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Synthesis and Structure of Bis(μ-1-methylhydantoinato-*N*,*O*)bis(*cis*-diammineplatinum(II)) Dinitrate. A Structural Analogue of Platinum Blues

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Platinum blues have long been of interest to chemists,[1-11] but to date, only *cis*-diammineplatinum α-pyridone blue has been fully characterized structurally.[3,4] However, comparative studies[2-5] suggest that all the known blue compounds are mixed-valent, metal–metal-bonded, amidate-bridged oligomers. Recently, nonblue compounds have been shown to display a geometry similar to that of the α-pyridone blue.[12-17] Here we report on such a compound, **1**, which is obtained, almost quantitatively, from the reaction of *cis*-diammineplatinum(II) with 1-methylhydantoin and which may be oxidized by H_2O_2 (pH 1, NO_3H) to a blue-green paramagnetic species, **2**.[18] It is noteworthy that nonsubstituted hydantoin reacts with $[Pt(NH_3)_2]^{2+}$ directly, leading to a blue-green product, **3**.[19] The infrared and Raman spectra of these three species look almost identical[21] as regards the bands related to the ligands and, analytically, they display the same platinum to ligand ratio, i.e., 1. At this stage, it was suspected that the yellow compound **1** would be a structural analogue of the α-pyridone yellow,[14] and therefore an X-ray crystal structure analysis[22] was initiated.

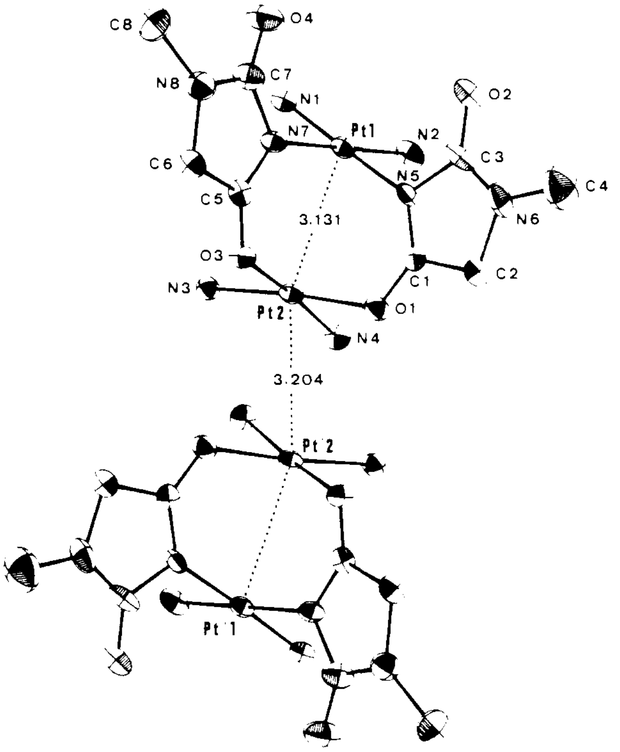

Figure 1. Structure of $[Pt_2(NH_3)_4(C_4H_5N_2O_2)_2]_2(NO_3)_4{\cdot}H_2O$ showing the 20% probability thermal ellipsoids and omitting nitrate ions, water molecule, and hydrogen atoms.

Table I. Selected Interatomic Distances and Angles[a]

	dist, Å		angle, deg
Pt1–Pt2	3.131	Pt1–Pt2–Pt'2	160.5
Pt2–Pt2'	3.204	N1–Pt1–N2	89.5
Pt1–N1	2.04	N1–Pt1–N5	177.5
Pt1–N2	2.03	N1–Pt1–N7	89.5
Pt1–N5	2.02	N2–Pt1–N5	89.6
Pt1–N7	1.98	N2–Pt1–N7	178.6
Pt2–N3	2.04	N5–Pt1–N7	91.0
Pt2–N4	2.04	N3–Pt2–N4	91.6
Pt2–O1	2.05	N3–Pt2–O1	174.9
Pt2–O3	2.05	N3–Pt2–O3	89.6
		N4–Pt2–O1	88.5
		N4–Pt2–O3	174.8
		O1–Pt2–O3	89.9

[a] Atoms are labeled as in Figure 1. Standard deviations in parentheses occur in the last significant figure.

A mixture of *cis*-diammineplatinum(II) hydrolysis products was prepared from 1.66 mmol of *cis*-$Pt(NH_3)_2Cl_2$ and 3.32 mmol of $AgNO_3$ in 10 mL of water. After removing the silver chloride by centrifugation, 10 mL of an aqueous solution containing 1.66 mmol of 1-methylhydantoin was added. The pH was adjusted to 5.0 with NaOH, and the resulting solution was left to stand in the dark at 40 °C. The pH was kept constant by continuous addition of NaOH. After 6–8 days, an equivalent amount of base was added, causing the ligand to be completely deprotonated and the reaction was stopped. Air evaporation of the solution provided

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(18) The solid-state EPR spectrum of **2** is approximately axial, having g values of 1.976 ($g_\parallel$) and 2.498 ($g_\perp$) with extensive hyperfine coupling.

(19) The study of this complex is still in progress. Its EPR spectrum is very similar to that of **2** ($g_\parallel \cong 1.97$; $g_\perp \cong 2.43$). It is suggested that this compound is identical with the species mentioned in ref 20.

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(21) The main infrared and Raman bands of **1** are as follows (solid sample, room temperature): IR 3260 (s), 3120 (sh), 2950 (m), 2920 (m), 1730 (s), 1630 (sh), 1610 (vs), 1480 (sh), 1445 (m), 1380 (s), 1350 (s), 1330 (s), 1240 (m), 1180 (sh), 1160 (m), 1040 (m), 985 (m), 900 (m), 865 (sh), 830 (sh), 820 (m), 765 (s), 727 (m), 665 (m), 660, 610 (s), 520 (w), 490 (w), 470 (m) cm^{-1}; Raman (514.5-nm excitation) 2945 (vs), 2910 (m), 2360 (m), 2300 (s), 1820 (w), 1730 (m), 1480 (w), 1460 (m), 1390 (m), 1250 (m), 1160 (s), 1060 (vs), 1040 (vs), 920 (m), 720 (s), 680 (m), 550 (sh), 520 (s), 510 (sh) cm^{-1}.

(22) X-ray analysis. compound **1** crystallized in the triclinic system (space group $P\bar{1}$) with the following cell parameters: $a = 8.5546$ (10), $b = 11.2325$ (12), $c = 13.3208$ (13) Å; $\alpha = 110.85$ (1), $\beta = 92.57$ (1), $\gamma = 105.97$ (2)°; $\rho_{obsd} = 2.40$, $\rho_{calcd} = 2.39$ g/cm^3 for $Z = 2$ formula units. The structure was solved by standard heavy-atom Patterson and Fourier methods by using 3877 reflections collected with a Nonius CAD-4 diffractometer ($2\theta_{max}$ 61.2°; radiation Mo Kα λ 0.710 69 Å). Refinement of the absorption corrected data with all atoms assigned anisotropic temperature parameters, except hydrogen and nitrate atoms, which were refined isotropically with constraints, has converged to a value of 0.048 for $R = \sum||F_o| - |F_c|/|\sum|F_o|$. Atomic positional and thermal parameters are provided as supplementary material.

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Table II. Geometric Properties of Selected "Dimer" and "Tetramer" Platinum Complexes[a]

		α-pyridone		1-methylthymine		1-methyluracile
	1	dimer-of-dimer[14]	blue[3,4]	head-to-tail dimer[12]	head-to-head dimer[13]	head-to-tail dimer[16]
Pt-Pt, Å	3.131	2.88	2.77	2.97	2.91	2.95
	3.204	3.13	2.88			5.10
Pt-NH_3 (av), Å	2.04	2.05	2.06	2.06		2.05
Pt-N (av), Å	2.00	2.05	2.05	2.04		2.05
Pt-O (av), Å	2.05	2.04	2.04	2.03		2.05
ϕ,[b] deg	38.6	30.0	27.4	36.1	29.5	35.8

[a] All the complexes are platinum(II) complexes but the α-pyridone blue, platinum oxidation state 2.25. [b] Tilting angle between adjacent Pt coordination planes.

microneedles of **1**. The yield was 0.576 g (85%) within 1-2 days. Slow recrystallization from water gave crystals up to 0.5 mm long. They have the composition[23] $[Pt_2(NH_3)_4(C_4H_5N_2O_2)_2]_2(NO_3)_4\cdot H_2O$.

The structure of the molecular cation is shown in Figure 1, and selected interatomic distances and angles are given in Table I. It may be regarded as a dimer-of-dimer, the two dimeric units being related through an inversion center. In each dimer, two roughly planar[24] *cis*-diammineplatinum(II) units are bridged in the cis position by two deprotonated ligands arranged head-to-head. Linkage of the two dimers is achieved by intrachain hydrogen bonds between the coordinated ammines of one dimer and the oxygen atoms of the neighboring dimer. The molecular cation is surrounded by four nitrate anions and a water molecule, leading to a platinum formal oxidation state of 2 in accordance with its diamagnetic behaviour.

In Table II, structural parameters of selected "dimer" and "tetramer" platinum complexes are compared. As expected for a platinum(II) species, the Pt-Pt distances in **1** are rather long. They are similar to those found in the *cis*-diammineplatinum(II) pyrophosphate dimer (3.229 and 3.11 Å)[25] but are somewhat longer than those observed for the platinum(II) α-pyridone dimer-of-dimer.[14] The lengthening is more pronounced for the bridged Pt-Pt distance than for the nonbridged one, and this causes the two metal-metal distances occurring in a tetramer unit to differ by only 0.07 Å. This lengthening of the Pt-Pt distance offers an explanation for the exclusive formation of **1** in the reaction of 1-methylhydantoin with *cis*-diammineplatinum(II) since it may reasonably be assumed that, in the partially oxidized compound **2**, the Pt-Pt distance would present a much shorter value (ca. 2.7-2.8 Å) to accomplish metal-metal interaction. The need of drastic conditions for converting **1** into **2** and the very low stability of **2** in solution support this rationale. However, the reasons for this lengthening still remain unclear. They do not originate in geometric requirements of the five-membered ligand since the N···O bite distance (average 2.4 Å) would easily accommodate a shorter Pt-Pt distance. Moreover the discrepancy between these two distances causes the canting of the adjacent coordination planes to be longer than in the other related dimers or tetramers reported so far (cf. Table II). Furthermore, short Pt-Pt distances (ca. 2.7 Å) have recently been found in a tan compound (platinum oxidation state 2.5) formed by a five-membered heterocyclic ligand, α-pyrrolidone.[26] A possible clue to the origin of this lengthening may lie in the occurrence of a repulsive interaction between the NH_3 and NCH_3 groups within each dimer.

Finally, the particular behaviour of 1-methylhydantoin has to be emphasized since it reacts with $[Pt(NH_3)_2]^{2+}$ to yield, almost quantitatively, a nonblue product, whereas similar ligands (pyrimidines, α-pyridone, α-pyrrolidone, hydantoin) chiefly lead to blue or tan species. Thus, this ligand allows a tetranuclear array of platinum atoms to form readily but disfavors the subsequent conversion into a partially oxidized species. In this respect, compound **1** can be viewed as a borderline case among the nonblue species. Other details of the structure and solution properties will be published later.

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Supplementary Material Available: Atomic positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(23) Anal. Calcd for $PtC_4H_{11.5}N_5O_{5.25}$: C, 11.75; H, 2.84; N, 17.13; Pt, 47.73. Found. C, 11.67; H, 2.51; N, 17.21; Pt, 47.58.

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Intramolecular [6 + 4] Cycloadditions: Intramolecular Control of Periselectivity

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Intramolecular cycloadditions are versatile methods for polycyclic natural product synthesis that often proceed with pronounced regioselectivity and stereoselectivity to generate bicyclic systems with the production of four new chiral centers.[1-3] We have expanded this repertoire beyond the usual six π electron cases to intramolecular cycloadditions involving ten π electrons. We report the intramolecular [6 + 4] cycloaddition and examples of side-chain and substituent control of regioselectivity and periselectivity in intramolecular cycloadditions.

Following the techniques developed for intramolecular Diels-Alder cycloadditions of *o*-xylylenes,[4,5] we have prepared a benzocyclobutene with a suitably disposed fulvene side chain by the method shown in Scheme I. Alkylation of cyanobenzocyclobutene,[6] **1**, with LDA and 5-chloro-2-pentanone ethylene ketal in THF containing HMPA gave **2** (70%), which was deprotected with acid and converted to the fulvene with sodium cyclopentadienide in THF to give **3**, a light yellow oil,[7] in 56% yield.

The fulvene **3** was heated at 180 °C in *o*-dichlorobenzene for 7 h to produce an inseparable mixture of cyclopentadiene isomers, **4**, in 60% yield (Scheme II). The major product, **4a**, has a methyl

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