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Platinum Blue Related Tetranuclear Platinum(III) Complex That Oxidizes Water to Molecular Oxygen

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"Platinum blue" is a class of mixed-valent complexes containing Pt(II) and Pt(III) in a tetranuclear zigzag chain structure. Several cations of a basically identical structure with different platinum oxidation states have so far been isolated: blue $[Pt_4(NH_3)_8L_4]^{5+}$ with average Pt oxidation state 2.25 (L = deprotonated α-pyridone,[2,3] α-pyrrolidone,[4] 1-methylhydantoin,[5] or 1-methyluracil[6]); dark brownish red $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ with average Pt oxidation state 2.50[7,8] (C_4H_6NO is deprotonated α-pyrrolidone); yellow $[Pt_4(NH_3)_8(C_5H_4NO)_4]^{4+}$ with average Pt oxidation state 2.0[9] (C_5H_4NO is deprotonated α-pyridone). From our recent studies, it was found that dark brownish red $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ (**1**) is reversibly reduced by water to blue $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ (**2**) and to a yellow complex which is presumably $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ (**3**), a corresponding analogue of yellow $[Pt_4(NH_3)_8(C_5H_4NO)_4]^{4+}$.[4] Moreover, **1** is reversibly oxidized by air in a strongly acidic solution to another yellow complex, whose average platinum oxidation state is 3.0.[4] In the present study, the yellow oxidation product has been isolated and found to be tetranuclear $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ (**4**). What is more interesting is that **4** is easily reduced by water to **1** even in solid and molecular oxygen is generated.

The yellow Pt(III) complex is synthesized as follows: 50 mg of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6{\cdot}2H_2O$[7,8] is dissolved in 1 mL of 1.8 M H_2SO_4 and 42 mg of $Na_2S_2O_8$ is added. On slight warming at 50 °C for a few minutes, the initially dark red solution turns to yellow. After cooling to room temperature, the yellow complex is precipitated by adding 67 mg of $H_3PW_{12}O_{40}{\cdot}29H_2O$. The precipitate is immediately dried in vacuo and stored over silica gel at 0 °C. Anal. Calcd for $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)(PW_{12}O_{40})_2{\cdot}20H_2O$:[10] C, 2.58; H, 1.19; N, 2.25; Pt, 10.45; P, 0.83; W, 59.13%. Found: C, 2.67; H, 1.06; N, 2.01; Pt, 9.9; P, 0.77; W, 57.3%. The yellow cation can also be prepared in 1.4 M NHO_3. Anal. Calcd for $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_2(PW_{12}O_{40})_2{\cdot}10H_2O$: C, 2.63; H, 0.94; N, 2.68%. Found: C, 2.83; H, 1.17; N, 2.77%. Similarly, $SiMo_{12}O_{40}^{4-}$ and ClO_4^- salts can be prepared by adding hydrated $H_4SiMo_{12}O_{40}$ and $LiClO_4$, respectively. Anal. Calcd for $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)(SiMo_{12}O_{40})_{3/2}{\cdot}32H_2O$: C, 4.13; H, 2.43; N, 3.61%. Found: C, 4.48; H, 2.63; N, 3.54%. Calcd for $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)_2(ClO_4)_4{\cdot}6H_2O$: C, 9.85; H, 3.11; N, 8.62%. Found: C, 10.20; H, 3.19; N, 8.91%. The perchlorate salt is precipitated by adding excess acetone to the aqueous solution. The yellow Pt(III) complex **4**, prepared by oxidation of **1** either with O_2, $Na_2S_2O_8$, or Ce(IV), is diamagnetic and shows the same visible-spectral behavior as mentioned later in this paper. The complex **4** is sensitive to humidty even in solid: if the powder sample is left in humid air at room temperature for several hours, it turns dark red.

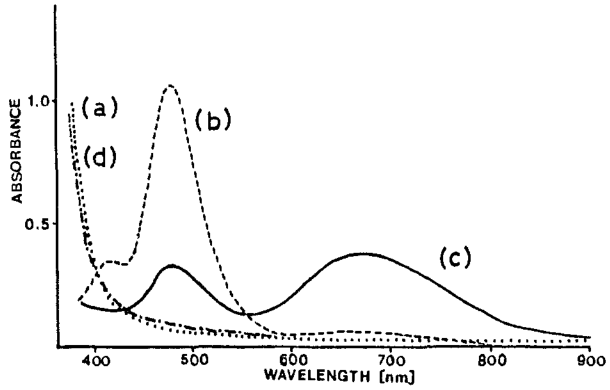

Figure 1. Visible absorption spectra of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$: (a) yellow $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)_2(ClO_4)_4{\cdot}6H_2O$ (2.2×10^{-3} M) in 4.5 M H_2SO_4; (b) dark red $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)_2(ClO_4)_4{\cdot}6H_2O$ left in humid air for 3 days (7.8×10^{-5} M) in 4.5 M H_2SO_4; (c) dark red $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)_2(ClO_4)_4{\cdot}6H_2O$ left in humid air for 2 weeks (2.6×10^{-3} M in 0.06 M H_2SO_4); (d) dark red $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)_2(ClO_4)_4{\cdot}6H_2O$ (2.2×10^{-3} M) with the addition of Ce(IV) (8.8×10^{-3} M) in 4.5 M H_2SO_4.

The visible absorption spectra of **4** and its reduction products by water are shown in Figure 1. The powder sample of the yellow compound $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)_2(ClO_4)_4{\cdot}6H_2O$ was left in humid air for various periods and the visible spectra were measured as aqueous solutions. Figure 1 suggests that **4** is reduced to **1** by water (λ_{max} = 478 and 415 nm for **1**).[4] The spectrum (Figure 1c) is considered to be a mixture of **1** and **2**, suggesting **4** is further reduced to **2** on long standing even in solid (λ_{max} = 680 nm for **2**).[4] If small excess of Ce(IV) is added to the dark red or blue reduction product, the solution turns yellow and the original spectrum is recovered (Figure 1d).

The reduction of **4** by water was also monitored by ESR (Figure 2). All the spectra in Figure 2 were measured as powders. The spectrum of **2** is characterized by a broad axial signal without any hyperfine splitting, whereas that of **1** is accompanied by an approximately nine-line hyperfine splitting due to four platinum atoms[3] (average separation in the axial component is 72 G).[11] Figure 2c is the signal of isostructural green complex, which is actually a mixture of 48% **1** and 52% **2**.[12] The signal (Figure 2c) is considered to be composed of paramagnetic **2** diluted with diamagnetic **1**. The relative signal intensities of the lower half-field part of the perpendicular component in Figure 2c are 3:8:19:45:64:100 (the central peak is normalized to 100) with the average separation of 69 G. These relative intensities are almost identical with what was theoretically calculated for blue α-pyridone complex $[Pt_4(NH_3)_8(C_5H_4NO)_4]^{5+}$, 0.3:3:8:2:48:62:100,[3] although the first smallest peak is not clearly observed in Figure 2c. The yellow cation **4** is completely diamagnetic (Figure 2d); however, on reaction with water, the powder sample of **4** becomes dark red and paramagnetic (Figure 2e). Signal e is basically identical with signal b and indicates that **4** is reduced to **1** and even to **2** in solid. This, in other words, signifies that the originally yellow complex **4** is also a tetranuclear structure. The approximately nine-line hyperfine splitting is indisputable evidence for a tetranuclear structure.

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[1] (a) Waseda University. (b) The University of Air.

[2] Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434.

[3] Barton, J. K.; Caravana, C.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 7269.

[4] Matsumoto, K. *Chem. Lett.* **1984**, 2061.

[5] Laurent, J.-P.; Legape, P.; Dahan, F. *J. Am. Chem. Soc.* **1982**, *104*, 7335.

[6] Mascharak, P. K.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6428.

[7] Matsumoto, K.; Fuwa, K. *J. Am. Chem. Soc.* **1982**, *104*, 897.

[8] Matsumoto, K.; Takahashi, H.; Fuwa, K. *Inorg. Chem.* **1983**, *22*, 4086.

[9] Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1230.

[10] The cation may be coordinated by the anions or water molecules at both ends of the platinum chain. However, at present, no definite evidence has been obtained concerning the coordination of the cation at the chain ends. Therefore, the molecular formulas are written as those in the text.

[11] Although the ESR signal of **1** is very weak compared with that of **2**, the signal intensity per weight is always constant from preparation batch to batch. If **1** itself exhibits an ESR signal, it must be that of $S = 1$, which would be definitely different from that of **2** ($S = {}^1/_2$), in terms of the number of ESR transitions. Therefore, the very weak signal (Figure 2), which is very close to Figure 2c in its hyperfine splitting structure, would be due to very small amount of **2** present in diamagnetic **1**. The reproducible appearance of signal b would indicate that very small part of **1** is reduced to **2** by atmospheric water or the compound **1** is nonstoichiometric, containing very small fraction of **2**.

[12] Matsumoto, K.; Takahashi, H.; Fuwa, K. *J. Am. Chem. Soc.* **1984**, *106*, 2049.

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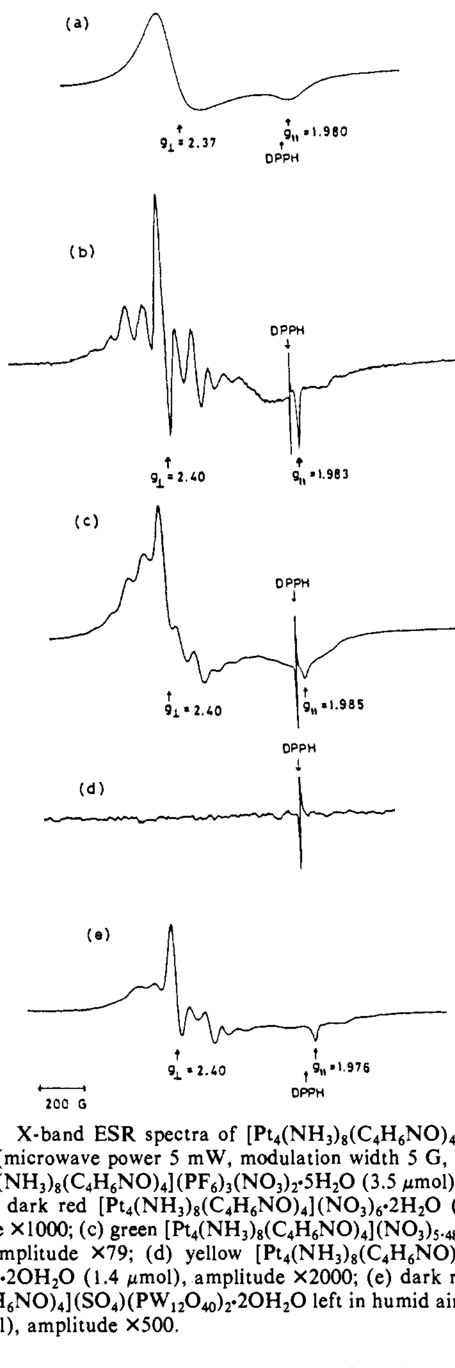

Figure 2. X-band ESR spectra of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ powder samples (microwave power 5 mW, modulation width 5 G, 77 K): (a) blue $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$ (3.5 μmol), amplitude ×50; (b) dark red $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ (6.7 μmol), amplitude ×1000; (c) green $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48} \cdot 3H_2O$ (5.1 μmol), amplitude ×79; (d) yellow $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)(PW_{12}O_{40})_2 \cdot 20H_2O$ (1.4 μmol), amplitude ×2000; (e) dark red $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)(PW_{12}O_{40})_2 \cdot 20H_2O$ left in humid air for 7 days (1.4 μmol), amplitude ×500.

It is important to know what the oxidized product of water is, as a result of the reduction of **1**. Gas-chromatographic analysis[13] of the gas in the head space of a sealed tube containing an aqueous solution of **4** showed that molecular oxygen is generated. Typically, 1.8 × 10^{-5} mol of $[Pt_4(NH_3)_8(C_4H_6NO)_4](SO_4)_2(ClO_4)_4 \cdot 6H_2O$, dissolved in 0.1 mL of H_2O and placed in a 3-mL sealed tube, gradually turned dark red and concomitantly O_2 was generated. The final O_2 amount detected was 2.9 × 10^{-6} mol. The visible and ultraviolet absorption spectrum of the solution after O_2 generation shows that the platinum species in the solution is a mixture of **1** and **4**. Addition of Ce(IV) almost quantitatively restores the original spectrum of **4**. Therefore, the reaction would be described as follows:

$$2[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+} + 2H_2O \rightleftarrows 2[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+} + O_2 + 4H^+$$

The backward reaction has been reported previously.[4] Mass spectrometric analysis[14] of the O_2 gas generated from the reaction of $H_2{}^{18}O$ with **4** confirmed that the oxygen really comes from water.

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[13] Column packing, Molecular Sieve 5A; carrier gas, Ar, 50 mL min^{-1}; column temperature, 30 °C; injection port temperature, 30 °C; TCD detector, 70 °C, 80 mA; retention time 1.14 min. Small amount of air leak was estimated by measuring both N_2 and O_2.

[14] GC MS was carried out with the same conditions as in ref 13, except that He was used as carrier gas instead of Ar. Both $^{18}O_2$ and $^{18}O^{16}O$ were detected.

Formation of N^{21},N^{22}-Etheno Bridged Porphyrins by the Reaction of Cobalt(III) Porphyrin π-Cation Radicals with Alkynes

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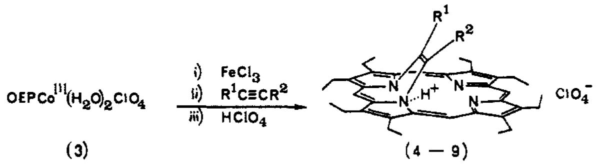
Metalloporphyrin π-cation radicals have been the focus of recent studies directed to elucidate the structure and function of hemoproteins.[1] In the case of cobalt octaethylporphyrin (OEP), two types of Co(III) π-cation radicals, $[OEPCo^{III}]^{2+}2Br^-$ (**1**) and $[OEPCo^{III}]^{2+}2ClO_4^-$ (**2**), have been regarded as representative of $^2A_{1u}$ and $^2A_{2u}$ states, respectively, on the basis of optical and ESR evidence, and the similarity of their optical absorption spectra to those of catalase compound I (CAT-I) and horseradish peroxidase compound I (HRP-I) was noted.[1a] NMR study of **1** and **2** was recently undertaken and the results were interpreted in terms of a thermal equilibrium of $^2A_{1u}$ and $^2A_{2u}$ states with the greater contribution being placed on $^2A_{1u}$ state for **2** in contrast to the previous formulation.[1i] From the viewpoint of reaction behavior, the reaction that is characteristic of metalloporphyrin π-cation radical is rather unknown and the cobalt(III) porphyrin π-cation radicals **1** and **2** have never been reported to react in a different manner, while π-dications of metalloporphyrins are known to react with nucleophiles giving meso-substituted metalloporphyrins via isoporphyrins as intermediates.[1b]

The present study demonstrates that **2** prepared by the oxidation of divalent and trivalent cobalt porphyrins with ferric perchlorate reacted smoothly with alkynes to give N^{21},N^{22}-etheno bridged octaethylporphyrins whereas **1** did not react at all.

An excess amount of alkynes was added to the reaction mixture of $OEPCo^{III}(H_2O)_2ClO_4$[2] (**3**) and $FeCl_3$ (1-2 equiv) in CH_2Cl_2 to result in the color change to reddish green immediately. The mixture was washed with 10% $HClO_4$ solution and then purified by chromatography on silica gel with $CHCl_3$-acetone (5:1). Table I summarizes the yields and the ^1H NMR data of the products **4-9** which were prepared from acetylene, 1-hexyne, propargyl



(3)

(4 — 9)

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[1] (a) Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J.; Felton, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 614. (b) Dolphin, D.; Muljiani, Z.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton, R. H. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 177. (c) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* **1974**, *7*, 26. (d) Gans, P.; Marchon, J.-C.; Reed, C. A.; Regnard, J. R. *Nouv. J. Chim.* **1981**, *5*, 203. (e) Phillippi, M. A.; Shimomura, E. T.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1322. (f) Buisson, G.; Deronzier, A.; Duee, E.; Gans, P.; Marchon, J.-C.; Regnard, J.-R. *J. Am. Chem. Soc.* **1982**, *104*, 6793. (g) Scholz, W. F.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R.; Lang, G. *Ibid.* **1982**, *104*, 6791. (h) Fujita, I.; Hanson, L. K.; Walker, F. A.; Fajer, J. *Ibid.* **1983**, *105*, 3296. (i) Morishima, I.; Takamuki, Y.; Shiro, Y. *Ibid.* **1984**, *106*, 7666. (j) Groves, J. T.; Quinn, R.; McMurry, T. J.; Nakamura, M.; Lang, G.; Bolo, B. *Ibid.* **1985**, *107*, 354.

[2] Sugimoto, H.; Ueda, N.; Mori, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3425.

0002-7863/86/1508-1309$01.50/0