$[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2$: A Novel Platinum(IV) Dimer with Two Bridging Peroxo Ligands that Provides Insight into the Mechanism of Aerial Oxidation of Platinum(II)

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Oxidation of Pt(II) to Pt(IV) usually requires a strong oxidant but facile aerial oxidation of Pt(II) complexes has been reported.[1−4] In these cases, facially coordinating tridentate ligands were present and it was suggested that they promoted oxidation but no indications as to the detailed mechanism of oxidation emerged. This paper describes the reproducible preparation of the first structurally characterized Pt(IV) dimer bridged by two peroxo ligands, $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2$. The O_2^{2-} ligands are derived from oxidative addition of atmospheric oxygen in the reaction between *cis*-$[Pt^{II}Cl_2(dmso)_2]$[5] (dmso = dimethyl sulfoxide) and 1,4,7-triazacyclononane ($[9]aneN_3$) in ethanol.[6] $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2$ is air-stable and stable to hydrolysis in ethanol or water for in excess of 1 week. The presence of Cl^- anions and water in the crystal lattice further indicate the stability of the $\{Pt(\mu_2\text{-}O_2)_2Pt\}$ moiety. The addition of NaCl to an aqueous solution of preprepared $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]^{2+}$ resulted in no reaction after 3 days.

The asymmetric unit of the crystal structure of $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2\cdot 4H_2O$ (Figure 1)[7] consists of the cationic complex located about a center of symmetry, one chloride anion and two water molecules of crystallization. The geometry about the Pt atoms is octahedral, three coordination sites being occupied by the triazacyclononane ligand, one by a chloro ligand and two by O (peroxo) atoms. Two such moieties are linked by the two peroxo ligands. Pt−N, Pt−Cl, and Pt−O bond lengths are consistent with the Pt(IV) oxidation state (Figure 1). The presence of one Cl^- anion per Pt in the lattice and the O−O bond length [1.39(1) Å], indicating that the dioxygen bridge is in the peroxo oxidation state, are in accord with this conclusion.

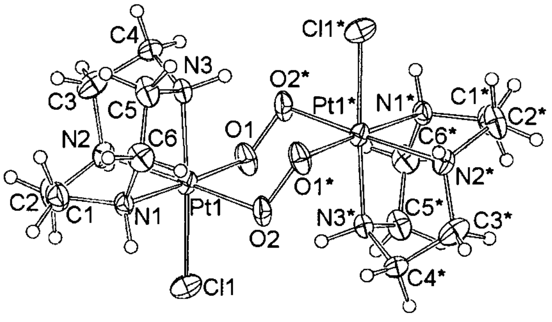

Figure 1. ORTEP plot of the cation of $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2\cdot 4H_2O$ giving the crystallographic atom numbering; 30% probability ellipsoids are shown. Important bond lengths (Å) are Pt(1)−N(1), 2.051(9); Pt(1)−N(2), 2.081(9); Pt(1)−N(3), 2.030(9); Pt(1)−O(1), 2.003(8); Pt(1)−O(2), 1.991(7); Pt(1)−Cl(1), 2.312(3); O(1)−O(2), 1.39(1) Å.

$[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2$ exhibits a strong $\nu(O_2)$ Raman peak at 808 cm^{-1} that is a weak absorption at 807 cm^{-1} in the IR spectrum. The position of this peak is typical of a peroxo stretching vibration.[8−10] The IR absorption of such a vibration is expected to be weak, because the peroxo groups bridge two symmetric Pt moieties and will not bring about a significant change in dipole moment upon stretching. The presence of this peak in the IR spectrum indicates that the Pt−O−O−Pt dihedral angle is not 180° (trans planar) where it would be IR-forbidden.[11] This angle is found to be ~83 ° by crystallography. In addition, assignment of the peak as resulting from a triazacyclononane ligand vibrational mode can be excluded by comparison against the spectra of 1,4,7-triazacyclononane, $[PtCl_2([9]aneN_3H)]_2(PtCl_4)$, $[PtCl_3([9]aneN_3)]Cl$, and $[PtCl_2([9]aneN_3)]$.[12]

The only other structurally characterized complex with two transition metals bridged by two μ_2-O_2 ligands was reported by Theopold and co-workers[13−15] studying O_2 binding to Co in systems bearing bulky trispyrazolylborate ligands.[16] They obtained a thermally unstable and air-sensitive transitory bridged $\{Co(\mu_2\text{-}O_2)_2Co\}$ species that decomposes after abstracting a H atom from the trispyrazolylborate ligand.[15] The O−O bond

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(6) Preparation of $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2\cdot 4H_2O$. *cis*-$[PtCl_2(dmso)_2]$ (0.5008 g, 1.19 mmol) was stirred with 1,4,7-triazacyclononane ($[9]aneN_3$) (0.1520 g, 1.19 mmol) in EtOH (6 mL) at 45 °C for 24 h. The reaction vessel was sealed, but the solution was not degassed. The initially pale yellow suspension deepens to orange-yellow over this time. The solid was filtered off and rinsed with EtOH and Et_2O, yielding $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2\cdot 4H_2O$ (0.2347 g, 42% based on Pt). IR (KBr, cm^{-1}) 3371 w, br, 3181 m, 3023 s, 3001 s, 2897 sh, 2842 m, 2781 mw, 1487 m, 1448 ms, 1377 w, sh, 1346 w, 1289 vw, 1266 w, 1226 vw, 1162 m, 1120 m, 1055 s, 1024 ms, 982 s, 892 w, 837 m, 807 m, 639 ms, 576 ms, 558 ms, 491 m. ^1H NMR (δ, ppm, D_2O (H_2O = 4.80 ppm)) 4.131, 4.016, 3.994, 3.909, 3.888, 3.724, 3.648, 3.598, 3.576, 3.441, 3.421, 3.210. Anal. Calcd: C, 15.56; H, 4.13; N, 9.07; Found: C, 15.72; H,4.03; N, 8.94.

(7) Crystal data for $[Pt_2Cl_2(O_2)_2([9]aneN_3)_2]Cl_2\cdot 4H_2O$: $Pt_2C_{12}H_{38}Cl_4N_6O_8$, FW = 926.46, T = 294 K; monoclinic, space group $P2_1/c$, a = 11.039(2) Å, b = 10.143(1) Å, c = 11.703(2) Å, β = 101.01(1)°, V = 1286.0(3) $Å^3$, Z = 2, ρ_{calc} = 2.392 g cm^{-3}, λ = 0.710 67 Å, μ = 114.86 cm^{-1}. For 2397 unique reflections and 146 parameters, $R(F_o)$ = 0.037, R_w = 0.034 (on 1586 observed reflections with $I > 2.5\sigma(I)$).

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(16) A Rh dimer with two bridging O_2^{2-} ligands has also been reported (see Bennett, M. J.; Donaldson, P. B. *J. Am. Chem. Soc.* **1971**, *93*, 3307−3308). However, the arrangement of the O atoms in the bridge differs with only one O on each peroxo ligand bridging the two metals.

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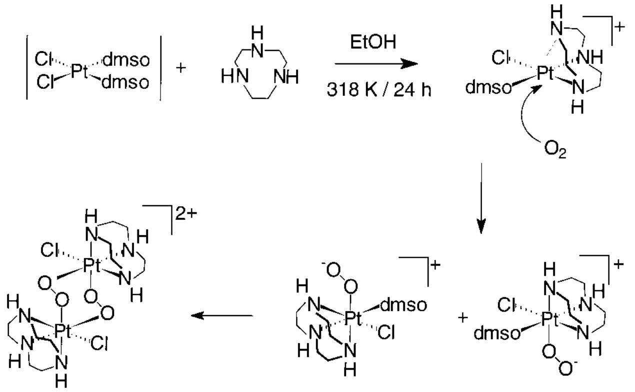
Scheme 1. Proposed $Pt^{II}-Pt^{IV}$ Oxidative Mechanism in the Presence of Facially Coordinating Tridentate Ligands



distance (1.354(5) Å) is intermediate between distances expected for superoxo and peroxo ligation. Interestingly, the two Co atoms are 5-coordinate, and based on Co−N and Co−O distances the complex was assigned as Co^{II}-superoxo.

Many workers have explored the reactions of Pt(II) and Pd(II) with facially coordinating tridentate ligands such as tacn, and related ligands with N and S donors.[1−4,17−27] The interest stems from the effect that a ligand that promotes octahedral coordination has on metals in oxidation states that are inherently square planar. It has been found that such Pt(II) complexes are readily oxidized to their Pt(IV) analogues, even by atmospheric oxygen,[1−4] but no previous report has been made of a peroxo- or superoxo-bound intermediate that could shed light on the mechanism of oxidation. This oxidation is evidently facilitated by the third (unbound) N or S of the tridentate ligand being held in the vicinity of an axial site of the square planar Pt(II) complex.[2,17,18,21,24] A proposed mechanism for the complexation of tacn to *cis*-$[PtCl_2(dmso)_2]$ and its oxidation to Pt(IV) is shown in Scheme 1. In the final step we have postulated that dmso ligands are displaced by peroxo ligands to give the stable dimer. Pt(IV) is kinetically inert but being a hard acid it will ultimately prefer binding to peroxo over the soft sulfur donor of the dmso and this may allow exchange to occur. Alternatively, two dioxygen ligands could bind to Pt(II) giving rise to Pt(IV) and two bound superoxo ligands and these could then bind to a second Pt(II) oxidizing it to Pt(IV), but this seems highly unlikely. Outer-sphere oxidation by O_2 followed by coordination of the peroxide cannot be excluded but other ligands such as water and Cl^- would be expected to compete with the peroxide.

Peroxo species were not isolated in previous studies where facile aerial oxidation of Pt(II) occurred in the presence of tridentate ligands.[1−4] Sarneski et al.[1] reported a bound water ligand[28] in the axial position and this may have been derived from O_2 binding, reduction to peroxide and decomposition of the peroxide. In all other cases[2−4] two tridentate ligands were present and it is probable that coordinated peroxide is displaced by the second of these ligands. Thus, our isolation of peroxo species is likely to be a consequence of the lack of additional strong ligands and the stabilization afforded by dimer formation.

Isolation of the bridged peroxo species under the conditions described above may be a consequence of having only two Cl^- anions per Pt atom in the reaction, although it must be added that not all of these Cl^- anions are bound to the Pt in the product, nor are water molecules that cocrystallized with the complex. Bhaduri et al.[29] in their study on the only $\{Pt(\mu_2\text{-}O_2)Pt\}$complex previously structurally characterized, $[Pt_2(OH)(O_2)(PPh_3)_4][ClO_4]\cdot 2C_6H_6$, found that in the presence of strong nucleophiles (e.g. Cl^- or Br^-) they were unable to isolate the peroxo complex. The complex reported by Bhaduri[29] has bridging peroxo and hydroxo groups. The O−O distance of 1.547(2) Å is at the long end of the peroxo range, whereas the distance in the structure reported here (1.39 (1) Å) is at the short end of the range.

In conclusion, a novel platinum(IV) dimer bridged by two peroxo ligands is reported. $[Pt_2Cl_2(\mu_2\text{-}O_2)_2([9]aneN_3)_2]Cl_2$ is stable in air as a solid and in alcoholic and aqueous solution. It is proposed that the $\{Pt^{IV}(\mu_2\text{-}O_2)_2Pt^{IV}\}$ moiety may represent a stable structural motif, or in the presence of strong nucleophiles, a transitory species in the oxidation of Pt(II) to Pt(IV) in aqueous media. Further physiochemical studies on this complex and on the generality of this reaction with other facially coordinating tridentate ligands are underway.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond lengths and angles (3 pages). Ordering information is given on any current masthead page.

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