A Trinuclear Palladium(II) Complex with Bridging 2-Hydroxyacetophenone N^4-Ethylthiosemicarbazone Ligands – An Unusual Dimethylformamide Promoted Deprotonation and Aggregation

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Received August 8, 1997

Keywords: Trinuclear *triangulo* palladium complex / 2-Hydroxyacetophenone N^4-ethylthiosemicarbazone / Dimethylformamide aggregation

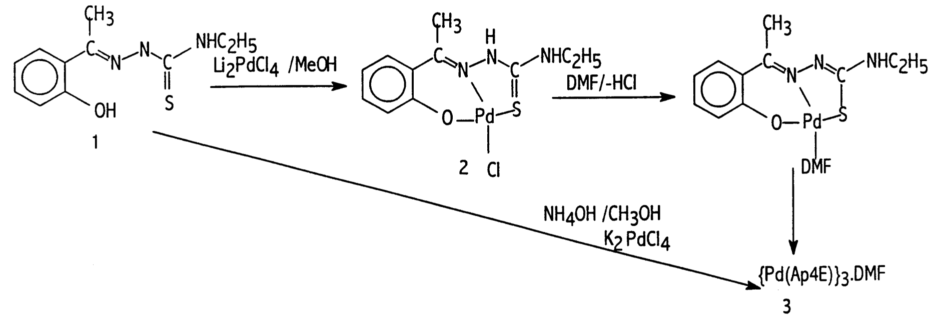
The X-ray crystal structure of a palladium(II) complex of 2-hydroxyacetophenone N^4-ethylthiosemicarbazone (H_2Ap4E) shows it to be a *triangular,* trinuclear complex with bridging thiosemicarbazonato sulfur atoms. This species can be formed from a monomer on dissolution in DMF or directly from Li_2PdCl_4 and the thiosemicarbazone in methanol-ammonia solution.

Thiosemicarbazones of aromatic *ortho*-hydroxy aldehydes and ketones have recently attracted considerable attention because of their potential biological properties[1] and catalytic activity[2]. These aromatic thiosemicarbazones most often coordinate as the dianion on loss of the phenoxy hydrogen and thiosemicarbazone moiety's to form mononuclear [M(ONS)X] (ONS represents the dianionic thioseicarbazone ligand coordinated via the phenoxy oxygen, azomethine nitrogen and thiolato sulfur and X represents a neutral molecule such as ammonia or pyridine)[3], or dinuclear $[M(ONS)]_2$ {M=Ni(II) or Cu(II) and M–O,O–M bridging pattern}[4][5][6][7] have been isolated on deprotonation of the ring hydroxy group and loss of the N(2) hydrogen of the thiosemicarbazone (tsc) moiety. Most recently, a trinuclear nickel(II) complex with both Ni–O,O–Ni and Ni–S,O–Ni bridging patterns has been reported[8]. Two monomers combine to form a butterfly-shaped dimer by Ni–O,O–Ni bonding and a third monomer binds to the dimer via Ni–S,O–Ni bridging. Palladium(II) complexes of tscs of 2-acetylpyridine have been studied with regard to their structural and biological properties, and some of them show remarkable antitumour activity[9][10][11]. Therefore, we expanded our studies of palladium(II) complexes to include other potentially tridentate tsc ligands and report here the structure of $[Pd(Ap4E)]_3 \cdot DMF$ (Ap4E is the dianion of 2-hydroxyacetophenone N^4-ethylthiosemicarbazone) with Pd–S–Pd bridging.

Although numerous dinuclear palladium complexes are known, only a few trinuclear palladium complexes have been reported[12][13]. Triangular complexes[12][13], as well as linear complexes[14], have been structurally characterized. Linear tripalladium structures have been found for the complexes $Pd_3[\eta^3\text{-1,3-di(pyvaloyl)allyl}]_2(\mu,\eta^2\text{-acetate})_4$[14b], $Pd_3[1\text{-}3\eta^3\text{-6-}(\alpha\text{-chloroethyl)cyclooctenyl}]_2Cl_4$[14c] and $[Pd_3(\mu\text{-SCy})_4Cl_2(PMe_3)2]$[14h] with four bridging ligands and palladium atoms at non-bonding distances. Bent trimetallic structures have been proposed for $[Pd_3(\mu\text{-PPh}_2)_2(\mu\text{-Cl})_2(PPh_3)_2]$[14f], $[NEt_4]_2[Pd_3(\mu\text{-Cl})_4Cl_2(C_6F_5)_4]$[14g], $[Pd_3(\eta^3\text{-1,2,3-tri(}p\text{-methoxyphenyl)allyl})_2(acac)_2]$[14d] and $[Pd_3(\eta^3\text{-2-methylallyl})_2(Cl)_4]$[14e]. In the case of allyl complexes, it is believed that the bent structures may result from crystal packing forces rather than steric interactions.

Palladium acetate has been found to be trinuclear with a triangular arrangement of non-bonded palladium[12f] and $[Pd_3(\mu\text{-O}_2CMe)_3(\mu\text{-MeSCHR})_3]$[13a] is a mixed-sphere palladium complex in which the solid state nuclearity and structure of palladium acetate is retained. Complexes that are cationic and triangular trinuclear with two triply bridging ligands include $[Pd_3(\mu_3\text{-SPPh}_2)_2(PhN{=}NC_6H_4)(PPh_3)_2]ClO_4$[13c] and $[Pd_3(C_6H_4CH_2NMe_2)_3(pyS)_2]BF_4$[13d] and with three bridging ligands, capped by a lone sulfur atom as $[Pd_3(\mu_3\text{-S})(SC)(\mu\text{-Ph}_2PCH_2PPH_2)_3][SCN]\cdot 3C_2H_4Cl_2$[13b] have been studied. Neutral tripalladium triangular complexes with two bridging ligands $[Pd_3(\mu\text{-SO}_2)_2(BuNC)_5]\cdot 2(C_6H_6)$[12b] and with three bridging ligands

Figure 1. The reaction path for the synthesis of $[Pd(Ap4E)]_3 \cdot DMF$



$[Pd_3(\mu\text{-}Pcy)_2(m\text{-}SPh)(PCyH)_2(SPh)]$[13e] have been studied. However, to our knowledge this is the first report of an approximately symmetric, *triangular* palladium(II) complex, $[Pd(Ap4E)]_3 \cdot DMF$, with three bridging ligands having the same formal charge and bonding pattern.

Results and Discussion

The reaction of Li_2PdCl_4 with HAp4E afforded the complex **2**. The microanalytical data are consistent with the empirical formula $C_{36}H_{46}N_{10}O_4Pd_3S_3$, which indicates the structure $[Pd(HAp4E)Cl]_n$, and suggests a mononuclear or binuclear structure. A mononuclear is suggested by the IR spectrum, which revealed the appearance of a strong band at 346 cm^{-1} consistent with a terminal ν(Pd−Cl) bond. Figure 1 shows the reactions used to form the trinuclear complex $[Pd(Ap4E)]_3 \cdot DMF$ with three doubly deprotonated phenolato-thiosemicarbazonato ligands and its molecular structure is shown in Figure 2. Each Ap4E ligand coordinates via its phenoxy oxygen and azomethine nitrogen atoms and bridges to another palladium(II) with its thiolato sulfur atom. The metal-ligand bond distances are as follows: Pd1−O1, 1.967(5) Å; Pd2−O1a, 1.993(5) Å and Pd3−O1b, 1.994(6) Å; Pd1−N1, 2.005(6) Å; Pd2−N1a, 2.002(6) Å and Pd3−N1b, 2.020(5) Å; Pd1−S1, 2.226(2) Å; Pd2−S1a, 2.250(2) Å and Pd−S1b, 2.231(2) Å. The bridging sulfur atoms are closer (ca. 0.1 Å) to one Pd atom, having distances of 2.332(2) Å, 2.315(2) Å and 2.337(2) Å to the second Pd atom. The distances between the palladium centres [Pd1−Pd2, 3.945(1); Pd2−Pd3, 4.146(1); Pd1−Pd3, 3.500(1)] indicate that there are no metal-metal bonds. The three bond angles involving bridging sulfur atoms are as follows: Pd1−S1−Pd2, 120.6(1)°; Pd2−S1a−Pd3, 129.3(1)° and Pd3−S1b−Pd1, 100.2(1)°.

Figure 2. Molecular structure of $[Pd(Ap4E)]_3 \cdot DMF$ and numbering scheme

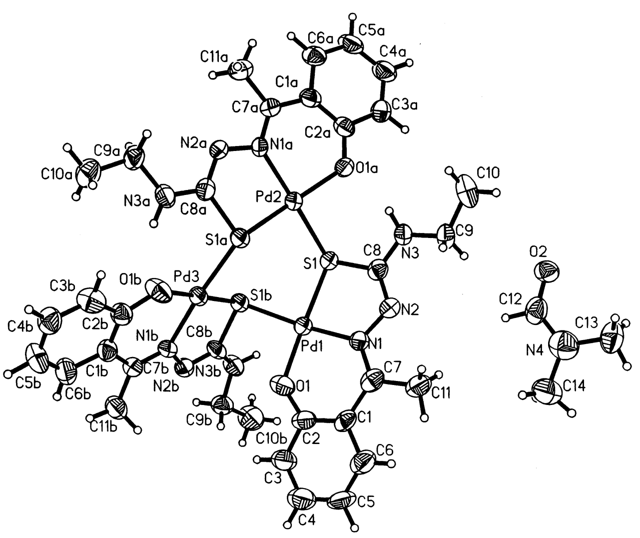
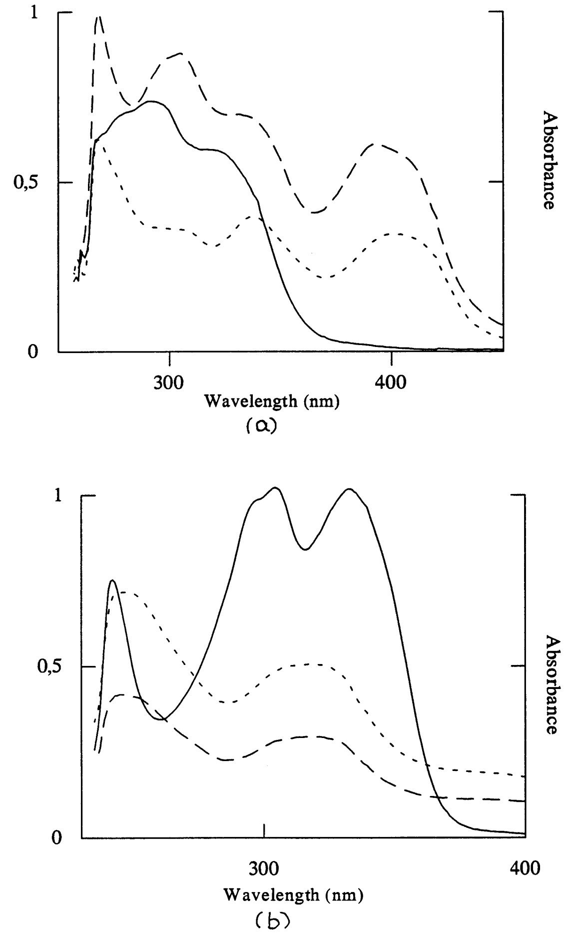


Figure 3. a) UV spectra of 5×10^{-5} M H_2Ap4E (——) [Pd(HAp4E)Cl] and (----) $[Pd(Ap4E)]_3 \cdot DMF$ (– –) in DMF and b) in $CHCl_3$



The coordination planes Pd1−O1−N1−S1−S1b, Pd2−O1a−N1a−S1a-S1 and Pd3−O1b−N1b−S1b−S1a have mean plane deviations of 0.066, 0.157 and 0.048 Å, respectively, and form dihedral angles of 42.24(6)°, 20.23(5)° and 43.98(6)° respectively, with Pd1−S1−Pd2−S1a−Pd3−S1b, which has a mean plane deviation of 0.436 Å.

A kinetically labile ligand and polar solvent like dimethylformamide affords the elimination of hydrogen chloride from **2** and the deprotonation of H_2Ap4E to form [Pd(Ap4E)]$_3$·DMF (Figure 1). The electronic spectra of the complexes **2** and **3** exhibit the same spectral pattern in $CHCl_3$, suggesting conversion of the trinuclear to the mononuclear complex (Figure 3). A different spectral pattern is shown in DMF solution, consistent with the slow transformation of the monomer to the trinuclear complex. Although transformation of **2** to **3** occurs in DMF solution (and the trinuclear complex can be prepared by this method), a non-coordinating, non-polar solvent such as $CHCl_3$ causes **3** to be reverted to **2** (Figure 3b). In contrast dinuclear complexes of copper(II)[5] and nickel(II)[6][7][8] when dissolved in solvents like DMSO and DMF are able to partly monomerize and crystals of a monomer were isolated from DMF solution[7].

Experimental Section

H_2Ap4E = 2-hydroxyacetophenone N^4-ethylthiosemicarbazone, **1**, was prepared by reacting equimolar amounts of 2-hydroxyacetophenone (2 mmol) and N^4-ethyl-3-thiosemicarbazide (2 mmol) in 30 ml ethanol. Two drops of concentrated sulfuric acid were added and the reaction mixture was refluxed for three hours. On partial evaporation of the solvent a white solid formed, which was filtered, washed with cold 2-propanol and dried. [Pd(HAp4E)Cl], **2**, was prepared by reacting lithium tetrachloropalladate (1.2 mmol) prepared in situ from palladium chloride and lithium chloride in methanol and H_2Ap4E (1 mmol) in methanol. The reaction mixture was stirred for 24 hours at room temperature and the resulting yellow powder was filtered, washed with methanol followed by ether and dried in vacuo over silica gel. Calcd for [Pd(HAp4E)Cl]·H_2O: C, 33.35; H, 4.04; N, 10.65; Cl, 8.95. Found: C, 33.05; H, 4.02; N,10.52; Cl, 9.10. Yield 43%. Slow evaporation of **2** from dimethylformamide gives dark red crystals of the complex **3** suitable for X-ray structural analysis. Also, the complex [Pd(Ap4E)]$_3$ was prepared directly from the reaction of K_2PdCl_4 (1.2 mmol) and H_2Ap4E (1 mmol) in 25 ml of H_2O, by adjusting the pH of the reaction to *ca.* 9 with drops of a 1.5 M NH_3 solution. Figure 1 shows the two routes to the trinuclear [Pd(Ap4E)]$_3$. Calcd for [Pd(Ap4E)]$_3$: C 38.66; H 3.80; N 12.30; found: C 39.13, H 4.10; N 12.40. Yield 50%.

Crystal Data: $C_{36}H_{46}N_{10}O_4Pd_3S_3$, molecular mass 1098.2, triclinic, space group *P*1bar, α = 8.874(2) Å, b = 15.680(2) Å, c = 16.273(2) Å, α = 97.80(2)°, β = 105.76(2)°, γ = 103.31(2)°, U = 2072.5(5) Å^3, Z = 2 , d = 1.760 Mg/m^3, F(000) = 1100, Mo*K*α (λ = 0.71073 Å). A red-wine prism with dimensions 0.36 × 0.10 × 0.08 mm was mounted in random orientation on a glass fiber and data were acquired with a Siemens P4 Four-Circle Diffractometer. The structure was solved with direct methods and missing atoms were found by difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic temperature factors. The H atoms were allowed to ride on the C atoms and assigned fixed isotropic temperature factor, U = 0.06 Å^2. Hydrogen atoms on a heteroatom, H3D, H3E and H3 C, were refined in found positions. Refinement of the structure was made by full-matrix least-squares. The minimized function was $S_w(F_o - F_c)^2$ with, $w^{-1} = [\sigma^2(F) + 0.0009(F)^2]$, with final g = 0.0005 for [Pd(Ap4E)]$_3$·DMF. Scattering factors were taken from International Tables for X-ray Crystallography (**1974**, Vol. IV). All calculations were done with the SHELXTL PC^{TM} program package.

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