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Bowl-Shaped and Highly Inert Bis(μ-hydroxo)platinum(II) Dimer

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Introduction

Bis-hydroxo-bridged dimers of platinum(II) and palladium(II) represent an important class of compounds. For instance, platinum-based dimers are toxic side products[1] in the hydrolysis reactions of the antitumor drug cisplatin, and analogous platinum complexes recently proved to be useful for homogeneous catalytic reactions.[2] Both platinum and palladium dimers were used in various stoichiometric reactions.[3] Palladium dimers were reported to act as catalyst precursors for carbonylation reactions[4] or novel, environmentally friendly oxidations.[5] An important feature is the possible interaction between the metal centers in the dimer, both from a theoretical point of view and from the fact that cooperative binding to a substrate could be governed by the intermetallic interaction. The latter is weakly bonding (up to 20 kJ/mol) and only significant in bent dimers.[6]

Dimers of the general type $[\{L_2M(\mu\text{-E}-\text{X})\}_2]$, M = d^8 metal, can be planar or hinged, depending on the bridging group E−X and the terminal ligand L. The metal−metal interaction in bent dimers and its contribution to the question "to bend or not to bend" have recently been reviewed.[6] The definition of the hinge angle is shown in Chart 1 along with the orbital overlap ($d_{z^2} \rightarrow p_z$) that results in a bonding interaction in bent dimers. The main conclusions reached concerning the stability of the bent versus the planar form are as follows: good σ-donors in the position of the terminal ligand L lead to a stronger metal−metal interaction and thus favor the bent form; a higher electronegativity for the bridging atom favors the planar form. Apparently, these rules apply well for dinuclear Pt complexes with oxygen bridges ("O$_2$"), viz., oxide, hydroxide, or alkoxide, where both bent and planar structures appear. Strong terminal σ-donors such as P, S, or C enable bending[7] (see Table 1) but are not sufficient to guarantee a bent structure, since the majority of the structures, even with these strong donors, are planar.[8] The σ-donor strength of nitrogen ligands is much lower, and consequently the known ("N$_2$")Pt^{II}("O$_2$")Pt^{II}("N$_2$") structures are planar or nearly so. The deviation from planarity is smaller than 15° in $[\{Pt(NH_3)_2(\mu\text{-OH})\}_2]^{2+}$,[9] $[\{Pt(N,N\text{-}Me_2en)(\mu\text{-OH})\}_2]^{2+}$,[10] $[\{Pt(phen)(\mu\text{-OH})\}_2]^{2+}$,[11] $[\{Pt(bipy)(\mu\text{-OH})\}_2]^{2+}$,[12] $[\{Pt(NO_2)_2$-

Chart 1

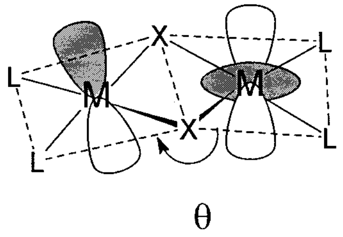

Table 1. Comparison of Hinge Angles (Calculated Using the Data from the Literature or the Cambridge Structural Database) for Bent Pt^{II} Dimers Containing the Pt(μ-O)$_2$Pt Substructure[a]

complex	deviation of hinge angle from planarity = 180°∠ θ	ref, refcode
$[\{Pt(Me_2phen)(\mu\text{-OH})\}_2]^{2+}$	43.1	this work (**1**)
$[\{Pt(1,3\text{-dppp})(\mu\text{-OH})\}_2]^{2+}$	39.6	7a, hejsiy
$[(1,5\text{-COD})_4Pt_4(\mu^3\text{-O})_2(\mu^2\text{-OH})]^+$	37.9	7b, fejtuj
$[\{Pt(PEt_3)_2(\mu\text{-OH})\}_2]^{2+}$	36.4	7c, hepptb
$[\{Pt(PPh_3)_2(\mu\text{-O})\}_2]$*LiBF$_4$	33.6	7d, kibteu10
$[\{Pt(Cl)(DMSO)(\mu\text{-OH})\}_2]$	33.5	7e, lespee
$[(1,5\text{-COD})_4Pt_4(\mu^3\text{-O})_2Cl_2]X_2$, X = F$_3CSO_3$	28.7	7f, fejtod
$[(1,5\text{-COD})_4Pt_4(\mu^3\text{-O})_2Cl_2]X_2$, X = BF$_4$	25.3	7f, fejtix

[a] Least squares planes were fitted through the approximately planar Pt^{II} coordination sphere, except for the cyclooctadiene complexes, where the PtO$_2$ planes were taken.

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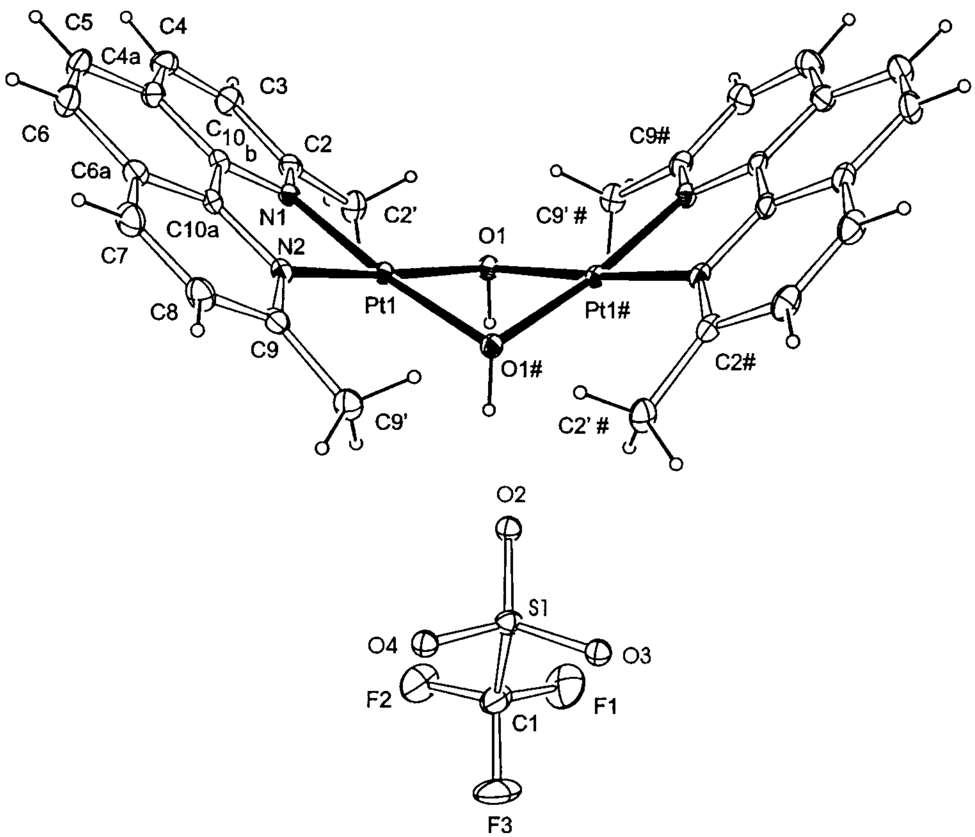

Figure 1. ORTEP plot (30% thermal ellipsoids) of the molecular structure of $[\{Pt(Me_2phen)(\mu\text{-}OH)\}_2]^{2+}$ (cation of **1**). Atoms labeled "#" are related by the symmetry operation "$-x$, y, $0.5 - z$". One trifluoromethanesulfonate ion is shown. Selected bond lengths (Å) and angles (deg.): Pt−N1, 2.031(3); Pt−N2, 2.024(3); Pt−O1, 2.023(3); Pt−O1#, 2.031(3); O1−Pt−O1#, 77.3(1); N1−Pt−N2, 81.8(1); Pt−O1−Pt, 96.4(2). Nonbonded distances (Å): Pt1−Pt1#, 3.022(1); O1−O1#, 2.53(1); C(methyl)−O(Pt), 2.90(1) (average); O1−O2, 2.72(2). Angle between the pyridine planes of a single Me_2phen moiety: 5.3°.

$(\mu\text{-}OH)_2\}_2]^{2-}$,[13] and $[\{Pt(N,N'\text{-disubstituted diimine})(\mu\text{-}OH)\}_2]^{2+}$.[14] The latter diimine system is relevant to the discussion of the factors influencing the bending along the hinge at the bridge, since the platinum complex is planar, but the palladium complex is bent. It seems that the palladium complexes are more easily bent, such that the modest strain exerted by the N-substituents is responsible for bending in the Pd case but not sufficient enough to enforce bending in the Pt complex. In this paper, we discuss a significant bending observed in a platinum complex in terms of steric strain. The Pd analogue of our system, which would provide an interesting comparison, has not yet been reported.

Results and Discussion

The structure and reactivity of an hydroxo-bridged dimer with nitrogen donor chelates, which turned out to be extremely bent, are reported. $[\{Pt(Me_2phen)(\mu\text{-}OH)\}_2](F_3CSO_3)_2$ (**1**; Me_2phen = 2,9-dimethyl-1,10-phenanthroline) has been prepared by chloride abstraction from the compound $[Pt(Me_2phen)Cl_2]$ using silver triflate. To investigate the influence of the 2,9-methyl groups on the structure of the dimer, a single-crystal X-ray structure determination was carried out. Crystals suitable for X-ray structure analysis were obtained by slow evaporation of a saturated solution from acetonitrile in air. Crystal data and details on structure refinement are summarized in Table 2; an ORTEP plot is provided in Figure 1, with selected bond lengths and angles in the legend of the plot. Close contact between an oxygen atom O2 of the triflate and the hydroxo bridge suggests a hydrogen bond between the dimeric cation and the anions. The most remarkable feature in the structure of **1** is the pronounced hinge, since it is a striking exception to the rules discussed above. Furthermore, this dimer appears to be the most bent Pt^{II}"O_2"Pt^{II} dimer presently known (see Table 1). It is interesting to compare the structure of this dimer with the planar structure of the parent compound $[\{Pt(phen)(\mu\text{-}OH)\}_2]^{2+}$. The Pt−O distances are identical with those reported for the planar nonmethylated analogue, and the Pt−N distances (2.03 and 2.02

Table 2. Crystal Data and Structure Refinement Details for $[\{Pt(Me_2phen)(\mu\text{-}OH)\}_2](F_3CSO_3)_2$ (**1**) and $[Pt(Me_2phen)(tu)_2](ClO_4)_2$ (**2**)

	1	**2**
chem formula	$C_{30}H_{26}N_4O_8Pt_2F_6S_2$	$C_{16}H_{20}Cl_2N_6O_8PtS_2$
fw	1138.83	754.49
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
T (K)	163(2)	163(2)
λ (Å)	0.710 73	0.710 73
a (Å)	21.908(8)	9.252(3)
b (Å)	8.984(3)	10.071(4)
c (Å)	18.310(6)	25.987(10)
β (deg)	112.902(4)	90.012(5)
V (Å^3)	3320(2)	2421.3(15)
Z	4	4
ρ_{calcd} (g cm^{-3})	2.28	2.07
μ (mm^{-1})	8.636	6.244
R1^a ($I > 2\sigma(I)$)	0.019	0.031
wR2^b (all data)	0.0481	0.083

^{a} $R1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

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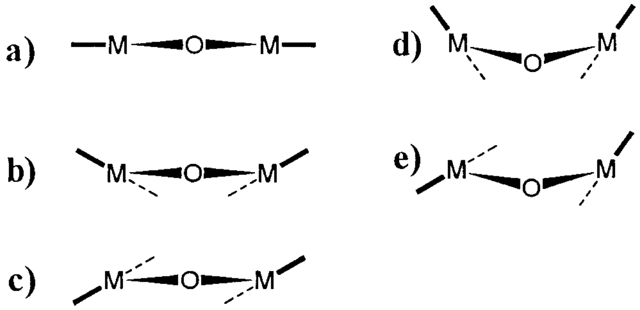

Figure 2. Schematic view along the O---O direction for conceivable structures of dimeric $(L_2)M(\mu\text{-}OH)_2M(L_2)$ complexes, where M is coordinated in a distorted square planar fashion. Hydroxo hydrogens are not shown. The bold lines represent metal−ligand bonds, whereas the dashed lines merely guide the eye. In the case of 2,9-dimethyl-phenantroline, the dashed lines represent the position of the methyl groups. (**a**) Planar structure with ligands coplanar; (**b** and **c**) "M_2O_2" core planar, ligand planes not coplanar, but syn in **b** and anti in **c**; (**d** and **e**) "M_2O_2" cores bent along the O---O hinge, but ligand planes syn in **d** and anti in **e**.

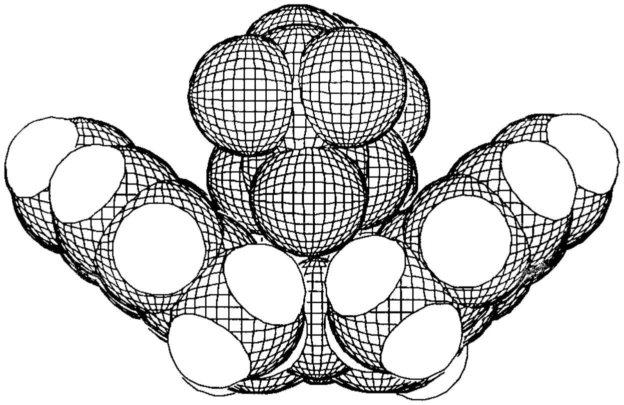

Figure 3. Space-filling model of **1**. Two triflate counterions are just visible and illustrate the packing of the CF_3 units into the cavity. Shortest Pt−F contacts: 3.43(2), 3.59(2) Å.

Å vs 1.99 and 2.01 Å) are only slightly larger.[11] The bond angles, however, exhibit significant differences compared to the parent compound. The O−Pt−O angle is smaller in **1** (77.3(1)° vs 81.0(4)°) and the Pt−O−Pt angle is also smaller (96.4(2)° vs 99.0(4)°). The most notable difference is the deviation of the hinge angle from planarity by 43° (N_2PtO_2 least squares planes). This is mainly due to the hinge at the bridging oxygen. A smaller contribution to this hinge angle comes from the distortion of the "square planar" environment, such that the N_2-Pt plane is in fact bent toward the corresponding O_2Pt plane by 8°. In addition, the ligand plane N1−C10b−C10a−N2 is bent in the same direction, such that the latter now forms an angle of 22° with the corresponding O_2Pt plane. The net result is that the two ligand planes in the dimer are almost perpendicular, with an angle of 101° between them.

Although there is no doubt that the methyl substituents cause the observed distortions in **1**, it is not immediately apparent in which way they are responsible for the hinge along the O---O axis. Structures that represent conceivable alternatives are shown in Figure 2 (**a**−**c**, **e**) along with the observed geometry (**d**). The completely planar structure **a** is easily ruled out. A model[15] based on the coordinates of $[\{Pt(phen)(\mu\text{-}OH)\}_2]^{2+}$ shows that the C_{methyl}---O distance would be 2.58 Å, much smaller than 3.50 Å, the sum of the van der Waals radii[16] of a methyl group (2.00 Å) and of oxygen (1.50 Å). An additional repulsive force should be the methyl−methyl repulsion between the two Me_2-phen ligands, since they would be only 3.32 Å apart. The sum of the van der Waals radii is 4.00 Å. The distortions in each half of the dimer resulting in the observed angle between the PtN_2 and PtO_2 planes reduce the strong methyl−oxygen repulsion, such that the corresponding C---O distance is in fact 2.90 (average) Å in **1**. There is precedence for this type of distortion in the structures of monomeric platinum(II) complexes of Me_2phen, e.g. $(Me_2phen)PtCl_2$.[17] The remaining structures **b**−**e** are equally well-suited to relieve this strain. Assuming an identical geometry within each half of the dimer, models predict also methyl−methyl distances which are almost identical for all of the structures **b**−**e**, in the narrow range from 3.78 to 3.96 Å. Furthermore, repulsion between the hydrogen on the hydroxo bridge and the methyl groups is also negligible in all these structures (see Supporting Information). It is therefore worthwhile discussing what might lead to a preference of **d**, the geometry observed in the crystal structure. The metal−metal interaction, weak but attractive in any case, should favor a hinge along the bridge. That this hinge does not occur for the other nitrogen-based bis-hydroxo-bridged dimers might be traced back to the fact that the Pt−O−Pt angle would be unfavorably small in a hinged structure. Not so, however, in the Me_2phen complex **1**, where the Pt−O−Pt angle can widen as a consequence of the more narrow O−Pt−O angle. This O−Pt−O angle is reduced by 3.7° relative to the parent phen dimer, very likely due to the methyl−oxygen repulsion. Accordingly, in complex **1**, a Pt−O−Pt angle of 96.4° is observed, which is larger than the predicted angle at oxygen for a hypothetical hinged $[\{Pt(phen)(\mu\text{-}OH)\}_2]^{2+}$. The nonmethylated compound, with its wider O−Pt−O angle, can less easily bend to the degree of hinging observed in **1**, since this would lead to an unfavorably small angle at oxygen, 93.1°, as demonstrated by a model. Following these arguments, structures **d** and **e** should be the most stable ones. An end-on orbital overlap, and thus also a possible bonding interaction, can be anticipated for **e**. The preference of **d** over **e** is most probably the result of hydrogen bonding in the crystal structure or weak packing forces.

A space filling model (Figure 3) shows that the triflate counterion is embedded into the bowl, at least in the crystal structure. Although triflate is not embedded but free in solution (^{19}F NMR, see Experimental Section), we are confident that stronger negatively charged donors could be found that would fit even better into the cavity and could indicate whether cooperative binding to the two metals is possible. It should be mentioned that the other bent dimers summarized in Table 1 appear less suitable for this purpose, since bulky groups on the terminal ligand L disfavor the entering of a guest molecule. In the present case, however, the phenanthrolines can direct a suitable guest molecule like a funnel toward the two metal centers, as observed for triflate in the crystal structure. The clear bowl shape of the bent structure suggests the application of this or similar dimers in molecular recognition studies.[18]

The structural results give rise to the question to what extent the bending enforced by the steric strain can affect the chemical

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(15) See Supporting Information on details of the discussed models, which were built using the program *MOPLO*: Thiele, G. *MOPLO 2.0*, Chemical Concepts/Wiley-VCH Software: Weinheim, Germany, 1994.

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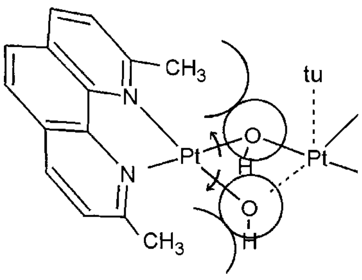
Chart 2



reactivity of bridge cleavage reactions. At first sight, it could be expected that the steric strain in the structure leads to a high reactivity, since it has been found for mononuclear complexes of Pt^{II} that displacement of phen by Me_2phen leads to enhanced reactivity both in the addition of unsaturated hydrocarbons[17,19] and in substitution reactions.[20] For the bent dimer, however, we found a reduced reactivity as compared to the planar phen analogue. This was already suggested by the procedure adopted during recrystallization of the complex, in which boiling acetonitrile gave the unreacted hydroxo-bridged dimer and not the monomeric acetonitrile complex. Attempts to cleave the dimer in acidic solution further demonstrated its inertness. After boiling the complex in water at pH 1.0 for 40 min, the solution still contained the bridged dimer. By way of comparison, these conditions were already reported to lead to the formation of the monomeric diaqua complex in the case of the planar parent dimer $[\{Pt(phen)(\mu\text{-}OH)\}_2]^{2+}$.[11]

More information on the inertness of the bent dimer was obtained from the reaction with thiourea, a strong nucleophile. Both $[\{Pt(Me_2phen)(\mu\text{-}OH)\}_2]^{2+}$ (**1**) and the planar, parent complex $[\{Pt(phen)(\mu\text{-}OH)\}_2]^{2+}$, selected for comparison purpose, showed pseudo-first-order behavior in the presence of a large excess of thiourea. The observed rate constants showed an excellent linear dependence on the thiourea concentration for both complexes, indicating a reaction that is first order in both complex and thiourea (Supporting Information Figure S2). The lines showed no significant intercept, which demonstrates that neither solvolysis nor reversibility in the thiourea reaction is observed. The final product was $[Pt(\text{‘}N_2\text{’})(tu)_2]^{2+}$ in both cases. Very notable is that $[\{Pt(Me_2phen)(\mu\text{-}OH)\}_2]^{2+}$ reacts ca. 100 times slower than the parent phen complex, with a rate constant of 0.107(1) as compared to 13.14(14) $M^{-1}\ s^{-1}$ at 25 °C, respectively. The rate-determining step in this bridge-cleavage reaction appears to be the attack of the first thiourea molecule, since no intermediates (such as $(\text{“}N_2\text{”})Pt(tu)(OH_2)^{2+}$) are observed. We propose the transition state structure schematically shown in Chart 2. Whereas the entering ligand thiourea (tu) does not encounter steric hindrance, the actual bridge-cleavage reaction has a higher activation barrier in the case of the Me_2phen complex than in the case of the phen complex, since the necessary widening of the O−Pt−O angle will encounter steric hindrance by the methyl groups.

We also conducted a crystallographic study on the product $[Pt(Me_2phen)(tu)_2]^{2+}$ (isolated as the perchlorate salt, **2**). A view along the N1−N2 vector is shown in Figure 4. The bond lengths in the Me_2phen ligand and in the bonded thiourea do not deviate significantly from those reported for other platinum complexes containing Me_2phen[19] or thiourea.[21] However, the Pt−N bond lengths are 0.075 Å longer than in the hydroxo-bridged dimer. This is obviously caused by the trans influence of each of the strong σ-donor sulfurs on the nitrogens, which weakens the Pt−N bonds. The fact that this chelate is stable is interesting in view of this trans influence and the strain observed in the structure.

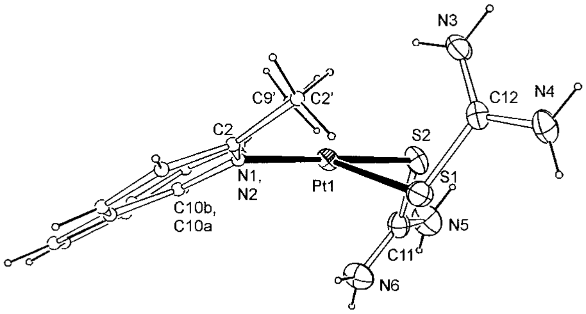


Figure 4. View along the N(1)−N(2) vector in $[Pt(Me_2phen)(tu)_2]^{2+}$ (cation of the perchlorate salt, **2**) illustrating the distortions in the crystal structure. Where thermal ellipsoids are shown, they correspond to 30% probability. The complete labeling scheme for Me_2phen is as in Figure 1. Selected bond lengths (Å) and angles (deg.): Pt−N1, 2.102(5); Pt−N2, 2.103(5); Pt−S1, 2.291(2); Pt−S2, 2.299(2); N1−Pt−N2, 79.8(2); S1−Pt−S2, 84.63(7). Interplanar angles (deg): {S1−Pt1−S2}/{N1−C10b−C10a−N2}, 38.8°; {N1−C10b−C10a−N2}/{N1−Pt1−N2}, 28.1; {N1−Pt1−N2}/{S1−Pt1−S2}, 13.9. The Pt−S1 bond is tilted away by 9.5° from the plane formed by the residual Pt coordination environment: N1, N2, Pt1, and S2 are nearly coplanar. Angle between the pyridine planes of Me_2phen (deg): 16.3. Torsion angles (deg): C9′−C9−N2−C10a, 12.0; C2′−C2−N1−C10b, 8.3.

The strain exerted by the van der Waals repulsion between the 2,9-methyl substituents on the ligand and the sulfur atoms on the platinum center is apparent from the large angle (38.8°) between the chelating N1−C10b−C10a−N2 substructure and the Pt−S1−S2 plane. The planes of the pyridine rings of Me_2phen are significantly (16.3°) bent together, in a bow-like manner. These distortions are very similar to those reported for $Pt(Me_2phen)Cl_2$ (38.8 and 16.4°, respectively).[17] This is reasonable since the van der Waals radius of S (1.85 Å) is only slightly larger than that of Cl (1.80 Å).[16] Another sterically caused distortion is observed in our complex in that the Pt−S1 bond is bent away from the residual coordination plane by ca. 10°.

Conclusions

In summary, it can be concluded that a strongly hinged structure is observed for $[\{Pt(Me_2phen)(\mu\text{-}OH)\}_2]^{2+}$ (**1**), where the distortions in the coordination sphere of platinum are relatively modest. The distortion of the chelating substructure away from the residual coordination plane and the bow-like distortion of the Me_2phen moiety itself are two and three times smaller in the dimeric hydroxo complex **1** than in the monomeric complex $[Pt(Me_2phen)(tu)_2]^{2+}$ (**2**), respectively. We propose that the methyl−oxygen repulsion is not only directly responsible for the distortions in the coordination plane of **1** but also mediated by a bond-angle effect for the hinging along the O---O axis. The same methyl−oxygen repulsion appears to be responsible for the low reactivity of **1** in comparison to the parent compound $[\{Pt(phen)(\mu\text{-}OH)\}_2]^{2+}$. The metal−metal interaction, which reduces the electrophilicity of the metal centers, could also contribute to the decrease in reactivity.

Finally, our results on the reactivity of the dinuclear complex **1** could assist the mechanistic understanding of the novel way in which Pd^{II} complexes of substituted phenanthrolines can

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generate hydrogen peroxide from dioxygen under biphasic conditions comprising an aqueous phase, as recently reported in the literature.[22] It was noted that the most active catalyst precursors had methyl substituents in the 2,9-positions. Tentatively, the explanation was offered that these substituents lead to steric hindrance preventing the formation of bridged dimers.[23] We found that 2,9-dimethyl substitution leads to *stabilization* of dimeric complexes in the case of Pt^{II}, thus making this hypothesis less likely. However, our dimeric complex releases strain, partially by achieving nonplanarity of the coordination environment, partially by forcing the bridging oxygens into close proximity (2.5 Å). A key intermediate in the proposed reaction mechanism for the Pd-catalyzed reduction of dioxygen to H_2O_2 is the [("N_2")Pd(O_2)] peroxo complex. Since the peroxo complex should have an even smaller oxygen−oxygen distance (ca. 1.5 Å), its formation will release strain in the case of "N_2" = Me_2-phen and will therefore be favored. We are confident that further studies on the stability of bridged dimers using substituents in the 2,9-positions of phenanthroline will lead to a more detailed understanding of several catalytic processes catalyzed by platinum or palladium complexes in aqueous solution.

Experimental Section

Syntheses. [{Pt(Me_2phen)(μ-OH)}$_2$](F_3CSO_3)$_2$ (1). The title compound was synthesized by a procedure similar to that already described for [{Pt(phen)(μ-OH)}$_2$] (F_3CSO_3)$_2$·2H_2O in ref 11. A suspension of 245 mg of [Pt(Me_2phen)Cl_2] (synthesized according to a literature procedure[17]) in 40 mL of water was stirred together with 400 mg of AgF_3CSO_3 in the dark at 75 °C for 4 h. The precipitate was separated from the solution via MILLIPORE filtration (0.2 μm) and washed several times using 100 mL of water. The product was extracted from the solution by stirring in hot acetone/H_2O (1:1, 300 mL). The AgCl precipitate was removed by MILLIPORE filtration. The solvent was evaporated and the product purified by recrystallization from boiling acetonitrile (400 mL) to give 181 mg of product. Yield: 61%. ^{1}H NMR ([D_7]DMF/D_2O, 1:1, 300.13 MHz): δ 8.49 [d, 4 H, $^3J_{H-H}$ = 7.5 Hz, H(4,7)]; 7.83 [s, 4 H, H(5,6)]; 7.67 [d, 4 H, $^3J_{H-H}$ = 7.5 Hz, H(3,8)]; 3.13 [s, 12 H, CH_3(2,9)]. ^{19}F NMR ([D_7]DMF/D_2O, 1:1, 282 MHz): δ 0.00 [s, F_3CSO_3] relative to F_3CSO_3Na under identical conditions. IR (KBr): 3212 (s, ν_{OH}), 3072 (w, ν_{CH}), 1029 (s, δ_{Pt-OH}), the OH vibrations are very similar to those of [{Pt(phen)(μ-OH)}$_2$]$^{2+}$.[28] X-ray quality crystals were obtained by slow evaporation of a saturated solution in MeCN in air. Anal. Calcd for $C_{30}H_{26}N_4O_8Pt_2F_6S_2$: C, 31.64; H, 2.30; N, 4.92; S, 5.63. Found: C, 31.75; H, 2.36; N, 4.91; S, 5.56.

[Pt(phen)(tu)$_2$](NO_3)$_2$. The complex obtained from the reaction of [{Pt(phen)(μ-OH)}$_2$]$^{2+}$ with thiourea (tu) shows an UV−vis spectrum identical with that previously reported.[11] Addition of a large excess of $NaNO_3$ and cooling led to the formation of dark yellow crystals which analyzed correctly as [Pt(phen)tu$_2$](NO_3)$_2$. Anal. Calcd for $C_{14}H_{16}N_8O_6S_2Pt$: C, 25.80; H, 2.48; N. 17.20; S, 9.84. Found: C, 25.96; H, 2.50; N, 17.00; S, 9.86.

[Pt(Me_2phen)(tu)$_2$](ClO_4)$_2$ (2). A solution of 170 mg (0.15 mmol) of 1 in 2 L of water was reacted with 1140 mg (15 mmol) of thiourea at ambient temperature. The pH was adjusted to 4.0 (F_3CSO_3H) before the reaction. After 1 h 45 min (99% conversion, calculated from the second-order rate constant), 380 g (!) of $NaClO_4$ was added. Vigorous shaking led to the formation of seed crystals. The solution turned cloudy and was cooled to 5 °C. After 1 day at 5 °C, the microcrystalline powder was separated by filtration. Yield: 130 mg (0.172 mmol) = 57%. A similar procedure (but without shaking) led to the formation of X-ray quality crystals within 1 week at 5 °C. ^{1}H NMR ([D_6]acetone, 300.13 MHz): δ 8.83 [d, 4 H, $^3J_{H-H}$ = 8.4 Hz, H(4,7)]; 8.18 [s, 4 H, H(5,6)]; 8.01 [d, 4 H, $^3J_{H-H}$ = 8.4 Hz, H(3,8)]; 3.30 [s, 12 H, CH_3(2,9)]. ^{13}C{^{1}H} NMR ([D_6]acetone, 75.48 MHz): δ 177.3 [$^2J_{Pt-C}$ = 12 Hz, C=S], 166.7 [J_{Pt-C}, not resolved, C ortho to N], 149.5 [J_{Pt-C}, not resolved, C ortho to N], 141.1 130.1, 129.0, 128.0 [4 C of aromatic system], 27.8 [CH_3(2,9)]. Anal. Calcd for $C_{16}H_{20}N_6O_8Cl_2S_2Pt$: C, 25.47; H, 2.67; N, 11.14; S, 8.50. Found: C, 25.79; H, 2.62; N, 11.04; S, 8.15.

X-ray Crystal Structures. Siemens P4/SMART CCD diffractometer, structure solution with direct methods, full matrix least squares method on F^2, all non-hydrogen atoms were anisotropically refined. The hydrogen atoms (except for the hydrogen on the hydroxo bridge of **1**, which was found in the difference map and not refined) were fixed in idealized positions and refined isotropically riding on their carrier atoms. Structure solution and refinement with the program SHELXTL.[24] Plots were generated and parameters calculated using ORTEP,[25] Pluton,[26] and XP.[27]

Kinetic Measurements and Instrumentation. The kinetics were followed by UV−vis spectroscopy using a Hewlett-Packard 89090A diode array spectrophotometer and a 0.88 cm tandem cuvette. At least 50 spectra were recorded covering at least three half-lives of the reaction. The pH was low enough to avoid the formation of the complex [Pt_2("N_2")$_2$(OH)$_3$]$^+$, which is formed above pH 7.[28] No salt was added for a constant ionic strength, since this would have led to precipitation due to the low solubility of the complexes. The data were analyzed using SPECFIT software.[29] Good pseudo-first-order behavior was found, although minor deviations in the kinetic traces were observed that could not be fitted with any reasonable kinetic model. These deviations are presumably due to changes in the ionic strength during the reaction and subsequent reactions that occur following the rate-determining bridge-cleavage process. The concentration dependence of the observed pseudo-first-order rate constants (Supporting Information Figure S2) is in excellent agreement with the assumption of a bimolecular bridge-cleavage reaction and shows no intercept, indicating that the reaction is truly irreversible. Chemical analyses were performed on a Carlo Erba Elemental Analyzer 1106.

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Supporting Information Available: Figures showing a plot of the observed pseudo-first-order rate constants for the bridge cleavage reactions as a function of the thiourea concentration, space-filling plots, and *xyz*-coordinates, text describing modeling procedures for the hypothetical alternative structures discussed in the paper, and tables showing procedures and coordinates and relative parameters for **1a**−**f**. X-ray crystallographic files, in CIF format, for the structure determinations of [{Pt(Me_2phen)(μ-OH)}$_2$](F_3CSO_3)$_2$ (**1**) and [Pt(Me_2phen)(tu)$_2$](ClO_4)$_2$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-145127 and CCDC-145126 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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