even demetalated chlorophyll, pheophytin, is photooxidized at 77 K in the presence of tetranitromethane.[31] The present ESR observation[32] of the photooxidation of (Chl a·H$_2$O)$_2$ and (Chl a·2H$_2$O)$_2$ by water in the absence of extraneous oxidants thus appears to be of significance in view of the current interest in the in vitro characterization of the primary light reactions in photosynthesis[33] and the in vitro photochemical splitting of water by the chlorophyll.[8]

References and Notes

(1) L. S. Levitt, *Science*, **118**, 696 (1953).
(2) (a) B. Commoner, J. Heise, and J. Townsend, *Proc. Natl. Acad. Sci. U.S.A.*, **42**, 710 (1956); (b) P. Sogo, N. Pon, and M. Calvin, *ibid.*, **43**, 387 (1957); (c) B. Commoner, J. Heise, B. Lippincott, R. Norberg, J. Passinneau, and J. Townsend, *Science*, **126**, 57 (1957); (d) H. Beinert, B. Kok, and G. Hoch, Biochem, *Biophys. Res. Commun.*, **7**, 209 (1962).
(3) J. R. Norris, R. A. Uphaus, H. L. Crespi, and J. J. Katz, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 625 (1971).
(4) B. D. C. Borg, J. Fajer, R. H. Felton, and D. Dolphin, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 813 (1970).
(5) A. Trebst and M. Avron, Ed., "Photosynthesis I", Springer-Verlag, Heidelberg, Germany, 1977.
(6) (a) C. B. Van Niel, *Cold Spring Harbor Symp. Quant. Biol.*, **3**, 138 (1935); (b) S. Ruben, M. Randall, M. D. Kamen, and J. L. Hyde, *J. Am. Chem. Soc.*, **63**, 877 (1941).
(7) H. J. Gorkum, J. J. Tamminga, and J. Haveman, *Biochim. Biophys. Acta*, **347**, 417 (1974).
(8) F. K. Fong, J. S. Polles, L. Galloway, and D. R. Fruge, *J. Am. Chem. Soc.*, **99**, 5802 (1977).
(9) F. Takshashi and R. Kikinchi, *Biochim. Biophys. Acta*, **430**, 490 (1976).
(10) Y. Toyoshima, M. Morino, H. Motoki, and M. Sukigara, *Nature*, **265**, 187 (1977).
(11) F. K. Fong and V. J. Koester, *Biochim. Biophys. Acta*, **423**, 52 (1976).
(12) F. K. Fong and V. J. Koester, *J. Am. Chem. Soc.*, **97**, 6888 (1975).
(13) F. K. Fong, V. J. Koester, and L. Galloway, *J. Am. Chem. Soc.*, **99**, 2372 (1977).
(14) H.-C. Chow, R. Serlin, and C. E. Strouse, *J. Am. Chem. Soc.*, **97**, 7230 (1975).
(15) H. J. Van Gorkom, M. P. J. Pulles, and J. S. C. Wessels, *Biochim. Biophys. Acta*, **408**, 331 (1975).
(16) L. Galloway, J. Roettger, D. R. Fruge, and F. K. Fong, *Bioelectrochem. Bioenerg.*, in press.
(17) B. Kok, *Biochim. Biophys. Acta*, **48**, 527 (1961).
(18) M. R. Wasielewski, M. H. Studier, and J. J. Katz, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 4282 (1976).
(19) S. Boxer and G. L. Closs, *J. Am. Chem. Soc.*, **98**, 5405 (1976).
(20) L. L. Shipman, T. M. Cotton, J. R. Norris, and J. J. Katz, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1791 (1976).
(21) R. H. Clarke and D. R. Hobart, *FEBS Lett.*, **82**, 155 (1977).
(22) In spite of this photochemical inactivity of the exo C-9 dimer and the notable differences between its optical spectrum and the light-induced absorption change spectrum of P700,[23,13] a number of workers[18-20,24-26] consider this dimer a viable model for the P700 reaction center aggregate in vivo. Significantly, the recent synthesis[27] of the covalently linked exo C-9 dimer of BChl a polyhydrate resulted in a molecular adduct that has an absorption maximum at ~800 nm closely matching the absorption maximum of the P800 photochemically inactive pair of BChl a molecules in bacterial photosynthesis.[28] The bacterial reaction center dimer has an absorption maximum at ~870 nm (P870).[28,29] Based on the available information, we propose that the exo C-9 dimer may be a suitable model for some long wavelength form of the light-harvesting system, such as the P800 in bacterial photosynthesis[28] and the antenna Chl a complex at 695 nm in plant photosynthesis.[30]
(23) J. Breton, *Biochim. Biophys. Acta*, **459**, 66 (1977).
(24) R. P. H. Kooyman, T. J. Schaafsma, and J. F. Kleibenker, *Photochem. Photobiol.*, **26**, 235 (1977).
(25) P. Loach, *Photochem. Photobiol.*, **26**, 87 (1977).
(26) J. S. Brown, *Photochem. Photobiol.*, **26**, 319 (1977).
(27) M. R. Wasielewski, U. H. Smith, B. T. Cope, and J. J. Katz, *J. Am. Chem. Soc.*, **99**, 4172 (1977).
(28) (a) D. W. Reed and R. K. Clayton, *Biochem. Res. Commun.*, **30**, 471 (1968); (b) G. Feher, *Photochem. Photobiol.*, **14**, 373 (1971).
(29) (a) J. R. Norris, M. E. Druyan, and J. J. Katz, *J. Am. Chem. Soc.*, **95**, 1680 (1973); (b) G. Feher, A. J. Hoff, R. A. Isaacson and L. C. Acherson, *Ann. N.Y. Acad. Sci.*, **244**, 239 (1975).
(30) J. P. Thornber, R. S. Alberte, R. A. Hunter, J. A. Shiozawa, and K.-S. Kan, *Brookhaven Symp. Biol.*, **No. 28**, 132–148 (1976).
(31) J. Fajer, D. C. Borg, A. Forman, R. H. Felton, D. Dolphin, and L. Vegh, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 994 (1974).
(32) A full experimental characterization of this observation in terms of action and light-induced absorption change spectra will be reported elsewhere.
(33) The in vitro approach to photosynthesis research hopefully provides the molecular basis for the increasing number of biophysical investigations into the structural arrangements in plant[23,34-36] and bacterial[37-39] photosynthetic systems. The observed dependence of the physicochemical and photochemical properties of the various Chl a–H$_2$O dimers on the stereospecific interactions responsible for these dimers suggests the

possibility that Chl a–protein interactions, which are in essence exogenous solvent interactions under physiological conditions, are complementary to the endogenous Chl a–H$_2$O interactions in maintaining the specific structures of the various forms of light harvesting[36] and photoreactive[34,35,37-39] Chl a complexes in vivo. The analogical properties of (Chl a·H$_2$O)$_2$ and P700, listed in Table I, thus indicate that the internal structures of the two species may be of the same molecular origin.
(34) W. Junge, H. Schaffernicht, and N. Nelson, *Biochim. Biophys. Acta*, **462**, 73 (1977).
(35) K. Vacek, D. Wong, and Govindjee, *Photochem. Photobiol.*, **26**, 269 (1977).
(36) M. Lutz, *Biochim. Biophys. Acta*, **460**, 408 (1977).
(37) A. Vermeglio, J. Breton, G. Paillotin, and R. Cogdell, *Biochim. Biophys. Acta*, in press.
(38) T. Mar and G. Gingras, *Biochim. Biophys. Acta*, **440**, 609 (1976).
(39) V. A. Shualov, A. A. Asadov, and I. N. Krakhmaleva, *FEBS Lett.*, **76**, 240 (1977).

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Determination of Local Structures of Platinum Uridine Blues and Purples by Extended X-Ray Absorption Fine Structure Spectroscopy

Sir:

A new class of water-soluble "platinum–pyrimidine blues" have been reported to be promising antitumor agents,[1,2] although more recent results suggest otherwise.[3] These compounds, formed when cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ and related species are reacted with pyrimidines or their analogues,[1] exhibit interesting colors ranging from purple to blue to green. In fact, the existence of deep blue platinum–amide complexes has been known for a long time.[4] Attempts to crystallize the pyrimidine blues for structural studies have met with little success, presumably because the various preparations represent an admixture of clusters with different degree of oligomerization.[1,4] By far the closest structural model to these complexes is that of cis-diammineplatinum α-pyridone blue recently reported by Lippard et al.[5] In an attempt to explore the structural variation of these apparently amorphous compounds, we report here the extended x-ray absorption fine structure (EXAFS) analysis of a purple and a blue compound derived from the reaction of "cis-Pt(amine)$_2$(H$_2$O)$_2$$^{2+}$"[6] with uridine (UH).

The purple compound was obtained by reacting cis-Pt(CPA)$_2$Cl$_2$ (CPA = cyclopropylamine) with uridine. In a typical experiment, 1 mmol of cis-Pt(CPA)$_2$Cl$_2$[7] and 1 mmol of uridine are dissolved in 15 mL of water, and the resulting mixture (pH 7.7) is stirred at 40 °C for 24 h, forming a deep purple solution. Addition of large amounts of ethanol or acetone at this point precipitates the water-soluble chloride salt of the purple cation. Alternatively, addition of an aqueous NaPh$_3$BCN solution to the purple reaction mixture precipitates the water-insoluble [Ph$_3$BCN]$^-$ salt. The [Ph$_3$BCN]$^-$ salt can be dissolved in methanol and purified via chromatography on Sephadex LH20-100 using methanol as eluent. Since the EXAFS spectra of these purple compounds are very similar (viz., independent of the nature of the counteranion such as Cl$^-$ or Ph$_3$BCN$^-$, and the degree of purification), we will describe herein only the EXAFS spectrum of the purified cis-[Pt(CPA)$_2$U](Ph$_3$BCN)$_x$ (**1**, where $x = 1.25 \pm 0.20$).

The blue compound was similarly prepared from cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ and uridine. A solution (pH 7.0) of "cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ (NO$_3$)$_2$$^-$"[6] and uridine (3 mmol each) in 20 mL of water was heated at 38 °C for 48 h to give
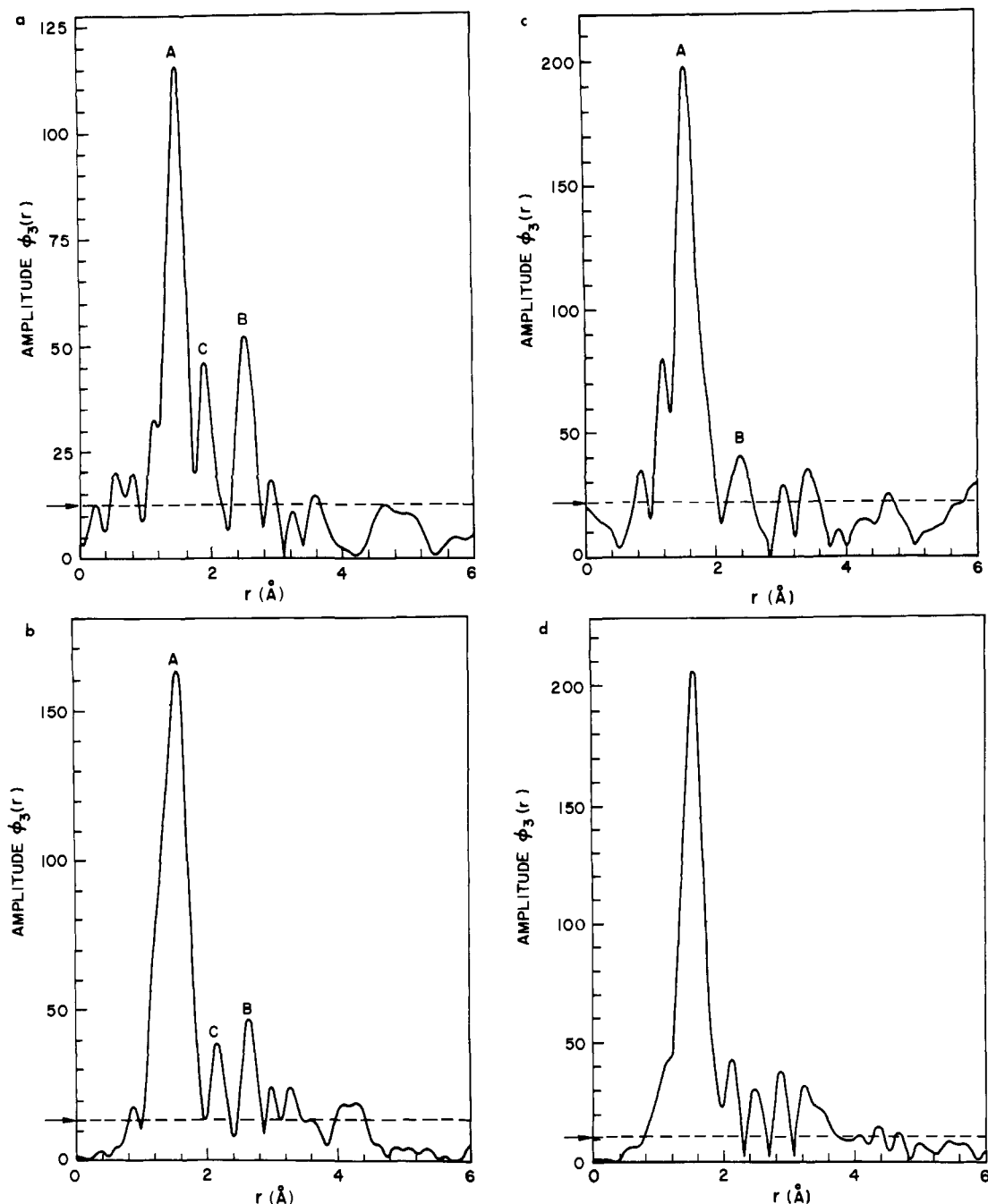
Figure 1. Fourier transforms $\phi_3(r)$ ($k = 2.5\sim15$ Å^{-1}) of the $k^3\chi(k)$ data of (a) platinum uridine purple (1); (b) platinum uridine blue (2); (c) Pt(en)$_2^{2+}$ (3); and (d) Pt(en)Guo$_2^{2+}$ (4). The interatomic distances (R) are related to the radial distribution peaks (r) by the phase shifts (see text).

a deep blue solution. The water-insoluble salt *cis*-[Pt-(NH$_3$)$_2$U](Ph$_3$BCN)$_x$ (2, where $x = 1.25 \pm 0.20$) was then precipitated with NaPh$_3$BCN. We note that the purple Pt-CPA-(pyrimidine) complexes, first reported by Thomson and co-workers,[8] are much more stable than the original Pt-NH$_3$-(pyrimidine) blues,[1] which slowly turn green upon exposure to air and/or light.

EXAFS spectra (Pt L$_1$ edge) in the form of $\mu x = \ln I_0/I$ as a function of x-ray photon energy E (13750$\sim$14750 eV) of 1 and 2 were recorded at room temperature with the synchrotron radiation of EXAFS I at SLAC-SSRL.[9] After conversion of E into photoelectron wavevector k ($k = [(2m/\hbar^2)(E - E_0)]^{1/2}$ where E_0 is chosen as 13 900 eV and varied in the subsequent curve fittings) and μx into $\chi(k) = (\mu - \mu_0)/\mu_0$, the data were multiplied by k^3 and the background removed by a cubic spline technique (four sections with $\sim$4 Å^{-1} each).[10a] Fourier transforms[10a] (in distance r space) of the resulting spectra (k

$= 2.5$-15 Å^{-1}) are shown in Figure 1a and 1b. For comparison, the Fourier transforms of the structurally well-characterized Pt(en)$_2^{2+}$ (3)[11a] and Pt(en)Guo$_2^{2+}$ (4) (en = ethylenediamine; Guo = guanosine)[11b] are also shown in Figure 1c and 1d. It is immediately apparent that the local platinum coordination of 1 is somewhat different from that of 2; both, however, are quite distinct from that of 3 and 4. The major peak (A) in both 1 and 2 can be assigned to the nearest neighboring atoms (N or O) of the coordination sphere.[12] The two smaller but distinct peaks (B and C)[13] in 1 and 2, which are well above the noise levels indicated by the dotted line, can be due to either Pt···C (or Pt···O) and/or Pt-Pt distances. We assign the peak at longer distance (B) to Pt-Pt scattering and the peak at shorter distance (C) to Pt···C and/or Pt···O back-scatterings based on the observation that the amplitude of B is 2$\sim$3 times larger than that would be expected for Pt···C or Pt···O scatterings of similar distance as observed in known systems such as 3 and 4 (cf.
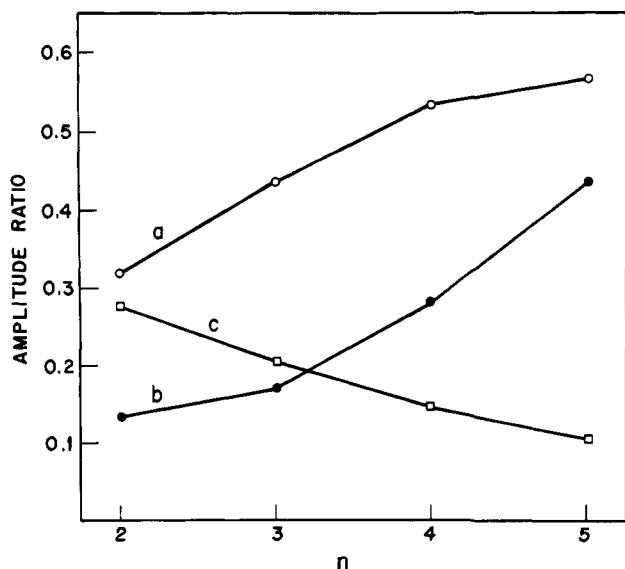
Figure 2. The amplitude ratio as a function of n for the Fourier transform $(\phi_n(r))$ peaks B/A (cf. Figure 1) for **1** (a), **2** (b), and **3** (c).

Table I. Interatomic Distances (from Fourier Transform, $\phi_3(r)$, and Curve Fitting of $k^3\chi(k)$) for the Platinum Uridine Purple (**1**) and Blue (**2**) Compounds and the Model Compounds $Pt(en)_2^{2+}$ (**3**) and $Pt(en)Guo_2^{2+}$ (**4**)

Distance		Purple (**1**)	Blue (**2**)	$Pt(en)_2^{2+}$ (**3**)	$Pt(en)Guo_2^{2+}$ (**4**)
Pt-N(O)[a]	(FT)	1.97	2.01	2.04[c]	2.01
	(CF)	1.97	2.01	2.04[c]	2.01
Pt$\cdots$C(O)	(FT)	2.36	2.63	2.86[c]	2.94
	(CF)	2.43	2.53	2.86[c]	2.92
Pt-Pt[b]	(FT)	2.79	2.93		
	(CF)	2.87	2.94		

[a] For comparison, the average Pt-N(O) distance found in the x-ray structure determination of *cis*-diammineplatinum α-pyridone blue is 2.05 Å.[5] The average Pt-N distance found in $Pt(en)Guo_2^{2+}$ is 2.00 Å.[11b] [b] Note that the intra- and interdimer Pt-Pt distances in *cis*-diammineplatinum α-pyridone blue are 2.779 and 2.885 Å, respectively.[5] [c] The crystallographically observed Pt-N and Pt$\cdots$C distances of 2.04 and 2.86 Å,[11a] respectively, were used to determine the phase shifts for the Pt-X (X = C, N, O) bonds.

Figure 1c and 1d). That is, since the EXAFS amplitude attenuates rapidly as the distance r increases due to the $1/r^2$, $e^{-2r/\lambda}$ (inelastic losses; λ is the electron mean free path) dependence as well as the possibility of either overlaps of similar distances (static disorder) or decreasing bond strength which results in an increase in Debye–Waller factor σ ($e^{-2\sigma^2 k^2}$ dependence), one would expect peak B to be much smaller in amplitude than C if they both involve the same type of scatterer(s).

To provide further evidence for this assignment, we first multiply the EXAFS data $\chi(k)$ (after removal of background) by k^n where n = 2, 3, 4, 5 followed by Fourier transforming the resulting $k^n\chi(k)$ spectra into $\phi_n(r)$. We reason that since heavy scatterers have amplitude envelopes ($\chi(k)$ in k space) which peak at higher k region than the light scatterers, it may be possible to differentiate scatterers with significantly different atomic numbers by calculating the ratio of the amplitude of a particular peak in the Fourier transforms ($\phi_n(r)$ in r space) with respect to a reference peak (such as the major coordination peak which involves only light scatterers) of known nature. Such a ratio should increase as n increases for a heavy scatterer as a result of the increasing weighting on the higher k region. On the other hand, the opposite (or little effect) may be true (vide infra) when a light scatterer is involved. Furthermore, owing to the nonlinearity of the phase shifts as a function of k (viz., the absolute value of the slope decreases as k increases), the position of a light scatterer peak in the Fourier transform will shift to (successively) larger distances as n increases. For heavy scatterers, this effect is less profound and therefore little or no shift will be observed. The amplitude ratios of peak B vs. peak A in **1–3** are shown in Figure 2. It is clear that the amplitude ratio of B/A in both **1** and **2** increases dramatically as n increases, strongly suggesting that peak B is due to a heavy scatterer (knowing that A is a light scatterer peak). Furthermore, while peak A in both **1** and **2** moves to higher distance (up to 0.07 and 0.12 Å in **1** and **2**, respectively) with increasing n, there is essentially no shift of peak B in the radial distribution curve. We therefore identify peak A with light scatterers N and/or O and peak B with heavy scatterer Pt in both **1** and **2**. In sharp contrast, the amplitude ratio of B/A in **3** shows a significant decrease as n increases. We believe that this can be attributed to the much larger Debye–Waller factor of B in comparison with that of A (0.077 vs. 0.050 Å via fitting).[14] Both peaks, however, shift to larger distances with increasing n, in accord with the identification

of both to light scatterers (Pt-N and Pt$\cdots$C, respectively). Finally, for peak C in **1** and **2**, it is difficult to determine its Fourier transform amplitude with respect to peak A accurately owing to the serious overlap of A and C (especially at high n values where A shifts to higher distances). A crude estimate of the amplitude ratio C/A as a function of n indicates that it goes through a maximum at n = 4 in **1** but increases at a slower rate than B/A in **2**. Such different behaviors are not surprising in view of the possible overlaps of two or more nonbonding Pt$\cdots$X (X = C, N, O) peaks at the proximity of these distances.

It is important to note that our assignment of the EXAFS spectra of this class of platinum uridine blues is in accord with other structural[5] or spectroscopic[5,15] evidence of different but nevertheless similar platinum blues. Specifically, our EXAFS data greatly substantiate the existence of distinct Pt-Pt bonding in these compounds.

Knowing the average Pt-N and Pt$\cdots$C distances of 2.043 and 2.855 Å, respectively, in $Pt(en)_2^{2+}$ (**4**)[11a] as well as the first-shell Pt-Pt distances of 2.775 Å in Pt metal,[11c] we obtain, for E_0 of 13900 eV, phase shifts of 0.46, 0.46, and 0.27 Å, for the Pt-N, Pt-C, and Pt-Pt vectors, respectively (for $\phi_3(r)$ only). Assuming that the phase shift for Pt-O is similar to either Pt-N or Pt$\cdots$C (0.46 Å), we tabulate in Table I the corrected interatomic distances for the four complexes[12] based on phase shift transferability.[16,17]

Another way of deducing interatomic distances from EXAFS spectra is via Fourier filtering[10a] followed by curve fitting.[10b] For closely spaced or multicomponent peaks this latter method gives more accurate data and higher resolution.[16c,17] The three major peaks in each of the Fourier transforms were filtered with smooth windows of widths ranging from 0.7 to 1.4 Å and transformed back into k space. The resulting EXAFS spectra were then fitted with experimentally determined Pt-N, Pt$\cdots$C (from $Pt(en)_2^{2+}$), and Pt-Pt (from platinum metal) amplitude and phase shift functions (assuming transferabilities for both[16,17]). Single distance models with four variables (overall scale, distance r, Debye–Waller factor σ and ΔE_0) described elsewhere were least squares refined.[17] The results are also listed in Table I.[17c] It is obvious that the two sets of distances agree quite well except in cases where the possibilities of multicomponent and/or multidistances prevail.

Judged from these interatomic distances, we conclude that the local platinum coordination of **1** and **2** involves Pt-X (where X = N or O) bonds of $\sim$2.00 Å and a "partial" but distinct Pt-Pt bond of $\sim$2.90 Å. The coordination sphere is

probably *cis*-Pt(amine)$_2$XY where X, Y = N$_3$, O$_2$, or O$_4$ of the uridinato ligand. A curious difference between **1** and **2** is the shortening of all three types of distances, suggesting a relief in steric hindrance despite the replacement of the unsubstituted amines by the bulkier cyclopropylamines. Furthermore, the shorter Pt···C(O) distance in **1** in comparison with that in **2** seems to suggest a smaller ring size involving the platinum coordination and the uridinate. While EXAFS spectroscopy does not provide detailed stereochemical information, it is not unreasonable to propose plausible structures based on the determined distances (cf. Table I) and other pertinent structural evidence of analogous systems. One possible structure is an oligomeric stack of platinums coordinated to two amines and N$_3$ and O$_4$ (or N$_3$ and O$_2$) of the uridinate in a square-planar configuration, giving rise to short Pt···C distances of ~2.5 Å within the four-membered PtNCO ring and Pt–Pt distances of ~2.9 Å perpendicular to platinum coordination plane (presumably through partial oxidation).[18] A second possibility is a structure analogous to *cis*-Pt(NH$_3$)$_2$(α-pyridone) blue,[5] with dimers of two *cis*-Pt(NH$_3$)$_2$ units in a somewhat twisted eclipsed configuration, one bonded to two nitrogen (or one nitrogen and one oxygen) and the other bonded to two oxygen (or one nitrogen and one oxygen) atoms of two separate uridinato ligands (here the nitrogen and the oxygen atoms refer to N$_3$ and O$_2$ or O$_4$, respectively). The metal atoms can form partial Pt–Pt bond(s) at ~2.9 Å. The heterocyclic five-membered Pt$_2$NCO rings give rise to no short Pt···C(O) contacts below 2.9 Å. However, slight tilting of the Pt–N$_3$ bond toward the uncoordinated oxygen atom O$_2$ (or O$_4$) can give rise to Pt···O$_2$ (or O$_4$) and/or Pt···C$_2$ (or C$_4$) distances of ~2.6 Å, in accord with the second shortest distance in the EXAFS spectrum. This weak but significant axial interaction is analogous to that of the nitrate ions in *cis*-Pt(NH$_3$)$_2$(α-pyridone) blue (Pt···ONO$_2$ distance of 3.30 Å).[18] As in the latter compound, two or more such units can be linked together to form higher oligomers. The extension of such Pt–Pt bonding could explain the observed color change from blue to green upon standing.[19] We believe that the large number of plausible isomers or oligomers (and the numerous reaction pathways for their interconversion) with similar local structures in these platinum pyrimidine blue complexes accounts to a large extent for the difficulty in crystallizing these amorphous materials.

In conclusion, EXAFS spectroscopy not only substantiates the existence of partial but distinct Pt–Pt bonding in "platinum-pyrimidine blues", but also provides indirect evidence about the local structure around the platinum coordination. The exact degree of oligomerization cannot be definitively established in this study. The degree of Pt···Pt bonding (due to partial oxidation), which manifests itself in the Pt–Pt distance, is reminiscent of that observed in a number of one-dimensional platinum complexes.[20] While the relevance of such partial Pt···Pt bonding to the possible antitumor activity of these complexes has yet to be demonstrated, it is tempting to speculate that, under real physiological conditions, these water-soluble platinum blues could be reduced back to platinum(II) complexes prior to their attack on DNA.

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References and Notes

(1) (a) J. P. Davidson, P. J. Faber, R. G. Fischer, Jr., S. Mansy, H. J. Peresie, B. Rosenberg, and L. Van Camp, *Cancer Chemother. Rep.*, **59**, 287 (1975); (b) B. Rosenberg, *ibid.*, **59**, 589 (1975).

(2) (a) R. J. Speer, H. Ridgway, L. M. Hall, D. P. Stewart, K. E. Howe, D. Z. Lieberman, A. D. Newman, and J. M. Hill, *Cancer Chemother. Rep.*, **59**, 629 (1975); (b) J. M. Hill, E. Loeb, A. MacLellan, N. O. Hill, A. Khan, and J. King, *ibid.*, **59**, 647 (1975).

(3) J. M. Hill, E. Loeb, A. S. Pardue, A. Khan, N. O. Hill, J. J. King, and R. W. Hill, *J. Clin. Hematol. Oncol.*, **7**, 681 (1977).

(4) For a relatively recent account of "Platinblau", see D. B. Brown, R. D. Burbank, and M. B. Robin, *J. Am. Chem. Soc.*, **91**, 2895 (1969).

(5) J. K. Barton, H. N. Rabinowitz, D. J. Szalda, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 2827 (1977), and references cited therein.

(6) The solution which results from the treatment of Pt(amine)$_2$Cl$_2$ with AgNO$_3$ was thought to contain primarily [Pt(amine)$_2$(H$_2$O)$_2$]$^{2+}$, but recent crystallographic evidence indicates that appreciable amounts of oligomeric species such as [Pt(amine)$_2$(OH)]$_2$$^{2+}$, [Pt(amine)$_2$(OH)]$_3$$^{3+}$, and [Pt(amine)$_2$(OH)]$_4$$^{4+}$ may also be present. See the following articles: (a) R. Faggiani, B. Kippert, C. J. L. Lock, and B. Rosenberg, *J. Am. Chem. Soc.*, **99**, 777 (1977); (b) C. J. L. Lock, J. Bradford, R. Fagglani, R. A. Speranzini, G. Turner, and M. Zvagulis, *J. Clin. Hematol. Oncol.*, **7**, 63 (1977).

(7) T. A. Connors, M. Jones, W. C. J. Ross, P. D. Braddock, A. R. Khokhar, and M. L. Tobe, *Chem. Biol. Interact.*, **5**, 415 (1972).

(8) A. J. Thomson, I. A. G. Roos, and R. D. Graham, *J. Clin. Hematol. Oncol.*, **7**, 242 (1977).

(9) For details of experimental setup, see (a) P. Eisenberger, B. Kincaid, S. Hunter, D. Sayers, E. A. Stern, and F. Lytle in *Proc. Int. Conf. Vacuum Ultraviolet Radiat. Phys., 4th*, 806–807 (1974); (b) B. M. Kincaid and P. Eisenberger, *Phys. Rev. Lett.*, **34**, 1361 (1975).

(10) Data analysis programs employed include (a) cubic spline background removal, Fourier transform, and Fourier filtering written by B. M. Kincaid; (b) least-squares curve-fitting written by A. L. Simons and B. K. Teo.

(11) (a) W. A. Freeman, *Inorg. Chem.*, **15**, 2235 (1976); (b) R. W. Gellert and R. Bau, *J. Am. Chem. Soc.*, **97**, 7379 (1975); (c) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 403.

(12) At this stage it is not possible to differentiate between the light atoms (C vs. N vs. O) or to resolve nonequivalent distances in a given shell.

(13) These "second-shell" distances are admittedly less accurate than the first-shell distances primarily due to their smaller amplitudes and the possibilities of overlaps of similar distances. However, it should be emphasized that these peaks cannot be due to either "side bands" of the major peak or random noise since different preparations of same (or similar) cationic species give rise to identical (or similar) spectra. Neither can these peaks be attributed to the residual structure from the preceding L$_{II}$ edge (608.9 eV lower in energy) since EXAFS of the L$_{II}$ edge attenuates well before it runs into the L$_I$ edge, especially for compounds with mainly light scatterers in the coordination sphere. The advantage of L$_I$ over L$_{II}$ or L$_{III}$ edges lies in the fact that only one phase shift is needed for each atom pair which greatly simplifies the interpretation.

(14) The larger Debye–Waller factor of peak B effectively attenuates the EXAFS amplitude at high *k* region such that as *n* increases the Fourier transform amplitude of B vs. A decreases.

(15) (a) B. Lippert and B. Rosenberg, quoted in R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *J. Am. Chem. Soc.*, **99**, 777 (1977); (b) B. Lippert, *J. Clin. Hematol. Oncol.*, **7**, 26 (1977).

(16) (a) E. A. Stern, D. E. Sayers, and F. W. Lytle, *Phys. Rev. B.*, **11**, 4836 (1975); (b) P. H. Citrin, P. Eisenberger, and B. M. Kincaid, *Phys. Rev. Lett.*, **36**, 1346 (1976); (c) S. P. Cramer, T. K. Eccles, F. Kutzler, K. O. Hodgson, and S. Doniach, *J. Am. Chem. Soc.*, **98**, 8059 (1976); (d) P. A. Lee and G. Beni, *Phys. Rev. B.*, **15**, 2862 (1977).

(17) (a) B. K. Teo, P. A. Lee, A. L. Simons, P. Eisenberger, and B. M. Kincaid, *J. Am. Chem. Soc.*, **99**, 3854 (1977). (b) P. A. Lee, B. K. Teo and A. L. Simons, *ibid.*, **99**, 3856 (1977). (c) The drastically different phase shifts and amplitude functions of Pt vs. N/O/C also serve as strong evidence supporting our assignments.

(18) However, we emphasize that we cannot rule out other possible stereochemistry with similar local structure. Some examples are (a) a dimer with two platinum atoms each coordinated to two amines (in a cis configuration), one N$_3$ from one uridinate, and the other platinum in a square-planar configuration; the oxygen atoms of each of the two uridinates can further weakly coordinate to the axial position(s) of the platinums from the same or adjacent molecules (the latter results in a three-dimensional polymeric structure); (b) a dimer with two *cis*-Pt(amine)$_2$ groups bridged symmetrically by two uridinates via N$_3$, O$_2$, or O$_4$; (c) etc.

(19) A solid sample of **2** was observed to turn green over a period of several months. The EXAFS spectrum of the green compound is very similar to that of **2**.

(20) A. H. Reis, Jr., and S. W. Peterson, *Inorg. Chem.*, **15**, 3186 (1976).

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