ELSEVIER

Inorganica Chimica Acta 332 (2002) 204–209

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Note

Synthesis, solution and spectral studies of palladium(II) complexes with 2-hydroxyacetophenone N(3)-propylthiosemicarbazone. Crystal structure of a tripalladium complex

Paras N. Yadav [a], Mavroudis A. Demertzis [a,*], Dimitra Kovala-Demertzi [a,*], Alfonso Castineiras [b], Douglas X. West [c]

[a] *Inorganic and Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece*
[b] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*
[c] *Department of Chemistry 351700, University of Washington, Seattle, WA 98195-1700, USA*

Received 11 July 2001; accepted 12 December 2001

Abstract

The reactions of palladium(II) salts with 2-hydroxyacetophenone N(3)-propylthiosemicarbazone, H_2Ap3Pr, are described. The synthesis and spectral characterization of a new *triangular*, trinuclear palladium(II) complex with the dianion, $Ap3Pr^{2-}$, are reported. The X-ray crystal structure determination of $[Pd(Ap3Pr_2)]_3 \cdot DMF$ shows it to contain a chair-form hexagon of alternating Pd and S atoms to form a molecular bowl. The spectrophotometric characterization of H_2Ap3Pr is also reported.

Keywords: Trinuclear *triangulo* palladium (II); 2-Hydroxyacetophenone N(3) propylthiosemicarbazone; One-dimensional extended network; Crystal structures; Dissociation constants

1. Introduction

Thiosemicarbazones of salicylaldehyde and 2-hydroxyacetophenone have recently attracted considerable attention because of their potential biological properties [1] and catalytic activity [2]. Binuclear copper(II) and nickel(II) [3] complexes of these types of N(3)-substituted thiosemicarbazones have phenoxy bridging based on spectral and structural characterization. Recently, two trinuclear palladium complexes [4] with sulfur bridging and a trinuclear nickel(II) complex with both Ni–O,O–Ni and Ni–S,O–Ni bridging patterns have been reported [5]. Palladium, in the form of the metal, as well as mononuclear and trinuclear compounds, is one of the best catalysts for a whole host of reactions [6]. For example, palladium acetate, $Pd_3(\mu\text{-}OAc)_6$, a trinuclear with a triangular arrangement of acetato bridged palladium atoms, is employed as a homogeneous catalyst in a large number of organic synthese [7]. Structures of both triangular and linear trinuclear palladium(II) complexes have been determined and have been reviewed [8]. For the Group 10 metals Ni, Pd, and Pt, M_3 triangulo clusters do not just act as building blocks for larger cluster compounds, but in addition they display a broad chemistry which increases on descending the triad [8,9]. Palladium compounds were found to exhibit potentially interesting biological activity [10]. Also, palladium(II) complexes of 2-formylpyridine and 2-acetylpyridine N(4)-substituted thiosemicarbazones have been studied with regard to their structural and biological properties, and some of them have shown remarkable antitumor activity [10]. Therefore, we continue to expand our studies of palladium(II) complexes to include other potentially tridentate thiosemicarbazone ligands and report here the structure of a trinuclear palladium(II) complex of 2-hydroxyacetophenone N(3)-propylthiosemicarbazone, $[Pd(Ap4Pr_2)]_3 \cdot DMF$, which has Pd–S–Pd bridging.

* Corresponding authors. Fax: +30-651-44825.
E-mail address: dkovala@cc.uoi.gr (D. Kovala-Demertzi).

0020-1693/02/$ - see front matter
PII: S0020-1693(02)00710-7

2. Experimental

2.1. Syntheses

Solvents were purified and dried according to standard procedures.

2.1.1. 2-hydroxyacetophenone N(3)-propylthiosemicarbazone, H_2Ap3Pr (1)

H_2Ap3Pr was prepared by reacting equimolar amounts of 2-hydroxyacetophenone (2 mmol), hydrazine hydrate (2 mmol) and propylisothiocyanate (2 mmol) in 10 ml methanol. The bright yellow powder was filtrated and washed with cold methanol and dried *in vacuo* under silica gel at 50 °C for 1 h, yield 35%; melting point (m.p.) 195 °C.

2.1.2. [Pd(HAp3Pr)Cl] (2)

[Pd(HAp3Pr)Cl] was prepared by reacting lithium tetrachloropalladate (1.2 mmol) prepared in situ from palladium chloride and lithium chloride in methanol and H_2Ap3Pr (1 mmol) in methanol. The reaction mixture was stirred for 24 h at room temperature (r.t.), and the resulting orange powder was filtered, washed with methanol followed by ether and dried in vacuo over silica gel. Calc. for [Pd(HAp3Pr)Cl]: C, 36.75; H, 4.11; Cl, 9.04; N, 10.7. Found: C, 36.50; H, 4.02; Cl, 9.40, N, 10.52%, m.p. 235 °C; yield: 78%.

2.1.3. $[Pd(Ap3Pr)]_3$ (3)

$[Pd(Ap3Pr)]_3$ was prepared from the reaction of K_2PdCl_4 (1 mmol) and H_2Ap3Pr (1 mmol) in 25 ml of H_2O, by adjusting the pH of the reaction to approximately 9.5 with drops of a 1.0 M NH_3 solution. Calc. for $[Pd(Ap3Pr)]_3$: C, 40.52; H, 4.25; N, 11.81. Found: C, 40.20; H, 4.30; N, 12.20%; m.p. > 300 °C; yield: 84%.

2.1.4. $[Pd(Ap3Pr)]_3 \cdot DMF$ (4)

Slow evaporation of dimethylformamide solutions of either **2** or **3** gives orange–brown crystals of the complex $[Pd(Ap3Pr)]_3 \cdot DMF$, **4**, suitable for X-ray structural analysis.

2.2. Physical measurements

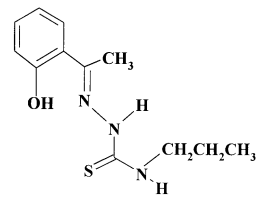
Infrared (IR) and far-IR spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer using KBr (4000–400 cm^{-1}) and polyethylene pellets (400–40 cm^{-1}). Electronic spectra were recorded on a JASCO V-570 spectrophotometer UV–VIS–NIR.

2.3. Structure determination

A yellow, prismatic crystal of $[Pd_3(Ap3Pr)_3] \cdot DMF$ was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $6.93 < \theta < 14.13°$ in a Enraf Nonius MACH3 automatic diffractometer [11,11a]. Data were collected at 293 K using Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω-scan technique, and corrected for Lorentz and polarization effects (Lp) [11b]. A semi-empirical absorption correction (ψ-scans) was made [11c] The structure was solved by direct methods [11d] and subsequent difference Fourier maps, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [11e]. One of the propyl groups (C29–C210–C211) showed disorder. All hydrogen atoms were located in their calculated positions (C–H, 0.93–0.97 Å) and were refined using a riding model. Atomic scattering factors from 'International Tables for X-ray Crystallography' [11f]. Molecular graphics are from PLATON98 [11g] and a summary of the crystal data, experimental details and refinement results are listed in Table 1.

Table 1
Crystal data and structure refinement for $[Pd(Ap3P)]_3 \cdot DMF$

	$[Pd(Ap3P)]_3DMF$
Empirical formula	$C_{39}H_{52}N_{10}O_4Pd_3S_3$
Formula weight	1140.29
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	9.682(7)
b (Å)	15.815(5)
c (Å)	16.069(6)
α (°)	98.06(3)
β (°)	101.27(4)
γ (°)	107.12(5)
V (Å^3)	2254(2)
Z	2
D_{calc} (Mg m^3)	1.680
Absorption coefficient (mm^{-1})	1.374
$F(000)$	1148
Crystal size (mm)	$0.20 \times 0.20 \times 0.20$
θ Range for data collection (°)	1.32–27.47
Index ranges	$0 \le h \le 12$, $-20 \le k \le 19$, $-20 \le l \le 20$
Reflections collected/unique	10956/10338 [$R_{int} = 0.0318$]
Completeness to $2\theta = 27.47$ (%)	100.0
Absorption correction	ψ-scans
Max/min transmission	0.775, 0.570
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	10338/0/537
Goodness-of-fit on $F\hat{}2$	1.007
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0397$, $wR_2 = 0.0989$
R indices (all data)	$R_1 = 0.0671$, $wR_2 = 0.1106$
Largest difference peak and hole (e Å^{-3})	0.826 and −1.195



Scheme 1.

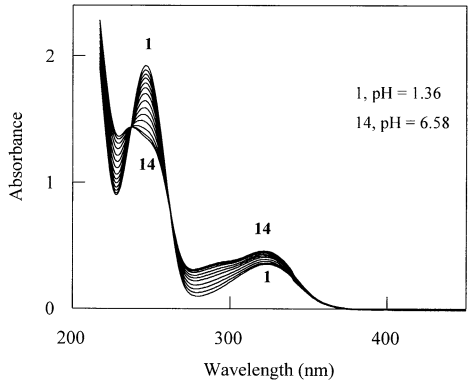


Fig. 1. Absorption spectra of the conjugate H_3A^+–H_2A pair in the pH region 1.36–6.58.

2.4. Dissociation constants

Due to the low solubility of H_2Ap3Pr, as well as its high k_{a1} and low k_{a3} values, spectrophotometry was used to study the dissociation constants. Aqueous H_2Ap3Pr solutions of constant ionic strength were prepared with distilled water obtained from a borosilicate autostill BICASA Spa, Model BE-115/R and used to determine dissociation constants by a methology reported previously [12]. A 1×10^{-4} M stock solution of H_2Ap3Pr was initially prepared by suspending in a water bath the appropriate amount of the compound in 0.01 M KOH until dissolution occurred, cooling to r.t., filling the flask to the required volume with 0.01 M KOH solution and mixing thoroughly. Exactly 5.0×10^{-5} M working ligand solutions, having different H_3O^+ ion concentrations and constant ionic strength ($\mu = 0.1$), where then prepared with standard HCl or KOH and KCl solutions. All absorption spectra and pH measurements were made at 25 °C with a JASKO 590 UV–VIS–NIR spectrophotometer guided by a personal computer and a Methrom 691 pH-meter.

3. Results and discussion

3.1. Concentration dissociation constants

2-Hydroxyacetophenone N(3)-propylthiosemicarbazone, H_2Ap3Pr, Scheme 1, designated in this paragraph as H_2A, possesses two function groups, –NH and –OH, with dissociative hydrogens, which undergo two deprotonation steps as a function of pH. In addition, H_2Ap3Pr, is also susceptible to a single protonation. Therefore, in aqueous solutions there are four independent species (i.e., H_3A^+, H_2A, HA^- and A^{2-}) properly shown by separate absorption spectra of the conjugate acid–base pairs. Fig. 1 is an example of the pair H_3A^+–H_2A. Thus, there are three separate dissociation steps given by Eqs. (1)–(3):

$$H_3A^+ + H_2O \overset{K_{a1}}{\rightleftharpoons} H_2A + H_3O^+ \quad (1)$$

$$H_2A + H_2O \overset{K_{a2}}{\rightleftharpoons} HA^- + H_3O^+ \quad (2)$$

$$HA^- + H_2O \overset{K_{a3}}{\rightleftharpoons} A^{2-} + H_3O^+ \quad (3)$$

The law of mass-action for these equations, based on the molar absorptivities of the various species, takes the form:

$$Ka1 = [H_3O^+]\frac{\varepsilon_{H_3A^+} - \varepsilon_o}{\varepsilon_o - \varepsilon_{H_2A}} \quad (4)$$

$$Ka2 = [H_3O^+]\frac{\varepsilon_{H_2A} - \varepsilon_o}{\varepsilon_o - \varepsilon_{HA^-}} \quad (5)$$

$$Ka3 = [H_3O^+]\frac{\varepsilon_{HA^-} - \varepsilon_o}{\varepsilon_o - \varepsilon_{A^{2-}}} \quad (6)$$

respectively. The terms ε_o, $\varepsilon_{A^{2-}}$, ε_{HA^-}, ε_{H_2A} and $\varepsilon_{H_3A^+}$ are the molar absorptivities of the observed solution, doubly negative ionized, singly negative ionized, molecular and positively charged species, respectively. In order to find the dissociation constants, the values of the molar absorptivities must be experimentally determined. However, in this particular instance a direct application of relationships (Eqs. (4) and (6)) for K_{a1} and K_{a3} determination is impossible, since $\varepsilon_{H_3A^+}$ and $\varepsilon_{A^{2-}}$ cannot be determined in solutions with ionic strength equal to 0.1. Ideally, A^{2-} and H_3A^+ predominate at very high alkaline or very low acid solutions, respectively. Perhaps the equilibrium steps (2) and (3) occur to an extent simultaneously, and the value of the common species HA^- cannot also be determined directly from absorption spectra. Therefore, instead of using relationships (Eqs. (4)–(6) it is expedient to use a proper rearrangement of them in the form:

$$\varepsilon_o = \varepsilon_{H_3A^+} - Ka1\frac{\varepsilon_o - \varepsilon_{H_2A}}{[H_3O^+]} \quad (7)$$

$$\varepsilon_o = \varepsilon_{HA^-} + \frac{1}{Ka2}(\varepsilon_{H_2A} - \varepsilon_o)[H_3O^+] \quad (8)$$

$$\varepsilon_o = \varepsilon_{A^{2-}} + \frac{1}{Ka3}(\varepsilon_{HA^-} - \varepsilon_o)[H_3O^+] \quad (9)$$

respectively, [13]. These relationships are useful to find the concentration dissociation constants of the ligand. The relative standard deviation (R.S.D.) of the slopes, their confidence limits, the correlation coefficients, the analytical wavelengths and the pK_a of the above relationships are shown in Table 2.

Table 2
Analytical parameters of calibration graphs for acid–base properties of H_2Ap3Pr

Equation	R.S.D. of slope (%)	Confidence limit of slope	Correlation Coefficient	Analytical wavelength (nm)	pK_a values
Eq. (7)	2.87	$-1.64\times10^{-2}\pm1.11\times10^{-3}$ [a]	0.9971	247	$pK_{a1}=1.79$
Eq. (8)	3.28	$6.89\times10^{8}\pm5.22\times10^{7}$ [b]	0.9957	306	$pK_{a2}=8.84$
Eq. (9)	4.66	$358\times10^{13}\pm4.29\times10^{12}$ [c]	0.9946	280	$pK_{a3}=13.55$

[a] $n=9$.
[b] $n=10$.
[c] $n=7$.

A good approach of confidence limit for the pK_a values is $pK_{a1}=1.79\pm0.03$, $pK_{a2}=8.84\pm0.03$ and $pK_{a3}=13.55\pm0.05$. The first of them ($pK_{a1}=1.79$) is assigned to the dissociation of the protonated thiosemicarbazone moiety by comparison toprotonated thiosemicarbazide, which has a value of 1.70–1.87 [14]. The second one ($pK_{a2}=8.84$) is assigned to the hydroxyl group by comparison with acetylphenol, which has a value of 9.89–9.94 [14] and the third value ($pK_{a3}=13.55$) to the thiol–thioamide group. The replacement of the N(2)-hydrogen by a methyl group prevents the observation of the third dissociation constant adding credence to our assignment [15].

3.2. Molecular structure of [Pd(Ap3Pr)]$_3$·DMF (4)

The interaction of K_2PdCl_4 with H_2Ap4Pr in acid and basic solution (pH ca. 4–9) afforded the mononuclear and trinuclear complexes **2**–**4** according to the reactions:

$$K_2PdCl_4 + H_2Ap4Pr \rightarrow [Pd(HAp4Pr)Cl],\ \mathbf{2} + 2KCl + 2HCl$$

$$3K_2PdCl_4 + 3H_2Ap4Pr \xrightarrow{CH_3OH-H_2O-NH_4OH} [Pd(Ap4Pr)]_3,\ \mathbf{3} + 6KCl + 6HCl$$

$$[Pd(Ap4Pr)]_3,\ \mathbf{3} + DMF \rightarrow [Pd(Ap4Pr)]_3{\bullet}DMF,\ \mathbf{4}$$

$$[Pd(Ap4Pr)],\ \mathbf{2} + DMF \rightarrow [Pd(Ap4Pr)]_3{\bullet}DMF,\ \mathbf{4} + HCl$$

The X-ray crystal structure of complex **4** 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, in this case dimethylformamide promoted deprotonation and aggregation. Alternatively, the same complex can be synthesized directly from Li_2PdCl_4 and the thiosemicarbazone in methanol–ammonia solution. The stoichiometry of the complexes indicates that palladium(II) is coordinated by the doubly charged anion $Ap4Pr^{2-}$ formed on the loss of the two protons from the phenolic oxygen and thioamide nitrogen, N2.

The palladium complex **4** crystallizes with a dimethylformamide solvate molecule. A perspective view of [Pd(Ap4Pr)]$_3$·DMF with the atomic numbering scheme is shown in Fig. 2 and selected bond distances and angles are listed in Table 3. The dianionic, tridentate ligand has a ZEZ configuration about the bonds C11–C16, N12–C17 and N13–C10 for the oxygen, nitrogen and sulfur donor centers. The whole structure forms into a type of bowl with the (3Pd–3S) ring as the base. This type of core has been reported previously for palladium complexes [4]. The core of **4** consists of a six-membered ring of alternating Pd(II) and S atoms in a chair configuration. The remaining two sites of each square planar Pd(II) center are occupied by the imine nitrogen and the phenoxy oxygen.

The distances between the palladium centers [Pd(1)–Pd(2), 3.404(2); Pd(2)–Pd(3), 4.171(3); and Pd(1)–Pd(3), 3.872(3) Å] indicate that there is no direct bond between the palladium atoms. However, a very weak interaction can be postulated in agreement with the reported values for polynuclear palladium complexes (2.549(2)–3.539(1) Å) [8]. The three bond angles

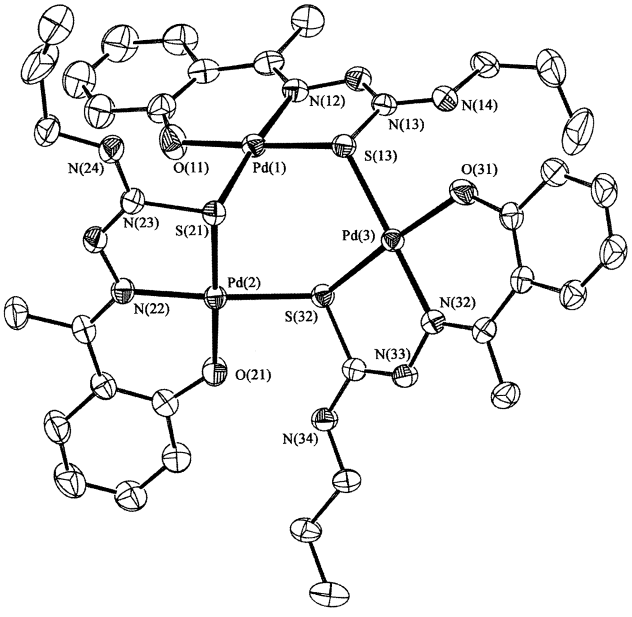


Fig. 2. Structural representation of [Pd(Ap3Pr)]$_3$·DMF with the labeling scheme; hydrogen atoms are omitted.

Table 3
Selected bond lengths (Å) and angles (°) for $[Pd_3(Ap3P)_3]\cdot DMF$

Bond lengths	
Pd(1)–O(11)	1.970(4)
Pd(1)–N(12)	2.009(3)
Pd(1)–S(13)	2.2251(18)
Pd(1)–S(21)	2.3282(14)
Pd(2)–O(21)	1.996(3)
Pd(2)–N(22)	2.010(3)
Pd(2)–S(21)	2.2353(17)
Pd(2)–S(32)	2.3386(15)
Pd(3)–O(31)	1.985(3)
Pd(3)–N(32)	2.015(3)
Pd(3)–S(32)	2.251(2)
Pd(3)–S(13)	2.3154(12)
Bond angles	
O(11)–Pd(1)–N(12)	93.85(15)
O(11)–Pd(1)–S(13)	177.56(14)
N(12)–Pd(1)–S(13)	85.91(11)
O(11)–Pd(1)–S(21)	90.54(12)
N(12)–Pd(1)–S(21)	174.99(10)
O(21)–Pd(2)–N(22)	92.55(14)
O(21)–Pd(2)–S(21)	178.07(10)
N(22)–Pd(2)–S(21)	86.26(12)
O(21)–Pd(2)–S(32)	88.77(10)
N(22)–Pd(2)–S(32)	173.57(10)
O(31)–Pd(3)–N(32)	93.00(13)
O(31)–Pd(3)–S(32)	170.05(13)
N(32)–Pd(3)–S(32)	85.84(10)
O(31)–Pd(3)–S(13)	85.92(10)
N(32)–Pd(3)–S(13)	173.51(10)

involving bridging sulfur atoms are as follows: Pd(1)–S(21)–Pd(2), 96.44(6); Pd(2)–S(32)–Pd(3), 130.65(6) and Pd(1)–S(13)–Pd(3), 117.02(6)°. The Pd–N bond distances range from 2.009(3) to 2.015(3) Å, the Pd–O distances from 1.970(4) to 1.996(3) Å and Pd–S distances from 2.2251(18) to 2.3386(15) Å and are similar to those found in other palladium complexes [4,10]. The greater *trans* influence of the iminic nitrogens can be observed in the lengthening of the *trans* Pd–S distances (2.3154(12) to 2.3386(15) Å) with respect to the Pd–S distances *trans* to the phenoxy oxygens (2.2251(18)–2.251(2) Å). The dihedral angles between the planes of the two chelate rings (Pd–S–C–N–N, A, and (Pd–N–C–C–O), B, are 4.00(15), 4.59(15) and 5.46(17)° for Pd(1), Pd(2) and Pd(3) indicating that there is deviation from planarity by the ligands. The plane of A of Pd(1) is tilted by 89.99(14) and 59.37(14)° with respect to the plane A of Pd(2) and Pd(3), respectively.

The negative charge of the dianionic ligand is delocalized over the thiosemicarbazonato moiety and the S–C bond distances are consistent with increased single bond character, while the imine C–N distances and both thioamide C–N distances indicate considerable double bond character. The dimethylformamide molecule appears to be linked *via* hydrogen bond. This hydrogen bond involves O1 on dimethylformaimide and the hydrogen on the N(24) atom, N(24)–H(24). Further, intramolecular and intermolecular hydrogen bonds and C–H–π interactions [16] stabilize this structure.

3.3. Spectroscopy

The significant IR bands of H_2Ap3Pr and the three complexes of palladium(II) are close in energy to those found in other compounds with tridentate coordination [4,17]. The bands at 1595 and 1616 cm^{-1} are assigned to ν(C=N). Coordination of the azomethine nitrogens causes ν(C=N) to shift to lower frequencies by 20–40 cm^{-1} and a band at 453–459 cm^{-1} is assignable to ν(Pd–N). Coordination *via* the thiolato sulphurs is indicated by a decrease in the frequency of the thioamide IV band found at 821 cm^{-1} in H_2Ap3Pr (80–100 to 720–740 cm^{-1}) and also by the presence of a band assignable to ν(Pd–S) at 380–429 cm^{-1}. The phenolic oxygen, on loss of the OH proton, occupies the third coordination site. A band at 257–292 cm^{-1} range in the spectra of the complexes is assignable to ν(Pd–O). Complex **2** exhibits a strong band at 339 cm^{-1} attributed to the ν(Pd–Cl).

The ^1H NMR spectrum of H_2Ap3Pr shows signals for OH and ^2NH at 10.83 and 8.79 ppm [16]. The peak at 10.83 ppm is consistent with the presence of a hydrogen bonding isomer (OH···N). The signals for OH and ^2NH are absent from the spectra of **3** and **4**, as expected because of their loss on complex formation. There is considerable shifting of the signals for the ring protons in the spectra of the complexes compared with their positions in H_2Ap3Pr indicating coordination *via* the phenoxy oxygen. The loss of electron density on complexation is most significant for the carbons ^3CH, ^4CH and ^6CH; their protons show downfield shifts, and an upfield shift occurs for ^5CH. The small upfield shift for ^5CH, the ring hydrogen expected to be least affected by coordination of the phenoxy oxygen and azomethine nitrogen, is probably a result of π-back-bonding. The large upfield of $^8CH_3$, which occurs on coordination of the azomethine nitrogen, may be due to π-back-bonding by the palladium(II) to the π* orbital of the azomethine moieties.

The bands of the H_2Ap3Pr at approximately 31 000 and 34 000 cm^{-1} are due to $n \rightarrow \pi^*$ transitions of the imine portion of the TSC moiety and the aromatic ring, respectively [4,18]. The energies of these two bands are affected by changes in organic solvents due to differences in the mode of hydrogen bonding. The band at approximately 33 000 cm^{-1} is due to the $n \rightarrow \pi^*$ transition of the thiosemicarbazone moiety (imine, thioamide) and charge transfer involving the TSC moiety ($L \rightarrow M$). The maximum at 29 000 cm^{-1} is affected by the nature of the solvent consistent with its assignment as a charge transfer transition. The broad band at

approximately 24 000–25 000 cm^{-1} is assignable to a combination of sulfur → Pd(II), imine nitrogen → Pd(II) charge transfer (L(π) → MCT) and Pd(II) d–d bands. The maxima are affected by the nature of the solvent; i.e. the L(π) → MCT band shifts to higher energy on increase in the polar character of the solvent, and the reverse occurs for the M → LCT band [4,17]. Labile and polar solvents e.g. DMF, DMSO, MeCN, afford the elimination of hydrogen chloride from **2** and slow transformation within 24 h to **3**, while no polar solvents (e.g. $CHCl_3$) affords the transformation of the trimer **3** to the monomer **2**.

4. Supplementary material

Crystallographic data for $C_{39}H_{52}N_{10}O_4Pd_3S_3$, CCDC 164884 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. Copies of available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or .www: http://www.ccdc.cam.ac.uk).

References

[1] D.X. West, S.B. Padhye, P.B. Sonawane, R.C. Chikate, Asian J. Chem. Rev. 1 (1990) 125.

[2] D.E. Barber, Z. Lu, T. Richardson, R.H. Crabtree, Inorg. Chem. 31 (1992) 4709.

[3] (a) D.X. West, Y.-H. Yang, T.L. Klein, K.I. Goldberg, A.E. Liberta, J. Valdés-Martínez, R.A. Toscano, Polyhedron 14 (1995) 1681;
(b) D.X. West, Y.-H. Yang, T.L. Klein, K.I. Goldberg, A.E. Liberta, J. Valdés-Martínez, S. Hernández-Ortega, Polyhedron 14 (1995) 3051.

[4] (a) D. Kovala-Demertzi, N. Kourkoumelis, D.X. West, J. Valdés-Martínez, S. Hernández-Ortega, Eur. J. Inorg. Chem. (1998) 861;
(b) D. Kovala-Demertzi, N. Kourkoumelis, M.A. Demertzis, J.R. Miller, C.S. Frampton, J.K. Swearingen, D.X. West, Eur. J. Inorg. Chem. (2000) 727.

[5] A. Berkessel, G. Hermann, O.-T. Racuch, M. Buchner, A. Jacobi, G. Huttner, Chem. Ber. 129 (1996) 1421.

[6] (a) J. Tsuji, Organic Synthesis with Palladium Compound, Springer, New York, 1980;
(b) R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, London, 1985.

[7] (a) G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, second ed., Wiley, New York, 1992;
(b) F.A. Cotton, S. Han, Rev. Chim. Miner. (1983) 496;
(c) F.A. Cotton, S. Han, Rev. Chim. Miner. (1985) 277;
(d) D.H.R. Barton, J. Khamsi, N. Ozbalik, M. Ramesh, J. Sharma, Tetrahedron 30 (1989) 4661;
(e) A.C. Skapski, M. Smart, J. Chem. Soc., Chem. Commun. (1970) 658.

[8] D. Kovala-Demertzi, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Synthesis and Reactivity of Tripalladium clusters in Metal Clusters in Chemistry, Wiley-VCH, New York, 1999.

[9] A.D. Burrows, D.M.P. Mingos, Coord. Chem. Rev. 154 (1996) 19 and references therein.

[10] (a) A. Papageorgiou, Z. Iakovidou, D. Mourelatos, E. Mioglou, L. Boutis, A. Kotsis, D. Kovala-Demertzi, A. Domopoulou, D.X. West, M.A. Demertzis, Anticancer Res. 17 (1997) 247;
(b) D. Kovala-Demertzi, A. Domopoulou, M.A. Demertzis, A. Papageorgiou, D.X. West, Polyhedron 16 (1997) 3625;
(c) D. Kovala-Demertzi, A. Domopoulou, G. Valle, M.A. Demertzis, A. Papageorgiou, J. Inorg. Biochem. 68 (1997) 147;
(d) D. Kovala-Demertzi, M.A. Demertzis, V. Varagi, A. Papageorgiou, D. Mourelatos, E. Mioglou, Z. Iakovidou, A. Kotsis, Chemotherapy 44 (1998) 421;
(e) Z. Iakovidou, E. Mioglou, D. Mourelatos, A. Kotsis, M.A. Demertzis, A. Papagoergiou, J.R. Miller, D. Kovala-Demertzi, Anticancer Drugs 12 (2001) 65.

[11] (a) B.V. Nonius, CAD4. Express Software, Ver. 5.1/1.2, Enraf Nonius, Delft, The Netherlands, 1994;
(b) M. Kretschmar, GENHKL. Program for the reduction of CAD4 Diffractometer data, University of Tuebingen, Germany, 1997;
(c) A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., Sect. A A24 (1968) 351;
(d) G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467;
(e) G.M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997;
(f) International Tables for X-ray Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995;
(g) A.L. Spek, PLATON. A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.

[12] (a) S.K. Hadjikakou, M.A. Demertzis, J.R. Miller, D. Kovala-Demertzi, J. Chem. Soc., Dalton Trans. (1999) 663;
(b) M.A. Demertzis, S.K. Hadjikakou, D. Kovala-Demertzi, A. Koutsodimou, M. Kubicki, Helvet. Chim. Acta 83 (2000) 2787.

[13] (a) R.W. Ramette, Chemical Equilibrium and Analysis, Addison-Wesley Publishing Company, London, 1981;
(b) J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, second ed., J. Wiley & Sons, New York, 1988.

[14] A.E. Martell, R.M. Smith, Crtitical Statistical Constants, vol. 4, Plenum Press, New York, 1977.

[15] E.W. Ainscough, A.M. Brodie, W.A. Denny, G.J. Finlay, J.D. Ranford, J. Inorg. Biochem. 70 (1998) 175.

[16] (a) T. Steiner, M. Tamm, A. Grzegorzewski, N. Schulte, N. Veldman, A.M.M. Schreurs, J. Kroon, J. van der Maas, B. Lutz, J. Chem. Soc., Perkin Trans. 2 (1996) 2441;
(b) G.R. Desiraju, Acc. Chem. Res. 24 (1991) 290;
(c) T. Steiner, Cryst. Rev. 6 (1996) 1.

[17] (a) D.X. West, Y. Yang, T.L. Klein, K.I. Goldberg, A.E. Liberta, J. Valdes-Martinez, R.A. Toskano, Polyhedron 122 (1995) 1681;
(b) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Wiley, New York, 1997.

[18] (a) A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, New York, 1984;
(b) D. Kovala-Demertzi, J.M. Tsangaris, H.O. Desseyn, B. Van der Veken, Bull. Soc. Chim. Belg. 1 (1987) 7;
(c) G.L. Estiu, A.H. Jubert, J. Costamagna, J. Vargas, Inorg. Chem. 35 (1996) 263;
(d) D. Kovala-Demertzi, M.A. Demertzis, P.N. Yadav, A. Castineiras, D.X. West, Trans. Met. Chem. 24 (1999) 642.