

in the 2.504-Å O...O distance, in the severe bending at these oxygens ($\angle C-O-Sr = 135.2^\circ$ for O17 and 137.8° for O31), and in the acute Sr-Sr-O angles of 70.46° (O17) and 78.29° (O31), as these ligands try to decrease the distance between their lone pairs. These latter bond angles and the longer distance to O17 mark it as the phenol ligand.

Solution spectroscopic studies (1H and ^{13}C NMR) at $25^\circ C$ in THF- d_6 show evidence for only a single phenyl environment. Even at $-90^\circ C$, some rapid fluxional process time averages the structurally inequivalent phenyl sites.

Visually, this compound appears to melt at $96-99^\circ C$. Thermal analysis of this solid under helium reveals well-defined transformations. DSC shows an endotherm (41 J/g) centered at $98^\circ C$, which is evident in the TGA profile as the weight loss of all six THF molecules. Further weight loss continues so that, by $200^\circ C$, all phenol has been lost. Additional weight loss accompanies further heating to $1000^\circ C$.

(22) O-O distances in the range 2.40-2.50 Å are classified as "strong". See: Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond*; North Holland: Amsterdam, 1976.

The above findings serve to demonstrate that the oxygen donor Lewis base THF, when combined with strontium and phenoxide/phenol, is sufficient to afford a discrete and soluble molecular aggregate in which Sr^{2+} attains a pseudooctahedral environment. The Lewis base is sufficiently strongly bound to prevent polymer formation in solution but too labile to give volatile molecular species. A donor substituent on the phenoxide might avoid this difficulty.

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Supplementary Material Available: A listing of positional and thermal parameters for $Sr_4(OPh)_8(PhOH)_2(THF)_6$ (3 pages). Ordering information is given on any current masthead page.

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Articles

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Hydrolysis and Dimerization of Nitrile to Diacetamide and Crystal Structures of Chloro(2,2,2',2',2'-hexachlorodiacetamido)(dimethyl sulfoxide)platinum(II) and cis-Aquadichloro(dimethyl sulfoxide)platinum(II)

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The reaction of $K[Pt(DMSO)Cl_3]$ with trichloroacetonitrile in aqueous solution adjusted to $pH \approx 7$ with NaOH produces, after 24 h, a blue solution from which blue crystals were grown and analyzed by X-ray diffraction. The compound is a monomeric chelate Pt(II) species containing a deprotonated imide ligand, formed from the dimerization of trichloroacetonitrile. The crystals of $Pt(DMSO)Cl(C_4NO_2Cl_6)$ are monoclinic, $P2_1/n$ space group, with $a = 11.214$ (9) Å, $b = 11.555$ (11) Å, $c = 13.841$ (9) Å, $\beta = 107.18$ (5)°, $V = 1714$ (2) Å³, and $Z = 4$. The structure was refined to $R = 0.040$ and $R_w = 0.039$. The bond distances are Pt-Cl = 2.301 (2), Pt-S = 2.217 (2), Pt-O(1) = 2.002 (5), and Pt-O(2) = 1.950 (5) Å. The imide ligand is planar, and its dihedral angle with the Pt(II) coordination plane is 1.7° . After being exposed to air more than 7 months, the crystal became yellow. The blue color was probably caused by a coating on the surface by a blue amorphous Pt complex. When the pH of the aqueous solution is not adjusted ($pH \approx 2$), $K[Pt(DMSO)Cl_3]$ reacts with trichloroacetonitrile to give a yellow powder and very pale yellow crystals, identified by diffraction methods as *cis*- $Pt(DMSO)(H_2O)Cl_2$. The crystals are orthorhombic, $P2_12_12_1$ space group, with $a = 8.900$ (3) Å, $b = 9.020$ (3) Å, $c = 10.493$ (4) Å, and $Z = 4$, and the structure was refined to $R = 0.044$ and $R_w = 0.052$. The Pt-Cl bonds are 2.337 (5) and 2.292 (5) Å, and the Pt-S distance is 2.191 (4) Å, while the Pt-O bond is 2.076 (16) Å. The crystal is stabilized by hydrogen bonds between the aqua ligand and one Cl ligand and O of DMSO.

Introduction

We have recently reported¹ the molecular and crystal structure of an analogue of "platinblau" reported in 1907,² whose exact structure is still unknown. It was suggested³ that platinblau contained deprotonated acetamide anions bound to platinum(II), the acetamide ligand being obtained by reaction of water with coordinated acetonitrile. But attempts to obtain platinblau by direct combination of platinum(II) with acetamide were not successful. It has been assigned a variety of monomeric and polymeric structures of platinum(II) and -(IV).⁴⁻⁸

More recently, "platinum blues" have been obtained from the reaction of cisplatin (*cis*- $Pt(NH_3)Cl_2$) with pyrimidines, especially uracil derivatives.⁹ It has been suggested that platinum blues might be promising as second generation platinum antitumor drugs. But these compounds have shown to be difficult to characterize. *cis*-Diammineplatinum pyrimidine blues were suggested to be amorphous polymers of varying chain lengths.^{9,10}

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Table I. Crystallographic Data for *cis*-Pt(DMSO)(H₂O)Cl₂ (I) and Pt(DMSO)Cl(C₄NO₂Cl₆) (II)

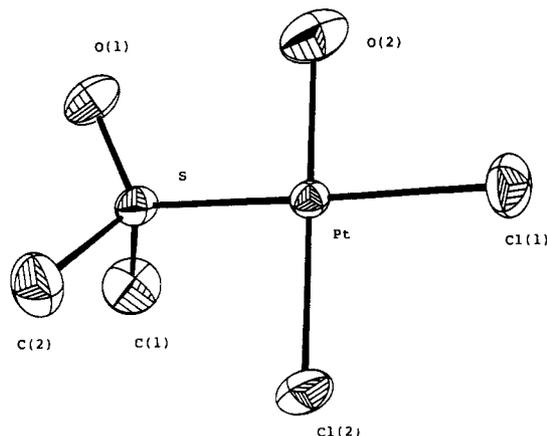
	I	II
chem formula	C ₂ H ₈ O ₂ SCl ₂ Pt	C ₆ H ₆ NO ₃ SCl ₂ Pt
fw	362.15	615.44
space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)	P2 ₁ /n (No. 14)
a, Å	8.900 (3)	11.214 (9)
b, Å	9.020 (3)	11.555 (11)
c, Å	10.493 (4)	13.841 (9)
β, deg	90	107.18 (5)
V, Å ³	842.4 (5)	1714 (2)
Z	4	4
F(000)	656	1144
ρ _{calcd} , Mg m ⁻³	2.855	2.385
λ(Mo Kα), Å	0.71069	0.71069
μ(Mo Kα), mm ⁻¹	17.64	9.49
transm coeff	0.061–0.124	0.095–0.639
T, K	295	295
R	0.044	0.040
R _w	0.052	0.039

Lippard et al. have prepared several of these compounds with α-pyridone and uracil derivatives. Three such platinum blues were characterized crystallographically.^{11,12} These were found to be tetranuclear mixed-valence platinum(2.25) compounds with bridging α-pyridonate or 1-methyluracilate ligands. Several similar non-blue complexes were reported with the same ligands.^{13–16} The intense color of platinum blues was suggested to arise from metal–metal charge-transfer transitions that vary in energy with metal–metal distances.¹²

We have been involved in the synthesis and study of sulfoxide Pt(II) complexes for several years. Recently we studied the reaction of K[Pt(DMSO)Cl₃] with CH₃CN, which gave a green compound on standing. Its crystal structure was determined, and we found that it was a dinuclear species with bridging acetamido ligands.¹ We repeated the synthesis several times, and we obtained crystals of different colors, yellow, green, gray, dark blue, and almost black. We studied all these crystals by X-ray diffraction, and we found that they were all identical, i.e. the dinuclear acetamido compound Cl(DMSO)Pt(μ-C₂H₄NO)₂Pt(DMSO)Cl.¹ We assumed that the compound was probably yellow and that the blue color was caused by a coating of some amorphous blue Pt complex on the surface of the crystal. We decided to continue the project by studying a similar reaction with another nitrile, namely trichloroacetonitrile. Again, we obtained yellow and blue compounds, but this time they seemed clearly different. The results of this study are discussed below.

Experimental Section

Syntheses. K[Pt(DMSO)Cl₃] was prepared as already reported.¹⁷ *cis*-Pt(DMSO)(H₂O)Cl₂ (I). A 0.15-g sample of K[Pt(DMSO)Cl₃] was dissolved in 15 mL of water. Trichloroacetonitrile (3 drops) was then added to the solution in a beaker that was covered with paraffin paper.

**Figure 1.** Labeled diagram of *cis*-Pt(DMSO)(H₂O)Cl₂.

The solution was left standing at room temperature. After 1 week, the yellow precipitate was filtered out. This product was found to contain at least two compounds, a yellow powder and very pale yellow crystals identified as *cis*-Pt(DMSO)(H₂O)Cl₂.

Pt(DMSO)Cl(C₄Cl₆NO₂) (II). A 0.5-mmol sample of K[Pt(DMSO)Cl₃] was dissolved in 20 mL of water, and the pH of the solution was adjusted to 7 with NaOH. Trichloroacetonitrile (2.5 mL), dissolved in about 10 mL of ethanol, was added. The beaker was sealed with waxed paper and left standing at room temperature. The next day the solution was dark blue, and a few days later, dark blue crystals were isolated. Yield: ~40%. Dec range: 115–120 °C. The compound is diamagnetic. IR (cm⁻¹): ν(C=O) 1585, ν(Pt–Cl) 347.

Crystallographic Measurements and Structure Resolution. The two crystals were selected after examination under a polarizing microscope for homogeneity. They were obtained directly from the reacting medium. The unit cell parameters were obtained by least-squares refinement of the angles 2θ, ω, and χ for 15 well-centered reflections on a Syntex P1 diffractometer using graphite-monochromatized Mo Kα radiation. Crystal data and other information are summarized in Table I. Scan rates and data treatment have already been described.¹⁸ Corrections were made for absorption and Lorentz–polarization effects. The anomalous dispersion terms of Pt, S, and Cl were included in the calculations.¹⁹

The coordinates of the Pt atom for the two crystals were determined from a three-dimensional Patterson map, and the positions of all the other non-hydrogen atoms were found by the usual Fourier methods. The refinements of the two structures were done by using full-matrix least-squares techniques, minimizing Σw(F_o – F_c)². In crystal II, the location of the O and N atoms of the bidentate ligand were clearly identified. Interchanging their positions resulted in negative or abnormal thermal factors. The H atoms could not be located. Isotropic secondary-extinction corrections²⁰ were included in the calculations. Individual weights w = 1/σ²(F) were applied. The refinement of the scale factor, coordinates, and anisotropic temperature factors of all atoms converged to R = 0.044 and R_w = 0.052 for I and to R = 0.040 and R_w = 0.039 for II. There were a few residual peaks (<1.1 (for I) and 1.5 (for II) e Å⁻³) in the close environment of the Pt atom.

The scattering curves of Cromer and Waber²¹ were used. The calculations were done on a Cyber 830 computer with programs already described.¹⁸

Results and Discussion

When K[Pt(DMSO)Cl₃] is dissolved in water (0.025 M), the pH of the solution is 2.35, indicating some hydrolysis reactions. When the pH of the solution is adjusted to ≈7 with NaOH, the complex reacts with trichloroacetonitrile to form a dark blue compound. Crystals adequate for X-ray diffraction analysis were obtained, and the crystal structure of the compound was determined. The results have shown that it is a monomeric chelate compound of Pt(II) with a deprotonated imide ligand: Pt(DMSO)Cl(C₄NO₂Cl₆) (compound II). When the pH of the solution is not adjusted, K[Pt(DMSO)Cl₃] reacts with trichloroacetonitrile and a yellow product can be obtained. Under the microscope, the product was found to be a mixture of at least

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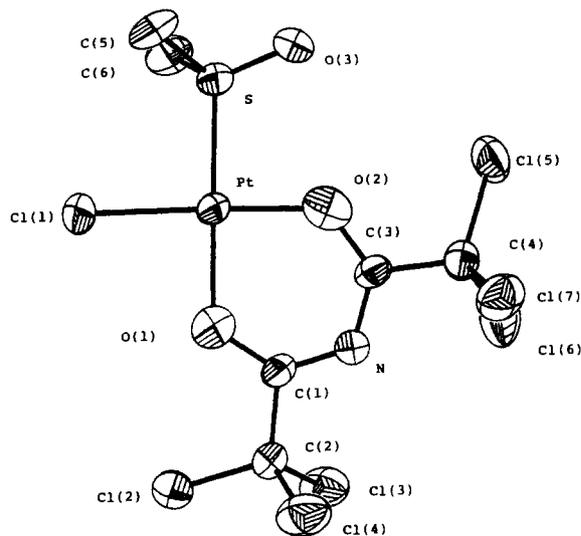


Figure 2. Labeled diagram of the molecule $\text{Pt}(\text{DMSO})\text{Cl}(\text{C}_4\text{NO}_2\text{Cl}_6)$.

two compounds, a bright yellow powder and some pale yellow crystals suitable for diffraction methods. The crystal structure of the latter compound was determined. The results of the study have shown that it is an aqua complex, $\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$ (compound I). The yellow compound is probably the expected product $\text{cis-Pt}(\text{DMSO})(\text{trichloroacetone})\text{Cl}_2$, which is produced in relatively small quantity. The IR spectrum of the mixture indicated a weak $\nu(\text{C}\equiv\text{N})$ band around 2300 cm^{-1} . Trichloroacetone is probably not a very good ligand for Pt(II), especially since aqua complexes can be isolated in its presence. The poor nucleophilicity of $\text{Cl}_3\text{CC}\equiv\text{N}$ is due to the presence of the three Cl atoms. Attempts were made to separate the two compounds by dissolving in different solvents, but the separation was never complete. Furthermore, the product seemed to undergo some changes.

The refined atomic parameters of the two structures are listed in Table II. Labeled diagrams of the molecules are shown in Figures 1 and 2. The bonds distances and angles are reported in Table III.

$\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$. The pale yellow crystals (I), which slowly crystallized after the addition of trichloroacetone to an aqueous solution of $\text{K}[\text{Pt}(\text{DMSO})\text{Cl}_3]$, are the aqua compound $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$. The crystal structure determination has shown that it is the cis isomer. DMSO has a large trans effect, and the formation of a cis isomer might seem at first surprising. But it is well-known that the disubstituted compound $\text{Pt}(\text{DMSO})_2\text{Cl}_2$, which is produced in aqueous solution, is the cis isomer.¹⁸ $\text{trans-Pt}(\text{DMSO})_2\text{Cl}_2$ is first produced, and there is rapid isomerization to the cis isomer.²² It has been suggested that the formation of the cis isomer was caused by the enhanced (d-d) π bonding, which is more effective in the cis configuration.²³ But this explanation is not adequate for aqua ligands, which cannot form π bonds. $\text{K}[\text{Pt}(\text{DMSO})\text{Cl}_3]$ is partly hydrolyzed in water, as shown by the low pH of its solution. There are probably several aqueous species in equilibrium, and $\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$ might be slightly more insoluble, leading to its crystallization on standing.

The coordination around the Pt atom is square-planar, with deviations (\AA) from the best weighted plane as follows: Pt, $-0.0001(6)$; S, $0.000(4)$; Cl(1), $0.000(2)$; Cl(2), $0.004(6)$; O(2), $0.040(18)$. Deviations (\AA) from the same plane for the other atoms: O(1), $-0.15(1)$; C(1), $1.51(3)$; C(2), $-1.25(2)$. The molecule is close to containing a mirror plane with the O atom of DMSO almost in the Pt coordination plane. The DMSO ligand is bonded through its S atom as expected. The Pt-Cl(1) bond distance ($2.337(5)\text{ \AA}$) trans to the DMSO ligand seems significantly longer than the Pt-Cl(2) bond distance trans to H_2O (2.292

Table II. Positional Parameters with Their Esd's and Temperature Factors ($\times 10^4$)

atom	x	y	z	$U_{\text{eq}}^a\text{ \AA}^2$
<i>cis-Pt</i> (DMSO)(H ₂ O)Cl ₂ (I)				
Pt	1137.6 (5)	5118.9 (6)	6252.8 (6)	248
Cl(1)	3548 (5)	5744 (6)	6953 (5)	507
Cl(2)	939 (6)	3295 (6)	7764 (5)	556
S	-1117 (4)	4590 (4)	5549 (4)	296
O(1)	-1686 (14)	5628 (14)	4555 (13)	448
O(2)	1318 (20)	6737 (17)	4855 (16)	851
C(1)	-1079 (27)	2782 (20)	4924 (27)	695
C(2)	-2476 (20)	4414 (27)	6859 (21)	510
Pt(DMSO)Cl(C ₄ NO ₂ Cl ₆) (II)				
Pt	365.2 (2)	5933.9 (2)	2541.2 (2)	327
Cl(1)	1002 (2)	4947 (2)	4051 (1)	587
Cl(2)	4205 (2)	4214 (2)	2273 (2)	687
Cl(3)	3187 (2)	4523 (2)	134 (1)	684
Cl(4)	4502 (2)	6383 (2)	1371 (2)	650
Cl(5)	-1453 (2)	8156 (2)	-495 (2)	617
Cl(6)	95 (2)	6844 (2)	-1414 (1)	800
Cl(7)	1090 (2)	8805 (2)	-148 (2)	577
S	-1414 (1)	6458 (2)	2807 (1)	407
O(1)	1949 (5)	5436 (5)	2275 (4)	585
O(2)	-126 (4)	6755 (4)	1253 (4)	590
O(3)	-2226 (4)	7168 (5)	1987 (4)	575
N	1625 (5)	6341 (5)	652 (4)	401
C(1)	2242 (6)	5701 (5)	1430 (5)	367
C(2)	3475 (6)	5231 (6)	1315 (5)	419
C(3)	538 (6)	6831 (6)	594 (5)	369
C(4)	66 (6)	7609 (6)	-330 (5)	411
C(5)	-1141 (7)	7202 (7)	3984 (5)	558
C(6)	-2268 (7)	5206 (7)	2995 (6)	597

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

(5) \AA), but the difference might not be significant. All the structures reported in the literature up to now have not shown any systematic lengthening of Pt-Cl bonds trans to DMSO.²⁴ The trans influence of DMSO is not believed to be very large. For example, the Pt-Cl bonds in $\text{cis-Pt}(\text{DMSO})_2\text{Cl}_2$ are normal ($2.306(3)$ and $2.312(2)\text{ \AA}$).¹⁷ The Pt-S bond length is $2.191(4)\text{ \AA}$. The S atom in the DMSO ligand is tetrahedral with the Pt-S-O angle ($117.0(3)^\circ$) slightly larger than the two Pt-S-C angles ($107.2(3)$ and $112.0(3)^\circ$), as observed in other Pt-DMSO complexes.²⁴ The S-O and S-C bond lengths are normal ($1.470(7)$, $1.794(10)$, and $1.798(10)\text{ \AA}$).

The Pt-O(2) bond is $2.077(17)\text{ \AA}$. This value is similar to those observed in other Pt-aqua complexes reported in the literature ($2.052(8)$,²⁵ $2.078(6)$,²⁶ and $2.099(5)$ ²⁷ \AA). The aqua ligand (O(2)) forms two hydrogen bonds, as observed in other Pt-aqua complexes. It is hydrogen-bonded to a chloro ligand and to O(1) of DMSO with distances $\text{O}(2)\cdots\text{Cl}(2) = 3.28(2)\text{ \AA}$ and $\text{O}(2)\cdots\text{O}(1) = 3.03(2)\text{ \AA}$ and with favorable angles $\text{Pt-O}(2)\cdots\text{Cl}(2) = 121.6(7)^\circ$ and $\text{Pt-O}(2)\cdots\text{O}(1) = 116.9(7)^\circ$. The packing of the molecules in the crystal is shown in Figure 3. It consists of layers of molecules parallel to the *ac* plane, held together by hydrogen bonding.

Pt(DMSO)Cl(C₄NO₂Cl₆). The compound (crystal II), formed at $\text{pH} \approx 7$, is a monomeric chelate complex of Pt(II) containing a deprotonated imide ligand formed from the dimerization of trichloroacetone. Several reaction mechanisms could account for such a dimerization. Two such mechanisms are shown in Figure 4. Trichloroacetone can hydrolyze into two tautomeric

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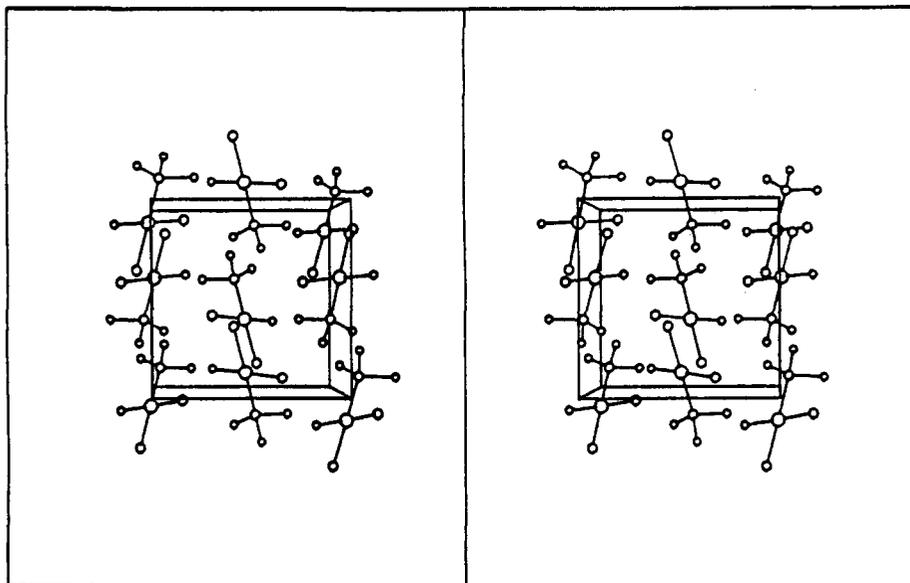


Figure 3. Stereoscopic view of the unit cell in the crystal *cis*-Pt(DMSO)(H₂O)Cl₂ (*a* axis vertical, *b* axis horizontal).

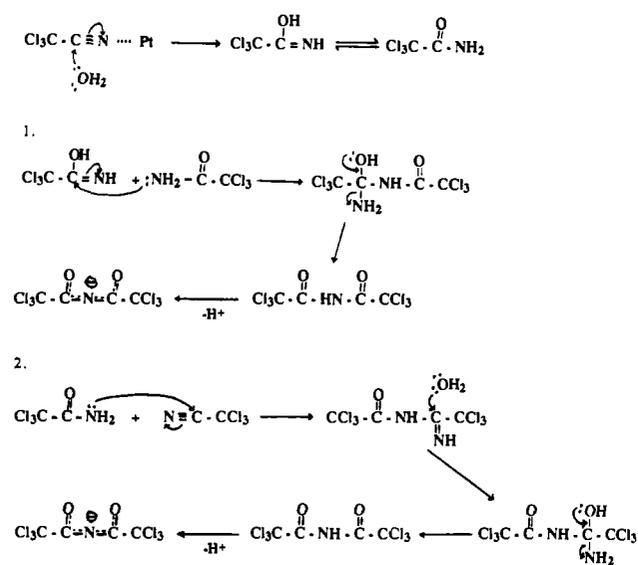


Figure 4. Proposed mechanisms for the dimerization of trichloroacetonitrile.

forms, an imine $\text{Cl}_3\text{CC}(\text{OH})=\text{NH}$ and an amide $\text{Cl}_3\text{CCONH}_2$. It is difficult to predict which form is predominant. In the first mechanism, the imine is assumed to react with an amide molecule to form the imide. In the second mechanism, the amide is assumed predominant and reacts with a molecule of trichloroacetonitrile to form the same deprotonated imide.

The IR spectrum of the compound showed no $\nu(\text{C}\equiv\text{N})$ band around 2300 cm^{-1} , but a $\nu(\text{C}=\text{O})$ band at 1585 cm^{-1} was observed. One $\nu(\text{Pt}-\text{Cl})$ band was also observed at 347 cm^{-1} . The compound is diamagnetic.

The platinum atom has the square-planar coordination expected for Pt(II) complexes. Deviations (\AA) from the weighted best planes: Pt, -0.0002 (3); Cl(1), 0.000 (2); S, 0.004 (2); O(1), 0.040 (6); O(2), 0.000 (5). The deprotonated bidentate ligand is also planar (except for the Cl atoms). Deviations (\AA) from the best plane calculated through O(1), C(1), N, C(3), and O(2): O(1), -0.009 (6); O(2), 0.009 (5); N, 0.002 (6); C(1), 0.014 (6); C(3), -0.017 (6); C(2), 0.038 (7); C(4), -0.149 (7). The latter plane is almost parallel to the Pt coordination plane with a tilt angle of 1.7° .

The Pt-Cl bond (2.301 (2) \AA) and the Pt-S bond (2.217 (2) \AA) located trans to the Pt-O(imido) bonds are normal.^{17,24} For α -pyridonate-bridged platinum complexes, it was observed that

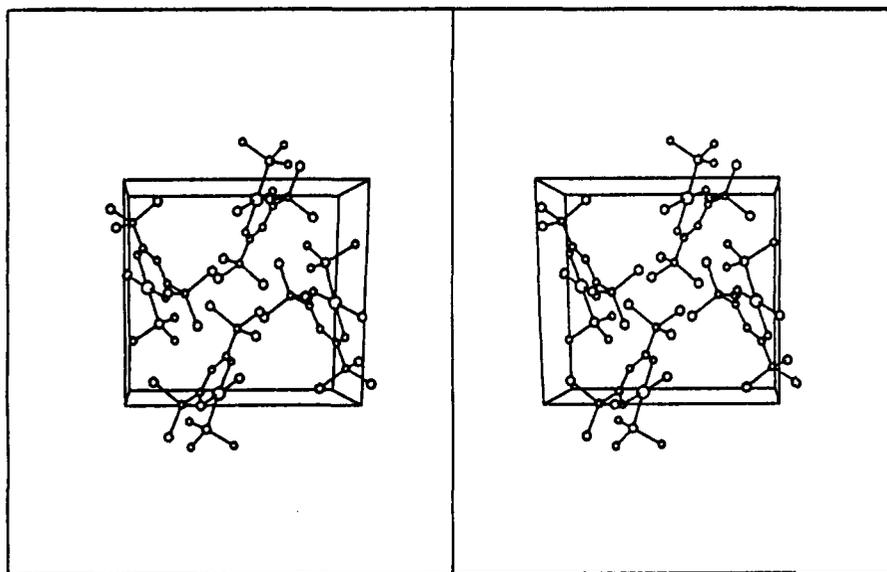


Figure 5. Stereoscopic view of the molecules in the crystal Pt(DMSO)Cl(C₄NO₂Cl₆) (*b* axis horizontal, *a* axis vertical).

Table III. Bond Distances (Å) and Angles (deg)

<i>cis</i> -Pt(DMSO)(H ₂ O)Cl ₂			
Pt-Cl(1)	2.337 (5)	Pt-Cl(2)	2.292 (5)
Pt-S	2.191 (4)	Pt-O(2)	2.076 (16)
S-O(1)	1.491 (14)	S-C(1)	1.76 (2)
S-C(2)	1.84 (2)		
Cl(1)-Pt-Cl(2)	91.5 (2)	Cl(1)-Pt-S	178.1 (2)
Cl(1)-Pt-O(2)	89.0 (5)	Cl(2)-Pt-S	90.4 (2)
Cl(2)-Pt-O(2)	178.8 (5)	S-Pt-O(2)	89.2 (5)
Pt-S-O(1)	114.2 (5)	Pt-S-C(1)	108.1 (8)
Pt-S-C(2)	111.7 (7)	O(1)-S-C(1)	109 (1)
O(1)-S-C(2)	111 (1)	C(1)-S-C(2)	102 (1)
Pt(DMSO)Cl(C ₄ H ₆ NO ₂) ₂			
Pt-Cl(1)	2.301 (2)	Pt-S	2.217 (2)
Pt-O(1)	2.002 (5)	Pt-O(2)	1.950 (5)
S-O(3)	1.476 (6)	S-C(5)	1.787 (8)
S-C(6)	1.795 (8)	O(1)-C(1)	1.340 (8)
O(2)-C(3)	1.340 (8)	N-C(1)	1.322 (8)
N-C(3)	1.323 (9)	C(1)-C(2)	1.537 (10)
C(3)-C(4)	1.525 (9)	C(2)-Cl(2)	1.780 (7)
C(2)-Cl(3)	1.770 (7)	C(2)-Cl(4)	1.747 (7)
C(4)-Cl(5)	1.768 (7)	C(4)-Cl(6)	1.749 (7)
C(4)-Cl(7)	1.766 (7)		
Cl(1)-Pt-S	92.15 (7)	Cl(1)-Pt-O(1)	88.3 (1)
Cl(1)-Pt-O(2)	178.2 (1)	S-Pt-O(1)	178.7 (1)
S-Pt-O(2)	89.7 (1)	O(1)-Pt-O(2)	89.9 (2)
Pt-S-O(3)	113.9 (2)	Pt-S-C(5)	111.3 (3)
Pt-S-C(6)	110.4 (3)	Pt-O(1)-C(1)	123.7 (4)
Pt-O(2)-C(3)	126.2 (4)	O(3)-S-C(5)	109.5 (3)
O(3)-S-C(6)	108.9 (3)	C(5)-S-C(6)	102.2 (4)
O(1)-C(1)-N	129.4 (6)	O(2)-C(3)-N	128.1 (6)
O(1)-C(1)-C(2)	118.0 (6)	O(2)-C(3)-C(4)	119.0 (6)
C(1)-N-C(3)	122.6 (6)	C(1)-C(2)-Cl(2)	112.7 (5)
C(1)-C(2)-Cl(3)	109.6 (5)	C(1)-C(2)-Cl(4)	109.1 (5)
C(3)-C(4)-Cl(5)	113.6 (5)	C(3)-C(4)-Cl(6)	109.4 (5)
C(3)-C(4)-Cl(7)	106.9 (5)	Cl(2)-C(2)-Cl(3)	107.6 (4)
Cl(2)-C(2)-Cl(4)	108.5 (4)	Cl(3)-C(2)-Cl(4)	109.4 (4)
Cl(5)-C(4)-Cl(6)	109.4 (4)	Cl(5)-C(4)-Cl(7)	107.5 (4)
Cl(6)-C(4)-Cl(7)	110.0 (4)		

the Pt-N (ammine or ethylenediamine) distances trans to pyridonate oxygen atoms were also normal.¹² In the acetamido-bridged compound [Pt(DMSO)Cl(μ -acetamido)]₂, the Pt-S bonds (2.185 (2) and 2.198 (2) Å) trans to the Pt-O (acetamido) bonds were slightly shorter than normal.¹ The S atoms in the DMSO ligands are in an approximate tetrahedral environment. The Pt-S-O angles (117.4 (2) and 116.8 (2)°) are slightly larger than the Pt-S-C (107.3 (3)-112.0 (3)°) angles, as observed in other Pt-DMSO complexes.^{17,24}

The Pt-O distances are 2.002 (5) and 1.950 (5) Å. We do not believe that the difference is significant. These bond distances

are slightly shorter than those observed in [Pt(DMSO)Cl(μ -acetamido)]₂ (2.039 (5) and 2.064 (5) Å)¹ and in the pyridonate and uracilate complexes reported by the group of Lippard (2.01-2.06 Å) cited above.¹²⁻¹⁵ The N-C bond distances in the bidentate ligand are normal (1.322 (8) and 1.323 (9) Å), while the O-C bond lengths are 1.340 (8) and 1.340 (8) Å, slightly longer than the values observed in the acetamido-bridged dimer (1.271 (7) and 1.282 (8) Å). Values between 1.287 (9) and 1.321 (15) Å have been reported in the pyridonate and uracilate complexes mentioned above.¹²⁻¹⁵ The order of the C-O bonds in our compound is probably lower due to resonance inside the chelate ring. The angles O(1)-C(1)-C(2) and O(2)-C(3)-C(4) are 118.0 (6) and 119.0 (6)°, indicating an sp² hybrid. The internal angles at O(1), C(1), N, C(3), and O(2) vary from 122.6 (6) to 129.4 (6)°. The angles around C(2) and C(4) are close to the tetrahedral value ranging from 107.5 (4) to 113.6 (5)°.

The packing of the molecules is shown in Figure 5. No hydrogen bonding is expected in this compound. Therefore the molecules are held together only by van der Waals forces.

The transparent crystals that were isolated from a dark blue solution were definitely dark blue. They were still colored after exposure to air for 6 months. But 8-9 months after they were removed from the blue solution, the crystals, which were still crystalline and in perfect shape, were found to be yellow. The blue color was probably caused by a coating on the surface of the crystals of some amorphous blue Pt complex, which eventually evaporated in the air.

In an attempt to determine if we could synthesize an analogue chelate compound with acetonitrile that would have the formulation Pt(DMSO)Cl(C₄H₆NO₂), we have studied the reaction of K[Pt(DMSO)Cl₃] with diacetamide, CH₃CONHCOCH₃, at pH \approx 7 (adjusted with NaOH). We have isolated yellow crystals, which were analyzed by X-ray diffraction methods. The results have shown that the compound is the acetamido-bridged dimer Cl(DMSO)Pt(μ -C₂H₄NO)₂Pt(DMSO)Cl, which we have reported earlier.¹ Therefore, there was a rearrangement of diacetamide in the presence of Pt resulting in an acetamido ligand. This is the reverse process of the reaction observed with trichloroacetonitrile. This study has proven most interesting, and the research project is being continued.

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Supplementary Material Available: Tables of experimental details of the X-ray diffraction studies (Table S1), anisotropic temperature factors (Table S2), and weighted least-squares planes (Table S3) (4 pages); listings of observed and calculated structure amplitudes (25 pages). Ordering information is given on any current masthead page.