Isomerism of the Metal Complexes Containing Multidentate Ligands. V.[1] Preparation and Properties of Optically Active Tris(diaminosuccinato)cobaltates(III)

Masaaki Kojima, Yuzo Yoshikawa, and Kazuo Yamasaki
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya, 464

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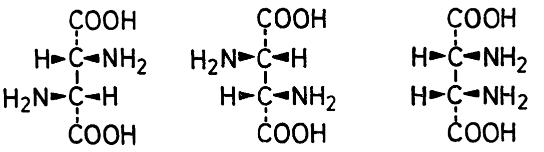
Tris(diaminosuccinato)cobaltates(III) with *meso, racemic,* and *laevorotatory* ligands were prepared and resolved by column chromatography on DEAE-cellulose and by the use of cinchonidine. The resolved complexes and their absolute configurations, assigned on the basis of the electronic and circular dichroism spectra, and on the basis of the elution order in cellulose column chromatography, are Δ-$(-)_{589}$-$[Co(mdas)_3]^{3-}$, Λ-$(+)_{589}$-$[Co(mdas)_3]^{3-}$, Λ(*lel*)-$[Co(ldas)_3]^{3-}$, and Δ(*ob*)-$[Co(ldas)_3]^{3-}$.

2,3-Diaminosuccinic acid is able to coordinate to metals with either amino groups or carboxyl groups. The copper and nickel complexes were studied in a previous report.[2] In the present paper, the preparations and properties of tris(diaminosuccinato)cobaltates(III) coordinating with amino groups will be described. The abbreviations $mdasH_2$, $rdasH_2$, and $ldasH_2$ are used for *meso, racemic,* and *laevorotatory* (589 nm) 2,3-diaminosuccinic acids respectively. Figure 1 shows three possible isomers of the ligand.



ldas H_2 (2*R*, 3*R*) ddasH_2 (2*S*, 3*S*) mdasH_2 (2*R*, 3*S*)

Fig. 1. Three possible isomers of 2,3-diaminosuccinic acid.

Experimental

Ligands. 2,3-Diaminosuccinic acid was prepared by the method of Toi *et al.*[3], while the *meso* and *racemic* forms were separated by the procedure of Farchy and Tafel.[4] To resolve racemic diaminosuccinic acid, the less soluble diastereoisomer of the benzoylated ligand[5] with cinchonidine was recrystallized several times from a 2: 1 mixture of water and ethanol. Then cinchonidine was precipitated by adding aqueous ammonia. The filtrate was acidified to obtain $(-)_{589}$-*N,N'*-dibenzoyldiaminosuccinic acid, which was then hydrolyzed with 6 M HCl to give $ldasH_2$.[6]

Preparation of the Complexes. The complexes with mdas, rdas, and ldas were prepared in a similar manner. To 2.4 g (9 mmol) of $[Co(NH_3)_6]Cl_3$ dissolved in 50 ml of water, a 4 g portion (27 mmol) of the ligand dissolved in 100 ml of the 0.5 M NaOH solution was added. After adding 0.5 g of active charcoal, the mixture was stirred for a few days at room temperature. The reaction mixture was then filtered, and the filtrate was subjected to column($\phi 2.7\times 120$ cm) chromatography on DEAE-Sephadex (A-25), with a 0.1 M sodium perchlorate as the eluent. A pink band was eluted first; it is a complex probably coordinating through both oxygen and nitrogen atoms of the ligand, but no further investigation of this complex was done. The main orange band, eluted slowly, was collected, and the effluent was evaporated to dryness *in vacuo.* After removing sodium perchlorate by extraction with methanol, the sodium salt was converted to the potassium salt by Dowex 50 W-X8 (K-form). The chemical compositions of the complexes thus prepared are given in Table 1.

TABLE 1. CHEMICAL COMPOSITIONS OF THE ISOMERS

Complex	Co (%)	N (%)	H_2O (%)
$K_3[Co(rdas)_3]\cdot 6H_2O$	8.06 (8.16)	11.31 (11.63)	14.57 (14.96)
$K_3[Co(mdas)_3]\cdot 6H_2O$	8.49 (8.16)	11.51 (11.63)	15.11 (14.96)
$(+)_{589}$-$Na_3[Co(ldas)_3]\cdot 6H_2O$	8.49 (8.74)	— —	16.03 (16.02)
$(-)_{589}$-$Na_3[Co(mdas)_3]\cdot 6H_2O$	8.75 (8.74)	12.59 (12.46)	15.88 (16.02)

Calculated values are given in parentheses.

Resolution of the mdas Complex with Cinchonidine. By the fractional crystallization of the diastereoisomers from water, the less soluble $(-)_{589}$-$(cinchonidine)_2K[Co(mdas)_3]\cdot 8\frac{1}{2}H_2O$ was obtained; it was then converted into the sodium salt by adsorption on DEAE-Sephadex and by subsequent elution with a 0.5 M sodium perchlorate solution (*cf.* Table 2). The resolved complex has the chemical composition of $(-)_{589}$-$Na_3[Co(mdas)_3]\cdot 6H_2O$ (Table 1).

TABLE 2. ABSORPTION AND CIRCULAR DICHROISM SPECTRA

Complex		Absorption		CD	
		$\tilde{\nu}_{max}$ (cm^{-1})	ε_{max}	$\tilde{\nu}_{max}$ (cm^{-1})	$\Delta\varepsilon_{max}$
$(+)_{589}$-$Na_3[Co(ldas)_3]\cdot 6H_2O$ Λ (lel) configuration	First Band	21100(473 nm)	110	20300(493 nm)	+3.21
	Second Band	29400(340 nm)	134	29000(345 nm)	−0.14
	CT Band	41700(240 nm)	10900	40000(250 nm)	−18
$(-)_{589}$-$Na_3[Co(mdas)_3]\cdot 6H_2O$ Δ configuration	First Band	21100(474 nm)	113	20300(493 nm)	−3.52
	Second Band	29400(340 nm)	139	29000(345 nm)	+0.15
	CT Band	41700(240 nm)	11000	40000(250 nm)	+12

CT: Charge transfer

Partial Resolution of the mdas Complex by Column Chromatography. The partial resolution of the mdas complex was accomplished by column chromatography on DEAE-cellulose, using a 0.1 M $NaClO_4$ solution as the eluent. The active complex resolved by the use of cinchonidine did not show any further increase in rotation when subjected to column chromatography on DEAE-cellulose, indicating a complete resolution.

The rdas complex too was resolved only partially by column chromatography.

Separation of the ldas Complex into Isomers. When the reaction mixture of $[Co(ldas)_3]^{3-}$ was eluted on a DEAE-cellulose column by the use of a 0.1 M $NaClO_4$ solution, it was separated into the fast-moving isomer I and the slow-moving isomer II. The chemical composition of the isomer II, which shows $(+)_{589}$, is given in Table 1. The isomer I, with a rotation of $(-)_{589}$, was obtained in only a minute amount, and so no chemical analysis has been done.

Measurements. All the measurements were carried out in the way described in previous papers.[1]

Results and Discussion

The mdas Complexes. The absorption (AB) and circular dichroism (CD) spectra of $(-)_{589}$-$Na_3[Co(mdas)_3]\cdot 6H_2O$ are shown in Fig. 2, while the data are listed in Table 2. This complex was tentatively assigned the *Δ* configuration, because it shows the following features required for that configuration: (a) The tris(diamine)cobalt(III) complex which has five-membered chelate rings and shows a major negative CD peak in the octahedral $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption region and a positive peak in the charge-transfer region generally has the *Δ* configuration, and (b) The tris(diamine)cobalt(III) complex, which is eluted first by HCl in a P-cellulose column, generally has the *Δ* configuration.[7]

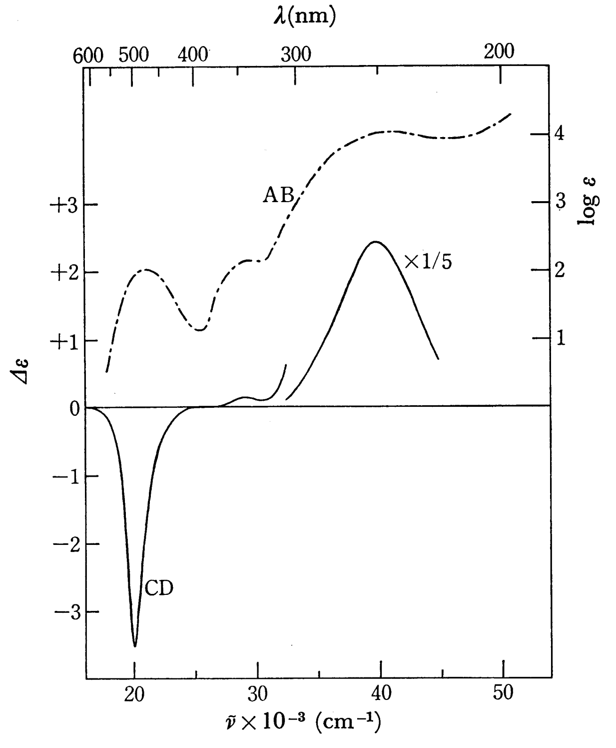


Fig. 2. AB and CD spectra of $(-)_{589}$-$Na_3[Co(mdas)_3]\cdot 6H_2O$.

For the mdas complex, two geometric isomers, *meridional* and *facial*, are possible from the alignment of the asymmetric carbons (*R* and *S*) for each of the absolute configurations, *Δ* and *Λ*. These isomers have not been detected by chromatography, although such isomers have been isolated for the tris(*meso*-2,3-butanediamine)cobalt(III) complex, which has a related structure.[8]

The ldas Complex. In Fig. 3 the AB and CD spectra of the isomer II, $(+)_{589}$-$Na_3[Co(ldas)_3]\cdot 6H_2O$, are shown, while the data are listed in Table 2. For the *Λ*(*lel*)-$[Co(d\text{-}pn)_3]^{3+}$ ion, a strong negative peak in the charge-transfer region has been found to be due to the contributions from both the configurational and vicinal effects with the same negative sign.[9] On the basis of this fact, and on the features mentioned above for the mdas complex, the absolute configuration *Λ*(*lel*) was assigned to the isomer II.

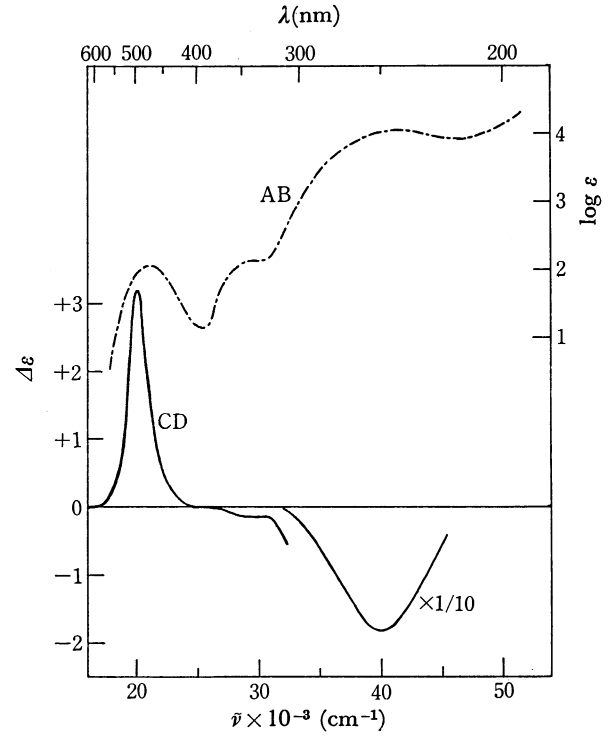


Fig. 3. AB and CD spectra of $(+)_{589}$-$Na_3[Co(ldas)_3]\cdot 6H_2O$.

As the *Λ*(*lel*) isomer was formed stereoselectively in a predominant amount, the absolute configuration of the ligand, $ldasH_2$, has been determined to be 2*R*,3*R* (Fig. 1). In this $(+)_{589}$-*Λ*(*lel*) complex, two carboxyl groups of the ligand assume equatorial positions with the *δ*(*lel*) conformation.

The CD spectrum of the isomer I, with the rotation of $(-)_{589}$, shows a negative peak at 480 nm in the d-d absorption region, and a negative and a positive peak in the charge-transfer region at 235 and 215 nm respectively. Taking into account the fact[9] that, in the charge-transfer region, the *Δ*(*ob*)-$[Co(d\text{-}pn)_3]^{3+}$ ion has a small negative CD peak at 240 nm and a relatively large positive peak at 212 nm, the isomer I is assigned the *Δ*(*ob*) configuration. The *Λ*(*ob*)-$[Co(l\text{-}pn)_3]^{3+}$ ion also shows almost the identical CD spectrum with the sign opposite to that of the $\Delta(ob)$-[Co(d-pn)$_3$]$^{3+}$ ion.[10]

The CD peak (480 nm) corresponding to the $^1E_a \leftarrow {}^1A_1(D_3)$ transition of the isomer I(*ob*) is at a shorter wavelength than that (493 nm) of the isomer II(*lel*); such a tendency has also been observed for the *lel* and *ob* isomers of the [Co(d-pn)$_3$]$^{3+}$ [9] and [Co(l-pn)$_3$]$^{3+}$.[10] The spectral data for the isomer I lack the intensity values because it is available in only a minute amount, and so no chemical analysis has been done.

Comparison between the mdas and ldas Complexes. For the tris(2,3-butanediamine)cobalt(III) ion, the $(+)_{589}$-bn complex has an absorption maximum (467 nm)[11] at a shorter wavelength than the *meso*-bn complex (473 nm).[8] This fact is consistent with the forced axial position of one of the two methyl groups for the latter complex, regardless of the chelate-ring conformation (δ or λ). For the das complex, however, the maximum of the octahedral $^1T_{1g} \leftarrow {}^1A_{1g}$ absorption of $\Lambda(lel)$-[Co(ldas)$_3$]$^{3-}$ is at almost the same wavelength as that of [Co(mdas)$_3$]$^{3-}$ (Table 2), although the latter has one axial carboxyl group. This spectral feature of the mdas complex is understandable on the basis of a hydrogen-bond formation between the oxygen atom of the axial carboxyl group and the hydrogen atom of the amino group on the adjacent chelate ring. In an acid solution, hydrogen bonds are usually weakened due to protonation. Actually, in 5 M HCl the first band maximum of the mdas complex* is shifted to a longer wavelength (483 nm) than that (479 nm) of the rdas complex.* A similar difference was observed in the solid state as well: 474 nm (mdas complex) and 470 nm (rdas complex).

For the complex, [Co(ldas)$_3$]$^{3-}$ two carboxyl groups are in the equatorial positions and it is difficult for strong intramolecular hydrogen bonds to be formed between the oxygen atom of the carboxyl group and the hydrogen atoms of the amino groups.

PMR Spectra. The PMR spectra for the mdas and rdas complexes* were measured in D_2O–D_2SO_4 at 60 MHz. The results, however, proved unfruitful, since no signal attributable to carboxyl groups was found down to 15 ppm, and furthermore other signals observed were too complicated and too broad to be analyzed.

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* In acid solutions these complexes are converted into the cations, [Co(mdasH$_2$)$_3$]$^{3+}$ and [Co(rdasH$_2$)$_3$]$^{3+}$ respectively. For the electronic and PMR spectral measurements where it is permissible, the rdas complex was used instead of the ldas complex because it is readily available.