Preparation and Characterization of (Amino carboxamidato-*N*,*N*′)(chloro)(dimethyl sulfoxide-*S*)-platinum(II) Complexes

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Several square-planar complexes of the [PtCl(aaa-*N*,*N*′)(dmso-*S*)] type were prepared (aaa=amino acid amidate, dmso=dimethyl sulfoxide). The crystal and molecular structures for *cis*(*NH*$_2$,*S*)-[PtCl(DL-alaa)(dmso)]·H$_2$O (**4**) and *trans*(*NH*$_2$,*S*)-[PtCl(DL-vala)(dmso)] (**3b**) were determined by X-ray diffraction (alaa=alaninamidate, vala=valinamidate). The crystal of **4** was triclinic, space group $P\bar{1}$ with a=9.144(2), b=9.172(3), c=7.371(2) Å, α=109.41(2)°, β=99.69(2)°, γ=76.13(3)°, Z=2, and final R=0.029 and R_W=0.034. The crystal of **3b** was monoclinic, space group $P2_1$ with a=7.158(2), b=9.948(2), c=8.741(2) Å, β=102.76(2)°, Z=2, and final R=0.041 and R_W=0.050. Both complexes were found to contain a carboxamidato group coordinating to platinum(II) through the nitrogen atom. A larger trans influence was observed for the coordinating carboxamidato nitrogen atom than for the amino one. The prepared complexes were characterized by NMR, visible and UV, and CD spectra in comparison with the complexes of [PtCl(aa-*N*,*O*)(dmso-*S*)] type (aa=amino acidate).

Amino carboxamides usually coordinate transition metal ions, such as copper(II), nickel(II), palladium(II),[1,2] cobalt(III),[3,4] ruthenium(II), and ruthenium(III),[5] through the amino nitrogen and one of the oxygen or nitrogen atoms of the carboxamide group. In Chart 1 the corresponding coordination modes (A and B) are shown together with the others found in various metal complexes of the carboxamide or carboxamidato group. Mode C and the corresponding amino-iminol-*N*,*N*′coordination of amino carboxamide are known concerning some complexes.[6]

Platinum(II) complexes with various carboxamides, containing peptides, pyridone, etc., have been actively investigated during the last two decades in connection with 'platinum blue' analogs or with antitumor

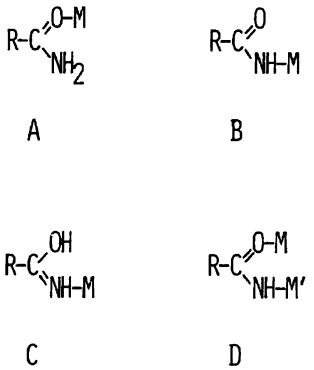

Chart 1.

effects. However, most of the complexes investigated contain the bridging mode D.[7—9] Information is unexpectedly limited, not only for the N,O- and N,N′-coordinations of amino carboxamide or amino carboxamidato ligands, but also for modes A and B of the carboxamides. Most of the information concerns only spectroscopic evidence.[7,10—13]

In the present paper we report on the preparation of several complexes of the [PtCl(aaa-*N*,*N*′)(dmso-*S*)] type, cis(*NH*$_2$,*S*) and trans(*NH*$_2$,*S*) isomers, which were confirmed by X-ray crystallography (Haaa=amino acid amide and dmso=dimethyl sulfoxide). The characterization of these complexes was made in comparison with analogous complexes of the [PtCl(aa-*N*,*O*)(dmso-*S*)] type (Haaa=amino acid).

Experimental

Materials. Haaa's and the starting complexes, *cis*-[PtCl$_2$(dmso)$_2$] (**1**) and K[PtCl$_3$(dmso)] (**2**), were prepared according to literature.[1,14]

The following abbreviations are used for individual aa and aaa ligands: ala=alaninate, leu=leucinate, ile=isoleucinate, phe=phenylalaninate, val=valinate, glya=glycinamidate, alaa=alaninamidate, leua=leucinamidate, ilea=isoleucinamidate, and vala=valinamidate.

Preparation of [PtCl(aaa)(dmso)]-Type Complexes. Elemental-analysis data of the complexes are given in Table 1.

***cis*(*NH*$_2$,*S*)-[PtCl(glya)(dmso)]·H$_2$O.** An aqueous solution of KOH (1 M (=1 mol dm^{-3}), 1 cm^3) was added

Table 1. Results of Elemental Analysis for [PtCl(L)(dmso)]·nH$_2$O

Complex				Found (Calcd)		
Isomer[a)]	L	n	Abbrev.	C/%	H/%	N/%
Cis	glya	1		12.00 (12.02)	3.41 (3.28)	6.86 (7.01)
Cis	L-alaa	0.5		14.56 (14.84)	3.44 (3.49)	6.66 (6.92)
Cis	DL-alaa	1	**4**	14.59 (14.51)	3.75 (3.65)	6.66 (6.77)
Cis	L-leua	0.5		21.66 (21.50)	4.50 (4.51)	6.23 (6.27)
Cis	L-ilea	1		21.14 (21.08)	4.58 (4.64)	6.12 (6.15)
Trans	L-vala	0	**3a**	19.86 (19.84)	4.04 (4.04)	6.56 (6.61)
Cis	L-vala	0		19.82 (19.84)	3.99 (4.04)	6.58 (6.61)
Trans	DL-vala	0	**3b**	19.80 (19.84)	4.06 (4.04)	6.56 (6.61)
Cis	DL-vala	2		18.34 (18.28)	4.80 (4.60)	6.05 (6.09)
Cis	L-ala	0.5		14.83 (14.80)	3.40 (3.23)	3.23 (3.45)
Trans	L-leu	0		21.89 (21.90)	4.06 (4.13)	3.15 (3.19)
Cis	L-leu	1		21.15 (21.03)	4.31 (4.41)	3.14 (3.07)
Trans	L-ile	1		21.01 (21.03)	4.45 (4.41)	3.03 (3.07)
Cis	L-ile	0		21.52 (21.90)	4.24 (4.13)	3.13 (3.19)
Trans	L-phe	1		26.84 (26.92)	3.74 (3.70)	2.83 (2.85)
Cis	L-phe	0		27.68 (27.94)	3.60 (3.41)	2.64 (2.96)
Trans	L-val	1		19.09 (18.99)	4.12 (4.10)	3.14 (3.16)

a) Cis and trans are referred to amino and dmso ligands.

dropwise to a suspension containing 422 mg (1 mmol) of **1** and 80 mg (1.1 mmol) of Hglya in 20 cm^3 of water. Complex **1** was gradually dissolved under stirring for 15 min. The reaction mixture was filtered once. The filtrate was evaporated under reduced pressure until a white precipitate appeared. After standing for 10 min the precipitate was filtered, washed with cold water and dried under reduced pressure. Yield, 70 mg.

***trans*(*NH*$_2$,*S*)-[PtCl(L-vala)(dmso)] (3a).** An aqueous solution of KOH (1 M, 1 cm^3) was added dropwise to a solution of 420 mg of **2** and 120 mg of L-Hvala in 20 cm^3 of water. After mechanical stirring for 20 min, a pale-yellow crystalline precipitate separated as needles or long plates. It was filtrated, washed with cold water, and dried under reduced pressure. Yield 210 mg.

***cis*(*NH*$_2$,*S*)-[PtCl(L-vala)(dmso)].** This isomer separated out as much larger colorless prisms after removing most of the trans isomer in the above-mentioned procedure. The contaminated trans isomer was removed by decantation. The obtained cis complex was dried in air.

The yields of the two isomers were roughly comparable; both isomers were sparingly soluble in water. Similar results were obtained by using **1** in place of **2** in the above-mentioned procedures.

***cis*(*NH*$_2$,*S*)- [PtCl(DL- vala)(dmso)]·2H$_2$O and *trans*(*NH*$_2$*S*)-[PtCl(DL-vala)(dmso)] (3b).** These complexes were prepared using DL-Hvala and **2** in a similar method to that described above for the optically active L-vala analogs. In this case, however, a cis isomer separated out first as colorless fine needles. After the cis isomer had been removed, a comparable amount of pale-yellow rectangular plates of trans isomer crystallized out from the mother solution.

Other Complexes of *cis*(*NH*$_2$,*S*)- [PtCl(aaa)-(dmso)]·nH$_2$O Type (aaa=L-alaa, n=0.5; aaa=DL-alaa, n=1; aaa=L-leua, n=0.5; and aaa=L-ilea, n=1). The desired precipitate of every complex was obtained as the first crop of precipitates in a procedure similar to that for the corresponding glya complex. The reaction time was 15—50 min, and the yields were 15—30%.

The prismatic crystals of *cis*(*NH*$_2$,*S*)-[PtCl(DL-alaa)-(dmso)]·H$_2$O (**4**) used for the X-ray analysis were obtained by standing a saturated aqueous solution in a desiccator under reduced pressure.

[PtCl(aa)(dmso)]-Type Complexes. Elemental-analysis data of the complexes are also given in Table 1.

***cis*(*NH*$_2$,*S*)-[PtCl(L-ala)(dmso)]·0.5H$_2$O.** An aqueous solution of KOH (1 M, 1 cm^3) was added dropwise to a suspension containing 422 mg (1 mmol) of **1** and 200 mg (2.2 mmol) of L-Hala in 15 cm^3 of water. After mechanical stirring for 15 min, the resulting solution was evaporated to a small volume under reduced pressure. The desired complex then precipitated as needle crystals. They were filtrated, washed with cold water, and dried under reduced pressure. Yield, 50 mg.

Other Complexes of *cis*(*NH*$_2$,*S*)- [PtCl(L- aa)-(dmso)]·nH$_2$O (aa=leu, n=1; aa=ile, n=0; and aa=phe, n=0). These complexes were also prepared according to the method described above for the L-ala complex.

Other Complexes of *trans*(*NH*$_2$,*S*)- [PtCl(L- aa)-(dmso)]·nH$_2$O (aa=val, n=1; aa=leu, n=0; aa=ile, n=1; and aa=phe, n=1). These complexes were prepared from **2** and the relevant Haa according to the literature method for the corresponding L-ala complex.[15,16]

Another Procedure for *trans*(*NH*$_2$,*S*)- and *cis*-(*NH*$_2$,*S*)-[PtCl(L-leu)(dmso)]. To a solution of 1.0 mmol of **2** in 15 cm^3 of water were added 1.0 mmol of L-Hleu and 1 cm^3 of 1 M KOH. After stirring for 20 min at 80 °C a yellow precipitate appeared. The reaction was continued for an additional 30 min, after which the resulting mixture was cooled to room temperature. The yellow precipitate of the deposited trans isomer was collected on a filter. Yield, 75 mg.

After the filtrate had been heated at 80 °C for 1 h and cooled to room temperature, a white precipitate of the cis isomer appeared. It was filtered, washed with cold water, and dried under reduced pressure. Yield, 80 mg.

Table 2. Crystal Data for **3b** and **4**

Compound	**3b**	**4**
Formula	$C_7H_{17}O_2N_2SClPt$	$C_5H_{15}O_3N_2SClPt$
Fw	423.83	413.79
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$(No. 4)	$P\bar{1}$(No. 2)
a/Å	7.158(2)	9.144(2)
b/Å	9.948(2)	9.172(3)
c/Å	8.741(2)	7.371(2)
α/°		109.41(2)
β/°	102.76(2)	99.69(2)
γ/°		76.13(3)
V/Å^3	607.1(2)	563.4(3)
Z	2	2
D_{calcd}/g cm^{-1}	2.318	2.439
Crystal size/mm	0.2×0.2×0.1	0.3×0.2×0.15
Crystal color	Pale yellow	Colorless
Crystal shape	Plate	Prismatic
2θ range/°	3 — 60	3 — 60
Temp/°C	23	23
No. of unique data	1886	3311
No. with $\|F_o\|>3\sigma\|F_o\|$	1650	2933
R[a)]	0.041	0.029
R_w[b)]	0.050	0.034

a) $R=\sum\||F_o|-|F_c|\|/\sum|F_o|$. b) $R_w=[(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2)]^{1/2}$; $w=1/\sigma^2|F_o|$.

This complex has proved to be identical with *cis*(NH_2,*S*)-[PtCl(L-leu)(dmso)]·H_2O prepared by the above-mentioned method based on IR measurements.[17]

Measurements. A Hitachi 330 spectrophotometer was employed to measure the visible and UV absorption (AB) spectra, and a JASCO model MOE-1 J-20 spectropolarimeter for the circular dichroism (CD) spectra. The AB and CD spectra were measured in 0.3 M KCl at room temperature. The ^{1}H NMR spectra were recorded with a JEOL JNM-GSX-400 spectrometer in D_2O containing sodium 3-(trimethylsilyl)propionate-d_4 as an internal standard.

X-Ray Structure Determination. Each crystal of **4** and **3b**, having suitable dimensions, was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). All calculations were performed using the TEXSAN crystallographic software package.[18,19]

The structures were solved by heavy-atom methods, and refined by full-matrix (**4**) and block-diagonal matrix (**3b**) least-squares techniques.[20] The non-hydrogen atoms were refined anisotropically. The arrangements of the atoms in and around the carboxamidato groups could be accounted for in terms of coordination mode B in both **3b** and **4**, as described below. Further descriptions concerning the coordination mode will be given in Results and Discussion. The refined position of hydrogen H(1) coinsided with one of the approximately trigonal planar coordination positions around N(1), and no hydrogen atom was found in the neighborhood of O(1) in **4**. For the latter complex, all of the hydrogen atoms were refined isotropically, except for the three hydrogen atoms of the alaa methyl group and the two of the water of crystallization. The methyl hydrogens were fixed at calculated positions. For **3b** all hydrogens were fixed at calculated positions.

The absolute configuration of the vala ligands in **3b** was determined to be of the L-form based on the following calculations. Without the anomalous-dispersion terms the R value was 0.053, whereas by including these terms the R values were 0.043 and 0.053 for the L- and D-vala complexes, respectively.

Results and Discussion

Molecular and Crystal Structures. Selected crystallographic data for *cis*(NH_2,*S*)-[PtCl(DL-alaa)(dmso)]·H_2O, **4**, and *trans*(NH_2,*S*)-[PtCl(L-vala)(dmso)], **3b**, are given in Table 2; the final atomic coordinates and equivalent isotropic temperature factors are given in Table 3. Important bond lengths and angles for **4** and **3b** are listed in Table 4.[20] ORTEP drawings of the complexes are shown in Fig. 1, together with the numbering scheme.

The square-planar coordination geometry is common to **4** and **3b**, where the aaa ligands are coordinated by an amino N(2) and an amidato N(1) atom, and the dmso ligands by sulfur. The positions of the Pt, Cl, S, N(1), and N(2) atoms deviate from the relevant least-squares plane by +0.019, −0.020, +0.010, +0.014, and −0.024 Å for **4** and by −0.070, −0.025, +0.059, −0.037, and +0.068 Å for **3b**, respectively.

The Pt–N(1) bond lengths are 1.988 for **4** and 1.89 Å for **3b**, the ligand atom trans to N(1) being S for **4** and Cl for **3b**. These data clearly show the well-known trans influence of the dmso S atom; this influence is also found in the Pt–N(2) lengths.

The Pt–S length is longer for **4** than for **3b**, while the

Table 3. Final Atomic Coordinates and B_{eq}(Å^2)[a] for **3b** and **4**

	3b				**4**			
Atom	x	y	z	B_{eq}	x	y	z	B_{eq}
Pt	0.07500(6)	0.25	0.19189(5)	1.85(2)	0.11475(2)	0.25734(2)	0.06413(3)	2.113(8)
Cl	−0.0960(7)	0.4149(6)	0.0196(6)	4.3(2)	0.3287(2)	0.1318(2)	−0.0953(2)	3.70(6)
S	0.3177(5)	0.2672(9)	0.0760(4)	2.3(1)	0.2335(2)	0.2506(2)	0.3492(2)	2.53(5)
O(1)	0.194(2)	0.019(1)	0.576(1)	3.1(5)	−0.2534(6)	0.3344(7)	−0.3132(7)	4.3(2)
O(2)	0.478(2)	0.178(1)	0.139(1)	2.9(5)	0.1462(6)	0.3427(5)	0.5137(6)	3.6(2)
N(1)	0.192(2)	0.124(1)	0.345(1)	2.3(5)	−0.0133(6)	0.2737(6)	−0.1774(7)	2.9(2)
N(2)	−0.128(2)	0.246(4)	0.326(1)	2.1(4)	−0.0862(6)	0.3601(6)	0.1773(7)	2.8(2)
C(1)	0.123(2)	0.097(2)	0.473(2)	2.3(5)	−0.1583(7)	0.3276(7)	−0.1728(9)	3.0(2)
C(2)	−0.047(2)	0.187(2)	0.484(2)	2.0(5)	−0.2113(7)	0.3951(9)	0.030(1)	3.5(3)
C(3)	−0.195(2)	0.112(2)	0.549(2)	2.7(6)	−0.348(1)	0.339(1)	0.046(1)	5.6(4)
C(4)	−0.348(3)	0.210(2)	0.586(2)	3.3(7)	0.410(1)	0.309(1)	0.391(1)	4.6(4)
C(5)	−0.295(3)	−0.003(2)	0.451(2)	3.3(7)	0.286(1)	0.0544(9)	0.360(1)	4.4(3)
C(6)	0.249(2)	0.262(6)	−0.128(2)	4.0(7)				
C(7)	0.408(3)	0.437(2)	0.090(3)	4.3(9)				
O(3)					0.8692(7)	0.1433(7)	0.3552(8)	5.0(3)

a) $B_{eq}=(8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{i,j}\, a_i^* a_j^* \boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 4. Interatomic Distances (Å) and Angles (°) for **3b** and **4**

	3b	**4**
Pt–Cl	2.376(5)	2.309(2)
Pt–S	2.202(4)	2.210(2)
Pt–N(1)	1.89(1)	1.988(5)
Pt–N(2)	2.06(1)	2.030(5)
S–O(2)	1.46(1)	1.464(4)
S–C(dmso)	1.75(1)	1.766(8)
	1.80(3)	1.773(7)
O(1)–C(1)	1.21(2)	1.243(8)
N(1)–C(1)	1.35(2)	1.302(8)
N(2)–C(2)	1.49(2)	1.492(8)
C(1)–C(2)	1.53(2)	1.530(9)
C(2)–C(3)	1.51(2)	1.50(1)
Cl–Pt–S	90.2(2)	93.37(6)
Cl–Pt–N(1)	173.4(4)	93.1(2)
Cl–Pt–N(2)	92.6(7)	174.0(1)
S–Pt–N(1)	96.0(4)	173.6(1)
S–Pt–N(2)	172.2(5)	92.2(2)
N(1)–Pt–N(2)	81.0(8)	81.4(2)
Pt–S–O(2)	114.5(6)	114.8(2)
N(2)···O(3)		2.854(8)
O(1)···O(3)		2.727(7)
O(2)···N(2)		2.915(7)
O(2)···N(1)		3.199(7)
O(1)···N(2)	2.91(4)	
O(2)···N(2)	3.01(2)	

Pt–Cl lengths of these complexes are in reverse order. These data indicate a larger trans influence of the N(1) over N(2) atoms, i.e., the amidato nitrogen over the amino nitrogen. The Pt–Cl length for **3b** (2.376 Å) is appreciably long compared to the usually found 2.29—2.34 Å.[6b,9,21]

The coordination geometry of chloro(glycyl-L-methioninato–*N*,*N*′,*S*)platinum(II) is interesting, since it is very similar to that of **3b**. The lengths of mutually trans Pt–N(1) and Pt–Cl are 1.98 and 2.30 Å in the former complex,[10] being considerably longer and shorter than those of **3b**, respectively. The trans influence of the coordinating amidato nitrogen seems to be weakened in the dipeptide complex by a steric effect or a substituent effect.

Regarding the geometry of the coordinating carboxamidato group in **3b**, it is worth noting that the C–N bond length (1.35) is very long, while the C–O length (1.21 Å) is short compared to those in the other aaa complexes. The data to be compared are: 1.302 and 1.243 in **4**; (1.313/1.323) and (1.267/1.245) in bis(L-prolinamidato)nickel(II);[2] and 1.334 and 1.244 Å in a glycinamidatoruthenium(III) complex.[5b] It may be supposed that the long C–N and short C–O lengths are closely associated with the 'very short' Pt–N(1) bond in **3b**.

One molecule of the complex in **4** is related by a center of symmetry to another, enantiomeric, molecule within a unit cell. Thus, **4** is a racemic compound. On the other hand, one complex molecule in **3b** is related by a spiral axis to another of the same chilarity within a unit cell. A crystalline aggregate of **3b** should thus be a racemic mixture.

A couple of weak hydrogen bonds of the same kind (N(2)···O(2)) doubly bind the enantiomeric pair of the complexes in **4**, as shown in Fig. 2. On the other hand, the complex molecules of each individual enantiomer are linked to each other by a set of successive hydrogen bonds (N(2)···O(3) and O(3)···O(1), where O(3) is of the water molecule). As a whole, the hydrogen-bond system constructs linear ribbons extending along the *C*-axis. The structure of the ribbon is reinforced by weak hydrogen bonds of another kind (O(2)···N(1)), which is

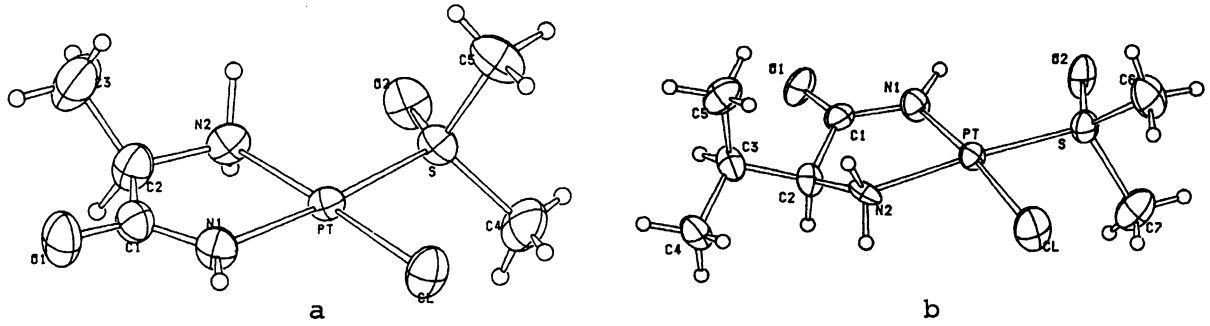

Fig. 1. Molecular structures and numbering of atoms for a) **4** and b) **3b**. Notation like N(1), C(2), etc. is used in the place of N1, C2, etc. in text.

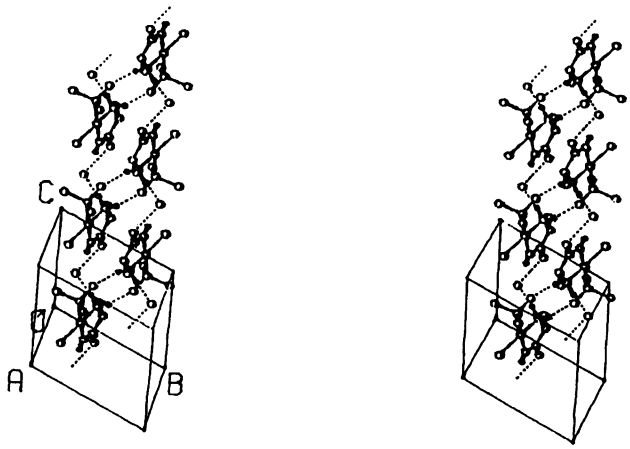

Fig. 2. The crystal structure of **4** by a stereo pair. Hydrogen bonds are indicated by broken lines. The hydrogen atoms other than those linked to nitrogen atoms are omitted.

omitted in Fig. 2.

In crystal **3b** a couple of successive hydrogen bonds (O(1)···N(2) and N(2)···O(2)) connect three complex molecules sequentially, where the amino nitrogen (N(2)) of the halfway molecule extends the two hydrogen bonds. The network of the hydrogen bonds forms layers lying in parallel with the *AB*-plane, as shown in Fig. 3.

The directions of the N(1)–H(1) bond in **4** and that of the O(1)···N(2) hydrogen bond in **3b** are clearly in harmony only with the assignment of the coordination mode B, not with that of the hypothetical mode derived by replacing N(1) by O(1) and O(1) by N(1) atom in mode B.

AB and CD spectra. The AB and CD spectra of the aaa and corresponding aa complexes are shown in Figs. 4 and 5, respectively. The AB spectra are given only for selected complexes. The CD curves are represented, if possible, by a particular type of line, indicating the common amino acid residue to a pair of the aa and aaa complexes.

The AB patterns are specific for geometrical isomers, and are almost independent of the bidentate ligands within each of the aaa and aa complexes, and were actually utilized to identify the isomers. The trans isomers generally show a weak AB band in the lower-wavenumber region than do the cis isomers among each of the aaa and aa complexes. As a result, aggregates of the crystals of the trans aaa complexes in many cases are pale yellow, whereas those of the cis isomers are colorless.

The resemblances of the AB and CD patterns are noticed between the complexes of an aaa and aa ligand bearing a common amino acid residue, especially at lower wavenumbers. On the other hand, an intense CD band at 45—48×10^3 cm^{-1} appears at lower wavenumbers for the trans isomer than for cis among each of the aaa and aa complexes.

Preparation. Only the cis isomers of [PtCl(aaa-*N*,*N*′)(dmso-*S*)] complexes could be isolated from the aqueous reaction mixture of the starting complex, **1** or **2**, KOH, and Haaa other than L- and DL-Hvala. It has not been checked, however, as to whether the trans isomers were actually formed or not in the reaction mixtures.

The use of the optically active ligand gave crystals of the trans isomer first in preparing the vala complexes, while the use of the DL-ligand gave colorless needles of the cis isomer prior to prismatic crystals **3b** of the trans isomer. In the case of the DL-ligand, the crystals of the trans isomer have proved to be a racemic mixture by the X-ray structure analysis. However, it has not yet been revealed whether or not the crystals of **3b** are isomorphous with **3a** prepared by using the optically active ligand.

The cis isomer of the L-vala complex was also isolated starting from the L-ligand. Recrystallization of this isomer was rather difficult because the trans isomer very easily crystallized as fine needles, and the two isomers have similar solubilities. The cis DL-vala complex, which has proved to have no water of crystallization, is suggested to be a racemic compound based on all the observations mentioned above.

For a comparison, the known aa complexes [PtCl(aa-*N*,*O*)(dmso-*S*)] were prepared using the starting complex **1** or **2**, Haa, and KOH.[15] Here, the reaction temperature can be increased because the Haa's are much more stable to heating than the Haaa's. Concerning

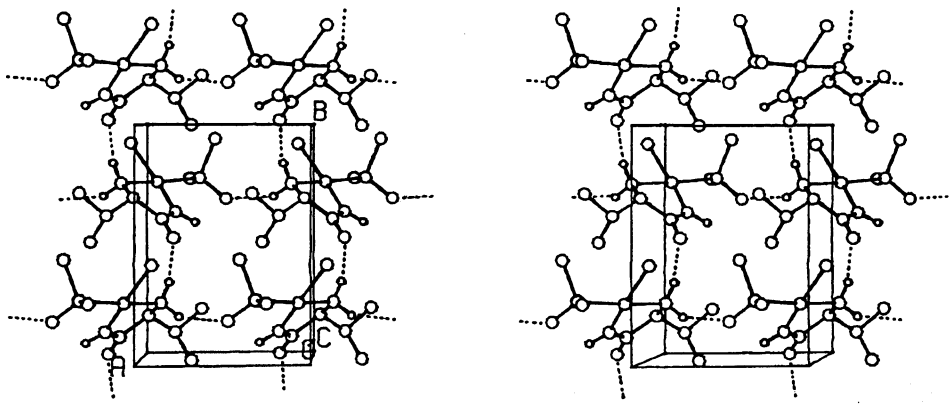

Fig. 3. The crystal structure of **3b** by a stereo pair. Hydrogen bonds are indicated by broken lines. The hydrogen atoms other than those linked to nitrogen atoms are omitted.

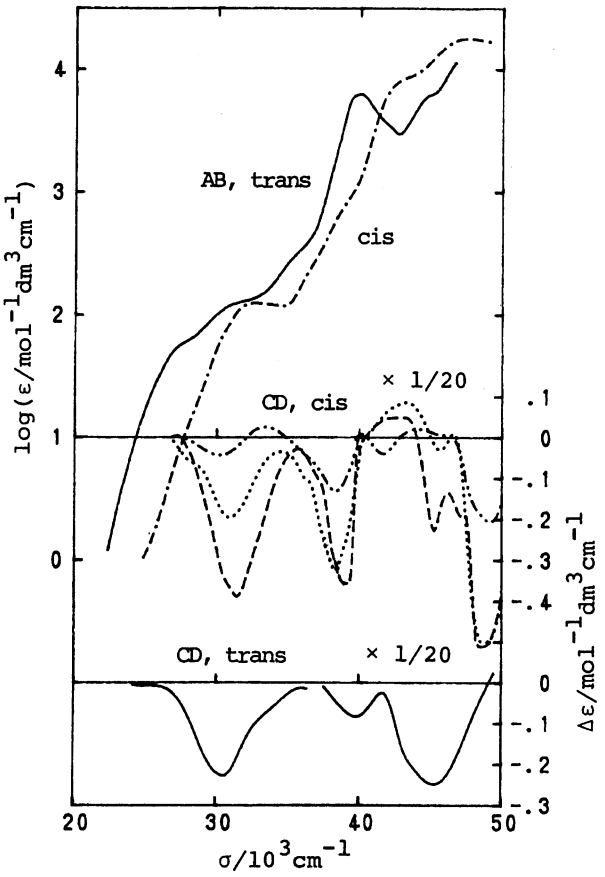

Fig. 4. The absorption and CD curves of *trans*(NH_2,*S*)- and *cis*(NH_2,*S*)-[PtCl(aaa)(dmso)] (aaa=DL- or L-vala, trans, ——; aaa=DL-vala, cis, –·–; aaa=L-alaa, cis, –··–; aaa=L-leua, cis, ····; aaa=L−ilea, cis, - - -) in 0.3 M KCl.

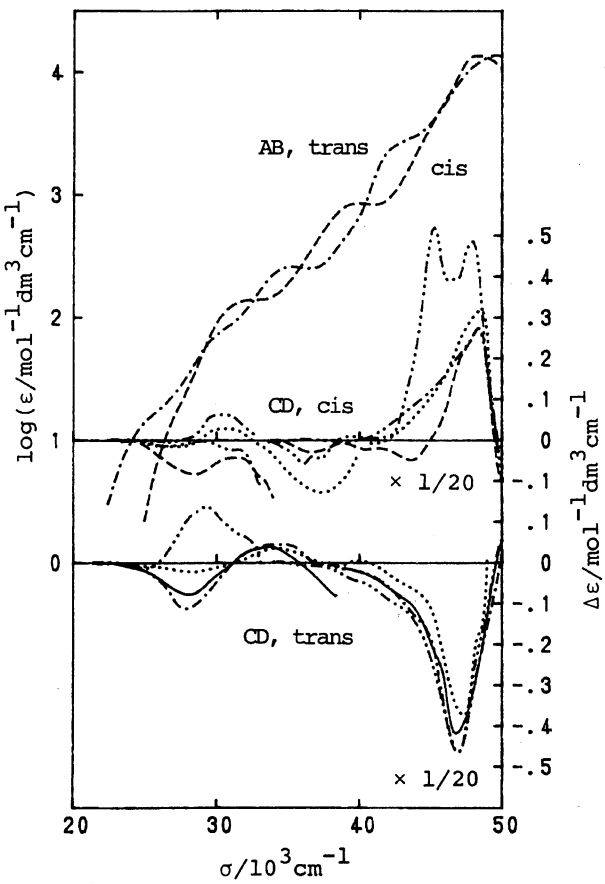

Fig. 5. The absorption and CD curves of *trans*(NH_2,*S*)- and *cis*(NH_2,*S*)-[PtCl(aa)(dmso)] (aa=L-val, trans, ——; aa=L-ala, cis, –··–; aa=L-leu, cis and trans, ····; aa=L-ile, trans, –·–; aa=L-ile, cis, - - -; aa=L-phe, cis and trans, –····–) in 0.3 M KCl.

the formation process of the aa complexes, it has been suggested from NMR studies[16] that the trans isomer is first formed, and is then isomerized to the thermodynamically more stable cis isomer. We observed that crystals of the trans isomer separated out first for the L-leu complex, as described in the Experimental section.

The first formation of the trans isomers has been explained based on the following hypotheses: a much larger trans effect of the coordinated sulfur atoms and a much larger reactivity of the amino nitrogen atoms than the carboxylato oxygen in aa ligands.[15,16,22] If the reactivity of the amino nitrogen is assumed to be dominant to that of the amidato nitrogen in aaa ligands, the exclusive formation of a trans isomer is expected

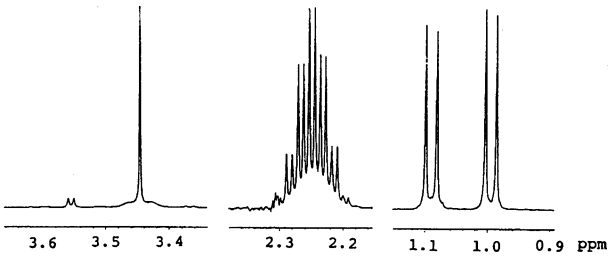

Fig. 6. ^{1}H NMR-spectrum (400 MHz) of *cis*(NH_2,*S*)-[PtCl(DL-vala)(dmso)] in D_2O. Relative intensities in the three regions are arbitrary.

Table 5. ^{1}H NMR Data for *trans*- and *cis*-[PtCl(DL-vala)(dmso)] in D_2O

Isomer[a]		Trans	Cis
Chemical shifts δ/ppm	α-CH	3.62	3.56
	CH_3(dmso)	3.51	3.45
	CH(isopropyl)	2.24	2.25
	CH_3(isopropyl)	1.10, 1.00	1.09, 0.99
^3J/Hz	Pt–S–C–H	20	13
	H–C–CH_3	7.1	7.1
	H–C–C–H	3.5	3.5

a) Trans and cis are referred to amino and dmso ligands.

in the initial stage of complex formation. However, no sign of this expectation was detected. Actually, both the cis and trans isomers of the aaa complexes could be isolated under mild conditions, and only the cis isomers were readily isolated in most cases. In addition, no sign of isomerization could be detected within 24 h in the ^{1}H NMR spectra for the cis and trans DL-vala complexes in aqueous solutions (Fig. 6 and Table 5). Based on these observations the reactivity of the amidato nitrogen atom may be inferred to be not smaller than that of the amino nitrogen.

The magnitude of the coupling constant ^3J{Pt–S–C–H} (13 Hz) for the *cis* DL-vala complex was significantly smaller than that of the trans isomer (20 Hz). The latter value is typical for the *S*-coordinating sulfoxides which are trans to the amino or carboxylato ligands in simple platinum(II) complexes,[23] including the aa complexes.[16] On the other hand, the former reveals a weakening of the Pt–S bond in the cis complex. This weakening, in turn, may be explained by the large trans influence of the coordinating amidato nitrogen, consistent with observations concerning bond-length data. The chemical shifts of dmso–CH_3 are within the range of the literature values for *S*-coordination;[23] the smaller deshielding for the cis complex is also in line with the large trans influence of the carboxamidato group.

References

1) T. Komorita, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **41**, 854 (1968); *Bull. Chem. Soc. Jpn.*, **42**, 168 (1969).
2) T. Tsukihara, Y. Katsube, K. Fujimori, and Y. Ishimura, *Bull. Chem. Soc. Jpn.*, **45**, 1367 (1972); T. Komorita, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **52**, 1832 (1979).
3) D. A. Buckingham, P. Morris, A. M. Sargeson, and A. Zanella, *Inorg. Chem.*, **16**, 1910 (1977).
4) D. A. Buckingham, C. E. Davis, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **92**, 5571 (1970).
5) a) Y. Ilan and H. Taube, *Inorg. Chem.*, **22**, 1655 (1983); *Inorg. Chem.*, **22**, 3144 (1983); b) Y. Ilan and M. Kapon, *Inorg. Chem.*, **25**, 2350 (1986).
6) a) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **91**, 3451 (1969); b) R. Cini, F. P. Fanizzi, F. P. Intini, L. Maresca, and G. Natile, *J. Am. Chem. Soc.*, **115**, 5123 (1993).
7) T. G. Appleton, J. R. Hall, T. W. Hambley, and P. D. Prenzler, *Inorg. Chem.*, **29**, 3562 (1990).
8) L. S. Hollis, M. M. Roberts, and S. J. Lippard, *Inorg. Chem.*, **22**, 3637 (1983); F. D. Rochon, R. Boughzala, and R. Melanson, *Can. J. Chem.*, **70**, 2476 (1992).
9) F. D. Rochon, R. C. Kong, and R. Melanson, *Inorg. Chem.*, **29**, 1352 (1990).
10) H. C. Freeman and M. L. Golomb, *J. Chem. Soc., Chem. Commun.*, **1970**, 1523.
11) M. F. Mogilevkina, V. I. Bessonov, and I. M. Cheremisina, *Russ. J. Inorg. Chem.*, **18**, 1396 (1973).
12) L. S. Tikhonova, L. I. Iozep, A. I. Stetsenko, A. A. Iozep, I. M. Ginzburg, and L. F. Strelkova, *Koord. Khim.*, **15**, 266 (1989).
13) B. E. Schwederski, H. D. Lee, and D. W. Margerum, *Inorg. Chem.*, **29**, 3569 (1990).
14) Yu. N. Kukushkin, Yu. E. Vyaz'menskii, L. I. Zorina, and Yu. L. Pazukhina, *Russ. J. Inorg. Chem.*, **13**, 835 (1968); J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, **11**, 1280 (1972).
15) Yu. N. Kukushkin and G. P. Gur'yanova, *Russ. J. Inorg. Chem.*, **15**, 1435 (1970).
16) L. E. Erickson and W. H. Hahne, *Inorg. Chem.*, **15**, 2941 (1976); L. E. Erickson, J. W. Cartmell, and N. G. Albrecht, *J. Coord. Chem.*, **5**, 135 (1976).
17) K. Tanimoto, unpublished work.
18) The crystal structure analyses were carried out at the X-Ray Diffraction Service of the Department of Chemistry.
19) "TEXSAN-TEXRAY Structural Analysis Package," Molecular Structure Corporation (1985).
20) Full crystallographic data, the positional parameters of the hydrogen atoms, the anisotropic thermal parameters, all of the bond distances and angles, and a list of the structure factors are deposited as Document No. 68028 at the Office of the Editor of Bull. Chem. Soc. Jpn.
21) L. J. Nicholls and W. A. Freeman, *Acta Crystallogr., Sect. B*, **B35**, 2392 (1979); W. A. Freeman, *Acta Crystallogr., Sect. B*, **B33**, 191 (1977); F. D. Rochon, P. C. Kong, and R. Melanson, *Inorg. Chem.*, **29**, 2708 (1990).
22) Yu. N. Kukushkin, Yu. E. Vyaz'menskii, and L. I. Zolina, *Russ. J. Inorg. Chem.*, **13**, 1573 (1968).
23) J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, **24**, 115 (1981).