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- [7] **6** [black crystals, m.p. 259–261°C; IR (KBr): 1610, 1595, 1570 cm⁻¹; ¹H-NMR (250 MHz, CH₂Cl₂): δ=4.27 (s, 6H, 5-OCH₃, 5'-OCH₃), 7.69 (s, 2H, H-12, 12') was synthesized from **1** by reduction with HI/HOAc, alkylation with Me₂SO₄/NaOH, and subsequent oxidative coupling (FeCl₃/DMF).
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Electrochemiluminescence of Tetrakis(diphosphonato)diplatinate(II)**

By Arnd Vogler* and Horst Kunkely

Intermolecular photoredox reactions of electronically excited transition metal complexes with reducing or oxidizing agents have been the subject of intensive study in recent years^[1]. The converse of such processes leads, under suitable conditions, to chemiluminescence (CL). A special case is electrochemiluminescence (ECL). So far only a few investigations have been carried out on the CL^[2] or ECL^[3] of metal complexes, even though such studies provide important information on the mechanism of redox reactions; hitherto, such investigations have been restricted to complexes which contain 2,2'-bipyridyl or related ligands. The luminescent states are almost exclusively of the charge transfer (metal→ligand)-type. Herein we report on the ECL of [Pt₂(P₂H₂O₅)₄]⁴⁻ (A^{4⊖}). Both the associated redox processes as well as the ECL itself lead to changes in the metal-metal bonding in the binuclear platinum complex.

In A^{4⊖} the two Pt^{II} centers are bridged by the dianions of the diphosphonic acid. The metal-metal interaction gives rise to the following series of MOs in order of increasing energy: 1a_{1g}(5d_{z²}) < 1a_{2u}(5d_{z²}) < 2a_{1g}(6p_z) < 2a_{2u}(6p_z)^[4]. The a_{1g} orbitals are bonding and the a_{2u} orbitals are antibonding. In the ground state of A^{4⊖}(1a_{1g}²1a_{2u}²) the formal Pt–Pt bond order is therefore 0. At room temperature and in solution, A^{4⊖} shows an intense photoluminescence of the lowest excited state (1a_{1g}²1a_{2u}¹2a_{1g}¹) with bond order 1^[4]. Both a weak fluorescence (λ_{max} = 407 nm) of the singlet ¹A_{2u} as well as an intense phosphorescence (λ_{max} = 517 nm) of the accompanying triplet ³A_{2u} is observed^[4].

A 1-cm spectrophotometer cell fitted with two platinum-foil electrodes was used for the ECL investigations. Solutions of A^{4⊖} as the tetrabutylammonium salt in oxygen-free anhydrous acetonitrile was subjected to an alternating current electrolysis with variable frequency (*sine-wave* generator, Kröncke Mod. 1246) using nBu₄N[⊕]BF₄[⊖] as supporting electrolyte. With an effective voltage of 4 V and frequency of 280 Hz and a current of 13 mA, a marked green luminescence was observed at one electrode, even with the naked eye. The electrochemiluminescence (Fig. 1) in the long wave region was identical with the photophosphorescence, but no short-wave fluorescence could be observed.

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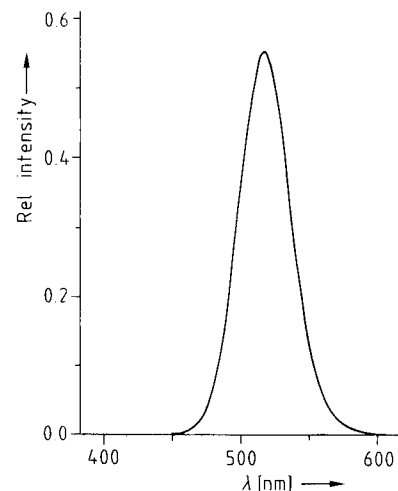


Fig. 1. Electrochemiluminescence spectrum of a solution of 2×10^{-4} M (nBu₄N)₄[Pt(P₂H₂O₅)₄] and 0.1 M (nBu₄N)BF₄ in CH₃CN; alternating current of 4 V and 280 Hz.

From these observations we conclude that A^{4⊖} is oxidized to A^{3⊖} during the anodic phase and reduced to A^{5⊖} during the cathodic phase. The recombination



furnishes sufficient energy to generate one of the two product molecules in the lowest excited state, the triplet ³A_{2u}(^{*}).

The Pt–Pt bond is strengthened (bond order 1/2), both in the oxidation of A^{4⊖} to A^{3⊖} (ground state: 1a_{1g}²1a_{2u}¹) and the reduction to A^{5⊖} (ground state: 1a_{1g}²1a_{2u}²2a_{1g}¹). On the other hand, the recombination involves both a bond-weakening (A^{4⊖} in the ground state) and bond-strengthening (A^{4⊖} in the excited state).

Since the ECL spectrum shows only the phosphorescence, and not the fluorescence, the potential difference between A^{3⊖} and A^{5⊖} is only sufficient to reach the lowest triplet ³A_{2u} (≈ 2.6 V). The energy of the superposing singlet ¹A_{2u} (≈ 3.3 V) is apparently not attained anymore.

The high frequency necessary for observation of the ECL would indicate that the oxidized (A^{3⊖}) or reduced complex (A^{5⊖}), or both, have a very short half-life. This has recently been confirmed: A^{3⊖} exists only in the solid state in the form of Pt₂ chains which are bridged by halide X[⊖]^[5]; in solution A^{3⊖} immediately disproportionates into A^{4⊖} and AX₂^{4⊖}. A^{5⊖} was generated by pulse radiolysis, but rapidly disappeared ($k = 2.9 \times 10^4$ s⁻¹)^[6]. It is therefore understandable that it was not possible to determine the redox potentials for the reversible one-electron process by cyclovoltammetry. On attempting to quench the photoluminescence of A^{4⊖} by electron donors and acceptors, it was however possible to estimate the redox potentials. Donors such as *N,N*-dimethylaniline ($E_{1/2} = 0.78$ V vs SCE) and *N,N*-dimethyl-*p*-toluidine ($E_{1/2} = 0.65$ V) could not quench the photoemission of A^{4⊖}. Even the strong reducing agent *N,N,N',N'*-tetramethyl-*p*-phenylenediamine ($E_{1/2} = +0.24$ V vs SCE) did not effect reduction of A^{4⊖} in the ³A_{2u} state. It follows, therefore, that the reduction of A^{4⊖} in the ground state requires at least $E_{1/2} = -2.3$ V vs SCE. In contrast, the phosphorescence of A^{4⊖} is quenched by relatively weak acceptors^[7]. It is estimated that the oxidation of A^{4⊖} takes place at potentials of less than $E^0 = +1.6$ V vs NHE. The alternating potential of 4 V (2 V

cathodic and 2 V anodic) necessary for observation of the ECL is needed for the reduction of $A^{4\ominus}$, whereas smaller potentials should suffice for the oxidation.

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Na_3P_{21} and Li_3P_{21} , the First Polyphosphides with Isolated P_{21}^{3-} Groups**

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We recently reported on the synthesis of the polyphosphides Li_3P_7 ^[1] and Li_2P_{16} ^[2] by nucleophilic cleavage of white phosphorus with lithium dihydrogen phosphide. Salts containing isolated P_n^{m-} anions are of current interest because of their structural relationship with the phosphorus hydrides P_nH_m and organophosphanes P_nR_m and because of their potential use as building blocks for the synthesis of novel polyphosphorus compounds. Herein we report on the synthesis of a trisodium hencosaphosphide and a trilithium hencosaphosphide containing isolated P_{21}^{3-} groups.

Na_3P_{21} **1**^[3] is formed on reaction of white phosphorus with substoichiometric amounts of sodium in 1,2-dimethoxyethane or tetrahydrofuran (THF). Other products of the reaction include Na_2P_{16} ^[4], Na_2HP_7 ^[4], and further, as yet unidentified polyphosphides. The product pattern is strongly dependent on the reaction conditions: The best crude yield of **1** (up to 75 P-% of the soluble reaction products) is obtained at a P:Na ratio of 2:1 (not 7:1!) in boiling THF. $\text{Na}_3\text{P}_{21} \cdot 15\text{THF}$, a solvent adduct of **1**, can be isolated analytically pure by crystallization at -20°C . On drying, the orange needle-shaped crystals lose a part of the solvent of crystallization with concomitant decomposition to Na_2P_{16} and other polyphosphides. Above -10°C liquefaction occurs, whereas at room temperature slow disproportionation takes place. The hencosaphosphide is only slightly sensitive to oxidation but strongly sensitive to hydrolysis.

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Li_3P_{21} **2** is formed as main product on reaction of Li_3P_7 ^[1,5] with iodine or 1,2-dibromoethane as well as on metalation of P_7H_3 ^[5] with lithium dihydrogen phosphide or *n*-butyllithium under suitable reaction conditions^[6]. **2** is also formed on decomposition of LiH_2P_7 ^[7] and Li_2HP_7 ^[7] at room temperature and on nucleophilic cleavage of white phosphorus^[8]. Because of the similarity to **1** we have not isolated **2**.

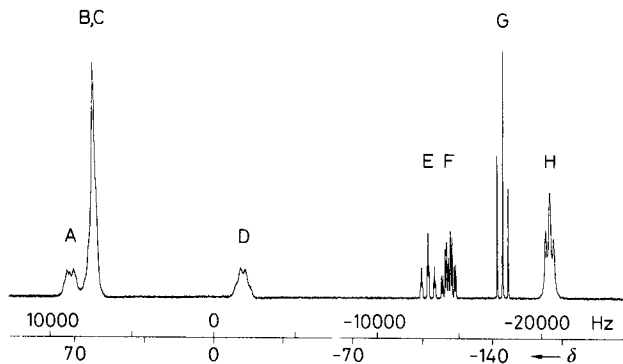
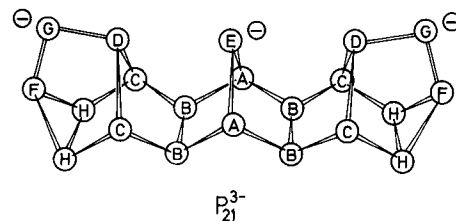


Fig. 1. ^{31}P -NMR spectrum of Na_3P_{21} in tetrahydrofuran/dimethylformamide (ca. 2:1) at 243 K (121.497 MHz).

1 and **2** show identical ^{31}P -NMR spectra, in which seven groups of signals occur at $\delta = +72$, $+61$, -15 , -108 , -118 , -146 and -169 (intensity ratio 2:8:2:1:2:2:4) (Fig. 1). The number and intensities of the groups indicate a symmetrical P_{21} skeleton. On the basis of their splitting patterns, chemical shifts and relative



intensities the signal groups D, F, G, and H are each to be assigned to five P atoms from two equivalent P_7 cages with nortricyclic structure^[9]. As evidenced by the triplet-like signal group E, a P_7 -substructure analogous to norbornane with negative charge on the P atom of the P_1 -bridge is present as linkage between the two cages. Correspondingly, from the intensities of the remaining signals it follows that the downfield group A arises from the two central bridgehead atoms^[10], while the neighboring intense signal B, C arises from the remaining two pairs of four equivalent P atoms.

The constitution of the P_{21}^{3-} ion as decacyclo-[9.9.1.0^{2,10}.0^{3,7}.0^{4,9}.0^{6,8}.0^{12,20}.0^{13,17}.0^{14,19}.0^{16,18}]hencosaphosphide(3-) is confirmed by the homoscalar-correlated 2D- ^{31}P -NMR spectrum (COSY spectrum^[11]) of **1** (Fig. 2). All $^1J(\text{PP})$ couplings of the directly linked and non-degenerated P atoms appear as cross-peaks.

The P_{21}^{3-} ion is the largest isolated $\text{P}_n(m)$ unit group known so far. In K_4IP_{21} synthesized by von Schnering et al.^[12] these P_{21}^{3-} groups are linked, after opening of their three-membered rings, to give a polymeric $[\text{P}_7]^-$ -structure. As a conjuncto-phosphane the isolated $\text{P}_{21}(3)$ skeleton is made up of a $\text{P}_7(5)$ unit analogous to