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Metal Complexes of Amino Acids. V.[1] μ-Aminocarboxylato Bi- and Tri-nuclear Complexes of Cobalt(III)

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Some new binuclear and trinuclear complexes containing μ-aminocarboxylato ligands, $[(NH_3)_5Co(OCORNH_2)Co\ NO_2(acac)_2](ClO_4)_2$ ($R=CH_2$, $(CH_2)_2$, and $CH(CH_3)$ for glycinato, β- and DL-alaninato ligands) and $[en_2Co\{(OCORNH_2)Co\ NO_2(acac)_2\}_2]ClO_4$ ($R=CH_2$ and $(CH_2)_2$), have been prepared and characterized on the basis of their elemental analyses, visible and ultraviolet absorption, infrared, and PMR spectra. It was concluded that the NH_2 end of the μ-aminocarboxylato bridge occupies a coordination position *trans* to the NO_2 ligand, and the COO ends of two μ-aminocarboxylato bridges in the trinuclear complex occupy positions *trans* to each other.

It is well-known that an aminocarboxylate anion or its parent acid coordinates to a cobalt(III) ion as a unidentate,[1–7] or a bidentate[8–12] ligand, and in some cases also as a tridentate ligand such as aspartate[13,14] and histidinate.[15] Previously we reported the $[Co(NH_3)_5(aaH)]X_3$,[2] *trans*-$[Coen_2(aaH)_2]X_3$,[3] and *cis*-$[Co(NH_3)_4(aaH)_2]X_3$[1] complexes containing various amino acids (abbreviated as aaH). The amino acid binds to a cobalt(III) ion as a unidentate ligand through its carboxylate group, the $-NH_3^+$ group being free. Recently the complexes of *N*-bonded unidentate amino acids, aminocarboxylates or amino acid esters were also prepared.[5–7] Pellizer *et al.*[16] suggested the occurrence of some μ-aminocarboxylato binuclear complexes in solution in the course of studies on the substitution reaction of a Vitamin B_{12} model complex.

In the present paper, formation and preparation of some μ-aminocarboxylato complexes by the reaction between the $[Co(aa)(NH_3)_5]^{2+}$ or *trans*-$[Co(aa)_2en_2]^{1+}$ ion and the $[Co(NO_2)_2(acac)_2]^-$ ion are reported. The complexes isolated are characterized on the basis of their elemental analyses, visible and ultraviolet absorption, infrared, and PMR spectra. The amino acids and their abbreviations (in parentheses) are as follows: glycine NH_2CH_2COOH (glyH), β-alanine $NH_2CH_2CH_2COOH$ (β-alaH), L- and DL-alanine $NH_2CH(CH_3)COOH$ (L- and DL-alaH), and γ-aminobutyric acid $NH_2CH_2CH_2CH_2COOH$ (γ-ambutH).

Experimental

Preparation of Starting Materials. *Pentaammine(amino acid)-cobalt(III) Complexes*: $[Co(NH_3)_5(glyH)](ClO_4)_3\cdot H_2O$, $[Co(NH_3)_5(\beta\text{-alaH})](ClO_4)_3$, $[Co(NH_3)_5(\text{L-alaH})](ClO_4)_3\cdot 2H_2O$, $[Co(NH_3)_5(\text{DL-alaH})](ClO_4)_3\cdot H_2O$, and $[Co(NH_3)_5(\gamma\text{-ambutH})](ClO_4)_3$, and the pentaammine(aminocarboxylato) complex, $[Co(gly)(NH_3)_5](ClO_4)_2$, were prepared by the method reported.[2] The *trans*-$[Co\ en_2(aaH)_2](ClO_4)_3$ (aaH= glyH, β-alaH, L-alaH and γ-ambutH) complexes were prepared by using the same method as that described.[3] These complexes were recrystallized from aqueous solution by addition of a small amount of ethanol and saturated sodium perchlorate solution. The glycine, β-alanine and γ-aminobutyric acid complexes are new ones.

Found: C, 15.44; H, 4.14; N, 13.42%. Calcd for $[Co\ en_2(glyH)_2](ClO_4)_3=C_8H_{26}N_6O_{16}Cl_3Co$: C, 15.31; H, 4.18; N, 13.39%.

Found: C, 18.12; H, 4.63; N, 13.11%. Calcd for $[Co\ en_2(\beta\text{-alaH})_2](ClO_4)_3=C_{10}H_{30}N_6O_{16}Cl_3Co$: C, 18.32; H, 4.62; N, 12.82%.

Found: C, 20.78; H, 4.94; N, 12.26%. Calcd for $[Co\ en_2(\gamma\text{-ambutH})_2](ClO_4)_3=C_{12}H_{34}N_6O_{16}Cl_3Co$: C, 21.08; H, 5.02; N, 12.29%.

Preparation of $Na[Co(NO_2)_2(acac)_2]$ complex was carried out by the method of Rosenheim and Garfunkel.[17]

Preparation of μ-Aminocarboxylato Binuclear Complexes. $[(NH_3)_5Co(gly)Co\ NO_2(acac)_2](ClO_4)_2\cdot 3H_2O$: The pH of an aqueous solution containing 2.5 g of $[Co(NH_3)_5(glyH)](ClO_4)_3\cdot H_2O$ in 25 ml of water was adjusted to 9.0 with sodium hydroxide (1 M). To this solution was added 1.8 g of $Na[Co(NO_2)_2(acac)_2]$. The resulting solution was kept in a water-bath at 30 °C for two hr and then kept in a refrigerator overnight. The brownish-red needle crystals formed were filtered and washed with a water–ethanol (1: 1) mixture and then with 95% ethanol. From the filtrate another crop of the complex was obtained by adding a saturated solution of sodium perchlorate. Recrystallization was carried out by adding a small amount of saturated sodium perchlorate solution to a concentrated solution and by keeping the mixture in a refrigerator. The separated complex was dried over $CaCl_2$ in a vacuum desiccator. The yield was *ca.* 2.3 g. The complex was readily soluble in water and acetone, but insoluble in absolute ethanol and ether.

Found: C, 18.74; H, 5.16; N, 12.62%. Calcd for $C_{12}H_{39}N_7O_{16}Cl_2Co_2$: C, 18.61; H, 5.09; N, 12.62%.

The same binuclear complex was also obtained from $[Co\ gly(NH_3)_5](ClO_4)_2$ (2.0 g) and $Na[Co(NO_2)_2(acac)_2]$, the yield being *ca.* 2.3 g.

$[(NH_3)_5Co(\beta\text{-ala})Co\ NO_2(acac)_2](ClO_4)_2$. Brown needle crystals were obtained by a similar procedure to that for the μ-gly binuclear complex except for the use of $[Co(NH_3)_5(\beta\text{-alaH})](ClO_4)_3$ (2.6 g) instead of $[Co(NH_3)_5(glyH)](ClO_4)_3\cdot H_2O$. This complex was more soluble in water than the μ-gly complex. The crystals obtained were dried over P_4O_{10} in a vacuum desiccator. The yield was *ca.* 1.5 g.

Found: C, 21.30; H, 5.00; N, 12.93%. Calcd for $C_{14}H_{37}N_7O_{16}Cl_2Co_2$: C, 21.26; H, 4.81; N, 13.36%.

$[(NH_3)_5Co(\text{DL-ala})CoNO_2(acac)_2](ClO_4)_3\cdot 2H_2O$. This complex was prepared by the same method as that employed for the μ-gly binuclear complex except for the use of $[Co(NH_3)_5(\text{DL-alaH})](ClO_4)_3\cdot H_2O$(2.6 g). The yield was 1.5 g.

Found: C, 20.24; H, 5.18; N, 12.89%. Calcd for $C_{13}H_{39}N_7O_{18}Cl_2Co_2$: C, 20.27; H, 5.11; N, 12.73%.

Preparation of the μ-L-ala binuclear complex was repeatedly attempted in the same way as for the DL-ala complex, but no pure complex was obtained. Preparation of the binuclear complex of γ-ambut was also unsuccessful, some dark brown crystals of an undesired composition being separated instead.

Preparation of μ-Aminocarboxylato Trinuclear Complexes. $[en_2Co\{(gly)CoNO_2(acac)_2\}_2]ClO_4 \cdot 1.5NaClO_4 \cdot 6H_2O$: The pH of an aqueous solution containing 2.5 g of *trans*-$[Co\text{-}en_2(glyH)_2](ClO_4)_3$ in 40 ml of water was adjusted to pH 9.0 with sodium hydroxide (1 M). To this solution was added 3.0 g of $Na[Co(NO_2)_2(acac)_2]$. The resulting solution was kept in a water-bath at 30 °C for two hours and cooled in an ice-bath. Crystals of the trinuclear complex deposited as brown flakes with addition of a saturated aqueous solution of sodium perchlorate. The crystals were filtered and washed with a saturated aqueous solution of sodium perchlorate, a small amount of ethanol and then with ether.

Recrystallization was performed from cold aqueous solution by addition of a saturated solution of sodium perchlorate, the resulting solution being kept in a refrigerator. The yield was *ca.* 1.3 g. The complex was soluble in water and acetone, but insoluble in absolute ethanol and ether.

Found: C, 25.52; H, 5.04; N, 8.55%. Calcd for $C_{28}H_{64}N_8O_{32}Cl_{2.5}Co_3$: C, 25.38; H, 4.87; N, 8.45%.

$[en_2Co\{(\beta\text{-}ala)CoNO_2(acac)_2\}_2]ClO_4 \cdot 3NaClO_4 \cdot 5H_2O$. A brown complex was obtained as flake crystals by a similar method to that for the μ-gly trinuclear complex. The yield was *ca.* 1.0 g.

Found: C, 23.14; H, 4.52; N, 7.61%. Calcd for $C_{30}H_{66}N_8O_{37}Cl_4Na_3Co_3$: C, 23.72; H, 4.39; N, 7.37%.

Repeated attempts were made to prepare trinuclear complexes containing DL-ala, L-ala and γ-ambut, but were unsuccessful.

Estimation for the Formation of μ-Aminocarboxylato Complex in Solution. The % formation of the μ-gly binuclear complex was estimated as follows. $[Co(NH_3)_5(glyH)](ClO_4)_3 \cdot H_2O$ (2.50 g, 4.67×10^{-3} mol) was dissolved in 25 ml of water (an almost saturated solution was obtained), the pH being adjusted to 9.0 with 1 M-NaOH. The solution was made 50 ml in volume with water and then kept in a water-bath with a thermostat. It was then mixed with an aqueous solution containing 1.78 g (4.67×10^{-3} mol) of $Na[Co(NO_2)_2(acac)_2]$ in 50 ml of water. The mixed solution was transferred to a 100 ml Erlenmeyer flask with a stopper and kept at an appropriate temperature (20.0, 30.0, 40.0 or 50.0±0.1 °C). A 10 ml portion of the reactant solution, picked up at intervals several minutes to several hours after mixing, was quickly poured into a short column (4.5 cm × 5.5 cm) containing 60 ml (syrup state) of cation-exchange SP-Sephadex (C-25). The unreacted complex anion, $[Co(NO_2)_2(acac)_2]^-$, was removed by washing with water. The adsorbed μ-gly binuclear complex was carefully eluted out with 2 M-NaClO$_4$. The unreacted complex cation ($[Co(gly)(NH_3)_5]^{2+}$ or $[Co(NH_3)_5(glyH)]^{3+}$) remained as a red band. The eluted solution was made 100 ml in volume with 2 M-NaClO$_4$ solution. The concentration of the binuclear complex was estimated by comparing the absorbance measured at 405 nm with that of the prepared complex. The absorbance at 405 nm of the unreacted gly complex, $[Co(gly)(NH_3)_5](ClO_4)_2$ or $[Co(NH_3)_5(glyH)](ClO_4)_3$, is negligible in comparison with that of the μ-gly binuclear complex (Fig. 5). Similar tests (at only 30 °C) were also performed for the L-ala, β-ala and γ-ambut complexes.

Tests of the di-μ-aminocarboxylato trinuclear complexes of gly, β-ala and γ-ambut at 30 °C were carried out in the same way as for the μ-gly binuclear complex except for the use of *trans*-$[Co\ en_2(aaH)_2]^{3+}$ (3.98×10^{-3} mol) and $[Co(NO_2)_2(acac)_2]^-$ (7.96×10^{-3} mol).

Measurements. The absorption spectra were measured in aqueous solutions with a Hitachi Model EDS-3T spectrophotometer. The infrared spectra were obtained with a JASCO IR-S infrared spectrophotometer. The PMR spectra were recorded on a JEOL Model MH-100 high-resolution spectrometer with DSS as an internal standard.

Results and Discussion

Formation of μ-Aminocarboxylato Complex. The % formation and pH value *versus* reaction time for the μ-gly binuclear complex at 20, 30, 40, and 50 °C are shown in Fig. 1. Formation of the μ-gly binuclear complex began instantly after mixing two aqueous solutions containing $[Co(gly)(NH_3)_5]^{2+}$ and $[Co(NO_2)_2(acac)_2]^-$, respectively. The maximum formation (*ca.* 72.5%) was observed after 2—3 hr at 30 °C. At higher temperatures (40 and 50 °C) the formation curve reached its maximum a few minutes after mixing and then began to decrease sharply. This indicates that rapid decomposition of the formed μ-gly binuclear complex occurs at higher temperatures. At lower temperature (20 °C) the formation curve indicated lower values than at 30 °C within 5 hr of reaction time, but higher values after 5 hr.

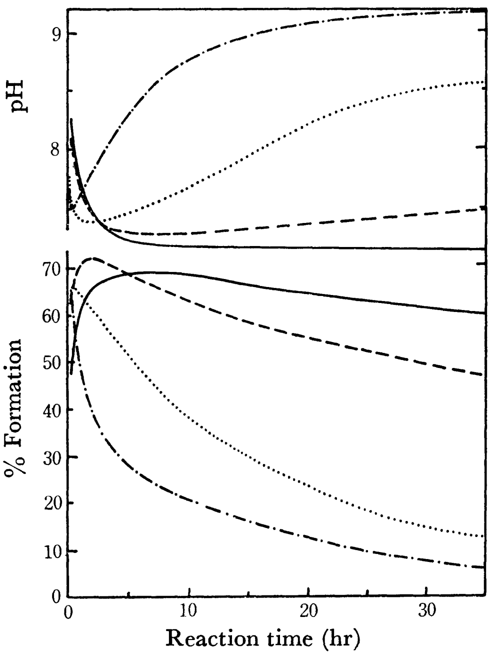

Fig. 1. % Formation and pH *vs.* reaction time for μ-gly binuclear complex at various temperatures, 20 °C (——), 30 °C (– – –), 40 °C (····), and 50 °C (–·–·–).

In order to coordinate the amino end of the pentaammine(O-glycine)cobalt(III) complex ion to another cobalt(III) ion, the amino end ($-NH_3^+$) should be deprotonated producing free amino group ($-NH_2$). It could be assumed that the p*K* value of the $[Co(NH_3)_5(glyH)]^{3+}$ is located at around 9. Formation tests and preparation of the μ-aminocarboxylato binuclear complexes were performed with use of pH-adjusted (*ca.* pH 9) solutions of the protonated complexes, $[Co(NH_3)_5(aaH)](ClO_4)_3$. A sharp decrease in the pH at the beginning of the reaction (Fig. 1) indicates the coordination of the amino group, and the increment

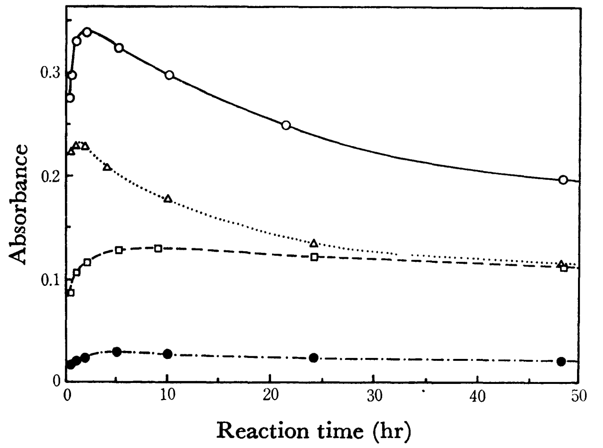

Fig. 2. The plots of absorbance *vs.* reaction time for binuclear complexes. μ-gly (—○—), μ-L-ala (••△••), μ-β-ala (--□--), and μ-γ-ambut (-•●•-).

of the pH with the progress of reaction at higher temperatures (40 and 50 °C) can be attributed to the detachment of the amino group or of ammonia molecule during the course of decomposition of the μ-gly binuclear complex.

The formation cruves of binuclear complexes are compared for gly, L-ala, β-ala, and γ-ambut (Fig. 2). The relative degree of formation is in the order

$$\text{gly} > \text{L-ala} > \beta\text{-ala} > \gamma\text{-ambut}.$$

Formation curves of the di-μ-aminocarboxylato trinuclear complexes for gly, β-ala and γ-ambut at 30 °C are compared in Fig. 3. The formation and decomposition of the μ-gly trinuclear complex proceeds rapidly as compared with those of β-ala and γ-ambut complexes. This phenomenon coincides with the case of the binuclear complexes. The maximum % formation which was estimated experimentally for the μ-gly trinuclear complex (*ca.* 24%) was considerably low as compared with that for μ-gly binuclear complex (72.5%).

The μ-aminocarboxylato binuclear and trinuclear complexes are relatively stable in aqueous solution in the pH region 3—8, but less stable for pH>9. Only one band appeared when these complexes were developed in a cation-exchange resin column, showing that they consist of one species each.

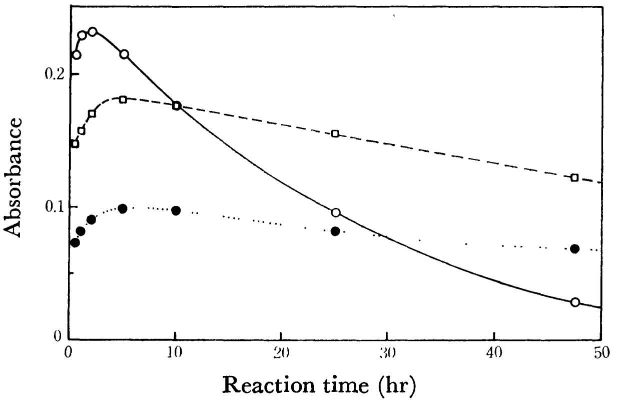

Fig. 3. The plots of absorbance *vs.* reaction time for trinuclear complexes. di-μ-gly (—○—), di-μ-β-ala (--□--), and di-μ-γ-ambut (••●••).

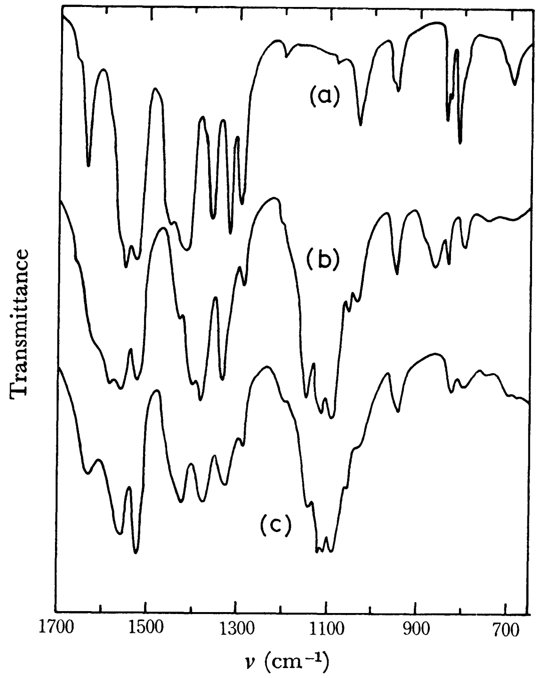

Fig. 4. Infrared spectra of (a) $Na[Co(NO_2)_2(acac)_2]$, (b) μ-gly binuclear, and (c) di-μ-gly trinuclear complexes.

In the preparation of binuclear complexes for L- and β-ala, and γ-ambut, in some cases complexes such as $[Co(NH_3)_5(aaH)][Co(NO_2)_2(acac)_2]_3$ were also separated. These complex-to-complex salts split into two bands brown and orange in color on the column, easily distinguishable from the μ-aa binuclear complexes.

Infrared Spectra. The infrared spectra of μ-gly binuclear and di-μ-gly trinuclear complexes are shown in Fig. 4 together with the spectrum of the starting acetylacetonato complex, $Na[Co(NO_2)_2(acac)_2]$.

These complexes show intense absorption bands in the 1520—1560 cm^{-1} region, which are assigned to the C⎓O and C⎓C stretching vibrations of the coordinated acetylacetonate.[18–20] The bands of 825 and 1325 cm^{-1} are assigned to the NO_2^- bending and asymmetric stretching modes,[19] respectively. The medium bands which appear near 1630 cm^{-1} are attributed to the coordinated carboxyl group. They are generally recognized in several aminocarboxylato cobalt(III) complexes. The present μ-aminocarboxylato complexes show intense bands characteristic of ClO_4^- in the 1060—1140 cm^{-1} region. This confirms that the complex ions are electro-positive.

Absorption Spectra. The absorption spectra of the μ-aminocarboxylato binuclear and trinuclear complexes show a similar behavior to that of the starting $Na[Co(NO_2)_2(acac)_2]$ complex (Fig. 5). The absorption spectra of acetylacetonato metal complexes in general have been studied.[18,20,21] Referring to these studies the band peaks observed at 515 and 535 nm for the bi- and tri-nuclear complexes, respectively, are attributed to the d—d transition ($^1A_{1g}\rightarrow{}^1T_{1g}$ in O_h per-

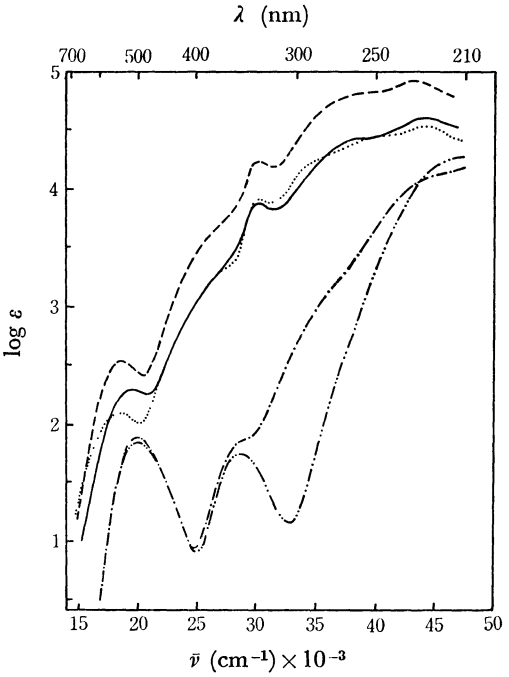

Fig. 5. Absorption spectra of μ-gly binuclear (——), di-μ-gly trinuclear (– – –), $[Co(NO_2)_2(acac)_2]^-$ (····), $[Co(gly)(NH_3)_5]^{2+}$ (-····), and $[Co(NH_3)_5(glyH)]^{3+}$ (–··–) complex ions in aqueous solutions.

centage).[18] A metal-enolate charge transfer band ($d_\varepsilon \rightarrow \pi^*$) appears in the 330—350 nm region. The broad and shoulder bands near 225 and 260 nm are attributed to the enolate $\pi \rightarrow \pi^*$ transitions. The absorption curves of the μ-gly binuclear and di-μ-gly trinuclear complexes coincided with the summation curves of $[Co(aaH)(NH_3)_5]^{3+}$ and $[Co(NO_2)(NH_3)(acac)_2]$[18] (1: 1 mixture), and of *trans*-$[Co\ en_2(aaH)_2]^{3+}$ and $[Co(NO_2)(NH_3)(acac)_2]$ (1 : 2 mixture), respectively. These results support the view that the complexes obtained consist of the binuclear and trinuclear compositions. Proposed structures for these bi- and trinuclear complex ions are shown in Figs. 6 and 7.

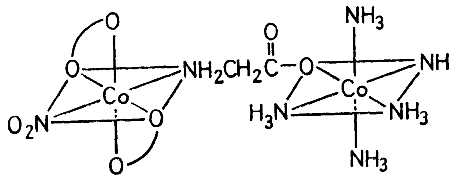

Fig. 6. The structure of μ-gly binuclear complex.

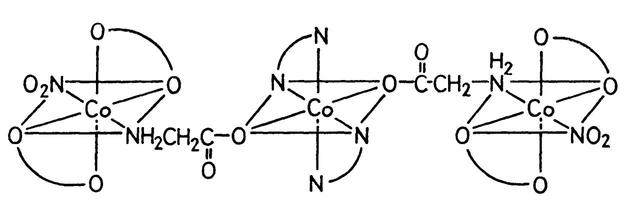

Fig. 7. The structure of di-μ-gly trinuclear complex.

Proton Magnetic Resonance Spectra. The PMR data of the μ-gly binuclear and trinuclear complexes are given in Table 1. These μ-gly complexes show a pair of singlet resonances in the 2.15—2.22 and 5.84—5.88 ppm regions corresponding to the methyl and methin protons, respectively, of acetylacetonato ligands. The singlet resonances suggest that four methyl groups and two methin groups in the μ-gly binuclear complex and eight methyl groups and four methin groups in the di-μ-gly trinuclear complex lie in the same chemical environment. Thus it is reasonable to conclude that the bi- and tri-nuclear complexes take the *trans* structure with respect to the NH_2 group of the μ-glycinato ligand and NO_2^- (Figs. 6 and 7). If these complexes take the *cis* structure, they would show a more complicated pattern of proton resonances.

Table 1. PMR[a] data of gly complexes

Complexes	Chemical shift (ppm)		
	CH_3(acac)	CH_2(gly)	CH(acac)
$Na[Co(NO_2)_2(acac)_2]$	2.14		5.67
$[Co(gly)(NH_3)_5](ClO_4)_2$		3.40	
$[Co(NH_3)_5(glyH)](ClO_4)_3$		3.79	
μ-Gly binuclear	2.15	3.03	5.88
Di-μ-gly trinuclear	2.22	2.85[b]	5.84

a) Internal standard is DSS in D_2O. b) Overlaps with CH_2 of ethylenediamine.

The center cobalt(III) of the di-μ-gly trinuclear complex is also expected to have the *trans* structure with respect to the carboxyl groups of the two μ-glycinato ligands from the appearance of a strong singlet resonance for methylene protons of ethylenediamine at 2.85 ppm.

Boucher and Bailar[18] reported the replacement of one NO_2^- ligand of $[Co(NO_2)_2(acac)_2]^-$ by several amine ligands, and suggested the *trans* structure of the starting dinitro complex and the product nitroamine complexes from the view point of *trans* effect of the NO_2^- ligand. In our case the replacement of one NO_2^- ligand in $[Co(NO_2)_2(acac)_2]^-$ by the amino end of $[Co(aa)(NH_3)_5]^{2+}$ also produces a complex having *trans* structure with respect to the NO_2^- and the amino end. In conclusion it is proposed that the present bi- and tri-nuclear complexes have structures such as shown in Figs. 6 and 7.

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