in both six-membered rings are widened significantly from their nominal values (Table VI). The Co–N2–C6 and Co–N3–C8 angles are the most strained. Comparison of the torsional angles (Table VIII) shows the six-membered rings' similarity.

The distortion from the "perfect chair" conformation amounts in the six-membered rings mainly to a flattening at the amine atoms. In the *trans*-dichloro ion the N2–C6 bond vector makes an angle of 27.3° with the N2–Co–N3 plane. In the Λ-*cis*-β the comparable angle is 28.3°. The N3–C8 bond vectors make angles of 29.4 and 32.7° with the N2–Co–N3 planes in the respective ions. These values are about 9° less than similar values in comparable structures.[20]

Acknowledgment. Thanks to Moo Jin Jun for furnishing a supply of the ligand. Also the provision of computer time by the University of Illinois at Chicago Circle Computer Center is gratefully acknowledged.

Registry No. *trans*-[Co(*SS*-pyht)Cl_2]ClO_4, 59202-14-1; *cis*-β-[Co(*SS*-pyht)(C_2O_4)]ClO_4, 59318-03-5.

Supplementary Material Available: A listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Structures and Circular Dichroism of Monomeric and Novel Dimeric Platinum(II) Complexes of the (*S*)-Methionine *S*-Oxides, Including the X-ray Crystal Structure of Bis[μ-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,μ-*N*]]-diplatinum(II)

WADE A. FREEMAN,* L. JEWEL NICHOLLS, and CHUI FAN LIU

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The preparation and characterization of four complexes containing equimolar platinum(II) and (*S*)-methionine *S*-oxide are reported. The crystal and molecular structure of bis[μ-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,μ-N]]-diplatinum(II), [Pt_2{(2*S*,*SS*)-methionine *S*-oxide(2−)}$_2$], $Pt_2[C_5H_9NO_3S]_2$, is reported from single-crystal three-dimensional X-ray data collected by counter methods. The dinuclear complex crystallizes as rhombic prismatic crystals in space group $P2_1$ (C_2^2; No. 4). Cell constants are $a = 11.4826$ (15) Å, $b = 12.5007$ (19) Å, $c = 5.5839$ (9) Å, and $\beta = 96.684$ (12)°. For $Z = 2$ this gives $d_{\text{calcd}} = 2.99$ g cm^{-3}; $d_{\text{obsd}} = 2.97$ (2) g cm^{-3}. There were 2826 independent measurements, and the structure was refined to an R value of 0.0257. The complex has two bridging imido nitrogens (ionized α-amino groups from the amino acid) that link the platinum(II) centers in a four-membered ring. Each four-coordinate platinum atom is surrounded by nearly coplanar N, S, and O atoms from one methionine *S*-oxide ligand and the bridging imido nitrogen from the other. The two planes of coordination meet at the bridging imido groups at an angle of 129.59 (3)°. The molecule lacks C_2 symmetry in the crystal lattice because of quite dissimilar hydrogen bonding arrangements involving the two imido nitrogen atoms and different oxygen atoms of a neighboring molecule in the crystal. The (2*S*,*RS*)-diastereomeric dimer is concluded to be similar in molecular structure by comparison of analyses, circular dichroism spectra, infrared spectra, and titration data. Comparison is also made with the structure and properties of the corresponding dichloromononuclear complexes.

Introduction

The details of the interaction of platinum(II) with optically active amino acids and peptides are of interest not only as coordination phenomena but also with respect both to the known biological activity of platinum(II) complexes[1] and to the means by which stereoselectivity is exerted. Circular dichroism spectra of such complexes are easy to get experimentally but present difficulty in interpretation.[2-4] Thus, during the characterization of the newly prepared dichloroplatinum(II) complexes of the diastereomeric ligands 2*S*,*SS*-methionine *S*-oxide and 2*S*,*SR*-methionine *S*-oxide, it was observed that, whereas in acid solution the CD spectra of the two were almost mirror images, in base the CD spectra of both changed, becoming quite similar. Both the original observation and the changes were unexpected. The changes were soon in fact confirmed to be caused by further reaction—the formation of two quite novel dinuclear platinum(II) complexes. These complexes represent the first cases of a double imido bridge in coordination compounds. They hold interest both for bonding theory and for the nature of the interaction of platinum(II) in biological systems.

In this paper the syntheses of the dinuclear complexes and their precursors are given, their structures established (by means that include X-ray crystal-structure studies), and their CD spectra interpreted on the basis of these structures.

Experimental Section

Preparation of Ligands. (2*S*,*SS*)- and (2*S*,*SR*)-methionine *S*-oxide were prepared and resolved by the method of Lavine.[5] The purity of the diastereomers was checked by comparing the rotation with that

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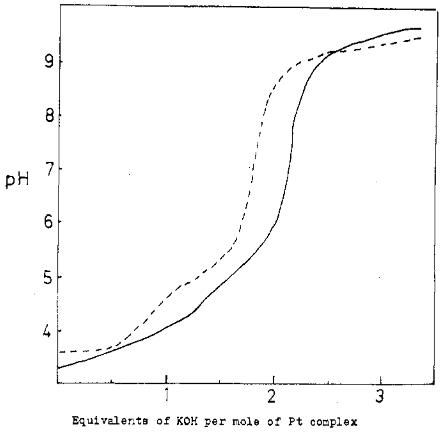

Figure 1. Titration of Pt((2*S*,*SR*)-methionine *S*-oxide)Cl_2 (- - -) and Pt((2*S*,*SS*)-methionine *S*-oxide)Cl_2 (—) with KOH at room temperature.

of the literature: 2*S*,*SS*-methionine *S*-oxide, $[\alpha]_D^{21}$ + 107° (lit. $[\alpha]_D^{25}$ +99°); 2*S*,*SR*-methionine *S*-oxide, $[\alpha]_D^{21}$ −62° (lit. $[\alpha]_D^{25}$ −71.0°).

Preparation of Complexes [Pt((2*S*,*SR*)-methionine *S*-oxide)]Cl_2. Potassium tetrachloroplatinate(II) and (2*S*,*SR*)-methionine *S*-oxide were reacted by the method used by Volshtein[6] for the related (*S*)-methionine complex with platinum(II). Anal. Calcd for $PtC_5H_{11}NSO_3Cl_2{\cdot}H_2O$: C, 13.37; H, 2.92; N, 3.12; Cl, 15.78. Found: C, 13.57; H, 2.97; N, 3.17; Cl, 15.89.

[Pt((2*S*,*SS*)-methionine *S*-oxide)]Cl_2. This diastereomer of the above complex was prepared by the same method. Anal. Calcd for $PtC_5H_{11}NSO_3Cl_2{\cdot}{}^1/_2H_2O$: C, 13.64; H, 2.74; N, 3.18; Cl, 16.11. Found: C, 13.94; H, 2.71: N, 3.33; Cl, 16.12.

Bis[*μ*-[(2*S*,*SR*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,*μ*-*N*]]-diplatinum(II). To a fresh solution of 0.10 g of Pt((2*S*,*SR*)-methionine *S*-oxide)Cl_2 in 20 mL of water was slowly added a 0.001 M KOH solution. The pH was monitored constantly as base was added. When a pH of 9 was reached and maintained the addition was ended. During the reaction, the solution changed from bright yellow to colorless. The solution was allowed to stand at room temperature for several days as very pale yellow crystals formed. During the evaporation the pH was held at 9 by addition of more KOH. The product was isolated, recrystallized from hot water, and air-dried. Anal. Calcd for $Pt_2C_{10}H_{18}N_2S_2O_6$: C, 16.76; H, 2.53; N, 3.91. Found: C, 17.25, 16.45; H, 2.58, 2.60; N, 3.91, 3.76; no chlorine.

Bis[*μ*-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,*μ*-*N*]]-diplatinum(II). This complex was prepared in the same manner as the previous, starting from the dichloroplatinum(II) complex of the (2*S*,*SS*) ligand. It was isolated as the dihydrate. Anal. Calcd for $Pt_2C_{10}H_{18}N_2S_2O_6{\cdot}2H_2O$: Pt, 51.84; C, 15.96; H, 2.95; N, 3.72. Found: Pt, 50.32; C, 16.05, 15.97; H, 2.69, 2.75; N, 3.61, 3.64; no Cl.

Titrations. The courses of the reactions giving the two dimers were followed with a Sargent-Welch pH meter. Solutions of approximately 7×10^{-4} M complex and standard KOH of 0.001 57 M were used. The solutions were stirred constantly using a magnetic stirrer as the KOH was slowly added. The procedure took about 1.5 h. Results of the titrations are shown in Figure 1.

Determination of Crystal Structure of Bis[*μ*-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,*μ*-*N*]]-diplatinum(II). Preliminary precession photographs showed monoclinic symmetry and the systematic absence 0*k*0 for *k* odd. Because the substance is optically active, it must crystallize in a noncentrosymmetric group and the space group was therefore definitely concluded to be $P2_1$ [C_2^2; No. 4]. A rhombic-prismatic crystal of approximate dimension 0.035 × 0.364 × 0.070 mm was mounted in a Picker FACS-1 computer-controlled four-circle diffractometer. The crystal was accurately centered and aligned with [001] coincident with the *ϕ* axis of the instrument. To determine the magnitude of the absorption problem the 003 reflection was measured (by repeated θ–2θ scans) at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The variation in intensity as a function of *ϕ* (defined as (maximum − minimum)/average) was large—64%. When the *ϕ*-scan data were later corrected (along with the primary data set) for the effects of absorption, the variation in intensity was reduced to 14%. Cell dimensions were determined by least-squares procedures based on the angular position of 12 high 2θ (2θ = 44 to 52°) reflections widely separated in reciprocal space.

Table I. Experimental Data for the X-ray Diffraction Study

(A) Crystal Parameters (at 21 °C)[a]

$a = 11.4826$ (15) Å
$b = 12.5007$ (19) Å
$c = 5.5838$ (9) Å
$\cos\beta = -0.1164$ (2)
$\beta = 96.684$ (12)°
$V = 796.05$ (26) Å^3
space group $P2_1$ [C_2^2; No. 4]
$Z = 2$
mol wt = 716.57
ρ(calcd) = 2.99 g cm^{-3}
ρ(obsd) = 2.97 (2) g cm^{-3} [b]
$F(000) = 656$ electrons

(B) Measurement of Intensity Data

radiation: Mo K*α*
filter(s): Nb foil at counter aperture (~47% transmission of Mo K*α*)
attenuators: Cu foil, inserted if $I > 10^4$ counts/s
takeoff angle: 3.0°
detector aperture: 5 mm × 5 mm
cryst–detector dist: 330 mm
cryst orientation: mounted along [001]
reflections measd: $+h \pm k \pm l$
max 2θ: 50°
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 2.0°/min
scan length: $\Delta(2\theta) = (1.10 + 0.692 \tan\theta)°$, starting 0.55° below the Mo Kα_1 peak
background measurement: stationary-crystal, stationary-counter; 20.0 s each at beginning and end of 2θ scan
standard reflections: three measured after every 48 reflections; rms deviations (after application of an isotopic linear decay correction) were 1.07% for 400, 1.17% for 040, and 1.24% for 003
reflections collected: 2826 independent measurements, 338 duplicate or equivalent measurements (averaged into primary data set), and 14 systematic absences

(C) Treatment of Intensity Data[c]

conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 8, using an "ignorance factor" of $p = 0.030$
absorption coefficient: $\mu = 187.6$ cm^{-1}; maximum and minimum transmission factors were 0.598 and 0.121, respectively[d]

(D) Details of Refinement

unique data used: 2826 (*none* rejected as "not significantly different from zero")
final no. of variables: 209 independent, 62 dependent (for "riding" H's)
final error in observation of unit wt: 1.27
final R_F: 2.57% R_{wF}: 2.95%[e]

[a] Based on λ(Mo Kα_1) = 0.709 300 Å: Bearden, J. A. *Rev. Mod. Phys.* **1967,** *39*, 78. [b] By neutral buoyancy in CCl_4/CBr_4. [c] Data reduction (including averaging, linear decay correction etc.) was performed using the Fortran IV program RDUS, by B. G. DeBoer. [d] Absorption corrections were carried out using the Fortran IV program DRABZ, by B. G. DeBoer.[8] [e] $R_F = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_{wF} = [\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{1/2}$; $w = \sigma^{-2}(|F_o|)$.

Data collection procedures and computer programs for the reduction of the data, for application of the absorption correction, and for solution and refinement of the structure have been described previously.[8] Calculations were done on an IBM 370/158 computer. Details pertinent to this structure are summarized in Table I.

The structure was solved without special difficulties by the heavy-atom method. After the platinum atoms were located from the Patterson synthesis, a difference Fourier map showed the locations of all the nonhydrogen light atoms. Atomic scattering factors for neutral nonhydrogen atoms were taken from Cromer and Waber[9] and for hydrogen from Stewart, Davidson, and Simpson.[10] Refinement included the use of anisotropic thermal parameters for all nonhydrogen atoms and insertion of all 18 hydrogen atoms as "riding" in idealized positions (based on d(C–H) = 0.95 Å and d(N–H) = 0.87 Å, as suggested by Churchill[11]). The methyl hydrogen atoms were placed so that they were conformationally staggered with respect to the S–Pt bond axis. All hydrogens had shifts in positional parameters held equal to the shifts of their attached atoms. The isotropic thermal parameters for the members of each set of hydrogen atoms bonded to a given nitrogen or carbon atom were held equal to each other during refinement. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = \sigma^{-2}(F_o)$.

Table II. Final Parameters for Atoms in Bis[μ-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,μ-*N*]]-diplatinum(II)[a, b]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt′	0.12568 (3)	−¹/₄	0.37670 (6)	1.599 (14)	1.587 (13)	1.979 (14)	0.047 (11)	0.175 (11)	0.169 (11)
S′	−0.0262 (2)	−0.3469 (2)	0.2258 (4)	1.76 (8)	2.12 (8)	2.12 (9)	−0.05 (6)	0.10 (7)	0.12 (6)
N′	0.1617 (7)	−0.3390 (5)	0.6821 (15)	1.3 (3)	1.9 (3)	3.1 (4)	−0.0 (2)	1.2 (3)	0.0 (2)
O(1)′	0.3565 (6)	−0.4579 (5)	0.8233 (14)	2.5 (3)	2.5 (3)	3.7 (4)	0.2 (2)	0.1 (3)	0.4 (2)
O(2)′	0.2502 (8)	−0.5957 (6)	0.9175 (18)	4.7 (4)	3.0 (3)	5.2 (5)	−0.2 (3)	−0.3 (4)	1.6 (3)
O(3)′	−0.5506 (6)	−0.3465 (6)	−0.0392 (13)	3.1 (3)	3.7 (3)	2.6 (3)	−0.3 (3)	0.5 (3)	0.1 (2)
C(1)′	0.2586 (9)	−0.5067 (7)	0.8234 (18)	2.8 (5)	1.9 (4)	2.5 (4)	0.2 (3)	0.1 (3)	0.6 (3)
C(2)′	0.1460 (10)	−0.4562 (7)	0.6943 (18)	2.9 (5)	1.8 (4)	2.2 (4)	0.2 (3)	0.7 (4)	0.4 (3)
C(3)′	0.1203 (10)	−0.5068 (8)	0.4479 (19)	3.6 (5)	1.8 (4)	2.9 (4)	0.1 (3)	−0.3 (4)	−0.4 (3)
C(4)′	−0.0011 (11)	−0.4840 (8)	0.3234 (27)	3.4 (5)	1.8 (4)	5.6 (7)	−0.7 (4)	−1.8 (5)	0.3 (4)
C(5)′	−0.1549 (8)	−0.3146 (10)	0.3555 (18)	2.5 (4)	3.8 (5)	−0.2 (4)	0.2 (4)	0.1 (3)	−0.3 (4)
Pt	0.33598 (3)	−0.31091 (3)	0.67068 (6)	1.746 (15)	1.667 (14)	1.830 (14)	0.095 (11)	0.095 (11)	0.085 (11)
S	0.5196 (2)	−0.2912 (2)	0.6039 (4)	1.71 (9)	2.39 (9)	2.32 (9)	0.02 (7)	0.06 (7)	−0.07 (7)
N	0.2724 (6)	−0.1702 (5)	0.5205 (13)	2.4 (3)	1.5 (3)	1.4 (3)	−0.4 (2)	0.5 (2)	−0.7 (2)
O(1)	0.1393 (6)	−0.1492 (5)	0.6929 (13)	2.7 (3)	2.5 (3)	2.3 (3)	−0.3 (2)	−0.2 (2)	0.9 (2)
O(2)	0.2610 (7)	−0.0385 (5)	0.0558 (13)	3.5 (3)	2.1 (3)	2.2 (3)	0.1 (2)	0.2 (3)	0.4 (2)
O(3)	0.5597 (6)	−0.3689 (6)	0.4322 (13)	2.9 (3)	4.1 (3)	2.9 (3)	0.7 (3)	0.5 (3)	−0.5 (3)
C(1)	0.2356 (9)	−0.6957 (6)	0.1074 (17)	2.4 (4)	1.4 (3)	2.3 (4)	0.1 (3)	0.4 (3)	0.2 (3)
C(2)	0.3203 (9)	−0.1040 (7)	0.3384 (18)	2.4 (4)	1.7 (3)	2.1 (4)	−0.4 (3)	0.5 (3)	0.3 (3)
C(3)	0.4387 (9)	−0.1429 (8)	0.2736 (19)	2.5 (4)	2.8 (4)	3.4 (5)	0.4 (3)	1.1 (4)	0.8 (4)
C(4)	0.5324 (9)	−0.1591 (8)	0.4882 (21)	2.3 (4)	3.1 (4)	3.8 (5)	−0.6 (3)	0.5 (4)	0.2 (4)
C(5)	0.6208 (9)	−0.2963 (9)	0.8642 (19)	2.3 (4)	3.0 (4)	4.0 (5)	0.1 (4)	−0.7 (4)	−0.3 (4)

atom[c]	*x*	*y*	*z*	B_{iso}, Å^2	atom	*x*	*y*	*z*	B_{iso}, Å^2
C(2)H′	0.0801	−0.4693	0.7783	3 (3)	C(5)H(2)′	−0.1741	−0.2414	0.3266	4 (2)
C(2)H	0.3327	−0.0360	0.4130	2 (2)	C(5)H(3)′	−0.1426	−0.3272	0.5242	
C(3)H(1)′	0.1752	−0.4791	0.3491	5 (2)	C(5)H(1)	0.6978	−0.2870	0.8212	6 (2)
C(3)H(2)′	0.1303	−0.5821	0.4633		C(5)H(2)	0.6041	−0.2411	0.9721	
C(3)H(1)	0.4670	−0.0924	0.1671	5 (2)	C(5)H(3)	0.6153	−0.3638	0.9401	
C(3)H(2)	0.4269	−0.2099	0.1942		NH′	0.1190	−0.3224	0.7953	2 (2)
C(4)H(1)′	−0.0552	−0.4998	0.4348	6 (3)	NH	0.2794	−0.1171	0.6216	
C(4)H(2)′	−0.0155	−0.5297	−0.1872						
C(4)H(1)	0.6083	−0.1492	0.4402	2 (1)					
C(4)H(2)	0.5198	−0.1082	0.6089						
C(5)H(1)′	−0.2175	−0.3582	0.2850	4 (2)					

[a] Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and were derived from the inverse of the final least-squares matrix. [b] Anisotropic thermal parameters are in units of Å^2 and enter the structure factor equation in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + B_{23}klb^*c^*)]$. [c] Esd's are identical with those of the atoms to which these hydrogen atoms are attached.

Both the real and imaginary components of the anomalous dispersion were included throughout the refinement for all nonhydrogen atoms, using the values of Cromer and Liberman.[12] During the final stages of refinement a reversal of handedness to the enantiomeric coordinates gave significant improvement in the discrepancy indices. The absolute configuration of the molecule was thus determined to be that given in Table II. The largest shift during the last cycle of refinement was 0.094σ. The "goodness of fit", defined as $|\sum w(|F_o| - |F_c|)^2/(m - n)|^{1/2}$, was 1.27. Final conventional R_F (see Table I) was 0.0257.

Spectra. Circular dichroism spectra were obtained using a Jasco Model ORD/UV5 spectrophotometer with an SS-20CD modification. All solutions were aqueous and dilute. Infrared spectra were run on a Perkin-Elmer 337 grating infrared spectrophotometer using the KBr pellet technique. The spectrophotometer was calibrated against polystyrene.

Analyses. All chemicals used were ACS reagent grade or better. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Discussion

Mononuclear Complexes. It is well-known that platinum(II) exhibits a considerable preference for sulfur (as compared to oxygen) donors when coordinating with ambidentate ligands that offer both.[13] For example, when platinum(II) is reacted with methionine, metal–ligand bonding occurs through the sulfur and nitrogen donors only, forming a six-membered chelate ring. The carboxylic acid group is left uncoordinated.[6] The X-ray crystal structure of this complex has been reported;[14] the chelate ring is in a chair conformation with the uncoordinated carboxylic acid group equatorial. By treating [Pt(methionine)Cl_2] with an equivalent of base, Volshtein[7] sought to force methionine to serve as a tridentate ligand. An insoluble complex with elemental analysis corresponding to [Pt(methioninate)Cl] was formed. IR and other evidence showed that this material did involve all three of the possible donor sites, but it was almost certainly a polymer (see below).

Use of the *S*-oxides of methionine as ligands introduces two complications: the possibility of coordination of the sulfoxide oxygen and an additional center of asymmetry (the sulfur atom). However, the *S*-oxide stretching frequency in the infrared spectra of these compounds turns out to be a good indication of mode of coordination. And the addition of another side group to the Pt–N–S chelate ring leads to subtle and interesting effects upon the conformation.

In the case of the two monomeric complexes, Pt((2*S*,*SR*)-methionine *S*-oxide)Cl_2 and Pt((2*S*,*SS*)-methionine *S*-oxide)Cl_2, the S–O stretching frequencies were 1090 and 1116 cm^{-1}, respectively. The uncoordinated ligands had values of 1020 and 1025 cm^{-1}, respectively. The shift to higher energy is typical of sulfur coordination.

Coordination through the sulfur is also argued by similarities found by comparison to the IR spectra of [Pt($Me_2SO)_2Cl_2$][15] and [Pt((*S*)-methionine)Cl_2];[14] the S–O stretching frequency is like that found in complexes of Me_2SO. In studies[15] of complexes of $(CH_3)_2SO$ with many metals, Cotton and coworkers concluded that platinum and palladium are coordinated to $(CH_3)_2SO$ through S rather than O because they found the S–O stretching frequency in those complexes to be higher than in the free ligand, while in complexes of metals of the first transition series the S–O stretching frequency is lower than in the free ligand.[16,17]

Finally, the asymmetric stretching frequencies of the C–O bonds are quite comparable (1718 and 1715 cm^{-1}) to those

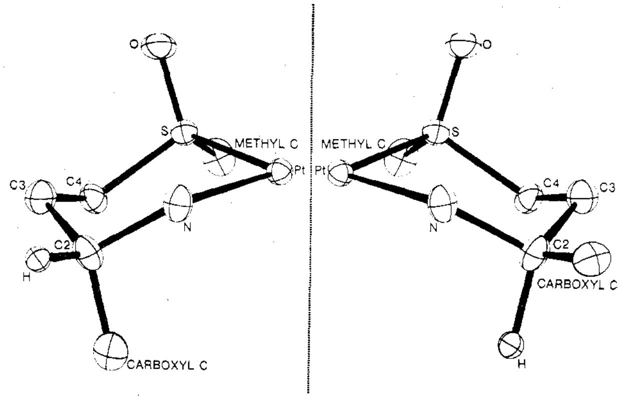

Figure 2. (a, left) Observed conformation of the chelate ring in the coordination of (2*S*,*SR*)-methionine *S*-oxide to platinum(II). The other ligands (the Cl^-'s) are omitted along with all hydrogens but the C(2) hydrogen. Also omitted are the carboxyl oxygens. The carbonyl C is "axial" and the S–O is also "axial". This diagram is based on X-ray crystallographic results.[18] (b, right) Proposed structure of the chelate ring in the coordination of (2*S*,*SS*)-methionine *S*-oxide to platinum(II). It is antimeric to the conformation of its coordinated diastereomer except that carboxyl C is "equatorial".

observed in Volshtein's [Pt(methionine)Cl_2] complex (1718 cm^{-1}). The conclusion is thus that the two dichloromethionine *S*-oxide complexes with Pt(II), like the [Pt(methionine)Cl_2] complex itself, involve coordination through S and N and not through the carboxyl oxygen.

This conclusion has been confirmed by an X-ray study on the [Pt((2*S*,*SR*)-methionine *S*-oxide)Cl_2] complex.[18] This complex, and therefore its diastereoisomer, are mononuclear, square planar, and involve N and S coordination only.

The six-membered N–Pt–S chelate ring in this complex could in general adopt either of two extreme chair conformations which, without regard to the disposition of any substituents, are mirror images. Also possible are intermediate boat and skew boat conformations. The crystal structure study cited above shows that for the (2*S*,*SR*)-methionine *S*-oxide complex, the conformation depicted in Figure 2a is actually found. This chair conformation has the –COOH group axial, the S–CH equatorial, and the S–O axial. Since the –COOH group in related complexes, like [Pt((*R*,*S*)-methionine)Cl_2], [Pt((*S*)-methionine)Cl_2], and [Pt((*R*,*S*)-methionine)Cl_2], is always equatorial, the conformation reported is unexpected. The antimeric chair conformation would have the –COOH equatorial, the S–CH_3 axial, and the S–O equatorial. The observation was rationalized in terms of the attainment of a geometry in which the S–O bond is better oriented to accept Pt(II) d electron density in a π^* molecular orbital.[18]

The coordinated S–O group prefers the axial disposition. Therefore the conformation in the [Pt((2*S*,*SS*)-methionine *S*-oxide)Cl_2] complex can confidently be expected to be that depicted in Figure 2b. Because of the different handedness at the sulfur atom this complex's chelate ring can have the S–O axial and the –COOH equatorial at the same time. As Figure 2 shows, the overall conformations in the two complexes are then nearly mirror images—the deviation being that in Figure 2a the –COOH is axial and in Figure 2b it is equatorial.

This relationship is of course entirely consistent with the observation of nearly mirror-image CD spectra in the region of the Pt(II) chromophore for the two complexes (Figure 3), bearing in mind as always that caution must be exercised in applied solid-state structural results to spectra taken in solution.

It is usual to attempt to separate CD spectra involving the central metal chromophore into contributions ascribed to configurational, conformational, and vicinal effects.[19] A first explanation for the differences between the CD's of [Pt((2*S*,*SS*)-methionine *S*-oxide)] and [Pt((2*S*,*SR*)-methionine *S*-oxide)] might be the different vicinal effect of the *S* and *R* sulfur atoms. But the above discussion shows how the actual differences are in fact conformational in origin. Thus, instead of the *difference* between the CD's of the two complexes representing twice the vicinal effect of the optically active sulfur, in fact the *sum* of the two represents twice the vicinal effect of the optically active 2-carbon!

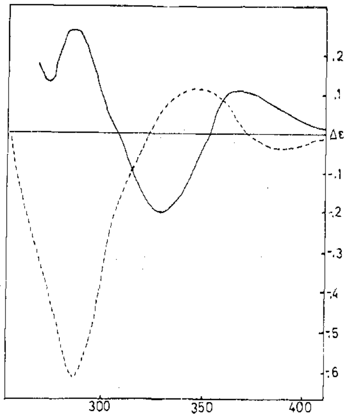

Figure 3. Circular dichroism spectra of [Pt((2*S*,*SR*)-methionine *S*-oxide)Cl_2] (- - -) and [Pt((2*S*,*SS*)-methionine *S*-oxide)Cl_2] (—) in 0.1 M HCl at room temperature. Horizontal axis is calibrated in nm.

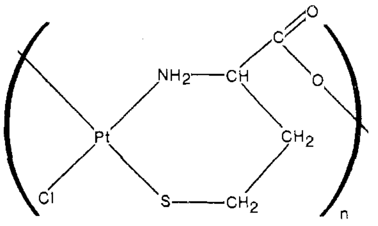

Figure 4. Probable structure of the [Pt(methioninate)Cl] complex of Volshtein.[7] The diagrammed sulfur is intended to be general for all the related methionine compounds—the remaining two tetrahedral positions at sulfur could be a pair of electrons and a methyl group (methionine) or an oxygen atom and a methyl group (methionine S-oxide).

Dinuclear Complexes. The synthesis of these compounds is dependent upon careful control of pH and the slow addition of base during the neutralization of the precursor compounds. Titration curves for the neutralizations are given in Figure 1. The [Pt((2*S*,*SS*)-methionine *S*-oxide)Cl_2] precursor gave a precipitate after the addition of 1 equiv of base, at pH 5. This precipitate redissolved upon further addition of base. The [Pt((2*S*,*SR*)-methionine *S*-oxide)Cl_2] did not give such a precipitate. When isolated, the precipitate proved intractable and quite insoluble in water. Its elemental analysis corresponded fairly closely to the formula [Pt((2*S*,*SS*)-methioninate *S*-oxide)Cl]. It is likely that this material is a mixture of Pt(II) polymers of the type represented in Figure 4. A similar polymeric structure also seems appropriate for the tridentate methionineplatinum(II) complex discussed by Volshtein.[7]

The similarity between the titration curves of the two diastereomeric mononuclear precursor complexes (Figure 1) supports the conclusion that similar reactions are taking place and similar products being formed. The addition of the first 2 equiv of base causes the neutralization of first the carboxylic acid group and then an amine proton on each ligand. The increase in acidity of amine protons upon coordination through the nitrogen is quite well-known.[20] The overall reaction:

$$2Pt(C_5H_{11}NSO_3)Cl_2 + 4OH^- \rightarrow Pt_2(C_5H_9NSO_3)_2 + 4H_2O + 4Cl^-$$

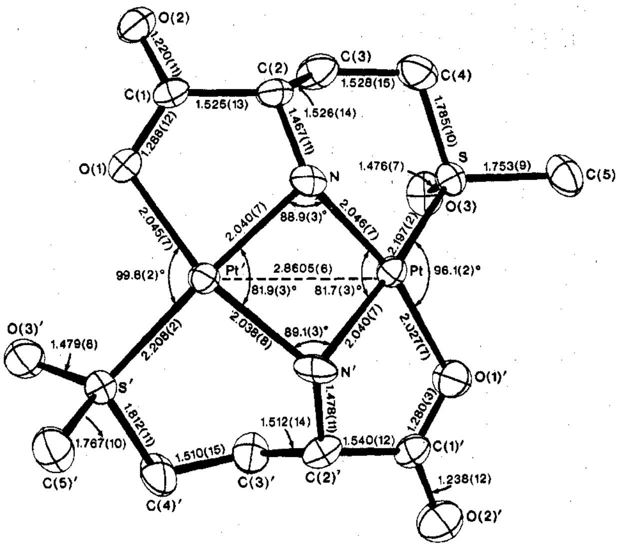

Figure 5. Perspective view of a molecule of $[Pt_2(C_5H_9NSO_3)_2]$. Hydrogen atoms are omitted for clarity. Interatomic distances are in Å. Esd's are shown in parentheses and are right-adjusted to the last digit of the preceding number. Their calculation includes the effect of all elements of the positional covariance matrix as well as the uncertainties in the unit cell dimensions. No corrections have been applied for the effects of thermal motion.

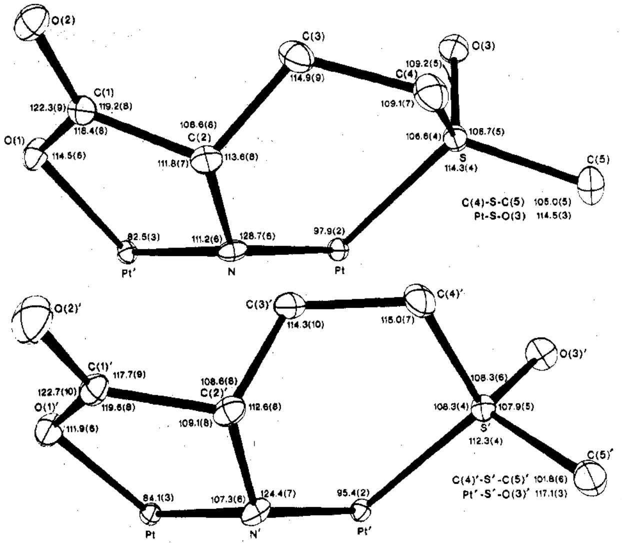

Figure 6. Comparison of the conformations of the independent ligands in $[Pt_2(C_5H_9NSO_3)_2]$. The upper portion of the figure shows a perspective view of the unprimed ligand looking parallel to the Pt–N–Pt′ plane. The lower portion of the figure is an exactly comparable view for the primed ligand. Bond angles are in degrees. Esd's are given as in the legend to Figure 5.

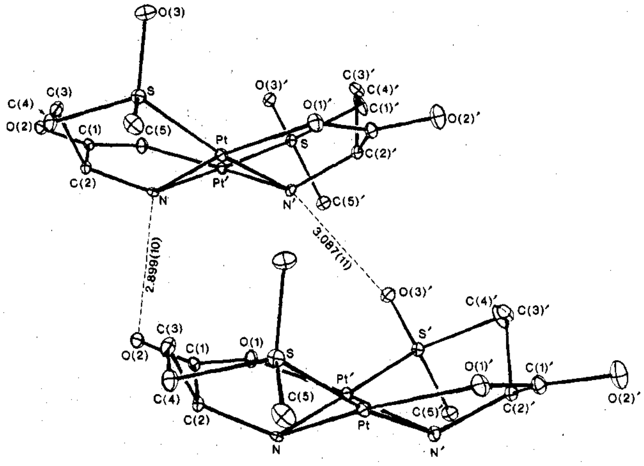

Figure 7. Perspective view of two $[Pt_2(C_5H_9NSO_3)_2]$ molecules related by translation along the *c* axis. Hydrogen bonds are indicated by dotted lines. They couple the "nitrogen side" of the upper molecule with the "oxygen side" of the lower.

Addition of a third equivalent of base was required before the loss of color (from yellow) which signified the reaction was complete.

The structure of one of the dinuclear complexes, that of the 2*S*,*SS* ligand, was determined by X-ray crystallographic means.[21] The similarity in the conditions of reaction, the titration curves, and of course the elemental analyses argue that the 2*S*,*SR* ligand gives a similar dinuclear complex. In addition, the frequencies of the asymmetric stretching mode of the carboxylate groups in the two dinuclear complexes are virtually identical (1620 and 1630 cm^{-1} for the 2*S*,*SS* and the 2*S*,*SR* ligand complexes, respectively). These values are typical of a coordinated carboxyl group.

The structure consists of discrete molecules. Each molecule comprises a system of a single four-membered, two five-membered, and two six-membered rings (see Figure 5). All of the rings are puckered. No two are in the same conformation. Coordination about each platinum atom is nearly planar. The largest deviation from the best least-squares plane defined by atom Pt and its four donor atoms is 0.096 Å; for the best least-squares plane defined by atom Pt′ and its donors, the corresponding figure is 0.066 Å. These two planes intersect in the line N–N′ at an angle of 129.59 (3)°. To allow coordination the bond angles about the bridging nitrogen atoms are severely distorted from the tetrahedral value (Figures 5 and 6).

The large angle between the planes of coordination means that the central four-membered ring is considerably puckered. This leaves the two nitrogen atoms exposed on the same side of the molecule. The molecule thus can be seen as possessing a nitrogen side and an oxygen side (Figure 7). Molecules are hydrogen bonded from the nitrogen side of one to the oxygen side of another along the crystallographic *c* axis.

The great difference in conformations between the two ligands (primed and unprimed labels) is surely a result of the different influences exerted upon them by hydrogen bonding. In the primed ligand the oxygen atom O(3)′ (the sulfoxide oxygen atom) is hydrogen bonded to the N′ atom in the neighboring molecule along the *c* axis. In contrast, in the unprimed ligand it is the oxygen atom O(2) (the carbonyl oxygen atom) that is hydrogen bonded to atom N in the same neighboring molecule. Figure 6 allows comparison of the two ligands' conformations.

A good way to compare and contrast the conformations of chelate rings is to consider angles formed among the lines and planes defined by the atoms comprising them. In the primed six-membered chelate ring in this compound the lines S′–C(4)′ and N′–C(2)′ form respectively angles of 69.5 (4)° and 72.3 (6)° to the C(2)′–C(3)′–C(4)′ plane. For the unprimed ligand the corresponding angles, of S–C(4) and N–C(2) to the C(2)–C(3)–C(4) plane, have quite different values: 87.2 (4)° and 53.0 (5)°, respectively. Equality or near-equality of these two angles in a six-membered ring means a symmetrical or near-symmetrical conformation; a great difference indicates a skew conformation. Thus the six-membered chelate ring involving the primed ligand is in a nearly symmetrical-boat conformation and the corresponding ring involving the unprimed ligand is in a skew-boat conformation. It is worth noting that the sums of the two above-defined angles are approximately equal for the primed and unprimed six-membered rings. For comparison's sake, in [dichloro-

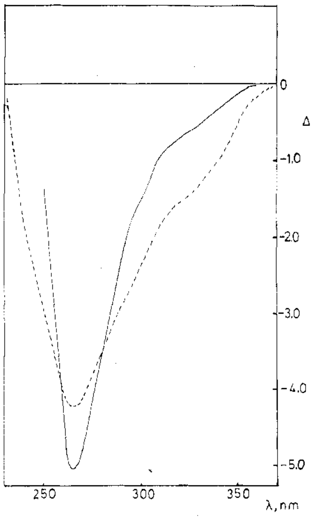

Figure 8. Circular dichroism spectra of $Pt_2[(2S,SR)$-methionine S-oxide$(2-)]_2$ (- - -) and $Pt_2[(2S,SS)$-methionine S-oxide$(2-)]_2$ (—) in water. The ordinate Δε is measured per mole of platinum chromophore for comparison with the monomeric species. The rotatory strengths of the dinuclear complexes are thus greater by a factor of about 10 than those of the monomeric species.

((2*S*,*SR*)-methionine *S*-oxide)platinum(II)], which contains a comparable six-membered ring, this time in a chair conformation, the angles corresponding to the above are respectively 74.5 (4)° and 70.4 (5)°.[18] Another way to view the difference between the two six-membered rings is to consider the angle of the line S–O(3) to the plane of coordination. For the symmetrical-boat, primed six-membered ring, this angle is 11.3 (4)°; for the skew-boat, unprimed ring, this angle is 26.5 (4)°.

For the five-membered chelate rings a useful comparison involves the dihedral angle between the planes N–C(2)–C(1) and O(1)–C(1)–C(2). In the unprimed five-membered ring this angle is 3.4 (5)°. In the primed ring the corresponding angle is 27.4 (5)°. This means that the unprimed five-membered ring is nearly flat. In fact the largest deviation from a best least-squares plane defined by the five ring atoms is 0.086 Å. In contrast an unprimed five-membered ring is much more puckered. The former situation is usual with α-amino acid chelate rings.[19]

In summary then, in the chelate rings involving the unprimed ligand, the five-membered ring is in a commonly found conformation and the six-membered ring is locked into the less common skew-boat conformation. For the primed ligand, the six-membered ring is in a symmetrical-boat conformation but the five-membered ring is forced to pucker far more than usual.

The N–N′–Pt and N–N′–Pt′ planes form an angle of 136.1°. The Pt atoms are 2.8605 (3) Å distant from each other. The puckering of the four-membered ring (Pt–N–Pt′–N′) brings the Pt atoms closer together than they would be were the ring planar. Approach between the two Pt atoms is achieved by compression of the Pt–N–Pt′ and Pt′–N′–Pt angles. Partial overlap between the d orbitals on the neighboring Pt atoms would compensate energetically for the strain at the N atoms in this ring. The formation of Pt–Pt bonds in crystalline platinum(II) complexes is well-known.[23]

The observed structure represents the first case of a double imido bridge in coordination compounds, although a di-μ-nitrogen-platinum(II) complex ion has previously been reported;[24] X-ray results on that dehydrodiimide-bridged species showed that the Pt_2N_2 moiety was planar. Also the ion involved "soft" phosphine ligands. It is therefore a very different bonding situation. Folded bridge systems are known with a series of dinuclear molybdenum complexes. An example involving dioxo bridging is $Na_2Mo_4O_4(cysteine)(H_2O)_2 \cdot 3H_2O$.[25]

Some preliminary X-ray crystallographic results on the (2*S*,*SR*) ligand dinuclear complex are of interest. The crystal is triclinic with $Z = 8$. Also, this substance was isolated with two waters of crystallization per molecule. The change in chirality at the S atom is obviously of great importance in the determination of the packing of the molecules into the crystal. This, too, is consistent with the nature of the hydrogen bonding scheme found in the crystal structure (Figure 7).

The CD spectra of the two dinuclear complexes are given in Figure 8. In contrast to the case of the CD spectra of the mononuclear precursors, Figure 3, these spectra are quite similar to each other. Also, the intensities of the CD spectra of the dinuclear complexes are on the order of ten times larger than the intensities of the mononuclear complexes. The Pt_2N_2 moiety in the dinuclear complexes is dissymetric in its own right. The asymmetry of the bridge nitrogen atoms in the structure of Figure 5 is determined only by the handedness at the 2-carbon atoms. In both dinuclear complexes, these 2 carbons are *S* in chirality. Thus in both the dinuclear complexes the Pt(II) chromophores have in their immediate environment a dissymetric influence of the same chirality. The influence of the asymmetric sulfur atoms, which was exerted heavily upon the Pt(II) chromophore in the mononuclear complex (by means of the chelate ring conformation) is submerged in the dinuclear complexes.

Registry No. [Pt((2*S*,*SR*)-methionine *S*-oxide)]Cl_2, 67651-07-4; [Pt((2*S*,*SS*)-methionine *S*-oxide)]Cl_2, 67670-63-7; bis[μ-[(2*S*,*SR*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,μ-*N*]]-diplatinum(II), 64916-28-5; bis[μ-[(2*S*,*SS*)-2-amino-4-(methylsulfinyl)butanoato(2−)-*S*,*O*,μ-*N*]]-diplatinum(II)·$2H_2O$, 67710-62-7.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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