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Regulation of the Ligand Field Strength of a Cobalt(III) Complex by Methyl Substitutions on a Tetraamine Ligand: An Important Factor for the Dissociation of a Generally Inert Chelated Amino Acidato Ligand from a Cobalt(III) Complex

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Introduction

Many physical properties of transition metal complexes are related to the ligand field. A major factor which contributes to the ligand field strength is the nature of the donor atoms, while chelate structure or substitutions on the ligands exert minor influences. The regulation of a ligand field by the modification of ligands is expected to be useful for systematic and delicate control of the properties or reactivities of metal complexes.

We previously reported that the chelated alaninato ligand dissociates when $[Co(alaninato)(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet^1)]^{2+}$ (**4**) is warmed in 0.1 mol dm^{-3} sodium carbonate aqueous solution.[2] It is currently known that amino acids form stable chelates with cobalt(III) and do not dissociate easily but result in racemization of the α-carbon center under basic conditions.[3] The dissociation of the alaninato chelate ligand observed for **4** is a characteristic phenomenon for a complex containing a substituted tetraamine. Since a remarkable lower energy shift of electronic absorption maxima is observed for **4**, the dissociation of the generally inert alaninato chelate ligand is expected to be a novel example of reactions which are regulated by the ligand field strength.

In this study, the effect of methyl substitutions on a tetraamine in the $[Co(alaninato)(tetraamine)]^{2+}$ system is examined by ^{59}Co NMR and electronic absorption spectroscopies, and the relation between the novel dissociation of the alaninato ligand and the ligand field strength is elucidated.

Experimental Section

Measurements. Electronic absorption spectra were recorded on a Shimadzu UV-210 spectrophotometer. Circular dichroism spectra were obtained on a JASCO J-20 recording spectropolarimeter. These measurements were made on aqueous solutions at concentrations near 2×10^{-3} mol dm^{-3}.

^{59}Co NMR spectra were obtained on a JEOL GX-400 at a concentration of 0.2 mol dm^{-3} in D_2O, at 22 °C. The observations were performed using 10 mm o.d. sample tubes. A saturated D_2O solution of $K_3[Co(CN)_6]$ was used as an external standard.

Preparations. $[Co(R\text{-}ala)(2,3,2\text{-}tet)](ClO_4)_2$[3b] (**1**), $[Co(R\text{-}ala)(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)](ClO_4)_2$[4a] (**2**), and $[Co(R\text{-}ala)(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)](ClO_4)_2$[4a] (**4**) were prepared by the reported procedures.[1]

$[Co(R\text{-}ala)(1,11\text{-}Me_2\text{-}2,3,2\text{-}tet)](ClO_4)_2$ (3) was prepared from *R*-alanine and *trans*-$[CoCl_2(1,11\text{-}Me_2\text{-}2,3,2\text{-}tet)](ClO_4)$[5] by the method used for the synthesis of **4**.[4a] The aqueous solution (40 mL) of *R*-alanine (0.21 g, 2.4 mmol) and *trans*-$[CoCl_2(1,11\text{-}Me_2\text{-}2,3,2\text{-}tet)](ClO_4)$ (0.84 g, 2.0 mmol) was adjusted to pH 5.5 with 0.1 mol dm^{-3} NaOH and heated for 1 h at 50 °C. The pH was then adjusted to 8.0, and heating was continued for an additional 3 h. The reaction mixture was poured onto a column of SP-Sephadex C-25 cation-exchange resin in the sodium form. The complex was eluted with 0.1 mol dm^{-3} $NaClO_4$. Concentration of the eluate from the main band gave red crystals. Anal. Calcd for $C_{12}H_{30}N_5O_{10}Cl_2Co$: C, 26.98; H, 5.66; N, 13.11. Found: C, 26.83; H, 5.79; N, 13.09. Electronic absorption spectrum, $\nu/10^3$ cm^{-3} (log ϵ): 19.8 (2.01), 27.7 (2.06). Circular dichroism spectrum, $\nu/10^3$ cm^{-3} ($\Delta\epsilon$): 18.4 (+0.19), 21.0 (+0.51), 27.4 (–0.12).

Caution! Although these perchlorate salts are moderately stable, they are potentially hazards and should therefore be handled with care and in small quantities.

$[Co(R\text{-}ala)(2R,4R,9R,11R\text{-}Me_4\text{-}3,2,3\text{-}tet)](ClO_4)_2\cdot H_2O$ (5) was prepared from *R*-alanine and *trans*-$[CoCl_2(2R,4R,9R,11R\text{-}Me_4\text{-}3,2,3\text{-}tet)](ClO_4)$[6] in the same manner as the preparation of **3**. Anal. Calcd for $C_{15}H_{38}N_5O_{11}Cl_2Co$: C, 30.31; H, 6.44; N, 11.78. Found: C, 30.42; H, 6.87; N, 11.95. Electronic absorption spectrum, $\nu/10^3$ cm^{-3} (log ϵ): 19.6 (2.12), 27.8 (2.18). Circular dichroism spectrum, $\nu/10^3$ cm^{-3} ($\Delta\epsilon$): 17.4 (+0.04), 19.8 (–1.70), 22.7 (+0.10), 27.8 (+0.42).

Dissociation of the Alaninato Ligand from the Complex. Samples (10-mg) of each complex were dissolved in 10 mL of 0.1 mol dm^{-3} Na_2CO_3 and allowed to react at 40 °C for 1.5 h. A 1-mL aliquot of the mixture was sampled, and the reaction was quenched by the addition of 1 mL of 1 mol dm^{-3} HCl. Alanine analyses were performed by on an HPLC system equipped with a TOSO IEX-2115 column. The reaction mixture was eluted with 0.2 N citrate buffer adjusted to pH 3.30, and dissociated alanine from the complex was detected fluorimetrically (λ_{em} = 460 nm, λ_{ex} = 340 nm) by the reaction with *o*-phthalaldehyde.

Results and Discussion

Preparations. Cobalt(III) complexes containing an alaninato and a tetraamine ligand were prepared by treating the *trans*-$[CoCl_2(tetraamine)]ClO_4$ complex with alanine at a pH of approximately 5.5 and at 50 °C for about 1 h, followed by adjusting the pH to 8.0 and continuing heating for an additional 3 h. ^{13}C NMR spectroscopy indicated that one of stereoisomers was obtained as a main product for **2**–**5**. **1** was a mixture of two stereoisomers, separation of which by the column chromatographic technique was not successful.

Under these reaction conditions, the amino acidato chelate ligand is expected to coordinate in the β_2 form.[3,7] The stereochemistry is supported by established structures of **2**[4a] and **4**.[4b] **1** is presumably a mixture of the Λ-β_2 and Δ-β_2 forms,[3] which are mirror images of each other apart from the alaninato moiety. Electronic absorption and circular dichroism spectroscopies indicate that the stereochemistry of **3** is similar to those of the above complexes. The very similar circular dichroism spectra of **5** and Δ-β-$[Co(oxalato)(2R,4R,9R,11R\text{-}Me_4\text{-}3,2,3\text{-}tet)]ClO_4$[8] indicate that the tetraamine takes the Δ-β configuration in **5**. The proposed stereochemistries of the complexes are summarized in Figure 1.

Effect of Methyl Substitutions of the Tetraamine on the Ligand Field Strength. Table I lists electronic absorption and ^{59}Co NMR

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(1) The following abbreviations are used throughout this paper: 2,3,2-tet = 1,9-diamino-3,7-diazanonane, 5*R*,7*R*-Me$_2$-2,3,2-tet = (4*R*,6*R*)-4,6-dimethyl-1,9-diamino-3,7-diazanonane, 1,11-Me$_2$-2,3,2-tet = 2,5,9,12-tetraazatridecane, 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet = (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane, 2*R*,4*R*,9*R*,11*R*-Me$_4$-3,2,3-tet = (2*R*,4*R*,9*R*,11*R*)-4,9-dimethyl-2,11-diamino-5,8-diazadodecane.

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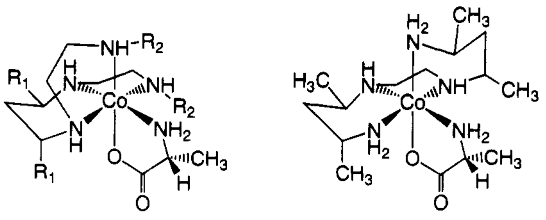

Λ-β_2 Δ-β_2

	R_1	R_2
1	H	H
2	CH_3	H
3	H	CH_3
4	CH_3	CH_3

5

Figure 1. Stereochemistry of the complexes. **1** is a mixture of isomers, presumably Δ-β_2 and Λ-β_2 forms.

Table I. Electronic Absorption and ^{59}Co NMR (95 MHz) Spectral Data for the [Co(alaninato)(tetraamine)]$^{2+}$ Complexes and Dissociation of Alanine from the Complexes

no.	λ_{max}/nm	δ/ppm	$\Delta\nu$/Hz	% dissociated alanine[a]
1	492, 352	7935	(2050)[b]	4
2	501, 357	8157	1380	17
3	506, 361	8347	3200	74
4	514, 367	8615	3000	95
5	511, 360	8620	4200	95

[a] Dissociated alanine from the complexes after treatment with 0.1 mol dm^{-3} Na_2CO_3 (pH 11.2) at 40 °C for 1.5 h. [b] A mixture of isomers (see text).

spectroscopic data. Absorption maxima are shifted to lower energy with an increase in the number of methyl substituents on the tetraamine. The first absorption maximum deviates from 492 nm for a complex containing a nonsubstituted tetraamine (**1**) to 514 nm for one containing a substituted tetraamine (**4**). Both *C*-methyl and *N*-methyl substitutions affect the ligand field, and the latter contribute more effectively. The effect of substitutions is also observed in the ^{59}Co NMR chemical shift. It is currently known that the ^{59}Co NMR chemical shift is closely related to the d–d transition energy of the complex.[9,10] With an increase in the number of methyl substituents, the ^{59}Co NMR signal shifts to lower field. The shift observed in absorption maxima shows good correlation with that of ^{59}Co NMR signals. The range of deviation is remarkably large for a series of complexes with the same donor atoms,[9] and thus the ligand field strength can be regulated effectively by the modification of the ligand.

The line width of the ^{59}Co resonance shows characteristic behavior. The line width for **3–5** is remarkably large compared with that for **2** or **1**. It is generally accepted that the line width of the ^{59}Co NMR signal mainly depends on quadrupolar relaxation.[10,11] The important factor which affects the line width is the symmetry of the configuration of electrons around Co. The very broad line width observed for **3–5** suggests a deviation from the regular octahedral geometry around cobalt(III) due to methyl substitutions.

Dissociation of the Alaninato Ligand from the Complex. It is well-known that amino acids from stable chelates with cobalt(III) and do not dissociate easily. Basic treatment of amino acidato complexes results in racemization at the α-carbon.[3] We previously reported that the chelated alaninato ligand dissociated from the complex when **4** was treated with Na_2CO_3 aqueous solution.[2] This reaction is useful in designing asymmetric reactions using cobalt(III) complexes because an amino acid can be recovered with retention its configuration at the asymmetric carbon. In order to obtain detailed information concerning this reaction, kinetic measurements were undertaken.

The reaction was followed by HPLC analysis of the dissociated alanine and exhibited pseudo-first-order kinetics.[12] The rate constant at 50 °C and pH 11.0 is $k = 1.8 \times 10^{-3}$ s^{-1}. This value is about 1 order larger than that for racemization of the alaninato ligand in [Co(en)(*S*-ala)]I_2 (1.6×10^{-4} s^{-1} at pH 11.0 and 50 °C).[3a] This is consistent with the result that the α-carbon of alanine maintains its configuration during dissociation from **4**.[2] Dissociation was also observed for **5**, whose rate constant was $k = 1.4 \times 10^{-3}$ s^{-1} at 50 °C and pH 11.0. Therefore, the reaction is a characteristic phenomenon for complexes containing a substituted tetraamine. The crystallographic study of **4** indicates that the alaninato ligand forms the usual five-membered chelate and that there is no notable distortion about the alaninato chelate.[4b] Therefore, the reaction is not attributed to steric repulsion between the ligands.

Dissociation was then investigated for a series of alaninato complexes containing tetraamines. Table I lists the results after 1.5-h reaction in 0.1 mol dm^{-3} Na_2CO_3 (pH 11.2) at 40 °C. The reaction time is about 3 half-lives of the reaction of **4** at these conditions ($t_{1/2}$ = 28 min). The amount of dissociated alanine is highly dependent on the tetraamine ligand. Both *N*- and *C*-methyl substitutions affect the reaction, and dissociation of the alaninato ligand proceeds more readily as the number of substituents is increased. Therefore, the influence of the ligand field strength on this reaction is strongly suggested.

Conclusion

Methyl substitutions on a tetraamine ligand affect the ligand field strength of a cobalt(III) complex considerably. Their remarkable effects were indicated by characteristic shifts of ^{59}Co NMR resonances, and of electronic absorption maxima. The ^{59}Co line width also provides information concerning the effect of the substitutions. The observation of ^{59}Co NMR spectra is useful for obtaining detailed information concerning the structure of cobalt(III) complexes. A decrease in the ligand field strength caused by substitutions on the ligand affects the stability of a chelate, and the chelated alaninato ligand, which is generally inert, dissociates readily. Therefore, modification of ligands by substitution is useful for a delicate design of the ligand field and thus for regulation of reactivities or properties of metal complexes.

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(12) The activation energy obtained from the temperature-dependent measurements of the rate constants is E = 110 kJ mol^{-1}. Although this reaction is quite novel, the value is not very different from that of a known reaction: e.g., the value for dissociation of the carbonato chelate ligand under basic conditions is E = 100 kJ mol^{-1} (Lapidus, G.; Harris, G. M. *J. Am. Chem. Soc.* **1963**, *85*, 1223).