

- interpreted in terms of a strong hydrogen bond, the O...O distance, according to the x-ray study,² was still thought to be long. An explanation of such an apparently conflicting situation has been given in the ab initio study of ref 8.
- (17) G. E. Bacon, *Acta Crystallogr., Sect. A*, **28**, 357 (1972).
- (18) F. W. B. Einstein and D. G. Tuck, *Acta Crystallogr., Sect. B*, **26**, 1117 (1969).

- (19) As it has been shown by several authors (e.g., Hamilton in ref 20), the net motion of the bridging hydrogen atom of the short O-H-O bond should be obtained from the "difference" ellipsoid defined by $\beta_{ij}(\text{H})-\beta_{ij}(\text{O})$. Usually the longest principal axis of this "difference" ellipsoid is found along the O-H-O direction and the two short axes perpendicular to it.
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The Molecular Structure and Absolute Configuration of *cis*-Dichloro[(*S*)-methyl *p*-tolyl sulfoxide][(*R*)-styrene]platinum(II)

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Received April 9, 1976

AIC60273C

The molecular structure and absolute configuration of the predominant diastereomer of *cis*-dichloro[(*S*)-methyl *p*-tolyl sulfoxide][styrene]platinum(II), $\text{Cl}_2[\text{CH}_3(\text{O})\text{S}(\text{C}_6\text{H}_4\text{CH}_3)]\text{Pt}(\text{C}_6\text{H}_5\text{HC}=\text{CH}_2)$, have been determined from three-dimensional x-ray data collected by counter methods. The molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. The unit cell dimensions are $a = 11.633$ (4), $b = 15.055$ (5), and $c = 9.776$ (3) Å. The structure has been refined by full-matrix least-squares techniques on F , using 2414 unique reflections for which $F^2 > 0$, to a final agreement factor of 0.0292. The complex adopts a square-planar coordination geometry, with the double bond of the coordinated olefin at an angle of 77.6 (6)° to the coordination plane. The absolute configuration at the asymmetric carbon atom which is formed upon olefin coordination has been determined by the Bijvoet method to be *R*.

Introduction

The absolute configurations of asymmetric metal-olefin complexes have been studied as a means of elucidating the causes of stereospecific nucleophilic additions to coordinated olefinic ligands.^{1,2} Thus, a substituted olefin $\text{H}_2\text{C}=\text{CHR}$ such as styrene, $\text{R} = \text{C}_6\text{H}_5$, can coordinate to a metal atom through either of two enantiotopic faces. Upon coordination the substituted carbon atom of the olefin becomes a site of asymmetry. If the metal complex contains an additional enantiomeric ligand, two diastereomers may be formed, not necessarily in equal amounts. If the formation of one diastereomer is favored to a significant extent, then the asymmetric environment so provided may cause nucleophilic attack upon the olefin to be stereospecific, thus resulting in an asymmetric synthesis. In order that an understanding of the reaction mechanism may be reached, a knowledge of the absolute configuration of the coordinated olefin is essential.^{2,3} Some progress in this field has recently been realized.⁴

Another area of interest in this laboratory is the study of the effects of the spatial distributions of asymmetric sites on the circular dichroism spectra of transition metal complexes.^{5,6} The title complex has two asymmetric sites, the chiral sulfur atom of *S* absolute configuration and the asymmetric carbon atom of the olefin ligand. We report here the crystal structure and absolute configuration of the predominant diastereomer of the complex *cis*-dichloro[(*S*)-methyl *p*-tolyl sulfoxide][styrene]platinum(II).

Experimental Section

Pale yellow crystals of *cis*-dichloro[(*S*)-methyl *p*-tolyl sulfoxide][styrene]platinum(II), $\text{Cl}_2[\text{CH}_3(\text{O})\text{S}(\text{C}_6\text{H}_4\text{CH}_3)]\text{Pt}(\text{C}_6\text{H}_5\text{HC}=\text{CH}_2)$, were kindly supplied by B. Bosnich and H. Boucher. Preliminary Weissenberg and precession photography showed the crystals to be orthorhombic with Laue symmetry *mmm*. The systematic absences observed, $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, unambiguously determine the space group to be $P2_12_12_1$, D_2^4 , No. 19.⁷

The crystal chosen for data collection was of approximate dimensions $0.04 \times 0.06 \times 0.19$ mm. It was carefully measured on a microscope fitted with a filar eyepiece to facilitate an absorption

Table I. Crystal Data

$\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{OPtS}$	Fw 524.38
$a = 11.633$ (4) Å	Space group $P2_12_12_1$
$b = 15.055$ (5) Å	$Z = 4$
$c = 9.776$ (3) Å	Cell vol = 1712.1 Å ³
$d(\text{obsd})^a = 2.04$ (1) g cm ⁻³	$d(\text{calcd}) = 2.03$ g cm ⁻³
$\mu = 189.9$ cm ⁻¹ for Cu $K\alpha_1$	

^a By neutral buoyancy in aqueous ZnI_2 .

Table II. Experimental Conditions for Data Collection

Radiation: Cu $K\alpha$, Ni foil prefilter, 0.018 mm
 Takeoff angle: 1.8° (gives 90% of maximum Bragg intensity)
 Aperture: 4 mm \times 4 mm, 32 cm from crystal
 Data collected: hkl and $h\bar{k}l$, for $0 < 2\theta < 110^\circ$
 Scan: $\theta-2\theta$, range 1.2° corrected for dispersion, at 1° min^{-1}
 Background: 20 s stationary crystal, stationary counter at limits of scan
 Standards: six recorded every 200 observations; 002, $00\bar{2}$, 040, 040, 200, $\bar{2}00$

correction. Ten faces of the forms $\{010\}$, $\{110\}$, and $\{011\}$ were identified by optical goniometry. The crystal was mounted on a Picker FACS-1 computer-controlled diffractometer with $[001]$ offset approximately 10° from coincidence with the spindle axis. Cell constants and an orientation matrix were obtained from a least-squares refinement of 26 intense, carefully centered reflections with $15 < 2\theta < 48^\circ$. Prefiltered Cu radiation was used, λ 1.54056 Å, at 20°C . Crystal data are given in Table I.

The conditions used for data collection are summarized in Table II. Several ω scans of intense, low-angle reflections were recorded as a check on crystal mosaicity. The average width at half-height was 0.08° . Measurement of standard reflections over the course of data collection and an examination of crystal mosaicity at the end showed no significant decomposition had occurred.

The intensity data were processed as previously described.⁶ The value for p , the "ignorance" factor, was determined to be 0.01 from a statistical examination of the variations in the standard reflections.^{8,9} An absorption correction was applied to all the data.¹⁰ The maximum and minimum transmission coefficients were 0.424 and 0.232, respectively. As a check on the quality of the data, the 2539 reflections collected included 75 pairs of reflections for the equivalent forms hkl

Table III. Final Atomic Positional and Thermal Parameters^a

Atom	x	y	z	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	2077.4 (3)	4030.8 (2)	7600.6 (4)	581 (2)	465 (2)	526 (2)	37 (2)	-8 (3)	3 (2)
Cl(1)	718 (2)	5080 (1)	7041 (3)	796 (16)	592 (13)	1008 (23)	-187 (13)	-96 (17)	13 (15)
Cl(2)	838 (2)	3537 (2)	9264 (2)	577 (15)	841 (16)	571 (16)	158 (13)	131 (14)	71 (14)
S	3433 (2)	3060 (1)	8285 (2)	501 (13)	494 (12)	447 (13)	65 (11)	12 (11)	-17 (11)
O	4623 (4)	3308 (3)	7997 (6)	452 (33)	653 (35)	777 (48)	110 (28)	-18 (31)	-14 (32)
C(1)	2722 (8)	4263 (6)	5494 (10)	801 (73)	717 (66)	607 (64)	47 (58)	96 (61)	-330 (54)
C(2)	3398 (9)	4710 (5)	6397 (9)	1227 (90)	500 (55)	505 (60)	357 (59)	25 (63)	-118 (48)
C(3)	3343 (9)	2875 (6)	56 (8)	860 (77)	634 (59)	358 (49)	-21 (60)	-118 (51)	-71 (49)
C(4)	2838 (10)	-467 (6)	5437 (9)	1286 (91)	587 (56)	639 (62)	27 (70)	-131 (77)	106 (51)
C(11)	2990 (9)	3429 (6)	4744 (8)	503 (58)	808 (68)	399 (52)	105 (62)	34 (56)	-168 (49)
C(12)	2114 (8)	3009 (7)	4031 (10)	631 (62)	964 (74)	508 (60)	8 (71)	58 (66)	-111 (58)
C(13)	2310 (9)	2206 (8)	3356 (10)	624 (73)	1200 (93)	496 (63)	155 (70)	148 (61)	-10 (66)
C(14)	3397 (10)	1840 (7)	3381 (10)	936 (83)	965 (81)	434 (63)	-188 (72)	98 (64)	-74 (59)
C(15)	4254 (9)	2271 (8)	4048 (10)	548 (66)	1248 (100)	534 (71)	-137 (73)	19 (63)	-22 (71)
C(16)	4068 (8)	3038 (8)	4721 (10)	491 (66)	1081 (88)	499 (65)	59 (68)	72 (55)	-160 (64)
C(21)	3196 (6)	1978 (4)	7587 (9)	512 (48)	462 (40)	374 (46)	39 (37)	40 (56)	14 (49)
C(22)	2126 (7)	1719 (5)	7145 (9)	571 (52)	515 (47)	700 (70)	-10 (47)	61 (64)	-7 (48)
C(23)	2022 (8)	904 (6)	6499 (9)	703 (61)	594 (55)	625 (57)	146 (63)	-90 (59)	1 (55)
C(24)	2947 (10)	372 (5)	6268 (9)	914 (72)	420 (50)	468 (54)	27 (60)	-22 (68)	-12 (43)
C(25)	3986 (9)	630 (5)	6754 (9)	846 (73)	527 (55)	529 (62)	-163 (53)	-46 (59)	84 (49)
C(26)	4134 (6)	1435 (5)	7409 (11)	509 (50)	679 (51)	530 (55)	-49 (43)	-82 (67)	10 (64)

^a Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. The positional and thermal parameters have been multiplied by 10^4 . ^b $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*) \text{ \AA}$. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

and $h\bar{k}0$. These reflections were averaged giving a weighted agreement factor of 0.019 based on F^2 .

Of the total number of reflections collected, 2224 had $F^2 > 3\sigma(F^2)$ and these were used in the solution and preliminary refinement of the structure.

Structure Solution and Refinement

The positional parameters for the Pt atom were determined from a three-dimensional Patterson synthesis. A series of structure factor and difference Fourier synthesis calculations revealed the positions of the remaining 20 nonhydrogen atoms. Refinement of atomic parameters was carried out by full-matrix least-squares techniques on F minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are respectively the observed and calculated structure factor amplitudes. The weighting factor w is given by $w = 4F_o^2/\sigma^2(F_o^2)$.

The scattering factors for the Pt, S, Cl, O, and C atoms were those of Cromer and Waber¹¹ while those for the H atom were taken from Stewart, Davidson, and Simpson.¹² The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were those of Cromer and Liberman¹³ and were included in the calculations for the Pt, Cl, and S atoms. One cycle of full-matrix least-squares refinement on the molecule with the two phenyl rings constrained as rigid groups (D_{6h} symmetry, C-C = 1.392 Å¹⁴) and varying the positional and anisotropic thermal parameters for the Pt, S, Cl, O, and C atoms of the olefin resulted in values of $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.053$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2} = 0.075$. At this point the enantiomorphic structure was refined under identical conditions to R_1 and R_2 values of 0.042 and 0.0556, respectively. Accordingly, this second model was used in the subsequent calculations.

Of the 18 H atoms present in the molecule, 14 were evident in a difference Fourier synthesis in geometrically feasible locations. The four which were not clearly discernible comprised one atom of the tolyl methyl group and the three olefinic H atoms. Idealized positional coordinates were computed, assuming sp^2 and sp^3 coordination geometries about the C atoms and an H-C bond distance of 0.95 Å for all the H atoms except those of the olefin. The H atoms were assigned isotropic thermal parameters 1.0 Å² greater than those of the atoms to which they are bonded. After two cycles of refinement a difference Fourier showed peaks in reasonable positions for two of the three olefinic H atoms while the third, coordinated to carbon atom C(2), remained a poorly defined smear of electron density. Two further cycles of full-matrix least-squares refinement with the group constraints removed and the C atoms of the phenyl rings refined as individual atoms assigned anisotropic thermal parameters, and the recalculated contributions from the H atoms included resulted in R_1 and R_2 values of 0.0249 and 0.0285, respectively. At this point the third H atom of the olefin still could not be adequately defined, so Fourier syntheses were calculated over the appropriate region as a function of $\lambda^{-1} \sin \theta$. The results were inconclusive and this H atom was not included

Table IV. Derived Hydrogen Atom Positional ($\times 10^4$) and Isotropic Thermal Parameters

Atom ^a	x	y	z	$B, \text{ \AA}^2$
HC(1)	2040	4315	5119	6.57
HC(2)	3157	5296	6679	6.83
HC(12)	1372	3272	4002	6.53
HC(13)	1701	1917	2886	7.11
HC(14)	3543	1291	2935	7.11
HC(15)	5006	2025	4040	7.10
HC(16)	4687	3315	5187	6.46
HC(22)	1473	2089	7281	5.70
HC(23)	1284	711	6208	6.05
HC(25)	4629	247	6641	5.99
HC(26)	4871	1610	7729	5.51
H1C(3)	3786	2367	287	5.86
H2C(3)	3633	3380	527	5.86
H3C(3)	2563	2780	301	5.86
H1C(4)	3471	-845	5627	7.61
H2C(4)	2141	-760	5674	7.61
H3C(4)	2829	-320	4492	7.61

^a H atoms are numbered according to the atom to which they are bonded; thus HC(1) is bonded to C(1), etc.

in the final model. An attempt to refine the H atom parameters did not result in a significant improvement in the model and accordingly further refinement included the contributions and did not refine any parameters of the H atoms.

After recalculation of the nonolefinic H atom positions the model was refined for three further cycles and, with 190 variables and 2414 observations for which $F^2 > 0$,¹⁵ converged at residuals of $R_1 = 0.0292$ and $R_2 = 0.0268$.

In the final cycle no parameter shift exceeded 0.006 of its estimated standard deviation. The error in an observation of unit weight is 1.86 electrons. A statistical analysis of R_2 in terms of $|F_o|$, diffractometer setting angles χ and ϕ , and $\lambda^{-1} \sin \theta$ showed no unusual trends. A total difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance. The highest peak, with fractional coordinates (0.325, 0.240, -0.280), located near the S atom, had an electron density of 0.52 (15) e Å⁻³. An examination of F_o and F_c showed no evidence for secondary extinction. Final positional and thermal parameters for the non-H atoms are given in Table III, and H atom parameters in Table IV. Structure factor amplitudes are presented in Table V.¹⁶

Determination of Absolute Configuration

The absolute configuration of the molecule, determined by the Bijvoet absorption edge technique, was confirmed by refinement of both models, including H atom contributions,

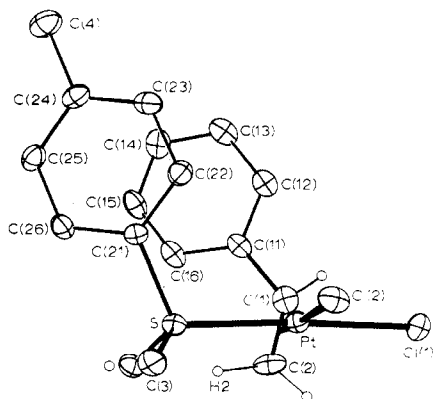


Figure 1. View of the $\text{Cl}_2\text{Pt}[\text{CH}_3(\text{O})\text{S}(\text{C}_6\text{H}_4\text{CH}_3)](\text{CH}_2\text{CHC}_6\text{H}_5)$ molecule. The H atoms, other than those on the olefin, are omitted. Atoms are represented by 50% probability ellipsoids, except for the H atoms which have been reduced.

to convergence. The chosen model had residuals of $R_1 = 0.0292$ and $R_2 = 0.0268$ while the enantiomeric structure gave agreement factors of $R_1 = 0.0442$ and $R_2 = 0.0472$. The R factor ratio test¹⁷ applied to R_2 shows that the alternate model may be rejected at less than the 0.005 significance level assuming no systematic errors in the data. Further illustration that the correct model was chosen is given in Table VI, which lists a selection of structure amplitudes for the chosen model for which $F_c(hkl)$ and $F_c(h\bar{k}l)$ differ by more than 25% based on the final positional parameters.

Molecular Structure

Some interatomic distances and selected bond angles are given in Table VII. A perspective view of a single molecule showing the atom numbering scheme is presented in Figure 1. A stereoview of the molecule including H atoms is shown in Figure 2. The inner coordination sphere of the Pt atom is of square-planar geometry, with the double bond of the olefin ligand approximately perpendicular to the plane. The angle between the olefin and the Pt-Cl(1)-Cl(2) plane is $77.6(6)^\circ$. A twist of this magnitude is commonly observed in platinum-olefin structures.¹ The two Pt-C distances to the olefin differ by 2.6σ , a difference, which while not unequivocal, does suggest a dissymmetric coordination of the two carbon atoms to the metal atom. This effect has been ascribed to the destabilizing influence of the olefin substituent on the olefin π^* orbitals.¹⁸ The olefin C-C double-bond distance of $1.360(11)$ Å is consistent with the range of values reported for other double bonds in platinum-olefin structures.¹

The asymmetric sulfoxide ligand has the S absolute configuration which is consistent with the R designation of free (+)-methyl p -tolyl sulfoxide.¹⁹ The internal structure of the sulfoxide ligand determined in this study shows no gross differences from the structure reported for the uncoordinated

Table VI. Determination of Absolute Configuration

hkl	$F_c(hkl)$	F_o relationship	$F_c(h\bar{k}l)$
143	12.15	<	19.16
162	31.12	>	23.35
165	14.42	<	22.76
271	19.60	>	10.07
222	37.80	<	53.30
452	21.77	>	15.03
422	10.21	<	17.43
532	17.39	>	12.60
554	17.83	<	24.81
631	29.29	<	39.11
2,13,5	13.22	>	9.13
2,10,3	18.41	>	12.34
327	20.52	<	28.79
378	9.62	<	15.09
458	13.01	>	7.88
556	11.73	<	7.17
282	12.78	>	17.46

Table VII. Selected Intramolecular Bond Distances (Å) and Bond Angles (deg)

Distances			
Pt-Cl(1)	2.301 (2)	S-O	1.461 (5)
	2.320 (2) ^a	S-C(3)	1.757 (8)
Pt-Cl(2)	2.297 (2)	S-C(21)	1.787 (7)
	2.308 (2) ^a	C(1)-C(2)	1.360 (11)
Pt-S	2.252 (2)	C(1)-C(11)	1.488 (12)
Pt-C(1)	2.219 (9)		1.555 (11) ^b
Pt-C(2)	2.188 (8)	C(4)-C(24)	1.508 (10)
Angles			
Cl(1)-Pt-Cl(2)	87.67 (9)	C(2)-C(1)-C(11)	128.0 (9)
Cl(2)-Pt-S	91.10 (8)	Pt-C(1)-C(11)	113.2 (5)
Cl(1)-Pt-C(1)	84.4 (2)	C(2)-C(1)-HC(1)	138.6
Cl(1)-Pt-C(2)	91.9 (2)	C(1)-C(2)-HC(2)	117.9
C(1)-Pt-C(2)	35.9 (3)		

^a Averaged over thermal motion, assuming Cl "riding" on Pt.

^b Averaged over thermal motion assuming independent motion.

sulfoxide. As might be expected, the bond distances to the S atom are somewhat shorter in the coordinated ligand compared to those in the free molecule, resulting from a reduction of electron density on the S atom upon coordination to the Pt atom. The Pt-Cl bond distances are Pt-Cl(1) = $2.301(2)$ Å and Pt-Cl(2) = $2.297(2)$ Å. Correction of these distances for thermal motion, assuming a model in which the Cl atoms "ride" upon the Pt atom, gave $2.320(2)$ and $2.308(2)$ Å, distances within the normal range.^{1,20} These values lie on the borderline of being significantly different (1.4σ uncorrected for motion, 4.2σ corrected) and reflect the assessment that both the styrene ligand and the sulfoxide have similar *trans* influences.

The two benzene rings in the molecule overlap in an interesting fashion. Weighted least-squares planes for the ring atoms were calculated, and the results are presented in Table

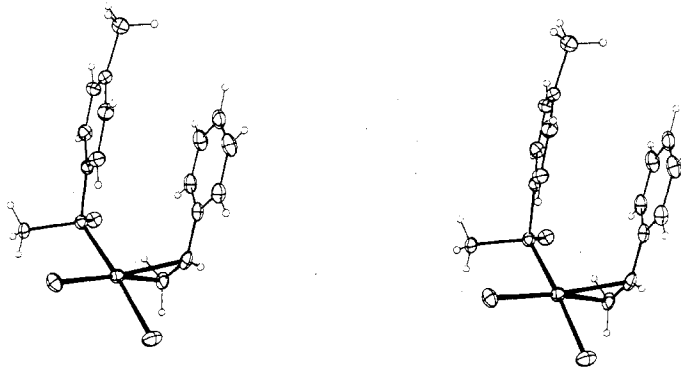


Figure 2. Stereoview of the complete molecule. The H atom temperature factors are arbitrarily reduced for clarity.

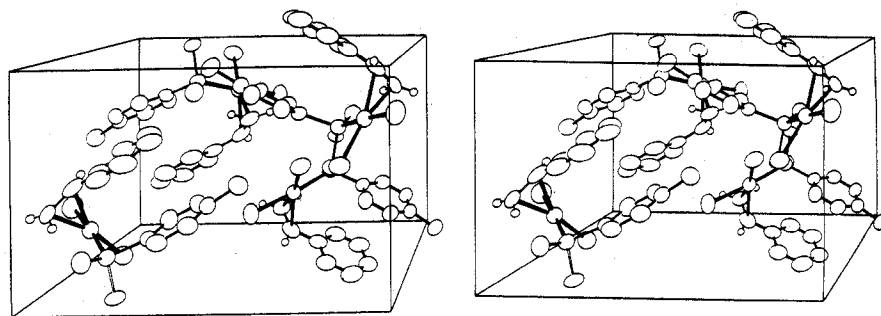


Figure 3. Stereoview of the contents of a unit cell showing the relative packing between adjacent molecules. The y and z axes are horizontal and vertical, respectively, with x toward the viewer.

Table VIII. Selected Weighted Least-Squares Planes

Plane 1 and Displacements from the Plane, \AA^a				
Pt	0.0028 (3)	C(1)	0.8166	
Cl(1)	-0.0838 (24)	C(2)	-0.4985	
Cl(2)	-0.0066 (23)			
S	-0.0656 (21)			
Plane 2 and Displacements from the Plane, \AA				
C(21)	-0.0110 (84)	C(24)	-0.0197 (82)	
C(22)	0.0017 (84)	C(25)	0.0129 (88)	
C(23)	0.0122 (84)	C(26)	0.0079 (96)	
Plane 3 and Displacements from the Plane, \AA				
C(11)	0.0091 (77)	C(14)	0.0092 (98)	
C(12)	-0.0116 (87)	C(15)	-0.0105 (98)	
C(13)	0.0027 (99)	C(16)	-0.0021 (92)	
Plane Equations of the Form $AX + BY + CZ - D = 0$				
	A	B	C	D
Plane 1	4.437	-9.949	6.319	-1.604
Plane 2	2.041	-6.682	-8.591	3.600
Plane 3	2.701	-7.653	-8.107	1.783

^a Displacements without esd's refer to atoms not included in the calculation of the plane.

VIII. The planes of the rings are almost parallel, Figure 2, with an angle between the plane normals of 5.68° . For example, the atoms of the styrene benzene ring lie between 3.36 and 3.62 \AA from the mean plane of the sulfoxide benzene ring. The mean value for the atom to ring separation is $3.49 (3) \text{ \AA}$, a distance strongly reminiscent of the $3.4\text{-}\text{\AA}$ separation between sheets in the structure of graphite. The mean C-C distance in the two phenyl rings is $1.37 (3) \text{ \AA}$, and the internal angles range from $117.6 (9)$ to $121.8 (10)^\circ$. The average displacement of ring atoms from the least-squares planes is approximately 0.01 \AA .

As shown by the diagram of a unit cell content in Figure 3 there appears to be no abnormal interaction between molecules in the crystal. The closest intermolecular interaction is 2.44 \AA between the H atom on C(12) of the styrene phenyl ring and the H atom on C(26) of the sulfoxide. The closest intermolecular Pt-Pt and Pt-Cl distances are $5.777 (1)$ and $5.471 (2) \text{ \AA}$, respectively.

Discussion

When an olefin which is unsymmetrically substituted at one or both carbon atoms coordinates to a metal atom, it may do so through either of two enantiotopic faces resulting in an R or S absolute configuration at these atoms.²¹ Thus an olefin of this type, such as styrene or *trans*-2-butene, which was optically inactive prior to coordination, forms an optically active complex upon coordination to a metal atom. When the metal atom is part of an enantiomeric complex, two diastereoisomers may be formed. These are not necessarily of equal thermodynamic stability, and in the present case the diastereoisomer ratio in solution is 75:25 in favor of the complex with the olefin in the R configuration in the presence of the

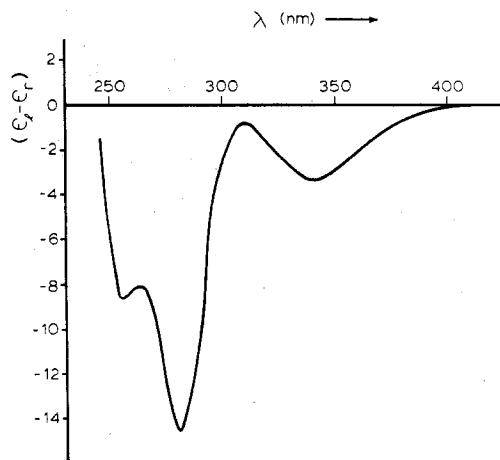


Figure 4. Solution CD spectrum of $\text{Cl}_2\text{Pt}[(\text{CH}_3(\text{O})\text{S}(\text{C}_6\text{H}_4\text{CH}_3)]-(\text{CH}_2\text{CHC}_6\text{H}_5)$ in CHCl_3 .

sulfoxide with S configuration.

In the configuration observed in the solid state, the phenyl rings approach within range of possible inter-ring interactions. This geometry we believe could arise from three sources: an $\text{O}\cdots\text{H}$ interaction between the sulfoxide and one of the H atoms on the olefin, crystal packing forces, or an attractive interaction between the phenyl rings. An $\text{O}\cdots\text{H}$ interaction could still be favorable with the H atoms of C(2) if the olefin were twisted 180° about the platinum-olefin bond, but hydrogen bonding to an olefinic H atom is not generally accepted as significant.²² There is nothing unusual in the crystal packing. At present we favor the latter explanation of an attractive interaction between the phenyl rings.

An examination of molecular models shows that for the diastereomer with the S configuration at the olefin, the two phenyl rings cannot get within the range observed in the present diastereomer without prohibitively close H atom interactions between the olefin and the sulfoxide methyl group. We feel therefore that this inter-ring interaction is important in determining the observed diastereomer population. We are currently looking at related structures to try to determine the importance of this interaction.

The presence of the asymmetric center formed by olefin coordination will affect the circular dichroism of the Pt d-d transitions, and this effect in square-planar Pt(II) complexes has been interpreted in terms of a quadrant rule.²³ This rule is based on the spatial disposition of the groups attached to the olefin determining the sign of the lowest energy transition of the CD spectrum of the complex. This particular band, arising from the Pt d-d manifold, is suggested by Mason to reflect the absolute configuration about the metal atom.²⁴ The CD spectrum⁴ and the quadrant rule projection for this complex are presented in Figures 4 and 5, respectively. The complex exhibits a negative CD band at 340 nm which, according to the rule, predicts the absolute configuration at C(1)

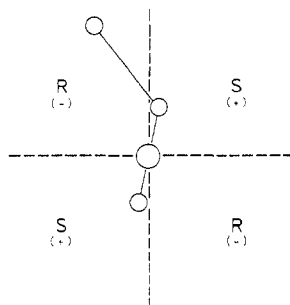


Figure 5. Projection of the platinum-olefin coordination geometry with respect to the quadrant rule. The capital letters refer to the absolute configurations and the signs to the sign of the CD band.

to be *R*. The configuration determined in this structural study is indeed *R*. This application of the regional rule to the CD spectrum has been made assuming that any contribution to the CD from the sulfoxide ligand does not affect the sign of the diagnostic band. This assumption is based on the observed results for analogous optically active amine platinum-olefin complexes.²³

Acknowledgment. We thank the National Research Council of Canada for financial support of this work.

Registry No. *cis*-Dichloro[(*S*)-methyl *p*-tolyl sulfoxide][(*R*)-styrene]platinum(II), 59821-93-1.

Supplementary Material Available: Table V, a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Optical and Magnetic Properties of Tetrakis(diethylamido)uranium(IV), a Five-Coordinate Dimeric Complex in the Solid State¹

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Received April 9, 1976

AIC602745

The volatile U(IV) compound $U[N(C_2H_5)_2]_4$ is dimeric in the solid state and exhibits an unusual and possibly unique five coordination about the U ion for an *f* series ion. The crystals are monoclinic, space group $P2_1/n$. At 23 °C $a = 9.326$ (4) Å, $b = 17.283$ (8) Å, $c = 13.867$ (6) Å, $\beta = 108.43$ (5)°, and $d_c = 1.65$ g/cm³ for $Z = 4$. X-ray diffraction intensity data were collected by an automated diffractometer using graphite monochromated Mo $K\alpha$ radiation. For 1809 reflections with $F^2 > 2\sigma(F^2)$, $R_1 = 0.035$ and $R_2 = 0.031$. The five-coordinate uranium atom is at the center of a distorted trigonal bipyramid of nitrogen atoms; two of these bipyramids share an edge to make a dimeric complex located on a center of symmetry. The nearest approach of the uranium atoms is 4.004 (1) Å. The three nonbridging U-N distances average 2.22 (2) Å whereas the bridging U-N distances are 2.46 and 2.57 Å. The N-U-N and U-N-U angles in the central cluster are 74.4 (3) and 105.6 (3)°, respectively. The optical and proton magnetic resonance spectra of $U[NET_2]_4$ at room temperature in various solvents are reported. Temperature-dependent magnetic susceptibility measurements on the solid show Curie-Weiss behavior from 10 to 100 K. Below 10 K the susceptibility becomes temperature independent and there is no indication of magnetic ordering. A greater tendency in U amide chemistry toward oligomerization than in the *d* transition series is suggested.

Introduction

The compound tetrakis(diethylamido)uranium(IV), $U[N(C_2H_5)_2]_4$, was first synthesized by Jones et al.² by the reaction of lithium diethylamide with UCl_4 in diethyl ether. After filtration of the LiCl and removal of the solvent the

uranium amide was purified by distillation under vacuum. An emerald-green liquid which crystallized at approximately 35 °C was obtained. This material was extremely reactive to oxygen and water and proved useful as an intermediate for preparing uranium(IV) mercaptides and alkoxides. Bagnall