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^{13}C NMR Study of the Cobalt(III) Complexes Containing Ethylenediamine-*N*-acetate (edma): [Co(edma)$_2$]$^+$ and [Co(ida)(edma)]

Tomoharu Ama,* Hiroshi Kawaguchi, and Takaji Yasui
Department of Chemistry, Faculty of Science, Kochi University,
Akebono-cho, Kochi 780

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The ^{13}C NMR chemical shifts of the glycinate ring (G-ring) carbons of edma's in the six geometrical isomers of [Co(edma)$_2$]$^+$ were measured. It was shown that the trans ligands and chelation form (meridional or facial form) influence the ^{13}C NMR chemical shifts of the G-ring carbons in the same way as the magnetic anisotropy generated on the cobalt(III) center does. The chemical shifts of the ethylenediamine ring (E-ring) carbons of coordinating edma's were also influenced by the trans ligands and the chelation form, similarly to those of the G-ring carbons. Four geometrical isomers of [Co(ida)(edma)] were newly prepared and their structural assignments were made according to their ^{13}C NMR behavior.

It is known that the ^{13}C NMR chemical shifts of a ligand in the cobalt(III) complexes are influenced by the magnetic anisotropy of the cobalt center,[1] the chelation forms[2,3] (e. g. mer- and fac- forms), and the nature of the ligating atom in the trans position to the ligand. The latter influence has been studied for the glycinate ligand in the [Co(ox)$_x$(gly)$_y$(en)$_z$] ($x+y+z=3$) series by Juranic et al.[4] However, their results have not yet been applied to the complexes of polydentate ligands having glycinate rings (G-ring).

In previous papers,[5,6] the structural assignments of the geometrical isomers of [Co(edma)$_2$]$^+$ (edma: $NH_2CH_2CH_2NHCH_2COO^-$) were reported. In this work we expand the results of Juranic et al. to the G-ring and to the ethylenediamine ring (E-ring) of edma in the six isomers of [Co(edma)$_2$]$^+$ and clarify which factor is the most important one to evaluate the ^{13}C chemical shifts of the coordinating edma's, comparing the three influences mentioned above. The result obtained for the [Co(edma)$_2$]$^+$ complex are applied to the newly prepared isomers of [Co(ida)(edma)] (ida: $NH(CH_2COO^-)_2$). The geometrical structures of the latter are discussed on the basis of absorption and ^{13}C NMR spectral data.

Experimental

Preparation of the Complexes. Four Isomers of the [Co(ida)(edma)] Complex: A solution containing 2.4 g of $CoCl_2\cdot 6H_2O$, 1.3 g of iminodiacetic acid (H$_2$ida) and 2.3 g of ethylenediamine-*N*-acetic acid dihydrochloride dihydrate (Hedma·2HCl·2H$_2$O) in 100 cm^3 of water was adjusted to pH 5 with a 2 mol dm^{-3} NaOH solution. The pH being kept constant at 5, 24 g of PbO_2 was stirred into the solution in small portions at 30 °C. After 1 h, insoluble materials were removed by filtration. A solution containing neutral complexes was obtained by passing the filtrate through an SP-Sephadex (K$^+$ form) column and a QAE-Sephadex (SO_4^{2-} form) column (eluent: water). This solution was evaporated to about 10 cm^3 and poured onto a QAE-Sephadex (Cl$^-$ form) column. A band adsorbed on the column was separated into three parts by recyclic developement with water: The first, a brown band; the second, two overlapped bands (violet and red-brown); and the third, a pink band. The second part was repeatedly developed on a QAE-Sephadex column (SO_4^{2-} form), by which means the violet (earlier eluate) and the red-brown (later eluate) bands were separated. Each solution eluted from the four bands was concentrated under reduced pressure, after which methanol was added to the concentrated solution to obtain crystals. Recrystallization was carried out from water by adding methanol except for the pink isomer which was recrystallized from warm water. Yields: The brown, 320 mg; the violet, 570 mg; the red-brown, 10 mg; and the pink isomer, 300 mg. Found for the brown isomer: C, 30.86; H, 4.76; N, 13.53%. Calcd for [Co(ida)(edma)]=$C_8H_{14}N_3O_6Co$: C, 31.28; H, 4.59; N, 13.68%. Found for the violet isomer: C, 29.24; H, 5.14; N, 12.74%. Found for the red-brown isomer: C, 29.54; H, 5.01; N, 12.96%. Found for the pink isomer: C, 29.51; H, 5.06; N, 12.90%. Calcd for [Co(ida)(edma)]·H$_2$O=$C_8H_{16}N_3O_7Co$: C, 29.55; H, 4.96; N. 12.92%.

Six Isomers of the [Co(edma)$_2$]X Complex: The preparation and separation were described in our previous paper.[5,6]

Spectral Measurements. The ^{13}C NMR spectra of the isomers were recorded on a JEOL FX-100 spectrometer, in the pulsed Fourier transform/proton noise decoupled mode. The field frequency ratio was stabilized by locking to internal D$_2$O. The peak positions were measured relative to internal dioxane (δ=67.40). No ^{13}C NMR spectra were obtained for the pink isomer of [Co(ida)(edma)] because of its low solubility in D$_2$O.

The two $-\underline{C}H_2-$ carbons neighboring to –NH– in coordinating edma ($-\underline{C}H_2NH\underline{C}H_2-$) were distinguished from one another by means of the ^{1}H selective decoupling method as the carbons were observed in the close magnetic fields in each isomer of [Co(edma)$_2$]$^+$; the methylene carbon of the G-ring appeared as a singlet peak when the glycinate $-CH_2-$ protons were decoupled. The signals which appeared near δ=180 and 40 were assigned to $-\underline{C}OO^-$ and $-\underline{C}H_2NH_2$ carbons, respectively.

The visible and UV absorption spectra were recorded on a HITACHI 557 spectrophotometer in aqueous solutions.

Results and Discussion

The numbering of the carbons in an edma ligand is as follows.

NH_2-CH_2-CH_2-NH-CH_2-COO^-
C-4 C-3 C-2 C-1

The $[Co(edma)_2]^+$ complex provides six geometrical isomers as shown in Fig. 1. The structural assignments of the geometrical isomers have been reported in the previous papers.[5,6] The ^{13}C NMR data of these isomers are listed in Table 1.

It is known that the chemical shifts of the ligands are influenced by the magnetic anisotropic effect of the cobalt(III) ion. The method of estimating this effect has been studied by Yoneda et al.[1] The anisotropy values (σ_{Co}) calculated for the coordinating edma's in $[Co(edma)_2]^+$ are presented in Table 1, together with the observed (δ^{obsd}) and corrected ($\delta^{cor}=\delta^{obsd}+\sigma_{Co}$) chemical shift values.

The ^{13}C NMR Chemical Shifts of the Complex Containing Facially Coordinating edma (*fac*-edma). The corrected chemical shift (δ^{cor}) of the C-1 carbons in coordinating edma's are classified into three types from the difference of two ligating atoms in the trans positions to two ligating atoms (N and O) of the G-ring of edma, as shown in Fig. 2(a); Types A, B, and C exhibit ^{13}C signals at lower, higher, and middle fields, respectively. Similarly to the C-1 carbons, the δ^{cor} values of the C-2 carbons can also be classified into three types as shown in Fig. 2(b). These results are in agreement with that obtained for the glycine ligand in the $[Co(ox)_x(gly)_y(en)_z]$ series by Juranic et al.[4] However, they do not describe the possibility of the classification for ethylenediamine (en) carbons. In the case of this series of the complex it is difficult to assign accurately each NMR signal to each carbon of

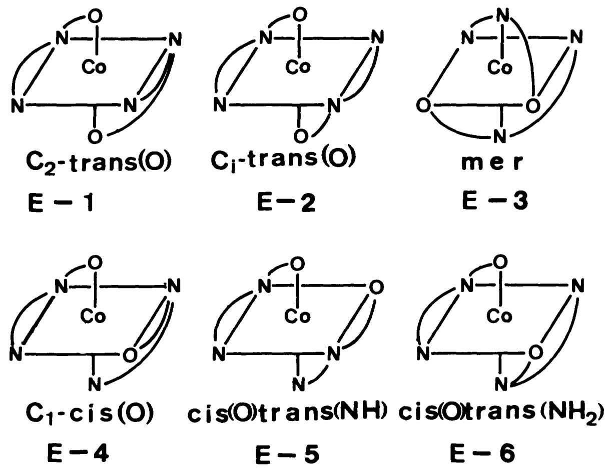

Fig. 1. The six geometrical isomers of the $[Co(edma)_2]^+$ ion.

Table 1. The Observed and Corrected ^{13}C Chemical Shifts and Magnetic Anisotropies from the Cobalt Center of the Isomers of $[Co(edma)_2]^+$ Ion

	C-1 Carbon				C-2 Carbon			
	δ^{obsd}	σ_{Co} c)	δ^{cor} d)	Type e)	δ^{obsd}	σ_{Co} c)	δ^{cor} d)	Type e)
C_2-*trans*(O)	185.61	+0.90	186.51	*fac* A	55.36	−0.06	55.30	*fac* B
C_1-*trans*(O)	185.41	+0.90	186.31	*fac* A	55.41	−0.06	55.35	*fac* B
C_1-*cis*(O)								
in-plane a)	184.30	+0.30	184.60	*fac* B	57.16	+0.27	57.43	*fac* A
out-of-plane b)	185.65	+0.13	185.78	*fac* C	57.16	−0.32	56.84	*fac* C
cis(O)*trans*(NH)	185.71	+0.13	185.84	*fac* C	57.16	−0.32	56.84	*fac* C
cis(O)*trans*(NH_2)	184.44	+0.30	184.74	*fac* B	56.53	+0.27	56.80	*fac* A
mer	184.74	+0.30	185.04	*mer* C	54.04	+0.27	54.31	*mer* C

	C-3 Carbon				C-4 Carbon			
	δ^{obsd}	σ_{Co} c)	δ^{cor} d)	Type e)	δ^{obsd}	σ_{Co} c)	δ^{cor} d)	Type e)
C_2-*trans*(O)	56.28	−0.53	55.75	*fac* C	41.76	−0.50	41.26	*fac* C
C_1-*trans*(O)	56.58	−0.53	56.05	*fac* C	42.25	−0.50	41.75	*fac* C
C_1-*cis*(O)								
in-plane a)	57.79	+0.06	57.85	*fac* A	40.59	−0.32	40.27	*fac* B
out-of-plane b)	55.99	−0.35	55.64	*fac* B	43.52	+0.02	43.54	*fac* A
cis(O)*trans*(NH)	55.36	−0.35	55.01	*fac* B	43.37	+0.02	43.39	*fac* A
cic(O)*trans*(NH_2)	58.53	+0.06	58.59	*fac* A	40.79	−0.32	40.47	*fac* B
mer	52.48	+0.06	52.54	*mer* B	47.51	−0.32	47.19	*mer* A

a) In-plane: in the plane of O-Co-O. b) Out-of-plane: out of the plane of O-Co-O. c) Anisotropies from cobalt(III), which were calculated according to Ref. 1. (+ value: to up-field). d) $\delta^{cor}=\delta^{obsd}+\sigma_{Co}$. e) See Fig. 2.

the en ligand because the chemical shifts of the en carbons are almost the same. On the contrary, as the chemical shift of C-3 is separated from that of C-4 in edma, it is to be easy to remove their erroneous signal assignments. In fact, our present data show that classifications similar to the C-1 and C-2 carbons are possible for the C-3 and C-4 carbons of the E-ring in edma (Table 1).

In both of the E- and G-rings, the difference in the chemical shifts between the Type A and Type B carbons (2—3 ppm) is larger than that caused by the magnetic anisotropy of a cobalt center (<1 ppm). However, the difference between the Types A and C or between the Types B and C is comparable to that caused by the anisotropy.

When a ligating N in the trans position to the ligating O of the G-ring is replaced by O, the C-1 carbon resonance is shifted to a lower field, while the C-2 carbon resonance is shifted to a higher field (alternation effect).$^{7)}$ (On the contrary, when a ligating N in the trans position to -NH- nitrogen of the G-ring is replaced by O, the C-1 carbon resonance is shifted to a higher field and the C-2 carbon resonance to a lower field.) That is, an influence from the trans position works alternately on the chemical shifts of the C-1 and C-2 carbons in the G-ring. A similar alternation effect is also observed for two neighboring carbons in the E-ring. This effect has been observed for the substituted alkenes and for the protonation shifts of alkylamines.$^{8,9)}$

^{13}C NMR Chemical Shifts of the Complex Containing Meridionally Coordinating edma (*mer*-edma). The chemical shifts of *mer*-edma are different from those of *fac*-edma, that is, the C-2 and C-3 carbons of *mer*-edma exhibit their chemical shifts in a higher field than those of *fac*-edma. This behavior is consistent with that of the $-CH_2NHCH_2-$ carbons of dien (dien: $NH(CH_2CH_2NH_2)_2$) and ida (The carbons in the mer-form resonate in a higher field than those in the fac-form.)$^{5,6)}$ On the contrary, the C-4 carbon signal of *mer*-edma appears at a lower field than that of *fac*-edma.

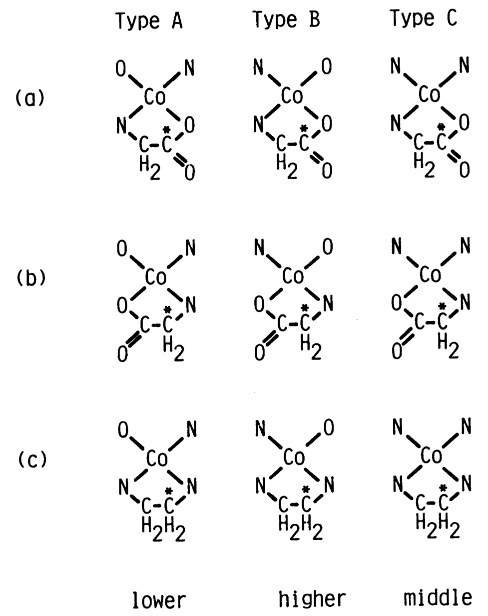

Fig. 2. Classification of the carbons in the coordinating edma: (a) for the C-1 carbon in the G-ring, (b) for the C-2 carbon in the G-ring, and (c) for the C-3 and C-4 carbons in the E-ring.

The chemical shift difference of C-2 between *mer*- and *fac*-edma's is about 2.5 ppm, and those of C-3 and C-4 are about 3 and 3.5 ppm respectively. These values are much larger than the chemical shift difference caused by the magnetic anisotropy effect of the cobalt center.

Structural Assignments of the Isomers of [Co(ida)(edma)]. Figure 3 shows the geometrical structures of four possible isomers of [Co(ida)(edma)], and Fig. 4 shows their electronic absorption spectra. The pink isomer shows a sharp band in the first absorption band region, while the violet, brown and red-brown isomers show only a broad band or a shoulder band. This behavior makes it possible to assign the pink isomer to *fac*(O) and other three isomers to *mer*(O).$^{10)}$ The red-brown isomer can be assigned to *mer*(O)*mer*(ch), because its first absorption band has the strongest intensity among the four geometrical isomers.$^{11)}$ Although the geometrical structure (*mer*(O)*cis*(NH) or *mer*(O)*trans*(NH)) of the other two isomers (violet and brown) can not be assigned solely by the visible absorption spectra, it is possible to assign them from their ^{13}C NMR data.

The chemical shift of the C-4 carbon in *mer*(O)-*mer*(ch) [Co(ida)(edma)] (containing *mer* A Type C-4 carbon) can be calculated, assuming that its $\delta^{\rm cor}$(C-4) value is nearly equal to that of the mer isomer of $[Co(edma)_2]^+$ (which contains *mer* A Type C-4

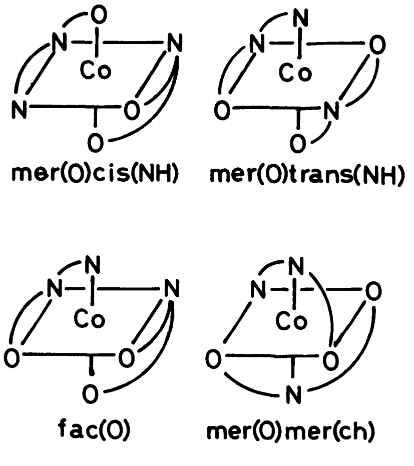
mer(O)cis(NH) mer(O)trans(NH)
fac(O) mer(O)mer(ch)

Fig. 3. The four geometrical isomers of [Co(ida)-(edma)].

Table 2. The Calculated and Observed Chemical Shifts of C-4 Carbons of edma in the Isomers of [Co(ida)(edma)]

	σ_{Co}	Type	Estimated δ^{cor} b)	δ^{cal} a)	Color of the isomer	δ^{obsd}
mer(O)*cis*(NH)	−0.5	*fac* B	40.4	40.9	Violet	41.08
mer(O)*trans*(NH)	−0.2	*fac* A	43.5	43.7	Brown	43.86
mer(O)*mer*(ch)	−0.2	*mer* A	47.2	47.4	Red-brown	47.22

a) $\delta^{cal}=\delta^{cor}-\sigma_{Co}$. b) The δ^{cor} values which appeared in Table 1 were averaged.

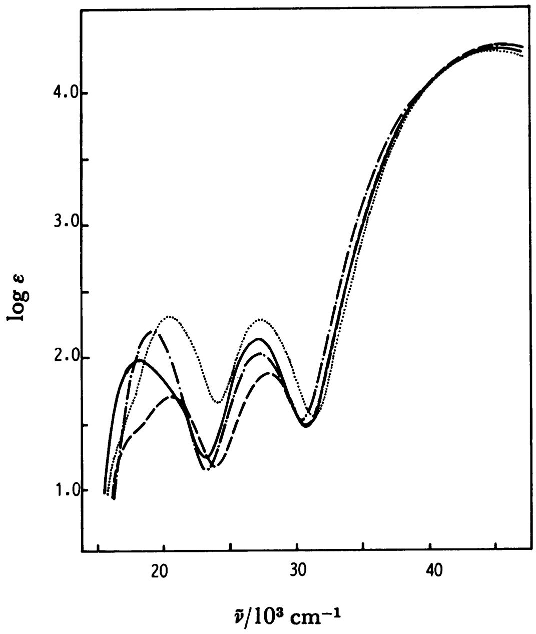

Fig. 4. Absorption spectra of the four isomers of [Co(ida)(edma)]; violet (——), brown (— —), red-brown (……), and pink (—·—).

carbon, too; δ^{cor}(C-4)=47.2) and that the equation, $\delta^{cal}(=\delta^{obsd})=\delta^{cor}-\sigma_{Co}$, is applicable to the isomer of *mer*(O)*mer*(ch) [Co(ida)(edma)] (the σ_{Co} value (−0.2 ppm) of this isomer is calculated by the method described in Ref. 1.). The δ^{cal}(C-4) value (δ=47.4) of the *mer*(O)*mer*(ch) isomer is nealy equal to the δ^{obsd}(C-4) value of the red-brown isomer (δ=47.22), but not to that of either the violet (δ=41.08) or the brown (δ=43.86) isomer (Table 2). On the basis of these results, the red-brown isomer is assigned to the *mer*(O)*mer*(ch). In the similar manner, comparing the δ^{cal}(C-4) value of the *mer*(O)*cis*(NH) (δ=40.9) or *mer*(O)*trans*(NH) (δ=43.7) [Co(ida)(edma)] with the δ^{obsd}(C-4) values of the obtained *mer*(O)-form isomers of [Co(ida)(edma)], the violet isomer is assigned to *mer*(O)*cis*(NH) and the brown isomer to *mer*(O)-*trans*(NH).

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