Pulse radiolysis allows us to study the reactions of Fe(IV) and Fe(V) in the absence of excess strong oxidants (e.g., $H_2O_2$). The immediate objective of these studies is not only to find other ligands and methods that will allow generation/stabilization of the Fe(IV) and Fe(V) species but also to measure their reactivity with various organic compounds. The characterization of the Fe(IV)/Fe(V) oxidation states in simple complexes will hopefully lead to the understanding of these iron forms in more complex systems.

**Acknowledgment.** This search was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank Dr. N. Sutin for stimulating discussions and constructive criticism of this manuscript.

**Registry No.** $Fe(OH)_4^-$, 29145-79-7; $FeO_4^{2-}$, 16836-06-9; $P_2O_7^{3-}$, 99783-30-9; $FeO_4^{3-}$, 37114-36-6; $Fe^{3+}$, 20074-52-6; $Fe^{6+}$, 14127-55-0.

---

# Additive Trans Influences of the Axial Ligand and Metal-Metal Bond in a Diplatinum(III) Complex Leading to an Asymmetric Structure with Penta- and Hexacoordination of the Two Metals

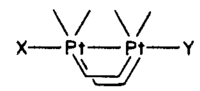
Bernhard Lippert,*[1a] Helmut Schöllhorn,[1b] and Ulf Thewalt[1b]

*Anorganisch-Chemisches Institut*
*Technische Universität München, 8046 Garching, FRG*
*Sektion für Röntgen- und Elektronenbeugung*
*Universität Ulm, 7900 Ulm, FRG*

*Received September 9, 1985*

Dinuclear Pt(III) complexes represent a relatively new class of compounds. In all crystallographically characterized examples reported so far, the two metals possess hexacoordination, regardless of whether the bridging ligands are symmetric (e.g., $CF_3COO^-$,[2] $SO_4^{2-}$,[3] $H_2P_2O_5^{2-}$,[4] $HPO_4^{2-}$,[5]) or asymmetric (e.g., pyridin-2-one,[6] 1-methyluracil,[7] pyrimidine-2-thione[8]) or if, in the latter case, they form a head-head,[6a] a head-tail arrangement,[6b,7] or a combination of both.[8] We herewith report the first crystal structure of a diplatinum(III) complex, $[(\mathit{N}O_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_3\cdot H_2O$ (with 1-MeU = monoanion of 1-methyluracil, $C_5H_5N_2O_2$), having one Pt atom hexacoordinated and the other Pt atom pentacoordinated only. Similar asymmetric structures have been proposed, on the basis of NMR spectroscopic evidence,[9] for $CF_3CO_2^-$-bridged diplatinum(III) complexes.

**Table I.** Pt-Pt Separations in 1-Methyluracilato-Bridged Diplatinum(III) Complexes



| | X | Pt-Pt, Å | Y | ref |
|---|---|---|---|---|
| | $\mathit{N}O_2^-$ | 2.607 (1) | | *a* |
| head-head | $Cl^-$ | 2.573 (1) | $Cl^-$ | *b* |
| | $Cl^-$ | 2.543 (1) | $Cl^-$ | *c* |
| | $\mathit{N}O_2^-$ | 2.574 (1) | $\mathit{O}H_2$ | *d* |
| head-tail | $\mathit{O}NO_2^-$ | 2.556 (1) | $\mathit{O}H_2$ | *e* |
| | $\mathit{O}NO_2^-$ | 2.560 (1) | $\mathit{O}H_2$ | *e* |

[a] This work. [b] $[Cl(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Cl]Cl_2$.[12] [c] $Cl(NH_3)_2Pt(1\text{-}MeU)_2PtCl_3$.[12] [d] $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3$.[7] [e] Two modifications of $[(\mathit{O}NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(\mathit{O}H_2)](NO_3)_3$.[11]

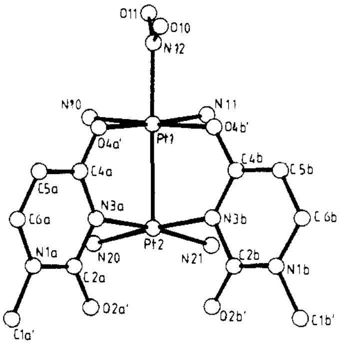


**Figure 1.** PLUTO drawing of the cation $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2]^{3+}$ of the title compound.

We believe that the difference in Pt coordination numbers in the here described complex is a consequence of the additive effects of the structural trans influence of the nitro ligand in the axial position of one Pt *and* the Pt-Pt bond for the following reasons: (i) Both the nitro ligand and the Pt-Pt unit on their own excert a strong trans influence.[6,10] (ii) In a related complex with head-tail orientation of the bridging ligands, $[(\mathit{N}O_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(\mathit{O}H_2)](NO_3)_3\cdot 5H_2O$,[7] the Pt-$OH_2$ bond trans to the $O_2\mathit{N}$-Pt-Pt unit is extremely long already, 2.253 (9) Å. This distance compares with 2.176 (11) and 2.171 (11) Å in the corresponding complexes with the $NO_2^-$ ligand replaced by $\mathit{O}NO_2^-$[11] and 2.122 (6) Å in a related complex of α-pyridone.[6a] (iii) If the nitro ligand of the title compound is substituted by a ligand of lower trans influence, e.g., $Cl^-$,[12] both Pt atoms become hexacoordinated, thus ruling against steric arguments (vicinity of exocyclic O2' oxygens of 1-MeU rings) for a lower coordination number of the second Pt.

In Table I the Pt-Pt distances of six diplatinum(III) complexes, containing two 1-MeU bridges each, are listed. The data confirm previous findings[6] on the structural trans influence of the nitro ligand on the Pt-Pt separation, but they suggest also that only head-head or head-tail dimers should be compared and that substitution of the equatorial $NH_3$ ligands (e.g., by $Cl^-$, footnote c in Table I) affects the Pt-Pt bond length as well.

Formation of the title compound is achieved by oxidation of the diplatinum(II) complex *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_2$[13] with $HNO_3$.[14] Orange crystals of the title compound are diamagnetic and EPR-inactive. The compound was characterized by elemental analysis,[15] X-ray analysis,[16] and

---

(1) (a) Technische Universität München. (b) Universität Ulm.

(2) Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938.

(3) (a) Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk SSSR* **1976**, *226*, 76. (b) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 2889.

(4) Che, C.-M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604.

(5) (a) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 1709. (b) Cotton, F. A.; Han, S.; Conder, H. L.; Walton, R. A. *Inorg. Chim. Acta* **1983**, *72*, 191.

(6) (a) Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2605. (b) Hollis, L. S.; Roberts, M. M.; Lippard, S. J. *Ibid.* **1983**, *22*, 3637.

(7) Lippert, B.; Schöllhorn, H.; Thewalt, U. *Z. Naturforsch., B* **1983**, *38B*, 1441.

(8) Goodgame, D. M. L.; Rollins, R. W.; Skapski, A. C. *Inorg. Chim. Acta* **1984**, *83*, L 11.

(9) Steele, B. R.; Vrieze, K. *Transition Met. Chem. (N.Y.)* **1977**, *2*, 169.

(10) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science: London, 1973.

(11) Schöllhorn, H.; Eisenmann, P.; Thewalt, U.; Lippert, B., unpublished results.

(12) Lippert, B.; Schöllhorn, H.; Thewalt, U., *Inorg. Chem.*, in press.

(13) Lippert, B.; Neugebauer, D.; Raudaschl, G. *Inorg. Chim. Acta* **1983**, *78*, 161.

(14) Preparation: 200 mg of powdered *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2\cdot H_2O$ (head-head) was added in small portions to 1 mL of concentrated $HNO_3$ with stirring. The solution rapidly became bluegreen and then suddenly deep red (after ca. 1.5 min). At this stage 2.5 mL of $H_2O$ were added and the now orange solution filtered from some precipitate and kept in a stoppered flask at 22 °C. After 24 h, 110 mg of orange-yellow, air-sensitive crystals were collected (dihydrate of title compound). If the solution was kept for 4 days instead of 1 days at 22 °C, 30 mg of orange, transparent, air-stable crystals of the title compound were obtained.

0002-7863/86/1508-0525$01.50/0

$^1$H NMR (cf. supplementary Material).

The molecular structure of the $[(NO_2)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2]^{3+}$ cation (Figure 1) consists of two *cis*-$(NH_3)_2Pt(III)$ units bridged by two 1-MeU ligands head-to-head, with Pt1 (coordinated to the two 04′ oxygens) carrying a nitro group in the axial position. Counting each Pt as one ligand for the second Pt, Pt1 has the coordination number 6, while Pt2 has 5 only. The Pt-Pt distance is 2.607 (1) Å, the Pt1-*N*$O_2$ distance is 2.06 (2) Å. Pt-$NH_3$ (2.03 (1)-2.07 (2) Å), Pt-N3 (2.02 (2) Å), and Pt-O4′ distances (2.01 (1), 2.04 (1) Å) are normal, as is the geometry of the nitro ligand (N-O 1.20 (2) Å, av O10-N12-O11 122 (2)°). The two Pt planes are tilted by 19° but almost eclipsed (twist angle about the Pt-Pt vector 3.6°, av).

Intermolecular hydrogen bonding involves $NH_3$ groups and nitrate oxygens, O11 of the $NO_2$ group and $NH_3$, $NH_3$ and lattice water, and lattice water and O2a′. None of these interactions are unusually short (≥2.74 Å), and there are no long-range Pt-Pt interactions (shortest intermolecular distance 6.3 Å).

**Acknowledgment.** We thank the DFG, Degussa (loan of $K_2PtCl_4$), and H. Vasquez, Universität Heidelberg (magnetic measurements).

**Supplementary Material Available:** Atomic positional and thermal parameter and $^1$H NMR data (2 pages). Ordering information is given on any current masthead page.

---

[15] Anal. Calcd for $[(NO_2)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2](NO_3)_3\cdot H_2O$: C, 12.53; H, 2.53; N, 17.54; O, 26.70. Found: C, 12.61; H, 2.49; N, 17.69; O, 26.35.

[16] X-ray analysis: Space group *C*2/*c*, $a = 19.257$ (5) Å, $b = 17.611$ (5) Å, $c = 15.389$ (2) Å, $\beta = 109.44$ (2)°, $V = 4924.2$ Å$^3$, $Z = 8$, $\rho_{obsd}$ 2.55 g cm$^{-3}$, $\rho_{calcd}$ 2.537 g cm$^{-3}$. Of 4450 reflections measured, 3415 reflections with $F_0 > 2\sigma F_0$ (PHILIPS PW 1100, $\lambda = 0.71069$ Å, $2\theta < 50°$, Lp and empirical ($\mu = 110$ cm$^{-1}$) absorption corrections) were used for the calculations. Refinement to $R = 0.074$, $R_{w(F)} = 0.072$ with H atoms ignored. The structure was solved by standard Patterson and difference Fourier methods.

---

# Iron K-Edge EXAFS Data on $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]_n$ ($n$ = 0–2). The Structure of an Iron(IV) Complex of *o*-Phenylenebis(dimethylphosphine)

Stephen K. Harbron, Simon J. Higgins, and
William Levason*

*Department of Chemistry, The University*
*Southampton S09 5NH, U.K.*

C. David Garner,* Andrew T. Steel, and Martinus C. Feiters

*Department of Chemistry, Manchester University*
*Manchester M13 9PL, U.K.*

S. Samar Hasnain

*The Daresbury Laboratory, Warrington WA4 4AD, U.K.*

*Received June 3, 1985*

Iron(IV) is a rare oxidation state, and relatively few thoroughly characterized compounds have been reported.[1] The presence of Fe(IV) in oxidized horseradish peroxidase was proposed over 30 years ago,[2] and the nature of the oxidation products of iron(III) porphyrins has remained a topic of considerable controversy. Recent studies have identified many of the one-electron oxidation products of iron(III) porphyrins as iron(III) porphyrin $\pi$-cation radicals; i.e., the oxidation is ligand rather than metal centered.[3-5] In a smaller number of cases, there is good evidence (especially from the $^{57}$Fe Mössbauer spectra) for the formation of Fe(IV)-porphyrin species, e.g., in horseradish peroxidase,[6] $\mu$-nitrido-[7] and $\mu$-carbido[8] dimers, a $\mu$-oxo polymer,[9] and most recently

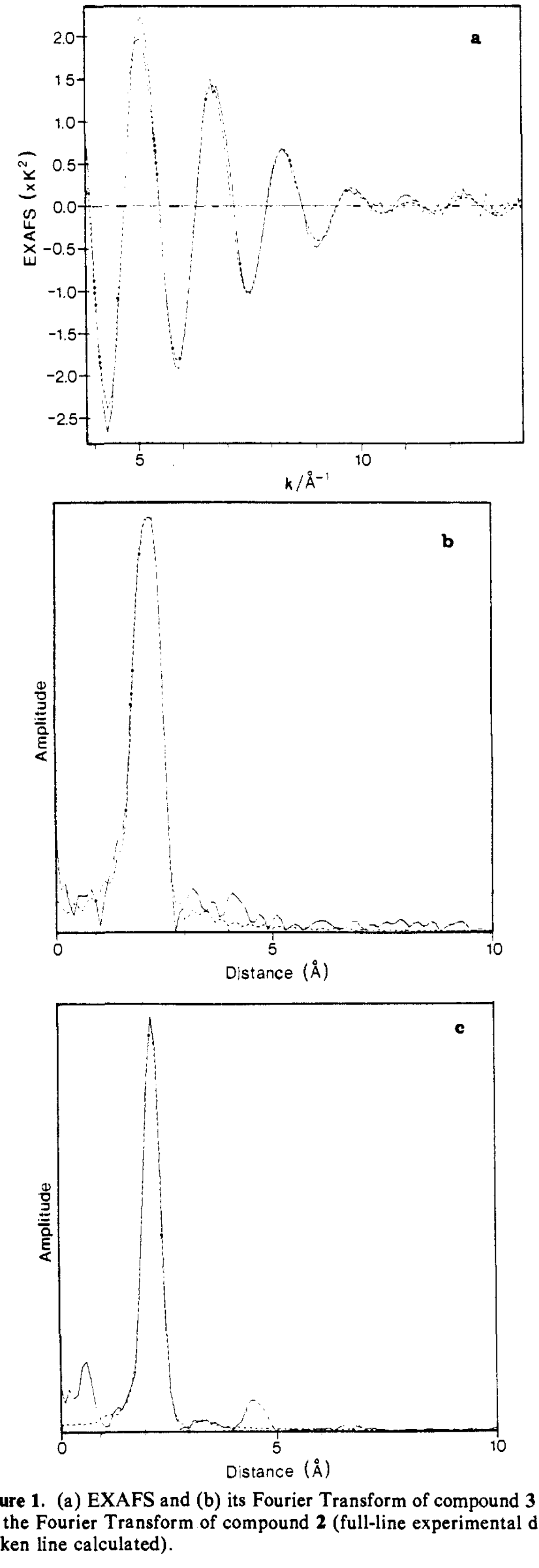


**Figure 1.** (a) EXAFS and (b) its Fourier Transform of compound **3** and (c) the Fourier Transform of compound **2** (full-line experimental data; broken line calculated).

---

[1] For a review of the earlier literature, see: Levason, W.; McAuliffe, C. A.; *Coord. Chem. Rev.* **1974**, *12*, 151-184.

[2] George, B.; Irvine, D. H.; *Nature* (*London*) **1951**, *168*, 164-165. George, P.; *Nature* (*London*) **1952**, *169*, 612-613.

[3] Shimomura, E. T.; Phillippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778-6780.

[4] Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6026-6034.

[5] Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1984**, *23*, 1671-1676 and references therein.

[6] Moss, T. H.; Ehrenberg, A.; Bearden, A. J. *Biochemistry* **1969**, *8*, 4159-4162.

[7] Kadish, K. M.; Rhodes, R. K.; Bottomley, L. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3195-3200.

0002-7863/86/1508-0526$01.50/0