taken to reflect a greater self-exchange rate associated with the corrin-derived reductant.

The alternate sequence, featuring reaction of protonated cob(I)alamin with NO_3^-, would not, on the basis of experience with more usual redox systems, be seriously considered, for it is recognized that protonation of an oxidant almost invariably converts it to a more effective acceptor,[22] whereas protonation of a reductant renders it less strongly reducing. However, the perceived hydride-like character of Co^I–H species[23] makes this mechanism a reasonable one. Thus, we cannot ignore the possibility that the reaction is initiated by a hydride transfer (formally a 2e transaction) to nitrate (eq 3) followed immediately by a Co^I–Co^{III} comproportionation (eq 4). The specific

$$Co^I\text{–}H + NO_3^- \rightarrow NO_2^- + Co^{III} + OH^- \quad (3)$$

$$Co^{III} + Co^I \rightarrow 2Co^{II} \quad (4)$$

rate for the latter transfer has been shown[7b] to be much greater than that for the reaction being considered here. Sequence (3)–(4) is closely similar to that proposed for the reduction of N_2O by B_{12s},[24] and it may be that reaction of Co(I) with aqueous acid to give H_2 proceeds, at least in part, in an analogous fashion. Additional points in favor of such a path are that the overall conversion to NH_3 is accomplished in four, rather than eight, transactions[25] and that it bypasses zerovalent nitrogen, which, in its diatomic form, should be reduced with difficulty.[26]

Note finally that the spectrum of the Co^{II} product exhibits significant variation with acidity (see Table I), reflecting the equilibrium between the protonated and nonprotonated species, II_{BH}^+ and II_B. This variation is most marked within the pH range 1.5–2.5, with a limiting spectrum observed near $[H^+] = 4 \times 10^{-4}$ M. A plot of $(A_{obsd} - A_{lim})$ vs. the quotient $(A_{obsd} - A_{lim})/[H^+]$ (where the A values refer to absorbances at 470 nm) is closely linear and yields, as its slope,[27] the acidity constant 0.0109 M ($pK_A = 1.96$). The value, which refers to 0.11 M ClO_4^-, may be compared to the recorded[6a] pK_A of 2.9, the latter measured in 1.6 M aqueous *p*-toluenesulfonate.[28,29]

Acknowledgment. The authors are grateful to Dr. James Espenson for initiating interest in this work and for valuable discussions.

Registry No. NO_3^-, 14797-55-8; HNO_3, 7697-37-2; vitamin B_{12s}, 18534-66-2; vitamin B_{12r}, 14463-33-3.

(21) Grube, G.; Breitinger, G. *Z. Elektrochem.* **1927**, *33*, 112. See also: Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 248.
(22) Exceptional cases involve inner-sphere oxidants in which the lead-in sites can be blocked off by protonation. See, for example: Loar, M. K.; Thomas, J. C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 2877.
(23) See, for example: Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1.
(24) (a) Banks, R. G. S.; Henderson, R. J.; Pratt, J. M. *J. Chem. Soc. A* **1968**, 2886. (b) A similar route has been suggested for the reduction of nitrate by Cr(II); see: Swaddle, T. W. *J. Am. Chem. Soc.* **1967**, *89*, 4338.
(25) Implicit in this argument is the assumption that if a 2e change is the preferred path for the initial step, it is also the preferred path for subsequent steps.
(26) A reviewer has pointed out that this must be so, since the entire series of reactions is carried out under N_2.
(27) See, for example: (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Ramette, R. W. *J. Chem. Educ.* **1967**, *44*, 647.
(28) Preliminary experiments indicate that HNO_2 undergoes a 6e reduction by cob(I)alamin at a specific rate near 10^3 M^{-1} s^{-1} (25 °C; $\mu = 0.10$; $[H^+] = 0.016$ M), i.e. that the reaction is considerably faster than the reduction of NO_3^- under comparable conditions.
(29) Two additional points raised by a reviewer merit response. First, there is a suggestion that eq 3 might be rewritten in terms of Co^I–H and undissociated HNO_3 to avoid the release of OH^- in acidic solution. It appears to us that, unless these protonated species were formed in a highly unusual manner, such a step would be reflected in a reaction rate proportional to $[H^+]^2$ under our conditions. It was further noted that the species HNO or NOH is a much more likely N(I) intermediate than N_2O, for although the latter is reduced by B_{12s},[24a] this reduction is slow compared to the reaction at hand. On this point we agree.

Contribution from the Institute of Physical Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

Optical Activity of Bis(thiocarbamide)bis(amino acid)platinum(II) Complexes

OLEG P. SLYUDKIN† and BENGT J. F. NORDÉN*

Received May 26, 1982

Unidentate amino acid platinum(II) complexes of the type *trans*-$[Pt(ZH)_2(Thio)_2]Cl_2$, where ZH = L-alanine (I), L-valine (II), L-tyrosine (III), and L-hydroxyproline (IV, V) and Thio = thiocarbamide, have been synthesized. Their electronic absorption and circular dichroism (CD) spectra have been studied in aqueous and in dimethylformamide (DMF) solution. A reversible change of CD with pH is observed for the alanine, valine, and tyrosine complexes in DMF. Similar CD spectra of DMF solutions of the complexes + 2 equiv of OH^- probably represent the contribution from the resulting asymmetric (deprotonated) nitrogen. With hydroxyproline (in contrast to the other amino acids) the complexes isolated from acid and alkaline solutions have quite different CD spectra, which is interpreted in terms of opposite absolute configurations of the asymmetrically coordinated nitrogen of the hydroxyproline ligand: Pt(S_N,S_C-hydroxyproline) (acidic medium), Pt(R_N,S_C-hydroxyproline) (alkaline medium) (S_C refers to C-2 of 4-hydroxyproline). This hypothesis is supported by chemical correlations and CD spectra of other proline complexes.

Introduction

Circular dichroism (CD) in the region of the d–d transitions of conformationally or vicinally chiral, planar metal complexes has been the subject of intense study (see e.g. Ref 1). Although the optical activity of planar complexes with chelated amino acids[2–4] has been studied in detail, very little has been done on unidentate amino acid complexes.[4] Such studies are of interest for understanding the mechanism of induction of chirality in d–d transitions. This kind of information could

† On leave from the Inorganic Chemistry Department, Novosibirsk State University, 630090 Novosibirsk, USSR.

(1) Jensen, H. P.; Woldbye, F. *Coord. Chem. Rev.* **1979**, *29*, 213.
(2) Hawkins, C. P. "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1971; Chapter 5.
(3) Gillard, R. D.; Slyudkin, O. P. *J. Chem. Soc., Dalton Trans.* **1978**, 152.
(4) Volstein, L. M.; Slyudkin, O. P. *Zh. Neorg. Khim.* **1980**, *25*, 231; **1981**, *26*, 991; *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 125; **1981**, *26*, 496.

0020-1669/83/1322-2637$01.50/0

also be of help for the interpretation of CD of biological molecules containing metal centers, where so far no effective theory has been developed. The use of protic (e.g. H_2O) as well as aprotic (e.g. DMF) solvents can also be of interest in relation to the effects of hydrophilic and hydrophobic environments in the biosystems.

The present study deals with unidentate amino acid Pt(II) complexes such as bis(thiocarbamide)bis(amino acid)platinum(II) chlorides (a few other Pt(II) unidentate amino acid complexes, *trans*-$[Pt(ZH)_2Cl_2]$ (ZH = L-ValH, L-TryH), have also been studied in DMF solution). Thiocarbamide binds to Pt(II) through the sulfur atom, the unidentate amino acid binds through the nitrogen atom of the amino group, and the noncoordinated carboxyl group can be protonated or deprotonated. When the L-hydroxyprolinate ion is coordinated as a bidentate ligand to platinum(II) (Pt–N and Pt–OCO bonds), the asymmetric environment of the donor nitrogen atom is known to correspond to the absolute configuration *S*.[4] In unidentate L-hydroxyproline, however, the asymmetric environment of the donor nitrogen atom may be either *S* or *R*. In this paper we report the isolation of two forms of *trans*-$[Pt(OproH)_2(Thio)_2]Cl_2$ with, according to CD, opposite absolute configurations of the asymmetric donor nitrogen atom of the unidentate coordinated hydroxyproline.

Experimental Section

Absorbance spectra were measured on a Cary 118 and a UV–vis Specord recording spectrophotometer; the CD spectra were measured on a Jasco J-500 spectropolarimeter and were also checked on a Jouan Model 2B dichrograph (IR spectra were recorded on a UR-20 spectrophotometer).

The methods of synthesis of the compounds containing the unidentate L-amino acids L-alaH, L-ValH, L-TyrH) differ somewhat from earlier methods[5] for the compounds with racemic amino acids because of different solubilities. The complexes with L-alaH, L-valH, and L-tryH were synthesized according to the reaction scheme

$$K_2[PtCl_4]\ (\text{red}) + 4ZH + 4KOH \xrightarrow[100\ ^\circ C]{H_2O\ \text{soln}} K_2[PtZ_4]\ (\text{uncolored}) + 4KCl + 2H_2O \quad (1)$$

$$K_2[PtZ_4] + 2HCl \xrightarrow[25\ ^\circ C]{} H_2[PtZ_4]\ (\text{white}) + 2KCl \quad (2)$$

$$H_2[PtZ_4] + 2HCl \xrightarrow[100\ ^\circ C]{\text{conc. HCl}} \textit{trans}\text{-}[Pt(ZH)_2Cl_2]\ (\text{yellow}) + 2HZ \quad (3)$$

$$\textit{trans}\text{-}[Pt(ZH)_2Cl_2] + 2\text{Thio} \xrightarrow{\text{brief heating}} \textit{trans}\text{-}[Pt(ZH)_2(Thio)_2]Cl_2\ (\text{white}) \quad (4)$$

The bis(thiocarbamide)bis(amino acid)platinum(II) chlorides were precipitated by addition of cold concentrated HCl.

The method is quite general, and further details for the preparation are only given for *trans*-$[Pt(ValH)_2(Thio)_2]Cl_2$ as an example. *trans*-$[Pt(ValH)_2Cl_2]$ (0.5 g), prepared as described before,[4,5] was added to a thiocarbamide solution (0.1 g in 5 mL of 10^{-3} M HCl), and the mixture was heated on a water bath for 20 s to give an uncolored solution. After cooling $[Pt(ValH)_2(Thio)_2]Cl_2$ was precipitated by addition of 5 mL of cold concentrated HCl. After 1 h the white product was filtered off, washed with 6 M HCl and acetone, and dried under vacuum at room temperature (yield 90%). The starting bis-chelate complex of platinum(II) with L-hydroxyproline was prepared by the published method[6] according to the scheme (S_C refers to C-2 of 4-hydroxyproline)

$$K_2[PtCl_4]\ (\text{red}) + \text{OproH} \rightarrow \underset{\text{mono chelate}}{K[Pt(S_N,S_C\text{-Opro})Cl_2]}\ (\text{yellow}) + KCl + HCl \quad (5)$$

$$\underset{\text{mono chelate}}{K[Pt(S_N,S_C\text{-Opro})Cl_2]}\ (\text{yellow}) + \text{OproH} \rightarrow \underset{\text{bis chelate}}{\textit{trans}\text{-}[Pt(S_N,S_C\text{-Opro})_2]}\ (\text{white}) + KCl + HCl \quad (6)$$

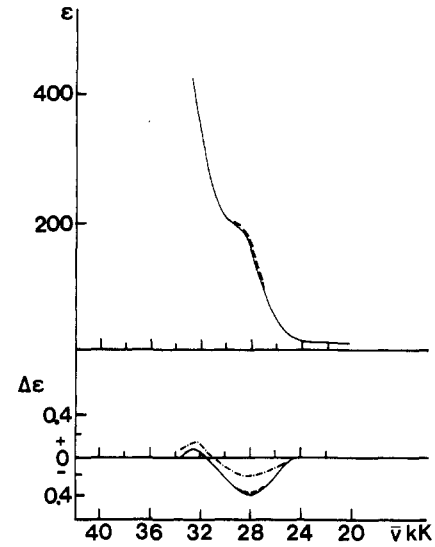

Figure 1. (——) Absorption and circular dichroism spectra of aqueous solutions of *trans*-$[Pt(S_C\text{-AlaH})_2(Thio)_2]Cl_2$ (I), (–·–) CD spectrum of *trans*-$[Pt(S_C\text{-ValH})_2(Thio)_2]Cl_2$ (II), and (---) absorption and circular dichroism spectra of I after addition of 2 equiv of OH^-.

The two different products with L-hydroxyproline were obtained according to the following reactions.

(a) From alkaline medium (stable isomer):

$$\underset{\text{bis chelate}}{\textit{trans}\text{-}[Pt(S_N,S_C\text{-Opro})_2]} + 2\text{Thio} \xrightarrow{+OH^-} \underset{\text{bis monodentate}}{\textit{trans}\text{-}[Pt(R_N,S_C\text{-Opro})_2(Thio)_2]}\ (\text{white}) \quad (7)$$

$$\textit{trans}\text{-}[Pt(R_N,S_C\text{-Opro})_2(Thio)_2] + 2HCl \rightarrow \textit{trans}\text{-}[Pt(R_N,S_C\text{-OproH})_2(Thio)_2]Cl_2\ (\text{white})$$

trans-$[Pt(Opro)_2]\cdot xH_2O$ (0.3 g in 3 mL of H_2O (pH 10)) and thiocarbamide (0.16 g in 2 mL of H_2O) were separately heated on a water bath and mixed. After 1 min the solution was cooled and the white precipitate filtered off and washed with cold water and acetone. This product was dissolved during vigorous stirring into ethanol (5 mL with a few drops of concentrated HCl). An excess of diethyl ether was then added and the white precipitate filtered off, washed with ether, and dried under vacuum at room temperature (yield 80%).

(b) From acidic medium (less stable isomer):

$$\textit{trans}\text{-}[Pt(S_N,S_C\text{-Opro})_2] + 2\text{Thio} + HCl \rightarrow \textit{trans}\text{-}[Pt(S_N,S_C\text{-OproH})_2(Thio)_2]Cl_2\ (\text{white}) \quad (8)$$

Solutions of *trans*-$[Pt(Opro)_2]\cdot xH_2O$ (0.3 g in 2 mL of H_2O) and thiocarbamide (0.16 g in 2 mL of 10^{-3} N HCl) were separately heated on a water bath and mixed for 30 s. After cooling the solution, 5 mL of cold concentrated HCl was added. The solution was poured, during vigorous stirring, into 20 mL of cold acetone. The white product was filtered off, washed with acetone, and dried under vacuum at room temperature (yield 60%).

The synthesis of the L-hydroxyproline Pt(II) complexes differs slightly from that of the L-proline Pt(II) complexes.[6] The composition of the complexes was confirmed within 1% by elemental analyses. IR spectra of the complexes in KBr disks all show a strong band near 1730–1750 cm^{-1}, which corresponds to the C=O stretching vibration of the protonated carboxyl group,[7] confirming the unidentate coordination of the amino acid to Pt(II) by the amino group.

Results and Discussion

Aqueous Solutions. Absorption and circular dichroism spectra of aqueous solutions of *trans*-$[Pt(S_C\text{-AlaH})_2(Thio)_2]Cl_2$, and of some of the other complexes, are shown in Figure 1 or 2 or summarized in Table I.

(5) Volstein, L. M. *Koord. Khim.* **1975**, *1*, 593.
(6) Slyudkin, O. P.; Zarukina, M. A. *Zh. Neorg. Khim.*, in press.
(7) Sluydkin, O. P.; Seliskaya, N. D.; Volstein, L. M. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1973**, *4*, 44.

Table I. Absorption (A) and Circular Dichroism (CD) Data of Aqueous Solutions of *trans*-$[Pt(ZH)_2(Thio)_2]Cl_2$[a]

		H_2O				H_2O + 2 equiv of OH^-			
		A		CD		A		CD	
complex	amino acid, ZH	$\bar{\nu}/10^3$ cm^{-1}	ϵ	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\epsilon$	$\bar{\nu}/10^3$ cm^{-1}	ϵ	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\epsilon$
I	L-AlaH	29.1	200	27.9	−0.38	29.1	210	28.0	−0.36
		33.0 sh	450	32.3	+0.10	33.0 sh	500	32.3	+0.10
II	L-ValH	29.1	210	27.3	−0.16	29.1	210	27.4	−0.16
		33.0 sh	450	32.3	+0.12	33.0 sh	500	32.3	+0.11
III	L-TyrH	28.4	140	27.8	−0.14	28	150	30.3	+0.2
						29 sh	300		
		33.0	600	36	−0.27			33.9	−0.47
IV	L-OproH	29.5	200	28.3	−1.3	30.0 sh	240	28.3	−1.4
	(from alkaline soln)	33.0	400	33.9	+0.15			33.9	+0.14
V	L-OProH			29.4	+0.25	30.0[b]	280[b]	28.0[b]	−1.0[b]
	(from acidic soln)	29.0	230						
		33.5	830						
				33.6	+0.5				

[a] sh = shoulder. [b] Small excess of OH^-.

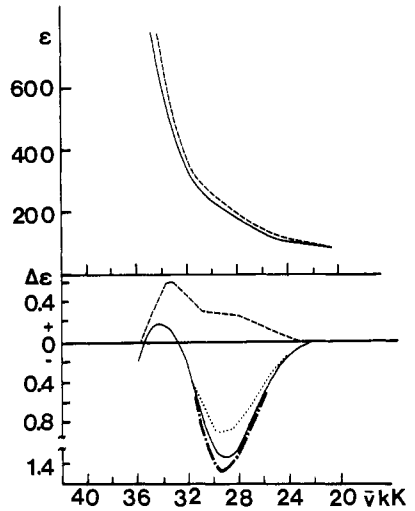

Figure 2. Absorption and circular dichroism spectra of aqueous solutions of (---) *trans*-$[Pt(S_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$ (V) and of (——) *trans*-$[Pt(R_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$ (IV) and CD spectra of aqueous solutions of (-·-) IV and (···) V after addition of 2 equiv of OH^-.

The absorption spectra of the alanine (I), valine (II), and tyrosine (III) complexes and the two hydroxyproline complexes (IV, V) all show a shoulder at about 29 × 10^3 cm^{-1} and one further band above 33 × 10^3 cm^{-1}. Under the 29 × 10^3 cm^{-1} absorption band, the alanine, valine, and tyrosine compounds show two CD bands of opposite signs, at ca. 27 and 32 × 10^3 cm^{-1}, which can be assigned as due to d–d transitions. The band at higher energy (33 × 10^3 cm^{-1}) is probably due to a metal–ligand charge transfer or to a local transition of the ligands. The CD spectrum of *trans*-$[Pt(R_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$ (IV) has a negative strong band at ca. 28 × 10^3 cm^{-1} and a positive band at ca. 34 × 10^3 cm^{-1}, whereas the CD spectrum of the other hydroxyproline complex (V) has two positive bands in the same spectral region (Figure 2, Table I).

As expected from the ionizing property of water as a solvent, the complexes with alanine (I), valine (II), tyrosine (III), and hydroxyproline (IV, V) are almost completely converted into the form $[Pt(H_2NCHRCOO^-)_2(Thio)_2]_{aq}$ ($pK \approx 2$–3 for the acid form). Thus, addition of 2 equiv of OH^- does not, as shown in Figure 1 in the case of *trans*-$[Pt(AlaH)_2(Thio)_2]Cl_2$, lead to any significant change either of the basic coordination geometry or of the rotamer populations.[8] With hydroxy proline, in contrast to the other amino acids, the complex *trans*-$[Pt(S_C\text{-OproH})_2(Thio)_2]Cl_2$, as seen from the two quite different CD spectra, comes out in two different forms from alkaline and acidic aqueous solutions. Addition of 2 equiv of OH^- to the "acid" form obviously leads to a change into a spectrum very similar to the form obtained in alkaline medium and also very similar to the CD spectra of the complexes I and II in Figure 1 and Table I. In this case, however, the reaction cannot be reversed by the addition of HCl. An analogous experiment carried out with the compound obtained from the alkaline solution (i.e., OH^- followed by subsequent HCl treatment), which is most probably *trans*-$[Pt(R_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$, gives a product that according to its CD spectrum is almost identical with the original compound (Figure 2). (It was found that some caution had to be taken here to avoid large excess of alkali or acid.)

It has been found that in strongly acidic medium the opening of the amino acid chelate ring in the L-proline Pt(II) chelates, where the asymmetric nitrogen atom has the *S* absolute configuration[3,9] (i.e., the conversion of bidentate proline (Pro) into unidentate (ProH)), is not accompanied by any inversion of the asymmetric nitrogen atom.[10,11] Alkaline medium however, promotes the inversion of the asymmetric nitrogen of unidentate ProH from the *S* configuration to the thermodynamically more stable *R* configuration (ΔG ca. 3 kcal mol^{-1} [11,12]). This conclusion is also supported by X-ray studies of solid *trans*-$[Pt(R_N,S_C\text{-ProH})(NH_3)Cl_2]$.[13]

The two products obtained in alkaline and acidic media are very likely to be diastereomers, with opposite absolute configurations of asymmetric nitrogen atoms. For the unidentate L-hydroxyproline we make the following assignments of absolute configuration: from alkaline solution, *trans*-$[Pt(R_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$ (IV); from acidic solution, *trans*-$[Pt(S_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$ (V).

Absorption and CD spectra of the aqueous solution of the tyrosine complex (III) differ from those of the alanine (I), valine (II), and hydroxyproline (IV, V) complexes. Addition of alkali to the tyrosine complex (in contrast to the situation for the other amino acidato complexes) changes the features of the CD spectrum from a (–,–) pattern to (+,–) (Table I).

(8) Erickson, L. E.; Erikson, M. D.; Smith, B. L. *Inorg. Chem.* **1973**, *12*, 412.
(9) Ito, T.; Marumo, F.; Saito, Y. *Acta Crystallgr., Sect. B* **1971**, *B27*, 1062.
(10) Volstein, L. M.; Slyudkin, O. P.; Kerzhentsev, M. A. *Zh. Neorg. Khim.* **1977**, *22*, 2774; *Russ. J. Inorg. Chem. (Engl. Transl.)* **1977**, *22*, 1506.
(11) Slyudkin, O. P.; Kerzhentsev, M. A. *Zh. Neorg. Khim.* **1979**, *24*, 3051; *Russ. J. Inorg. Chem. (Engl. Transl.)* **1979**, *24*, 3051.
(12) Slyudkin, O. P.; Kerzhentsev, M. A., to be submitted for publication.
(13) Sluydkin, O. P.; Minacheva, L. M.; Kerzhentsev, M. A.; Sadikov, G. G.; Antsyshkina, A. S.; Poray-Koshits, M. A. *Koord. Khim.* **1980**, *6*, 1097.

Table II. Absorption (A) and Circular Dichroism (CD) Data of DMF Solutions of *trans*-$[Pt(ZH)_2(Thio)_2]Cl_2$[a]

		DMF				DMF + 2 equiv of OH^-			
		A		CD		A		CD	
complex	amino acid, ZH	$\bar{\nu}/10^3$ cm^{-1}	ϵ	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\epsilon$	$\bar{\nu}/10^3$ cm^{-1}	ϵ	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\epsilon$
I	L-AlaH	29.0	150	26.7	−0.21	29.3	190	29.1	−0.86
				29.8	+0.03				
		33.0 sh	450	32.9	−0.26	33.0 sh	550	34.2	−1.1
II	L-ValH	29.5	140	25.0	−0.01	29.3	193	29.0	−0.75
		32.8 sh	470	29.4	+0.10	33.1 sh	610	33.9	−0.8
						28.8	250		
III	L-TyrH	29.4	360	25.5	−0.03	30.5 sh	400	28.7	−0.48
		32.9 sh	650	32.8	−0.04			33.6	−0.51
IV	R_N-OproH	30	300	27.5	−0.6	30 sh	220	28.1	−0.64
		33.0	500	31.8	−0.55			34.2	−0.5
V	S_N-OproH	30	320	28.6	−0.4	30 sh	260	28.5	−0.6
				35.1	+0.4			34.2	−0.45

[a] sh = shoulder.

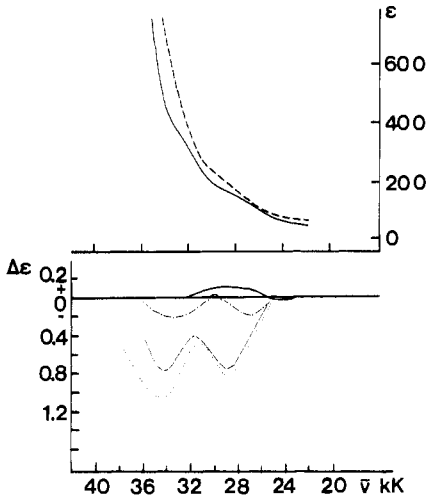

Figure 3. Absorption and circular dichroism spectra of DMF solutions of (——) *trans*-$[Pt(S_C\text{-ValH})_2(Thio)_2]Cl_2$ (II), CD spectrum of (-·-) *trans*-$[Pt(S_C\text{-AlaH})_2(Thio)_2]Cl_2$ (I), and absorption and CD spectra of (---) II and CD spectrum of (···) I after addition of 2 equiv of OH^-.

It seems that in the complex III, the bulky hydroxyphenyl group plays a dominant role in determining the observed rotational strength for the d–d transition. We finally notice that, while the sign of the observed Cotton effect of the band at ca. 28×10^3 cm^{-1} remains negative for the complexes I–III (with *S* configuration), the rotational strength is sensitively dependent on the substituent at the asymmetric center, varying in the order (in water) $CH_3 > CH(CH_3)_2 > CH_2C_6H_4OH$.

DMF Solutions. Figure 3 shows absorption and CD spectra of *trans*-$[Pt(S_C\text{-ValH})_2(Thio)_2]Cl_2$ and CD of *trans*-$[Pt(S_C\text{-AlaH})_2(Thio)_2]Cl_2$ in DMF. Table II summarizes the results for all the amino acids. In contrast to the fairly similar absorption spectra of the DMF and aqueous solutions, the CD spectra differ substantially (Figure 3, Table II). The CD spectra of the complexes I and II in DMF also differ markedly from each other, while they are very similar in aqueous solution.

Absorption and CD spectra of all the complexes in protonated form, $[Pt(ZH)_2(Thio)_2]Cl_2$, in DMF solution remain constant for at least 3 h at room temperature. This indicates that DMF does not enter into the inner coordination sphere. Addition of 2 equiv of OH^- to the alanine, valine, and tyrosine complexes (conversion to the deprotonated forms) leads in all three cases to a CD pattern with two negative strong bands at 28 and 34×10^3 cm^{-1}. The reaction is reversible and can be brought back and forth by adding equivalent quantities of acid and alkali. In contrast to the case in pure aqueous solutions, one may thus in DMF obtain the amino acids in both protonated and deprotonated forms in the complexes. The CD of the protonated form varies from complex to complex, whereas with the deprotonated forms there is only little variation in CD with the choice of amino acid. In the corresponding study of the second type of unidentate amino acid complexes, *trans*-$[Pt(ZH)_2Cl_2]$, the effect of adding alkali is less significant (Figure 4, Table III). The CD spectrum of *trans*-$[Pt(S_N,S_C)OproH)_2(Thio)_2]Cl_2$ in DMF is strongly

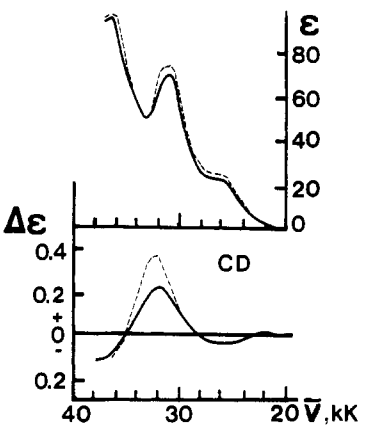

Figure 4. (——) Absorption and circular dichroism spectra of a DMF solution of *trans*-$[Pt(S_C\text{-ValH})_2Cl_2]$ (VI) and (---) of VI after addition of 2 equiv of OH^-.

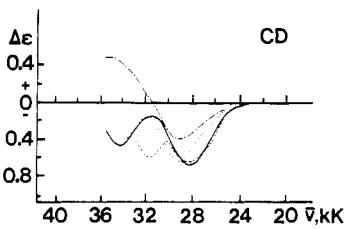

Figure 5. Circular dichroism spectra of DMF solutions of (---) *trans*-$[Pt(R_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$ (IV) and (-·-) *trans*-$[Pt(S_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$ (V) and of (——) IV and (···) V after addition of 2 equiv of OH^-.

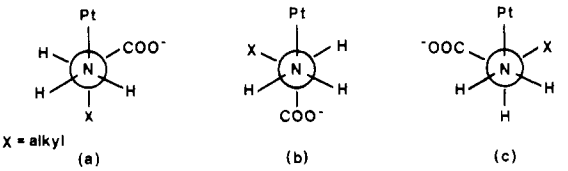

Figure 6. Three conformers associated with rotation about the N–C bond of unidentate amino acid.

Table III. Absorption (A) and Circular Dichroism (CD) Data of DMF Solutions of *trans*-$[Pt(ZH)_2Cl_2]$[a]

		DMF				DMF + 2 equiv of OH^-			
		A		CD		A		CD	
complex	amino acid, ZH	$\bar{\nu}/10^3$ cm^{-1}	ϵ	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\epsilon$	$\bar{\nu}/10^3$ cm^{-1}	ϵ	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\epsilon$
VI	L-AlaH	26.6	23	22.4	+0.03				
		31.2	70	25.7	−0.06				
		37.0	98	31.9	+0.26				
				37.7	−0.18				
VII	L-ValH	26.6	25	22.5	+0.02	26.9	25	22.4	+0.02
		31.2	68	25.4	−0.03	31.2	75	25.6	−0.03
		36.6	98	31.7	+0.24	36.5	100	31.7	+0.38
				37.3	−0.10			37.0	−0.28
VIII	L-TyrH	27.0	28	22.2	+0.03	27.0	25	22.2	+0.02
		31.7	90	25.6	−0.05	−32.0	70	25.7	−0.11
		36.6	CT	31.5	+0.34			31.5	+0.32
				>34.5	+(CT)			>34.5	+(CT)

[a] CT = charge-transfer band.

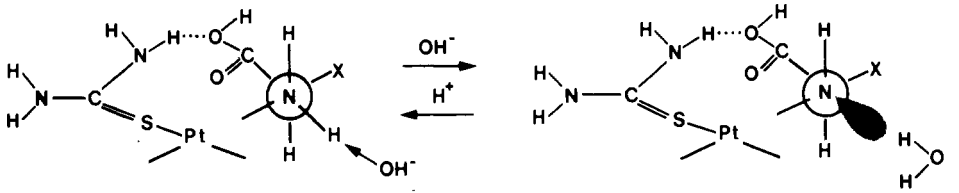

Figure 7. Possible mechanism for creation of an asymmetric donor nitrogen.

changed by addition of OH^-, just as in the aqueous solution. Addition of OH^- also changes the character of the CD spectrum of the other diastereomer, *trans*-$[Pt(R_N,S_C\text{-OproH})_2(Thio)_2]Cl_2$, in the region of the high-energy band (Figure 5, Table II).

The different behavior of the amino acid complexes in water and DMF can be explained by the preference for different rotamers of the unidentate ligand. (In DMF the equilibrium between protonated and deprotonated forms generally shifts to favor the protonated form[14] whereas in the aqueous solutions the deprotonated form tends to dominate.) In Figure 6 the conformers that are likely to occur in the aqueous solution are presented. We may thus expect that the conformer (a) is strongly favored by the possibility of hydrogen bonding between the carboxyl group and the neighboring thiocarbamide ligand and also by nonbonded interaction of the hydrophobic substituent (X). The variation (observed in Figures 1 and 3) between the different amino acid complexes may then be related to different conformer populations due to the size and chemical nature of the substituent.

In the case of the hydroxyproline diastereomers, we have besides the above-mentioned conformational effects also the effect of the chiral discrimination due to the asymmetric donor nitrogen. This latter effect is probably exclusively responsible for the CD variations observed in the aqueous solution, whereas in DMF the protonation of the hydroxyproline carboxyl group may lead to a conformational change similar to those of the other amino acids.

The similarity between the CD spectra of the deprotonated amino acid complexes (Figure 3) is, for steric reasons, not very likely due to identical conformations of the amino acid chelate rings but rather, as we will propose here, to the probability that the d–d CD of the Pt ion is dominated by another common source of optical activity.

The two N–H protons of the amino group are diastereotopic, and because of their different orientations with respect to the asymmetric carbon atom substituents they are susceptible to approach by OH^- (or solvent) to different extents. The stereoselective interaction of the NH_2 group depends of course on the preferred conformation. Thus the action of OH^- on the amino group can be expected to promote the formation of a chiral (sp^3-hybridized) nitrogen, but its handedness is selected by the chirality of the neighboring asymmetric carbon (mechanism in Figure 7). This effect is then supported by the formation of a "chelate" ring (which will narrow the conformational distribution) by the interaction between the carboxylic group and the adjacent thiocarbamide ligand. It is well-known that sulfur-coordinated ligands such as thiocarbamide and *S*-oxides have a strong acidifying effect in aqua and amino Pt(II) complexes.[16,17] For example, in $[Pt(H_2O)_2(Thio)_2]^{2+}$ the first acid constant, K_1, is too high to allow determination at ordinary concentrations and also K_2 is very high (10^{-3} M^{-1}).[16] Also, the methionine *S*-oxide Pt(II) complex is a strong acid, because of the acidity of the amino group, when coordinated in the cis position of the sulfur of the same ligand.[17] This is also consistent with a series ordering various ligands according to their influence on the acidity in aqua complexes, that thiocarbamide makes the platinum(II) aqua complexes more acidic than does the *S*-oxide ligand.[16] The observed behavior of the different amino acid complexes in DMF and DMF + OH^- solutions may thus be explained in terms of the strong acidity of amino groups when coordinating together with thiocarbamide to platinum(II).

The racemization mechanism of any asymmetric environment of the nitrogen must be very slow in DMF as was pointed out in ref 18. A great support for the model (mechanism, Figure 7) is of course the reversibility observed in DMF and the similarity between the CD spectra of the DMF + 2 OH^- solutions of the Pt(II) complexes with the ordinary amino acid and those with L-OproH with an intrinsically asymmetric nitrogen. However, if the carboxylic group or amine groups of thiocarbamide would happen to be more acidic than the amino group of the amino acid (in DMF), it is still possible

(14) Jantz, G. J.; Danyluk, S. S. *Chem. Rev.* **1960**, *60*, 209.
(15) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1978**, *17*, 1701, 1712.
(16) Kukushkin, Yu. N.; Trusova, K. M.; Sibizskaya, V. V.; Samuseva, V. N. *Zh. Neorg. Khim.* **1977**, *22*, 2781.
(17) Freeman, W. A.; Nicholls, L. J.; Liu, C. F. *Inorg. Chem.* **1978**, *17*, 2989.
(18) Hawkins, C. J.; Laurance, G. A.; Palmer, J. A. *Aust. J. Chem.* **1978**, *31*, 2399; **1977**, *30*, 2115.

to imagine a chiral environment of the coordinated nitrogen due to different *solvation* of the two hydrogens.[18,19] Thus, although our mechanism (Figure 7) is a very probable one, we cannot from the present evidence exclude other possibilities. Different models can be expected to provide different kinetic responses to hydrogen ion activity, and studies along these lines are in progress.

Acknowledgment. This work was performed during the visit of O.P.S. to Sweden within the framework of the collaboration between the Russian and Swedish academies of science.

Registry No. I, 86309-45-7; II, 30538-13-7; III, 86309-46-8; IV, 86309-47-9; V, 86362-14-3.

(19) Bosnich, B.; Harrowfield, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 898, 3425.

Notes

Contribution from the Department of Chemistry, The University, Southampton SO9 5NH, U.K.

Synthesis and Properties of Tetrahydrofuran Complexes of Chromium(III). $[Cr(THF)_3X_3]$ (X = Cl, Br, I), $[Cr(THF)_2X_4]^-$ (X = Cl, Br, I, NCS), and "$[Cr(THF)_6](BF_4)_3$"

Peter J. Jones, Annette L. Hale, William Levason,* and Francis P. McCullough, Jr.[1]

Received July 9, 1982

Since its preparation in 1958,[2] trichlorotris(tetrahydrofuran)chromium(III), $[Cr(THF)_3Cl_3]$, has been widely used as a starting material for the synthesis of coordination and organometallic[3] compounds of chromium. Surprisingly little is known about other Cr(III)–THF adducts,[4] although solutions of CrX_3 (X = Br, I) in THF have been prepared (from anhydrous CrX_3, THF, and zinc dust) and used in situ to prepare tertiary phosphine complexes.[5] In our experience the latter approach is not completely satisfactory since (a) some CrX_3 usually remains unreacted, making it difficult to control the Cr:ligand ratio accurately, and (b) the large excess of THF present as solvent can compete with weak donor ligands for the chromium. Even with polydentate phosphines, we have found that better yields and purer products are obtained from $[Cr(THF)_3Cl_3]$ and L in CH_2Cl_2 or CH_2Cl_2/toluene than in neat THF. Here we report the synthesis and properties of the title compounds, which are valuable starting materials for the preparation of Cr(III) complexes.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk tube and drybox techniques. Physical measurements were made as described previously.[6] Tetrahydrofuran (BDH Ltd.) was dried by refluxing over sodium wire for 3 days and distilled from $LiAlH_4$ immediately before use. Anhydrous chromium trichloride (Fluka) was used as supplied.

Anhydrous $CrBr_3$ was made in a manner similar to that described for $PaBr_5$.[7] Electrolytic grade chromium metal (20 mmol) was crushed and placed in a silica apparatus (20-mm diameter by 250-mm length) with a small side arm. The apparatus was flamed out under vacuum and cooled and then a 2-fold excess of anhydrous bromine (BDH) was transferred into the side arm. After suitable degassing, the silica apparatus was sealed off from the vacuum line. The tube was placed horizontally with the end containing the chromium inside a tube furnace at 500 °C. After approximately 2 days the tube was cooled, the excess bromine condensed in the side arm, and the tube sealed off. Yields were estimated to be in excess of 95% on the basis of bromine used.

For anhydrous CrI_3 no side arm was required, and the tube was held in a vertical position. The lower end of the tube was heated to 500 °C for 3 days. The excess iodine was sublimed away from the CrI_3 with the tube held horizontally.

$[Cr(THF)_3Cl_3]$. This was prepared in essentially quantitative yield as described.[2] Anal. Calcd for $C_{12}H_{24}Cl_3CrO_3$: C, 38.5; H, 6.4; Cl, 28.4; Cr, 13.9. Found: C, 38.7; H, 6.4; Cl, 29.4; Cr, 14.3.

$[Cr(THF)_3Br_3]$. This was prepared by extraction of a mixture of anhydrous $CrBr_3$ (ca. 5 g) and zinc dust (0.5 g) with THF (250 cm^3) in a Soxhlet apparatus under nitrogen for 24 h. The brown solution was concentrated under reduced pressure, dry petroleum ether added, and the mixture stirred to give a fine powder. This was filtered off, dried in vacuo (ambient temperature (0.1 torr) throughout), and stored in sealed ampules (60%). Anal. Calcd for $C_{12}H_{24}Br_3CrO_3$: C, 28.3; H, 4.7; Br, 47.2. Found: C, 28.0; H, 4.9; Br, 47.6.

$[Cr(THF)_3I_3]$. This was prepared in a manner similar to that for the bromide (40–60%). Anal. Calcd for $C_{12}H_{24}CrI_3O_3$: C, 22.2; H, 3.7. Found: C, 22.4; H, 3.7.

$[n\text{-}Bu_4N][Cr(THF)_2X_4]$ (X = Cl, Br, I). $[n\text{-}Bu_4N]X$ were dried by heating at 80 °C (0.01 torr) for 2 days. The appropriate finely powdered $[n\text{-}Bu_4N]X$ (2 mmol) was added to $[Cr(THF)_3X_3]$ (2 mmol) in dichloromethane (25 cm^3) and the mixture stirred for 3 h. For X = Br, the solution rapidly became green, but for X = Cl or I, no obvious color change occurred. The solutions were filtered and concentrated in vacuo at room temperature and the resulting oils/solids stirred with dry petroleum ether (40–60 °C). The resulting solids were dried in vacuo.

$[n\text{-}Bu_4N][Cr(THF)_2Cl_4]$. Anal. Calcd for $C_{24}H_{52}Cl_4CrNO_2$: C, 49.6; H, 9.0; Cl, 24.4; N, 2.4. Found: C, 49.7; H, 9.6; Cl, 23.6; N, 2.2.

$[n\text{-}Bu_4N][Cr(THF)_2Br_4]$. Anal. Calcd for $C_{24}H_{52}Br_4CrNO_2$: C, 37.9; H, 6.8; Br, 42.2; N, 1.8. Found: C, 37.4; H, 6.6; Br, 42.6; N, 1.7.

$[n\text{-}Bu_4N][Cr(THF)_2I_4]$. Anal. Calcd for $C_{24}H_{52}CrI_4NO_2$: C, 30.4; H, 5.5. Found: C, 29.7; H, 6.0.

$K[Cr(THF)_2(NCS)_4]$. $CrCl_3 \cdot 6H_2O$ (1.1 g, 4 mmol) and KCNS (2.3 g, 24 mmol) were refluxed in ethanol (50 cm^3) for 5 h, and the mixture was concentrated and filtered. The blue filtrate was stirred with petroleum ether until it produced a solid material, which was dried in vacuo. The material was refluxed for several hours with THF (30 cm^3), producing a purple solution, which was filtered and concentrated to yield a purple solid. This was washed with petroleum ether and dried (60 °C). Anal. Calcd for $C_{12}H_{16}CrKN_4O_2S_4$: C, 29.8; H, 3.3; N, 11.6; NCS, 48.7. Found: C, 30.4; H, 3.5; N, 11.8; NCS, 49.3.

"$[Cr(THF)_6](BF_4)_3$". A solution of $[Cr(THF)_3Cl_3]$ (0.37 g, 1 mmol) in THF (20 cm^3) was stirred overnight with $AgBF_4$ (0.59 g, 3 mmol) and the precipitated AgCl filtered off. The deep green filtrate decomposed on evaporation to yield a purple oil.

Results and Discussion

The brown $[Cr(THF)_3X_3]$ (X = Br, I) were made by reaction of the appropriate anhydrous CrX_3 with THF and a

(1) Present address: Dow Chemical Co., Freeport, TX.
(2) Herwig, W.; Zeiss, H. H. *J. Org. Chem.* **1958**, *23*, 1404.
(3) Sneedon, L. A. "Organochromium Compounds"; Academic Press: New York, 1975.
(4) Although $CrX_3 \cdot 3THF$ (X = Br, I) are mentioned by Parris (Parris, G. *Synth. React. Inorg. Met.-Org. Chem.* **1973**, *3*, 245), it does not appear that pure compounds were isolated and no data were reported.
(5) Howell, I. V.; Venanzi, L. M.; Goodall, D. C. *J. Chem. Soc. A* **1967**, 395.
(6) Gulliver, D. J.; Levason, W.; Smith, K. G.; Selwood, M. J.; Murray, S. C. *J. Chem. Soc., Dalton Trans.* **1980**, 1872.
(7) Brown, D.; Jones, P. J. *J. Chem. Soc. A* **1966**, 262.

0020-1669/83/1322-2642$01.50/0