July, 1994] © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 1825—1827(1994) 1825

Stereoselective Preparation and Characterization of $[Cr(amino\ acidato)_2(amino\ acidato\text{-}N)(Me_2SO)]$ Complexes

Hisaya Oki,* Yoshiki Kitagawa, and Ryuji Nakata
Department of Chemistry, Faculty of Education, Fukui University, Bunkyo 3-9-1, Fukui 910

(Received December 20, 1993)

New complexes of the type $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$, where AA stands for L-amino acidato ligands (valinato, isoleucinato, and leucinato) and AA-*N* represents monodentate L-amino acidato ligands with an amino nitrogen as a donor atom, were prepared by heating mixtures of $Cr(NO_3)_3 \cdot 9H_2O$ and sodium salts of amino acids in Me_2SO. For all the amino acids used, only complexes of the type $(+)_{546}$-$[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ were obtained. The presence of a Me_2SO molecule as a ligand was shown by the IR spectra of the crystals of the complexes. The bis-type complexes with L-valine and L-isoleucine were converted to $(-)_{546}$-isomers in MeOH and the resulting products were isolated. All the new complexes were confirmed to have facial configuration, $[Cr(O)_3(N)_3]$ from their UV-vis absorption spectra, as well as the corresponding tris-type complexes, $[Cr(AA)_3]$.

We have prepared *fac*-tris(amino acidato)chromium(III) complexes stereoselectively by solid-phase[1,2] or liquid-phase reactions in EtOH,[3] but the marked stereoselective preparation of *fac*-tris(amino acidato)chromium(III) has not been explained. To obtain deeper insight into this stereoselectivity, it is very important to try to prepare complexes of the type bis(amino acidato)(amino acidato-*N*)(solvent molecule) chromium(III), because such a complex is considered to be the precursor of the *fac*-tris(amino acidato)chromium(III) complex in a liquid-phase reaction. However, no study has been reported concerning the preparation of such bis-type chromium(III) complexes except for $[Cr(\text{L-phe})_2(\text{D-phe-}N)(OH_2)]$.[4]

We have succeeded in the preparation of some new bis(amino acidato)(amino acidato-*N*)(dimethyl sulfoxide) chromium(III) complexes containing L-valine, L-isoleucine, and L-leucine by using $Cr(NO_3)_3 \cdot 9H_2O$ as a starting material. We report here the preparation methods and characterization of these new complexes.

Experimental

Preparation of $(+)_{546}$-$[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$. $Cr(NO_3)_3 \cdot 9H_2O$ (1.20 g, 3 mmol as Cr) and the sodium salt of L-valine (1.504 g, 9 mmol) were dissolved in Me_2SO (15 cm^3) and the mixture was heated at 90 °C in a water bath for 3 h. The pink crystals produced during the heating were filtrated after being cooled to room temperature. The crystals obtained were $(+)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)] \cdot 0.5Me_2SO \cdot 1.5H_2O$. In the case of L-isoleucine or L-leucine, no complex was deposited on heating (reaction time: 3 h). Therefore, at the end of the reaction, the resulting solution was concentrated to half of its original volume, yielding $(+)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)] \cdot 0.5Me_2SO \cdot 1.5H_2O$ or $(+)_{546}$-$[Cr(leu)_2(leu\text{-}N)(Me_2SO)] \cdot H_2O$ as pink crystals.

Preparation of $(-)_{546}$-$[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$. $(+)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)] \cdot 0.5Me_2SO \cdot 1.5H_2O$ (0.20 g, 0.36 mmol) was dissolved in MeOH (50 cm^3). The solution was kept standing in a sealed flask at 25 °C for 2 d. The resulting solution was evaporated to dryness under reduced pressure, yielding $(-)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)] \cdot 0.5Me_2SO \cdot 1.5H_2O$ as pink crystals. $(-)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)] \cdot 4H_2O$ was also obtained as pink crystals by the same method, but the preparation of $(-)_{546}$-$[Cr(leu)_2(leu\text{-}N)(Me_2SO)]$ coluld not be accomplished.

The yields and elemental analyses for the complexes obtained are summarized in Table 1.

Measurements. The UV-vis spectra were recorded on a Hitachi 220A spectrophotometer. The CD measurements were made with a JASCO-J-500A spectropolarimeter and the optical rotations were measured with a JASCO-DIP-4 digital polarimeter. The IR spectra were taken on a Hitachi grating infrared spectrophotometer Model EPI-G3 by the KBr method.

Results and Discussion

UV-vis Absorption Spectra. The absorption spectra of $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ in Me_2SO were measured for three kinds of amino acid complexes. The spectral data of these complexes are listed in Table 2. All the spectra of the $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ complexes have similar shapes and peak positions. These spectra are also similar in the first peak position to the corresponding *fac*-$[Cr(AA)_3]$ complexes spectra, but the second peak positions in these complexes are shifted to lower wavelengths. In addition, the absorption coefficients of the first and second bands of these complexes are lower than those of the *fac*-$[Cr(AA)_3]$ complexes as seen in Fig. 1, which is drawn for the case of L-leucine. Their peak positions suggested that the $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ complexes, as well as $[Cr(AA)_3]$, have a facial configuration $[Cr(O)_3(N)_3]$ with respect to the nitrogen and oxygen donor atoms. Accordingly, the configuration of the new complexes obtained was presumed to be as follows; the two amino acidato ligands formed chelate rings, whereas the third amino acidato ligand coordinated to Cr^{3+} through its nitrogen atom as a monodentate, and so a solvent molecule also coordinated to Cr^{3+} through an oxgen atom. It will be shown later, based on the IR spectra, that the solvent molecule as a ligand in the crystal is not water but Me_2SO. For this type of complex, two possible structures can be considered, that is, cis and trans configurations with respect to the mutual position of the coordi-

Table 1. Analytical Data and Yields of $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$

Complexes	C (%)		H (%)		N (%)		Yield
	Calcd	Found	Calcd	Found	Calcd	Found	%
$(+)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)]\cdot 0.5Me_2SO\cdot 1.5H_2O$	39.69	39.91	7.77	7.31	7.72	7.71	80
$(-)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)]\cdot 0.5Me_2SO\cdot 1.5H_2O$	39.69	39.60	7.77	7.38	7.72	7.94	80
$(+)_{546}$-$[Cr(leu)_2(leu\text{-}N)(Me_2SO)]\cdot H_2O$	44.59	44.59	8.17	7.72	7.80	7.74	20
$(+)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)]\cdot 0.5Me_2SO\cdot 1.5H_2O$	42.97	42.95	8.18	7.82	7.16	7.08	15
$(-)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)]\cdot 4H_2O$	40.52	40.77	8.44	7.21	7.09	7.06	80

Table 2. Absorption Maxima and CD Maxima of $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$

Complexes	Absorption maxima (nm) and $\log \varepsilon$				CD maxima (nm) and $\Delta\varepsilon$			
	λ	$(\log \varepsilon)$	λ	$(\log \varepsilon)$	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$
$(+)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)]$	522	(1.90)	377	(1.87)	506	(+2.12)	390	(−0.72)
$(-)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)]$	522	(1.91)	377	(1.87)	494	(−2.20)	384	(+0.43)
$(+)_{546}$-$[Cr(leu)_2(leu\text{-}N)(Me_2SO)]$	522	(1.89)	376	(1.87)	502	(+2.08)	394	(−0.80)
$(+)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)]$	523	(1.88)	375	(1.81)	504	(+1.93)	394	(−0.67)
$(-)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)]$	523	(1.88)	375	(1.81)	493	(−2.57)	387	(+0.50)

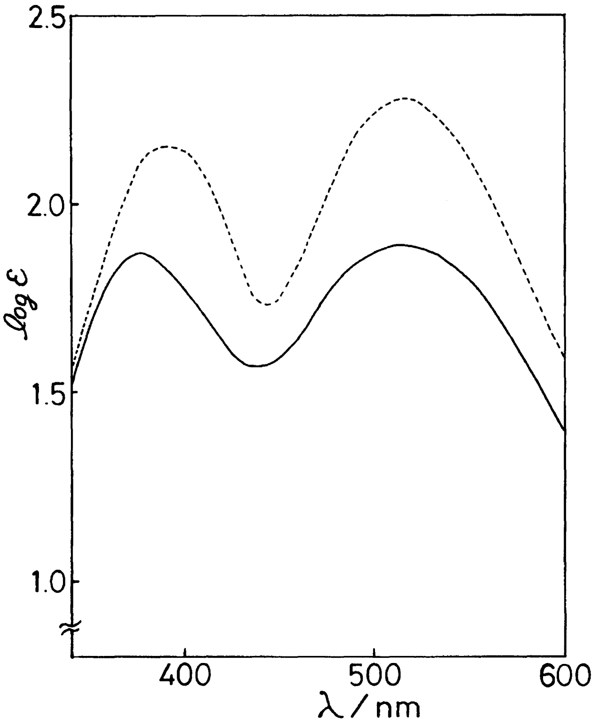

Fig. 1. Absorption spectra of *fac*-$(+)_{546}$-$[Cr(leu)_3]$ (---) and $(+)_{546}$-$[Cr(leu)_2(leu\text{-}N)(Me_2SO)]$ (—) in Me_2SO.

nating Me_2SO and the nitrogen atom of the monodentate amino acidato ligand. All complexes obtained were optically active as described below. These facts suggest that $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ complexes have cis configutations.

CD Spectra. The CD spectra for $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ were measured in Me_2SO. Their numerical data are summarized in Table 2. The CD spectra for $[Cr(ile)_2(ile\text{-}N)(Me_2SO)]$ and *fac*-$[Cr(ile)_3]$ are shown in Fig. 2. The shape and peak positions of the CD curves of $(+)_{546}$- or $(-)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)]$ are similar to those of the corresponding *fac*-$[Cr(ile)_3]$ complexes, and they are also very similar to those of $(+)_{546}$- or $(-)_{546}$-$[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ containing other amino acids, respectively. The magnitude of $\Delta\varepsilon$ showed that those complexes obtained were of fairly highly optical purity, although the separation of these

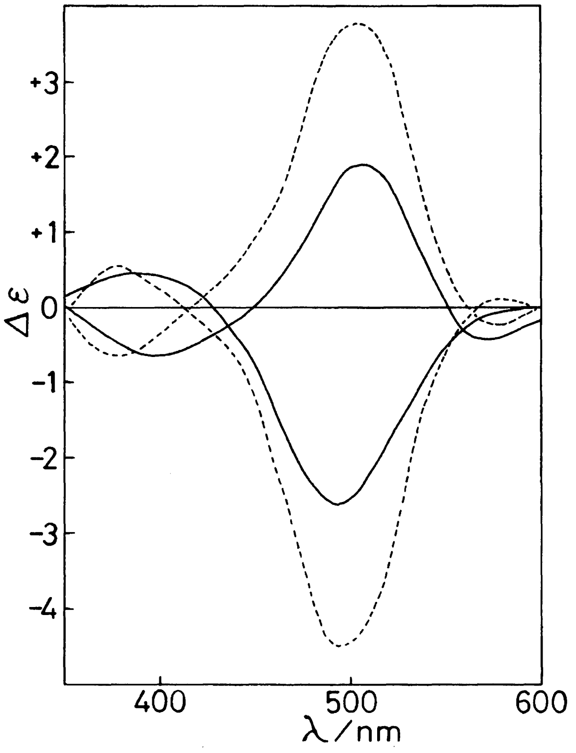

Fig. 2. CD spectra of *fac*-$(+)_{546}$- and *fac*-$(-)_{546}$-$[Cr(ile)_3]$ (---) and $(+)_{546}$- and $(-)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)]$ (—) in Me_2SO.

optical isomers was not always perfect. Their configurations could be reasonably identified as Λ for the $(+)_{546}$-isomer and Δ for the $(-)_{546}$-isomer by comparing the CD curves of the present complexes with those of *fac*-Λ, Δ-$[Cr(AA)_3]$.

IR Spectra. The IR absorption spectra of $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ were measured in the range of 4000 to 400 cm^{-1} and compared with those of *fac*-$[Cr(AA)_3]$. It is known that the S=O stretching frequency of Me_2SO complexes (980—930 cm^{-1}), in which coordination occurs through oxygen, is lower than that of free Me_2SO (1100—1055 cm^{-1}).[5] In the range of 1000 to 900 cm^{-1} in the spectra of Λ-$(+)_{546}$-, Δ-$(-)_{546}$-$[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$, and *fac*-$\Lambda$-$[Cr(AA)_3]$, it was seen that the absorption peaks assigned to the S=O stretching frequency appeared at ca. 950 cm^{-1} for the two former complexes, but that the corresponding peak did not appear for the latter. These results were in accord with expectations based on the UV-vis absorption spectra, in which it was suggested that the coordination with a solvent molecule occurred through oxgen in a bis-type complex. Since the crystallization of $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ for X-ray crystallographic analyses is unsuccessful at present, the existence of a Me_2SO molecule as a ligand could only be evidenced by observing this IR absorption peak. The M–O stretching band of the Me_2SO complex is also observed in the range of 500—400 cm^{-1},[5] and the spectra of the $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ complexes are certainly different from those of *fac*-$[Cr(AA)_3]$ in this absorption region. However, it was impossible to distinguish the M–O stretching band for Me_2SO in $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ from both the M–O and M–N stretching bands of the amino acidato ligands, which were also observed in this wavenumber region. Also, the absorption peak assigned to the COOH stretching vibration did not appear at 1730—1700 cm^{-1} in any spectrum of the $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ or *fac*-$[Cr(AA)_3]$ complexes, but a peak shifted to about 1620 cm^{-1} did appear. Accordingly, it is concluded that the carboxyl group of a monodentate amino acidato is in the form COO^-, though it cannot be determined whether the carboxyl group is linked by a hydrogen-bond to the amino group of the amino acidato ligands or not.

Reactions of $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ in Solutions. Complexes of the type $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ were much more soluble in MeOH, EtOH, or *N*,*N*-dimethylformamide (DMF) than the *fac*-$[Cr(AA)_3]$ complexes and the resulting solutions exhibited different behaviors according to the solvents used as described below. In water, purple crystals precipitated, which were considered to be a dimeric form. As mentioned in the experimental section, Λ-$(+)_{546}$-$[Cr(val)_2(val\text{-}N)(Me_2SO)]$ and Λ-$(+)_{546}$-$[Cr(ile)_2(ile\text{-}N)(Me_2SO)]$ isomerized to the corresponding Δ-$(-)_{546}$-isomers in MeOH, but Λ-$(+)_{546}$-$[Cr(leu)_2(leu\text{-}N)(Me_2SO)]$ racemized. The existence of a Me_2SO molecule as ligand in the Δ-$(-)_{546}$-isomer was confirmed by IR spectra measurements of crystals isolated from MeOH solutions. All $[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ in EtOH underwent similar behaviors, but in concentrated EtOH solutions, $[Cr(ile)_2(ile\text{-}N)(Me_2SO)]$ and $[Cr(val)_2(val\text{-}N)(Me_2SO)]$ gave the precipitates of the corresponding *fac*-Λ-$[Cr(AA)_3]$ on standing at room temperature, in spite of the fact that UV-vis spectra and optical rotations of the remaining solutions showed the predominant presence of Δ-$(-)_{546}$-$[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$. Accordingly, with regard to the stereoselective preparation of *fac*-Λ-$[Cr(AA)_3]$ in EtOH reported in the previous paper,[3] complexes of the type $[Cr(AA)_2(AA\text{-}N)L]$ must serve as a kind of precursor, that is, the stereoselective precipitation of *fac*-Λ-$[Cr(AA)_3]$ was supposed to occur owing to the sparingly soluble character of *fac*-Λ-$[Cr(AA)_3]$ formed by structural changes of $[Cr(AA)_2(AA\text{-}N)L]$, where L denotes a solvent molecule as a ligand. On the other hand, in DMF, which is a less polar aprotic solvent than Me_2SO, the isomerization from Λ-$(+)_{546}$-$[Cr(AA)_2(AA\text{-}N)(Me_2SO)]$ to the Δ-$(-)_{546}$-isomer, accompanied by the exchange of a solvent molecule as a ligand, was confirmed by measuring optical rotations of solutions and IR spectra of crystals isolated from the DMF solution.

From the results described above, it has become apparent that complexes of the type $[Cr(AA)_2(AA\text{-}N)L]$ are stable and isomerize from the Λ-isomer to the Δ-isomer readily in non-aqueous solvenrs such as MeOH, EtOH, DMF, or Me_2SO. Furthermore, under certain conditions, the conversion from $[Cr(AA)_2(AA\text{-}N)L]$ to $[Cr(AA)_3]$ also occurs. In order to understand the solution behavior of (amino acidato)chromium(III) complexes in non-aqueous solvents, more detailed experiments on the equilibria between $[Cr(AA)_2(AA\text{-}N)L]$ and $[Cr(AA)_3]$ are in progress and will be presented elesewhere.

References

1) H. Oki and K. Otsuka, *Bull. Chem. Soc. Jpn.*, **49**, 1841 (1976).

2) H. Oki, *Bull. Chem. Soc. Jpn.*, **50**, 680 (1977).

3) H. Oki and A. Kuwamura, *Synth. React. Inorg. Met. -Org. Chem.*, **21**, 1313 (1991).

4) H. Oki, M. Enomae, and Y. Yoshimura, *Synth. React. Inorg. Met. -Org. Chem.*, **19**, 1085 (1989).

5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, John Wiley & Sons, New York (1970), p. 210.