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Supplementary Material Available: An ORTEP diagram of 3 and Tables SI–SVI, listing respectively complete X-ray data, hydrogen atom positional parameters, intramolecular atomic distances, intramolecular bond angles, least-squares planes, and anisotropic thermal parameters for 3 (11 pages); Table SVII, listing calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department, Université du Québec à Montréal,
P.O. Box 8888, Succ. A, Montréal, Canada H3C 3P8

Molecular and Crystal Structures of a "Platinblau" Analogue, Bis(μ-acetamido)dichlorobis(dimethyl sulfoxide)diplatinum(II), and of *cis*-(Acetonitrile)dichloro(dimethyl sulfoxide)platinum(II)

F. D. Rochon,* P. C. Kong, and R. Melanson

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The reaction of K[Pt(DMSO)Cl_3] with acetonitrile in aqueous solution produces *cis*-Pt(DMSO)(CH_3CN)Cl_2 after a few days, but if the compound is allowed to stay in solution, a green compound can be isolated after several weeks. The green species can also be synthesized more rapidly by adjusting the pH of the solution to about 8.0 with NaOH. The crystal structures of the two compounds were determined by X-ray diffraction. *cis*-Pt(DMSO)(CH_3CN)Cl_2 is monoclinic with space group $P2_1/n$, a = 9.566 (4) Å, b = 9.996 (4) Å, c = 9.995 (3) Å, β = 93.18°, and Z = 4. The structure was refined to R = 0.036 and R_w 0.030. The Pt–Cl(2) bond (2.282 (2) Å) in trans position to the CH_3CN is shorter than the other Pt–Cl(1) bond (2.324 (2) Å). The Pt–S bond is normal (2.225 (2) Å) while the Pt–N bond is also short (1.976 (7) Å). The green compound was found to be a dinuclear species bis(μ-acetamido)dichlorobis(dimethyl sulfoxide)diplatinum(II). The crystals are triclinic, space group $P\bar{1}$ with a = 8.944 (6) Å, b = 10.228 (7) Å, c = 11.180 (10) Å, α = 83.31 (7)°, β = 66.73 (6)°, γ = 68.06 (5)°, and Z = 2, and the structure was refined to R = 0.027 and R_w = 0.035. The acetamido-bridged dimer is the head-to-tail isomer with Pt···Pt distance = 3.008 (0.3) Å. The Pt–N bonds (2.011 (6) and 2.017 (6) Å) are in cis position to the DMSO ligands while the Pt–O bonds (2.064 (5) and 2.039 (5) Å) are trans to DMSO. The Pt–S bonds (2.185 (2) and 2.198 (2) Å) are slightly shorter than normal. The acetamido ligands are planar. The dihedral angle between the two square-planar Pt planes is 137.1°. This compound is believed to be an analogue of "platinblau" which probably contains bridging acetamido bidentate ligands.

Introduction

Yellow *cis*-Pt(CH_3CN)$_2$$Cl_2$ has been known for a long time,[1] and its cis configuration has been confirmed a few years ago.[2] When it is treated with aqueous silver sulfate or nitrate and the resulting solution left to stand in air, an intense blue color is formed. "Platinblau" or platinum blue was the name originally assigned to the blue compound formed.[3] It was suggested that "platinblau" contained deprotonated acetamide anions bound to platinum(II), the acetamide ligand being obtained by reaction of water with coordinated acetonitrile. The empirical composition was found to be Pt(CH_3CONH_2)$_2$·H_2O. The infrared spectrum has shown an absorption band at 1623 cm^{-1}, which was assigned to a carbonyl stretching vibration. 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 mostly of platinum(II). Chernyaev and his co-workers[4] suggested the presence of chelate acetamido ligands, but later, without presenting any evidence, they suggested a linear structure containing the unit H_2O–Pt–Pt–OH_2.[5] One structure involving diazocyclobutadiene as a ligand was also suggested in 1959.[6] In 1964, Gillard and Wilkinson[7] argued that the chemical and spectroscopic evidence best fitted a polymeric structure involving acetamido bridges, with the water molecules hydrogen-bonded within the crystal. Brown, Burbank, and Robin[8] purified the blue compound and on the basis of a new elemental analysis and their results on a blue trimethylacetamide complex suggested a new formulation that could be written as a tetravalent complex with two hydroxo ligands Pt^{IV}(CH_3CONH)$_2$(OH)$_2$.

More recently, "platinum blues" have been obtained from the reaction of cisplatin, (*cis*-Pt(NH_3)Cl_2) with pyrimidines, especially uracil derivatives.[9] Cisplatin is a good antitumor agent, and it has been suggested that "platinum blues", which also have good antitumor properties, 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] 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 lig-

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Table I. Experimental Details of the X-ray Studies of $Cl(DMSO)Pt(\mu\text{-}C_2H_4NO)_2Pt(DMSO)Cl$ (I) and *cis*-$Pt(DMSO)(CH_3CN)Cl_2$ (II)

	I	II
compd	$C_8H_{20}N_2O_4S_2Cl_2Pt_2$	$C_4H_9NOSCl_2Pt$
fw	733.47	385.18
space group	$P\bar{1}$	$P2_1/n$
a, Å	8.944 (6)	9.566 (4)
b, Å	10.228 (7)	9.996 (4)
c, Å	11.180 (10)	9.995 (3)
α, deg	83.31 (7)	90.
β, deg	66.73 (6)	93.18 (3)
γ, deg	68.06 (5)	90.
volume, Å^3	871 (1)	954.3 (6)
Z	2	4
F(000)	672	704
ρ_{calcd}, Mg m^{-3}	2.796	2.681
λ(Mo Kα), Å	0.71069	0.71069
μ(Mo Kα), mm^{-1}	16.76	15.58
cryst faces [dimens, mm]	$(001-(00\bar{1})$ [0.086] $(010)(0\bar{1}0)$ [0.500] $(201)-(\bar{2}0\bar{1})$ [0.924] $(221)-(\bar{2}\bar{2}\bar{1})$ [0.750]	$(1\bar{1}0)-(\bar{1}10)$ [0.076] $(100)-(\bar{1}\bar{1}0)$ [0.116] $(1\bar{1}1)-(0\bar{1}\bar{1})$ [0.24 av]
transm factor range	0.016–0.237	0.167–0.354
2θ max, deg	60	57
quadrants	$h,\pm k,\pm l$	$h,k,\pm l$
h,k,l	0 to +12, −13 to +14, −14 to +15	0 to +12, 0 to +13, −13 to +13
scan technique	$2\theta/\theta$	$2\theta/\theta$
std reflcns	600, 008, $06\bar{2}$	140, 002, $21\bar{3}$
temp, K	295	295
no. of indep reflcns	5112	2719
no. of obsd reflcns ($I > 2.5\sigma(I)$)	4216	1843
R	0.027	0.036
R_w	0.035	0.030
std dev (unit weight)	1.8	1.46

ands. Several similar nonblue complexes were reported with the same ligands.[13-15] 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 have attempted to prepare mixed-ligand–Pt compounds with sulfoxides and nitriles. The reaction of $K[Pt(DMSO)Cl_3]$ with CH_3CN gave on standing a green compound. Its crystal structure was determined, and we found that it was a dinuclear species with bridging acetamido ligands. No bridging-acetamido–platinum complex has been reported yet. The crystal structure of bis(μ-acetamido)dichlorobis(dimethyl sulfoxide)diplatinum(II) (crystal I) is now described in this paper.

If the reaction conditions are slightly changed, bright yellow crystals of *cis*-$Pt(DMSO)(CH_3CN)Cl_2$ can be isolated. The crystal structure of this compound (crystal II) was determined and is also reported below.

Experimental Section

Syntheses. $K[Pt(DMSO)Cl_3]$ was prepared as already reported.[16]

***cis*-$Pt(DMSO)(CH_3CN)Cl_2$.** A 0.5-mmol quantity of $K[Pt(DMSO)Cl_3]$ (0.22 g) was dissolved in 10 mL of water. Acetonitrile (1.5 mL) was then added to the solution in a beaker that was covered with paraffin paper. The solution was left standing at room temperature. After a few days, the yellow crystals were filtered. Yield: 80%. Mp: 170 °C dec. IR (cm^{-1}): 2338 w, 2312 w, 1315 m, 1287 w, 1148 s, 1030 s, 980 m, 937 m, 769 m, 728 m, 440 s, 376 s, 359 s, 354 sh; ν(Pt–Cl) 318 s, 313 sh.

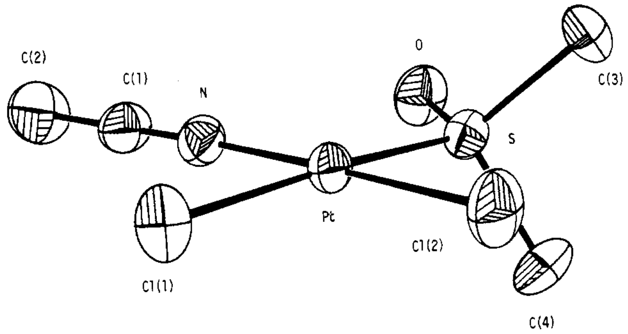

Figure 1. Labeled diagram of *cis*-$Pt(DMSO)(CH_3CN)Cl_2$.

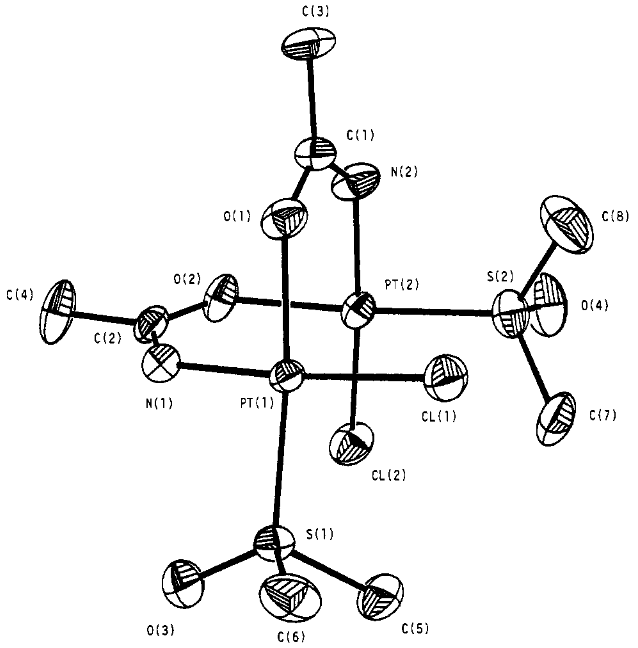

Figure 2. Labeled diagram of the molecule $Cl(DMSO)Pt(\mu\text{-}C_2H_4NO)_2Pt(DMSO)Cl$.

$(DMSO)ClPt(\mu\text{-}C_2H_4NO)_2PtCl(DMSO)$. A 0.5-mmol sample of $K[Pt(DMSO)Cl_3]$ was dissolved in 30 mL of water. Acetonitrile (2.5 mL) was added, and the pH of the solution was adjusted to 8.0 with NaOH. Two days later, the greenish crystals were filtered. Yield: 60%. Dec pt: 195–215 °C. The compound is diamagnetic. IR (cm^{-1}): 3311 m (large), 1585 s, 1566 sh, 1315 w, 12.99 w, 1257 w, 1235 s, 1141 s, 1020 s, 983 w, 955 m, 937 w, 919 w, 724 m, 703 m, 623 m, 598 w, 450 s, 444 s, 383 m, 363 w; ν(Pt–Cl) 338 m.

Crystallographic Measurements and Structure Resolution. The two crystals were selected after examination under a polarizing microscope for homogeneity. 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 $P\bar{1}$ 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.[17] Corrections were made for absorption and Lorentz-polarization effects. The anomalous dispersion terms of Pt, S, and Cl were included in the calculations.[18]

The coordinates of one Pt atom for crystal I were determined from the three-dimensional Patterson map. The position of the second independent Pt atom was obtained by structure factor and difference Fourier map calculations. The rest of the structure was solved by the usual methods. The coordinates of the Pt atom in crystal II were determined

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Table II. Positional Parameters ($\times 10^4$) with Their Esd's and Temperature Factors ($Å^2 \times 10^4$) ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j$)

atom	x	y	z	U_{eq}
	Cl(DMSO)Pt(μ-C_2H_4NO)$_2$Pt(DMSO)Cl			
Pt(1)	2661.0 (2)	1041.6 (2)	1876.6 (2)	183
Pt(2)	530.9 (3)	4056.7 (2)	1627.0 (2)	210
Cl(1)	445 (2)	238 (2)	3143 (2)	320
Cl(2)	1000 (2)	5196 (2)	3034 (2)	332
S(1)	3585 (2)	863 (1)	3451 (1)	231
S(2)	−2186 (2)	4500 (1)	2982 (2)	290
O(1)	2092 (5)	872 (4)	296 (4)	260
O(2)	2914 (6)	3938 (4)	269 (4)	317
O(3)	5181 (6)	1142 (5)	3146 (5)	355
O(4)	−3345 (6)	5976 (5)	3193 (6)	479
N(1)	4555 (6)	1717 (5)	651 (5)	258
N(2)	248 (7)	3121 (5)	279 (5)	303
C(1)	1115 (7)	1820 (5)	−189 (5)	230
C(2)	4374 (7)	2918 (6)	54 (5)	225
C(3)	884 (10)	1346 (8)	−1312 (7)	376
C(4)	5952 (9)	3160 (7)	−941 (7)	408
C(5)	1918 (9)	1951 (7)	4854 (7)	322
C(6)	3848 (10)	−877 (6)	4064 (8)	423
C(7)	−2273 (10)	3825 (7)	4527 (7)	437
C(8)	−3196 (11)	3572 (9)	2523 (10)	509
	cis-Pt(DMSO)(CH_3CN)Cl_2			
Pt	998 (1)	5573 (1)	8532 (1)	296
S	−703 (2)	6167 (2)	7041 (2)	332
Cl(1)	2871 (3)	4963 (2)	9984 (3)	470
Cl(2)	1552 (3)	7766 (2)	8904 (3)	470
N	597 (8)	3650 (7)	8258 (7)	357
O	−1630 (7)	5098 (6)	6506 (7)	460
C(1)	479 (10)	2503 (9)	8206 (10)	394
C(2)	297 (12)	1078 (10)	8105 (13)	609
C(3)	110 (11)	6979 (10)	5685 (10)	492
C(4)	−1757 (10)	7500 (9)	7650 (10)	461

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

Cl(DMSO)Pt(μ-C_2H_4NO)$_2$Pt(DMSO)Cl			
Pt(1)–Cl(1)	2.310 (2)	Pt(2)–Cl(2)	2.307 (2)
Pt(1)–S(1)	2.185 (2)	Pt(2)–S(2)	2.198 (2)
Pt(1)–N(1)	2.011 (6)	Pt(2)–N(2)	2.017 (6)
Pt(1)–O(1)	2.064 (5)	Pt(2)–O(2)	2.039 (5)
S(1)–O(3)	1.461 (6)	S(2)–O(4)	1.460 (5)
S(1)–C(5)	1.800 (7)	S(2)–C(7)	1.767 (8)
S(1)–C(6)	1.796 (7)	S(2)–C(8)	1.762 (11)
O(1)–C(1)	1.271 (7)	O(2)–C(2)	1.282 (8)
N(1)–C(2)	1.313 (7)	N(2)–C(1)	1.311 (7)
C(1)–C(3)	1.508 (10)	C(2)–C(4)	1.499 (11)
Pt(1)–Pt(2)	3.008 (0.3)		
Cl(1)–Pt(1)–S(1)	92.61 (6)	Cl(2)–Pt(2)–S(2)	90.73 (6)
Cl(1)–Pt(1)–O(1)	87.9 (1)	Cl(2)–Pt(2)–O(2)	88.6 (1)
Cl(1)–Pt(1)–N(1)	175.4 (1)	Cl(2)–Pt(2)–N(2)	175.4 (2)
S(1)–Pt(1)–O(1)	170.4 (1)	S(2)—Pt(2)–O(2)	171.4 (1)
S(1)–Pt(1)–N(1)	91.8 (1)	S(2)–Pt(2)–N(2)	93.0 (2)
O(1)–Pt(1)–N(1)	87.6 (2)	O(2)–Pt(2)–N(2)	87.4 (2)
Pt(1)–S(1)–O(3)	117.4 (2)	Pt(2)–S(2)–O(4)	116.8 (2)
Pt(1)–S(1)–C(5)	111.5 (2)	Pt(2)–S(2)–C(7)	110.7 (3)
Pt(1)–S(1)–C(6)	107.3 (3)	Pt(2)–S(2)–C(8)	112.0 (3)
Pt(1)–O(1)–C(1)	128.7 (4)	Pt(2)–O(2)–C(2)	127.4 (4)
Pt(1)–N(1)–C(2)	127.7 (4)	Pt(2)–N(2)–C(1)	127.2 (5)
O(1)–C(1)–C(3)	116.1 (6)	O(2)–C(2)–C(4)	116.0 (6)
N(1)–C(2)–C(4)	119.5 (6)	N(2)–C(1)–C(3)	120.0 (6)
O(1)–C(1)–N(2)	123.9 (6)	O(2)–C(2)–N(1)	124.5 (6)
cis-Pt(DMSO)(CH_3CN)Cl_2			
Pt–Cl(1)	2.324 (2)	Pt–S	2.225 (2)
Pt–Cl(2)	2.282 (2)	Pt–N	1.976 (7)
S–O	1.470 (7)	N–C(1)	1.153 (11)
S–C(3)	1.794 (10)	C(1)–C(2)	1.437 (13)
S–C(4)	1.798 (10)		
Cl(1)–Pt–Cl(2)	89.2 (1)	Pt–S–O	117.0 (3)
Cl(1)–Pt–S	176.4 (1)	Pt–S–C(3)	107.2 (3)
Cl(1)–Pt–N	88.2 (2)	Pt–S–C(4)	112.0 (3)
Cl(2)–Pt–S	90.4 (1)	Pt–N–C(1)	172.5 (7)
Cl(2)–Pt–N	177.4 (2)	N–C(1)–C(2)	178.1 (9)
S–Pt–N	92.2 (2)	O–S–C(3)	109.4 (4)
C(3)–S–C(4)	101.3 (5)	O–S–C(4)	108.9 (4)

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 minimizing $\sum w(F_o - F_c)^2$. The H atoms could not be located. Isotropic secondary-extinction corrections[19] were included in the calculations. Individual weights $w = 1/\sigma^2(F)$ were applied. The refinement of the scale factor, coordinates, and anisotropic temperature factors of all atoms converged to $R = 0.027$ and $R_w = 0.035$ for I and to $R = 0.036$ and $R_w = 0.030$ for II. There were a few residual peaks (<1.3 for I and 1.7 e $Å^{-3}$ for II) in the close environment of the Pt atom.

The scattering curves of Cromer and Waber[20] were used. The calculations were done on a Cyber 830 with programs already described.[17]

Results and Discussion

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.

***cis*-Pt(DMSO)(CH_3CN)Cl_2.** The yellow crystals that precipitated after the addition of acetonitrile to an aqueous solution of K[Pt(DMSO)Cl_3] are the expected compound Pt(DMSO)(CH_3CN)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 seems at first surprising. But it is well-known that the disubstituted compounds Pt(DMSO)$_2Cl_2$ and Pt(CH_3CN)$_2Cl_2$, which are produced in aqueous solution, are also cis isomers.[2,17] *trans*-Pt(DMSO)$_2Cl_2$ is first produced and there is rapid isomerization to the cis isomers. *trans*-Pt(benzyl methyl sulfoxide)$_2Cl_2$ and *trans*-Pt(di-*n*-propyl sulfoxide)$_2Cl_2$ have been isolated in the few first minutes of reaction.[21] The crystal structure of *trans*-Pt(di-*n*-propyl sulfoxide)$_2Cl_2$ has recently been reported.[22] It has been suggested that the formation of the cis isomers was caused by the enhanced (d-d)π bonding, which is more effective in the cis configuration.[23] Acetonitrile can also form π bonds with Pt. Therefore, the reaction of CH_3CN with K[Pt(DMSO)Cl_3] should first produce the trans isomer, which would isomerize quite rapidly to the more stable *cis*-Pt(DMSO)(CH_3CN)Cl_2. The infrared spectrum of the compound showed one ν(Pt-Cl) band at 318 cm^{-1} with a slight shoulder around 313 cm^{-1}.

The coordination around the Pt atom is square planar. The DMSO ligand is bonded through its S atom and acetonitrile through its lone pair of electrons on the N atom. The Pt-Cl(2) bond distance (2.282 (2) Å trans to the acetonitrile ligand is significantly shorter than the Pt-Cl(1) distance trans to DMSO (2.324 (2) Å). Short Pt-Cl bond lengths were also observed in *cis*-Pt(CH_3CN)$_2Cl_2$ (2.263-2.277 Å)[2] while it is normal in *cis*-Pt(DMSO)$_2Cl_2$.[17] The trans influence of acetonitrile seems to be very small. The Pt-S (2.225 (2) Å) bond length is normal, but the Pt-N bond (1.976 (7) Å) is slightly short (compared to Pt-N(amine)) as observed in *cis*-Pt(CH_3CN)$_2Cl_2$ (1.95-1.99 Å).[2] Acetonitrile contains empty π^* orbitals that can accept electron density from the metal. The nitrile ligand is linear with angles Pt-N-C(1) = 172.5 (7)° and N-C(1)-C(2) = 178.1 (9)° as obseved in the crystal structure of *cis*-Pt(CH_3CN)$_2Cl_2$.[2] The C(1)-N and C(1)-C(2) bond distances are 1.153 (11) and 1.437 (13) Å, close to the values found in *cis*-Pt(CH_3CN)$_2Cl_2$. The S atom in the DMSO ligand is tetrahedral with the angle Pt-S-O angle (117.0 (3)°) slightly larger than the two Pt-S-C angles (107.2 (3) and 112.0 (3)°). The S-O and S-C bond lengths are normal (1.470 (7), 1.794 (10), and 1.798 (10) Å). The molecule is close to contain a mirror plane with the O atom of DMSO in the Pt coordination plane. The deviations (Å) from the best

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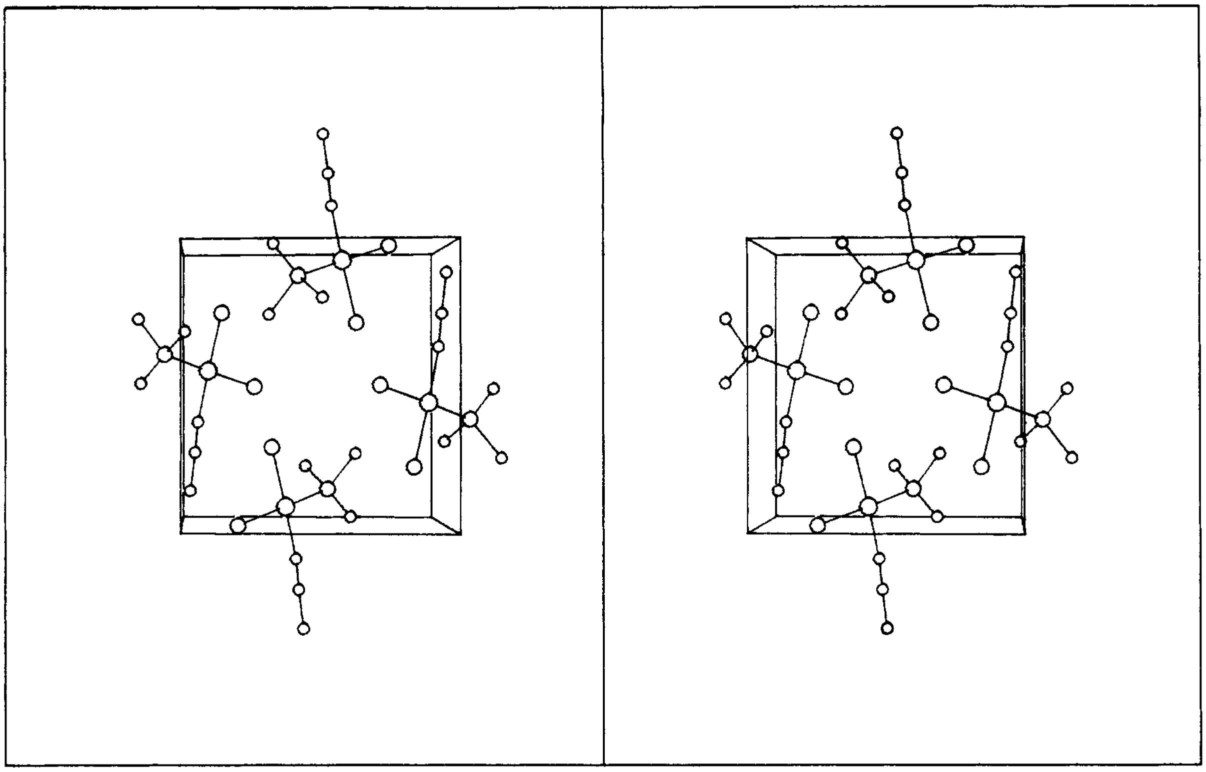

Figure 3. Stereoscopic view of the unit cell in the crystal *cis*-Pt(DMSO)(CH_3CN)Cl_2 (*b* axis vertical; *a* axis horizontal).

Table IV. Torsion Angles (deg) in the Crystal Cl(DMSO)Pt(μ-C_2H_4NO)$_2$Pt(DMSO)Cl

S(1)-Pt(1)-O(1)-C(1)	-171.7 (6)	S(1)-Pt(1)-N(1)-C(2)	-120.4 (5)
Cl(1)-Pt(1)-O(1)-C(1)	95.0 (5)	Pt(1)-O(1)-C(1)-C(3)	-176.9 (4)
Pt(1)-O(1)-C(1)-N(2)	-1.1 (9)	O(1)-C(1)-N(2)-Pt(2)	11.7 (9)
C(3)-C(1)-N(2)-Pt(2)	-172.7 (5)	C(1)-N(2)-Pt(2)-S(2)	-120.0 (6)
C(1)-N(2)-Pt(2)-O(2)	68.6 (6)	N(2)-Pt(2)-O(2)-C(2)	-88.7 (5)
S(2)-Pt(2)-O(2)-C(2)	178.7 (7)	Cl(2)-Pt(2)-O(2)-C(2)	93.4 (5)
Pt(2)-O(2)-C(2)-C(4)	-175.5 (4)	O(2)-C(2)-N(1)-Pt(1)	7.5 (9)
C(4)-C(2)-N(1)-Pt(1)	-173.2 (5)	C(2)-N(1)-Pt(1)-O(1)	69.2 (6)
N(1)-Pt(1)-O(1)-C(1)	-85.3 (5)	Pt(2)-O(2)-C(2)-N(1)	3.8 (9)

weighted plane are as follows: Pt, -0.019; S, +0.054; Cl(1), +0.049; Cl(2), -0.006; N, -0.017. Furthermore, the deviations (Å) for the other atoms from the same plane are as follows: C(1), -0.026; C(2), -0.030; O, -0.093; C(3), +1.614; C(4) -1.122.

The packing of the molecules in the crystal is shown in Figure 3. It consists of layers of molecules parallel to the *ac* plane. No important H bonds are expected in this crystal.

Cl(DMSO)Pt(μ-C_2H_4NO)$_2$Pt(DMSO)Cl. The greenish compound (crystal I) is a dinuclear species of Pt(II) with two acetamido bridging ligands formulated as Cl(DMSO)Pt(μ-C_2H_4NO)$_2$Pt(DMSO)Cl. The IR spectrum of the compound showed no band around 2300 cm^{-1}, but two new bands at 1585 and 1566 cm^{-1} were observed. These bands were assigned to carbonyl stretching of the acetamido ligands. One ν(Pt-Cl) band was observed at 338 cm^{-1}. The compound is diamagnetic, and the crystal studied was found to be the head-to-tail isomer. The DMSO ligands, which are bonded to Pt by S, are in trans positions to the acetamidate oxygen atoms while the chloro ligands are trans to the acetamido nitrogen atoms. The relatively short Pt(1)⋯Pt(2) distance (3.008 (0.3) Å) is produced by the geometric requirements imposed by the two bridging acetamido ligands. This structure is similar to the head-to-tail dimer $[Pt_2(NH_3)_4(\mu\text{-}C_5H_4NO)_2]^{2+}$ and the head-to-head dimer $[Pt_2(en)_2(\mu\text{-}C_5H_4NO)_2]^{2+}$ with bridging α-pyridonate ligands reported by Lippard and his coworkers.[13,14] These two compounds are yellow with Pt⋯Pt distance of 2.8981 (5) and 2.992 (1) Å, respectively.

Each platinum atom has the square-planar coordination expected for Pt(II) complexes, but there are important square-pyramidal distortions. The Pt atoms are out of the plane formed by the four coordinating atoms by 0.1116 (2) Å for Pt(1) and 0.1139 (2) Å for Pt(2) toward each other. When the planes are calculated through the five atoms, the acetamido O atoms are clearly out of the plane. The deviations (Å) from the best planes are as follows: Pt(1), -0.0014 (2); Cl(1), +0.003 (2); S(1), +0.034 (1); O(1), +0.310 (4); N(1), +0.030 (5); Pt(2), -0.0014 (2); Cl(2), +0.007 (2); S(2), +0.034 (1); O(2), +0.270 (4); N(2), +0.083 (5). The tilt angle between the two Pt planes is 42.9°.

The Pt-Cl bonds (2.310 (2) and 2.307 (2) Å) are normal, but the Pt-S bonds (2.185 (2) and 2.198 (2) Å) are slightly shorter than the average value (2.21 Å) reported for Pt-DMSO complexes.[17,24] This might seem at first surprising since it was observed in α-pyridonate-bridged platinum complexes that the Pt-N (ammine or ethylenediamine) distances trans to pyridonate oxygen atoms were significantly longer than those trans to pyridonate nitrogen atoms, revealing a larger trans influence of the O atom. Lippard and his co-workers suggested that this trans influence originated in more extensive σ-overlap of the Pt-N (pyridonate) bond relative to the Pt-O (amidate) bond.[12,25] In our compound, the Pt-S bonds which are located in trans position to the Pt-O (acetamido) bonds are slightly shorter than normal, indicating a greater π-character of the Pt-S bond. The S atoms in the DMSO ligands are in 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

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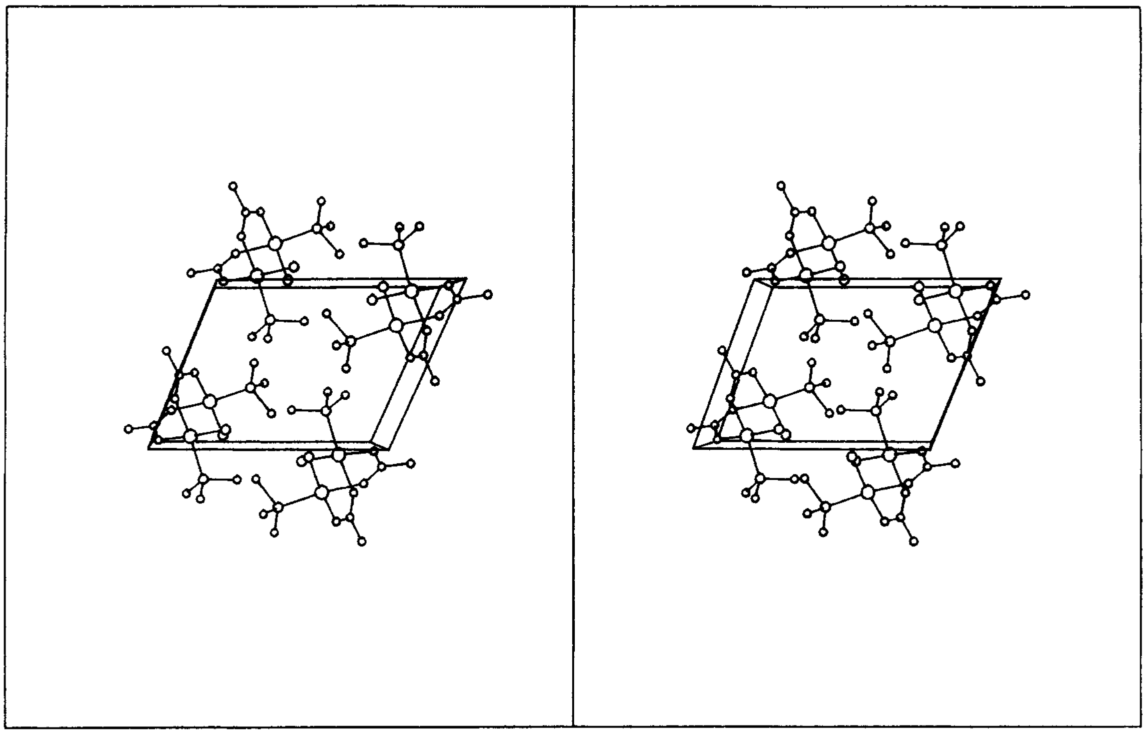

Figure 4. Stereoscopic view of the molecules in the crystal Cl(DMSO)Pt(μ-$C_2H_4NO)_2$Pt(DMSO)Cl (down the *b** axis; *c* axis horizontal).

other Pt–DMSO complexes.[17,24]

The Pt–O (2.064 (5) and 2.039 (5) Å) and Pt–N (2.011 (6) and 2.017 (6) Å) seem normal and agree well with values found in the pyridonate and uracilate complexes mentioned above. No acetamido–Pt complex has been reported yet. The bond lengths and angles in the two bridging acetamido ligands are also normal. The N–C bond distances are 1.313 (7) and 1.311 (7) Å while the O–C bond lengths are 1.271 (7) and 1.282 (8) Å. The angles around C(1) and C(2) are in the range 116.0 (6)–124.5 (6)°, indicating a sp^2 hybrid. The internal angles at N(1), N(2), O(1), and O(2) are very similar: 127.7 (4), 127.2 (5), 128.7 (4) and 127.4 (4)°, respectively. It was not possible to locate the H atoms on N(1) and N(2). The acetamido ligands are planar, and the dihedral angles between the acetamido planes and the Pt planes are 84.7 and 65.3° for Pt(I) and 68.3 and 83.8° for Pt(II). The two acetamido planes are almost perpendicular to each other with a dihedral angle of 95.0°. The torsion angles have been calculated and are shown in Table IV.

The packing of the molecules is shown in Figure 4. It consists of layers of molecules parallel to the *ab* plane. The environment of the acetamide N atoms was closely examined for the presence of hydrogen bonds. There might be such an intermolecular interaction with N(1)···O(1) distance = 3.056 (7) Å and angles Pt(1)–N(1)···O(1) = 107.1 (2)° and C(2)–N(1)···O(1) = 122.6 (4)°. The closest such contact around N(2) is O(2) with a distance of 3.464 (7) Å and angles of 96.4 (2) and 136.4 (4)°. Therefore, hydrogen bonding does not seem a very important stabilizing factor in this crystal structure.

This compound is believed to be an analogue of "platinblau", which should also contain acetamido ligands. Three such structures of Pt(II) has been suggested for "platinblau": a mononuclear chelate compound Pt(acetamido)$_2$,[4] a polymeric chain with bridging acetamido ligands (Pt(acetamido)$_2)_n$,[7] and a dinuclear species with a Pt–Pt bond and chelate acetamido compound (Pt(acetamido)$_2H_2O)_2$.[5] A tetravalent complex of formulation Pt(acetamido)$_2(OH)_2$ was also proposed.[8] The work of Lippard and his co-workers has shown that all the blue compounds with pyridonate or related ligands contained Pt–Pt bonds. It seems reasonable to believe that "platinblau" should also contain metal–metal bonds. If this is so, the two mononuclear structures should be eliminated. In our compound Cl(DMSO)Pt(acetamido)$_2$Pt(DMSO)Cl, the Pt···Pt distance is 3.008 (0.3) Å, which is slightly long for a strong metal–metal interaction. The color is also quite different from the one of "platinblau". We have prepared several batches of our greenish compound, and we have found that the color varied. Some crystals were definitely green, others were gray, and one time they were greenish yellow. The IR spectra of the different batches were all identical. X-ray diffraction has also shown that they were the same. The compound was found too insoluble to measure the electronic spectrum. We suggest that our greenish compound has an intermediate structure between "platinblau" and the usual yellow Pt(II) complexes. We cannot at the moment suggest a better formulation for the structure of "platinblau", but we intend to continue our research on this project.

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Supplementary Material Available: Anisotropic temperature factors (Table S1) and weighted least-squares planes (Table S2) (4 pages); observed and calculated structure factor amplitudes (Table S3) (30 pages). Ordering information is given on any current masthead page.