i**) has already been reported by Johnson and Everett in 1972 in their first paper demonstrating the measurable $^2H$ NMR spectra of paramagnetic metal complexes [31]. The present measurement of this complex gives an almost identical $^2H$ NMR spectrum with the reported one. $[Cr(acac\text{-}d_6)(O)_4]$ type complexes (**i, ii, iii**) exhibit only one NMR signal in nearly the same region as each other. As the number of nitrogen ligators in this type of complex increases by substituting nta, en and bpy ligands for the acac as in the **v, vi, vii** and **viii** complexes, the NMR signals of the acac are shifted to lower field as shown in Table 2. Moreover, the gly and nta complexes (**iv, v**) exhibit two $^2H$ NMR signals with small intervals as shown in Fig. 5, whereas only one signal is observed for the ethylenediamine complex (**vi**). This NMR behavior is in contrast to that of the corresponding malonato complexes as mentioned before. Since two methyl deuterons in the acac complexes are located at unequal distances from the in-plane ligators coplanar with the acac chelate, but at an equal distance from the out-of-plane atoms as shown in Fig. 2(g) and (h), the two NMR signals for the nta complex (**v**) may be due to the discrimination of two methyl groups in the acac ligand with respect to the oxygen and nitrogen ligators of nta both of which are coplanar with the acac chelate. The two signals observed for the bis(acac)glycinato complex (**iv**) with 3:9 integrated intensity ratio confirms this discrimination. In this case, it is likely that the differences in the $\sigma$ bond type interactions between Cr(III) and in-plane ligators are responsible for the discrimination by the in-plane ligating atoms according to the following consideration assuming the $C_{2v}$ point group similarly to the case of the malonato complexes. Unlike the malonato ligand, a set of two C–$CH_3$ $\sigma$ bonds of the acac ligand forms a $b_2$ orbital, which has the $\sigma$ bond symmetry with respect to the central metal d orbital. The orbital can interact with the $d_\sigma$ ($b_2$) orbitals of the Cr(III) ion through the C–O $\sigma$ bond ($b_2$) orbitals in the acac ligand. Therefore, the NMR signals of the acac complexes may be affected by the $\sigma$ bonds between the Cr(III) and the in-plane ligating atoms *trans* to the acac oxygen ligators. This is in keeping with the insensitivity of the NMR shifts to the in-plane nitrogen or oxygen ligators, because Cr–ligand $\sigma$ interactions are not so different from each other as revealed from the AOM parameter values

TABLE 2. $^2H$ NMR chemical shifts of the acetylacetonato Cr(III) complexes

| No. | Complexes | Chemical shifts (ppm) (degeneracy) | | |
|---|---|---|---|---|
| **i** | $[Cr(acac\text{-}d_7)]_3$ | 39.0(18) | | 28.0(3)[a] |
| **ii** | $[Cr(mal)(acac\text{-}d_6)_2]^-$ | 38.5(12) | | |
| **iii** | $[Cr(mal)_2(acac\text{-}d_6)]^{2-}$ | 38.1(6) | | |
| **iv** | $[Cr(acac\text{-}d_6)_2(gly)]$ | 46.6(3) | 42.0(9)[b] | |
| **v** | $[Cr(acac\text{-}d_6)(nta)]^-$ | 44.0(6) | 42.7(6) | |
| **vi** | $[Cr(acac\text{-}d_6)_2(en)]^+$ | 45.1(12) | | |
| **vii** | $[Cr(acac\text{-}d_6)_2(bpy)]^+$ | 49.5(12) | | |
| **viii** | $[Cr(acac\text{-}d_6)(en)_2]^{2+}$ | 61.1(6) | | |
| **ix** | *mer*-$[Cr(tfa\text{-}d_4)_3]$ | 59.8(9) | | 28.7(3)[a] |
| **x** | $[Cr(malon\text{-}d_3)_3]$ | 23.0(6) | | −8.50(3)[a] |
| **xi** | $[Cr(acaBr\text{-}d_6)_3]$ | 41.0(18) | | |
| **xii** | $[Cr(acaNO_2\text{-}d_6)_3]$ | 43.0(18) | | |

[a]The signal for the 3-deuteron of the $\beta$-diketones. [b]From the relative integrated intensities.

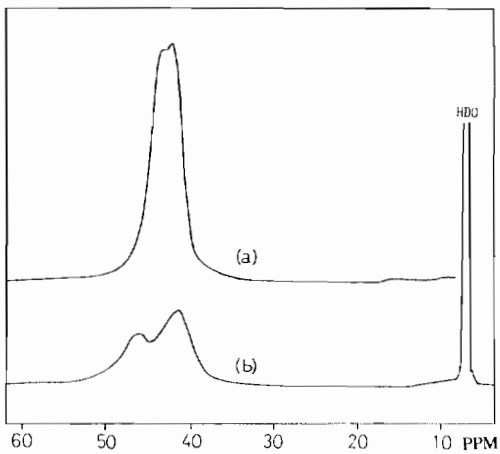


Fig. 5. $^2H$ NMR spectra of $[Cr(acac\text{-}d_6)(nta)]^-$ (**v**) (a) and $[Cr(acac\text{-}d_6)_2(gly)]$ (**iv**) (b).

(expressed as $e_\sigma$ (N) and $e_\sigma$(O) for the N and O ligators, respectively [32]).

$Cr(tfa\text{-}d_4)_3$] (**ix**) prepared in $D_2O$ by Sharma's direct method [28] was found to take the *mer* structure from the absorption spectra, X-ray powder pattern and melting point data, though two *mer* and *fac* geometrical isomers of this complex were prepared and separated by a different method [33]. Only one set of $^2H$ NMR signals is observed for the methyl and methine deuterons at 59.8 and 28.7 ppm, respectively, as previously reported [34], though two sets of signals are expected for this *mer*-type complex. This is in accordance with the fact that $^2H$ NMR signals for $\beta$-diketonato methyl groups are insensitive to the difference in the in-plane ligators as found for the mixed ligand acac complexes.

*The origin of contact shifts*

Most of the malonato complexes exhibit $^2H$ NMR contact shifts at low field. This may be accounted for in terms of the spin-polarization mechanism for four intervening bonds between a Cr(III) ion and deuterons as proposed previously [12].

The $^2H$ NMR spectra of $[Cr(malon\text{-}d_3)_3]$ (**x**) which are partially deuteriated at 2- and 1,3-methines show two signals. These signals at 23 and $-8.5$ ppm are assigned to 2-methine and 1,3-methine deuterons, respectively, as compared with the $^2H$ NMR spectra of $[Cr(acac\text{-}d_6)_3]$ with only deuteriated methyls and $[Cr(acac\text{-}d_7)_3]$ with both methyl and methine deuterons. This behavior of the contact shifts is consistent with that predicted by the spin-polarization mechanism. The alternation of the spin or sign inversion of the contact shifts occurs from 2,4-methyl deuterons in the acac complex to 1,3-methine ones in the malon one. That is, four bonds intervene between a Cr(III) ion and deuterons of the 2-methine and the 2,4-methyl, respectively, for the malon and the acac complex, whereas there is a three-bond intervention for the 1,3-methine deuteron of the malon. Moreover, the contact shifts of methyl groups for the 3-bromo- or 3-nitro-substituted acetylacetonato complex (**xi** or **xii**) are not so much different from each other as shown in Table 2, in spite of the significant change of the intraligand $\pi$–$\pi^*$ and/or charge transfer $d_\pi$–$\pi^*$ transition energies on going from the acac (**i**) to the acaBr or $acaNO_2$ complexes (**xi** or **xii**) [22, 24]. This suggests that the spin-polarization mechanism through the $\sigma$ bonding, not through the $\pi$ one, is operative in accordance with the results from the positional dependence of the in-plane ligating atoms for the acac complexes, but contrary to the previous theoretical study based on the INDO calculation, which was carried out by taking into consideration both the ligand-to-metal and metal-to-ligand spin transfers involving the $\pi$ bonding and $\pi^*$ antibonding orbitals [35].

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