SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF PALLADIUM(II) COMPLEXES CONTAINING EDTA TETRAALKYL ESTER LIGANDS

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contribution to the area of organometallic synthesis and catalysis.

The reaction of solutions of tetraalkyl ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate esters (alkyl = Me, **1a**; Et, **1b**) with $H_2[PdCl_4]$ led to the complexes $[PdCl_2(R_4EDTA)]$ (R = Me, **2a**; Et, **2b**). The coordination of R_4EDTA ligands to palladium(II) ions occurs through the two nitrogen donor atoms, as confirmed by IR, ^{1}H and ^{13}C NMR spectroscopies and X-ray crystallography.
Keywords: Palladium complexes; Crystal structure; X-ray diffraction; EDTA ligands; Coordination chemistry; Chelates.

Metal complexes involving ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetatic acid (H_4EDTA) have been widely described in literature[1]. Complexes that include tetraalkyl esters of H_4EDTA acid (Fig. 1) are few[2–6]. Complexes with Me_4EDTA were described for Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), Hg(II), Zn(II) and Sn(II) and Et_4EDTA complexes for Cu(II), Co(II) and Ni(II)[2–4]. The Me_4EDTA ligand was found to be flexidentate exhibiting a $\kappa^2 N,N'$ coordination (e.g. $[HgCl_2(Me_4EDTA\text{-}\kappa^2 N,N')]$)[2] or a multidentate *N* and *O* coordination (e.g. $[NiCl(H_2O)(Me_4EDTA\text{-}\kappa^4 N,N',O,O')]$)[2–4]. In other cases, there are conflicting reports on the proposed coordination mode based on conductivity and IR and reflectance spectra[2]. However, apart from the protonated species **1a**H^+ in the cluster $(\mathbf{1a}H)_2[W_6(\mu_3\text{-}Cl)_8Cl_6]$ [6], only

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Cu(II) and Zn(II) complexes, with κ^4*N*,*N′*,*O*,*O′* coordination of the ligand, have been structurally characterized[4]. Here, we report on the synthesis, characterization and crystal structures of palladium(II) complexes with these ligands.

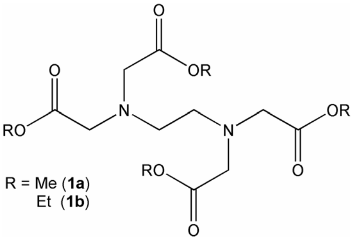

FIG. 1
Tetramethyl (**1a**) and tetraethyl EDTA (**1b**) ligands

EXPERIMENTAL

The elemental analyses (C, H, N) were carried out on a CHNS-93 (LECO) elemental analyzer. Infrared spectra were recorded in KBr pellets on a Mattson Galaxy 5000 FT-IR spectrometer, covering the region 4000–300 cm^{-1}. The ^{1}H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) were recorded on a Varian Unity 500 NMR spectrometer in $CDCl_3$ at 27 °C. Tetramethyl (Me_4EDTA; **1a**)[3] and tetraethyl ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate (Et_4EDTA; **1b**)[7] were synthesized by the procedures reported in the literature.

1a: ^{1}H NMR (500 MHz): 2.73 s, 4 H ($NC\mathbf{H}_2C\mathbf{H}_2N$); 3.45 s, 8 H ($NC\mathbf{H}_2CO_2$); 3.52 s, 12 H ($C\mathbf{H}_3$). ^{13}C NMR (125 MHz): 51.1 ($\mathbf{C}H_3$); 51.9 ($N\mathbf{C}H_2\mathbf{C}H_2N$); 54.7 ($N\mathbf{C}H_2CO_2$); 171.1 ($\mathbf{C}O_2$).

1b: ^{1}H NMR (500 MHz): 1.23 t, $^3J_{H,H}$ = 7.10, 12 H ($C\mathbf{H}_3$); 2.87 s, 4 H ($NC\mathbf{H}_2C\mathbf{H}_2N$); 3.56 s, 8 H ($NC\mathbf{H}_2CO_2$); 4.12 q, $^3J_{H,H}$ = 7.10, 8 H ($CO_2C\mathbf{H}_2CH_3$). ^{13}C NMR (125 MHz): 14.2 ($\mathbf{C}H_3$); 52.3 ($N\mathbf{C}H_2\mathbf{C}H_2N$); 55.2 ($N\mathbf{C}H_2CO_2$); 60.4 ($CO_2\mathbf{C}H_2CH_3$); 171.3 ($\mathbf{C}O_2$).

Synthesis

Dichloro(tetramethyl ethylenediamine-N,N,N′,N′-tetraacetate)palladium(II) (**2a**). To a suspension of $PdCl_2$ (200 mg, 1.13 mmol) in dilute HCl (10 ml H_2O + 0.5 ml concentrated HCl) stirred for 20 min, **1a** (393 mg, 1.13 mmol) was added in one portion. The solution was stirred for a period of 5 h. The yellow precipitate formed was filtered off and dried in air. Yield 423 mg (71%). ^{1}H NMR (500 MHz): 3.42 s, 4 H ($NC\mathbf{H}_2C\mathbf{H}_2N$); 3.79 s, 12 H ($C\mathbf{H}_3$); 4.10 d$^{1)}$, 4 H ($NC\mathbf{H}_2CO_2$); 4.73 broad$^{1)}$, 4 H ($NC\mathbf{H}_2CO_2$). ^{13}C NMR (125 MHz): 52.5 ($\mathbf{C}H_3$); 53.0 ($N\mathbf{C}H_2\mathbf{C}H_2N$); 56.9 ($N\mathbf{C}H_2CO_2$); 168.6 ($\mathbf{C}O_2$). IR: 3009 w; ν_{as}(CH) 2957 w, 2901 w;

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1) H atoms of the NCH_2CO_2 group are chemically not equivalent.

ν_{as}(COO) 1740 vs; ν_s(COO) 1438 s, 1387 m; δ_s(CH) 1359 m, 1239 m, 1254 m, 1212 s, 1083 s, 1017 s, 936 w, 807 w, 753 w, 592 w; ν_{as}(PdN) 527 w; ν_s(PdN) 430 w; ν(PdCl) 319 s. For $C_{14}H_{24}Cl_2N_2O_8Pd$ (525.7) calculated: 31.69% C, 4.87% H, 5.23% N; found: 31.99% C, 4.60% H, 5.33% N.

Dichloro(tetraethyl ethylenediamine-N,N,N′,N′-tetraacetate)palladium(II) (**2b**). This complex was prepared as **2a** using **1b** (456 mg, 1.13 mmol) instead of **1a**. Yield 423 mg (66%). ^{1}H NMR (500 MHz): 1.21 t, $^3J_{H,H}$ = 7.15, 12 H (C**H**$_3$); 3.32 s, 4 H (NC**H**$_2$C**H**$_2$N); 3.97 d1), 4 H (NC**H**$_2$CO$_2$); 4.17 q, $^3J_{H,H}$ = 7.08, 8 H (CO$_2$C**H**$_2$CH$_3$); 4.57 broad1), 4 H (NC**H**$_2$CO$_2$). ^{13}C NMR (125 MHz): 13.8 (CH$_3$); 52.9 (NCH$_2$CH$_2$N); 56.7 (NCH$_2$CO$_2$); 61.4 (CO$_2$CH$_2$CH$_3$); 167.8 (CO$_2$). IR: 2985 w; ν_{as}(CH) 2937 w, 2875 w; ν_{as}(COO) 1738 vs; ν_s(COO) 1444 s, 1378 s; δ_s(CH) 1350 m, 1275 m, 1251 m, 1205 s, 1088 s, 1018 s, 968 w, 958 w, 817 w, 754 w, 592 w; ν_{as}(PdN) 530 w; ν_s(PdN) 435 w; ν(PdCl) 323 s. For $C_{18}H_{32}Cl_2N_2O_8Pd$ (581.8) calculated: 37.16% C, 5.54% H, 4.81% N; found: 37.14% C, 5.74% H, 4.67% N.

X-ray Crystallography

Crystals of the [PdCl$_2$(R$_4$EDTA)] complexes (**2a**·CDCl$_3$ and **2b**) suitable for X-ray diffraction measurements were obtained from chloroform solution (for **2a**·CDCl$_3$) by slow evaporation of the solvent. Intensity data were collected on a STOE-STADI IV diffractometer at 293(2) K using graphite fine-focus sealed tube MoKα radiation (λ = 0.71073 Å). A survey of the crystallographic data, data collection parameters, and refinement parameters is given in Table I. The structures were solved by direct methods with SHELXS96 [8] and refined using full-matrix least-squares routines against F^2 with SHELXS97 [9]. Absorption corrections (ψ-scan) were applied.

Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined with fixed displacement parameters (riding model). Deuterium atom in **2a**·CDCl$_3$ was treated as H atom. The software used for the preparation of the crystallographic material for publication: PLATON[10] and ORTEP III[11].

CCDC 633397 (**2a**) and 633398 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Synthesis and Spectra

The addition of R$_4$EDTA (R = Me, **1a**; Et, **1b**) to a solution of H$_2$[PdCl$_4$] produced yellow precipitates (Eq. (*1*)).

$$\begin{array}{rcl} R_4EDTA + [PdCl_4]^{2-} & \xrightarrow{H^+} & [PdCl_2(R_4EDTA)] + 2\,Cl^- \qquad \text{Eq. (1)} \\ R = Me,\ \mathbf{1a} & & \mathbf{2a} \\ Et,\ \mathbf{1b} & & \mathbf{2b} \end{array}$$

The IR spectra of complexes **2a** and **2b** showed very strong asymmetrical/symmetrical ν(COO) absorption bands at 1740/1438 and 1738/1444 cm^{-1}, respectively (ligands: **1a** at 1744/1437, **1b** at 1736/1447 cm^{-1})[3,7,12]. Asymmetric CH_3 stretching vibrations were found at 2957 and 2937 cm^{-1} while those due to the degenerate symmetric vibrations appeared at 1359 and 1350 cm^{-1} for complexes **2a** and **2b**, respectively[12,13]. Bands at 527 and 430 cm^{-1} (**2a**) and 530 and 435 cm^{-1} (**2b**) were assigned to Pd–N asymmetrical and symmetrical stretching vibrations[14], respectively, indicating coordination of the R_4EDTA ligand via *N* donor atoms. The Pd–Cl stretching mode at 319 (**2a**) and 323 cm^{-1} (**2b**) are in agreement with the values reported in literature[14].

TABLE I
Crystal data, data collection and refinement parameters for **2a**·$CDCl_3$ and **2b** complexes

Complex	**2a**·$CDCl_3$	**2b**
Empirical formula	$C_{15}H_{24}Cl_5DN_2O_8Pd$	$C_{18}H_{32}Cl_2N_2O_8Pd$
M, g mol^{-1}	645.02	581.76
Crystal size, mm	0.38 × 0.46 × 0.62	0.46 × 0.57 × 0.66
T, K	293(2)	293(2)
Crystal system, space group	triclinic, $P\bar{1}$ (No. 2)	orthorhombic, $P2_12_12_1$ (No. 19)
a, Å; α, °	7.4624(7); 94.14(1)	10.765(2); 90
b, Å; β, °	11.7377(8); 98.19(1)	11.022(2); 90
c, Å; γ, °	15.398(2); 107.87(1)	21.587(5); 90
V, $Å^3$; *Z*	1260.9(2); 2	2561.3(9); 4
D_c, g cm^{-3}	1.699	1.509
F(000); μ(MoKα), mm^{-1}	648; 1.307	1192; 0.975
θ range, °; data completeness, %	1.8–25.1; 99.7	1.9–25.1; 99.8
hkl range	–8/8, –13/13, –18/18	–12/12, 0/13, 0/25
No. of unique diffractions	4447	4533
No. of observed diffractions	3562	3902
No. of parameters	284	284
R_{int}; Flack parameter	0.0405; –	0.0473; 0.03(7)
R, *wR* for observed diffractions, %	4.46, 10.90	5.72, 14.89
R, *wR* for all data, %	6.52, 12.08	7.26, 16.67
GOF for all data	1.06	1.08
T_{min}/T_{max}	0.70/0.86	0.46/0.64
Residual electron density, e $Å^{-3}$	1.07, –1.09	0.52, –0.58

All shifts found in the ^{1}H and ^{13}C NMR spectra are in the expected range. The coordination-induced shifts of the methylene hydrogen atoms from the EDTA moieties were found to be shifted to low field by 0.69 (**2a**) and 0.45 ppm (**2b**). Furthermore, the AB spin systems of the CH^{A}H^B protons of the glycine moieties at δ 4.10/4.73 (**2a**) and 3.97/4.57 ppm (**2b**) (free ligands **1a**: 3.45, **1b**: 3.56 ppm) strongly indicate a $\kappa^2 N,N'$ coordination mode of R$_4$EDTA ligands to palladium(II) ion.

*Crystal Structures of **2a**·$CDCl_3$ and **2b***

The complexes **2a**·$CDCl_3$ and **2b** crystallized in the triclinic space group $P\text{-}\bar{1}$ and in the orthorhombic space group $P2_12_12_1$, respectively. Both complexes crystallized as isolated molecules without any unusual intermolecular interactions. The $CDCl_3$ solvent molecule in **2a**·$CDCl_3$ exhibited no unusual contacts to complex **2a**. The molecular structures are shown in Figs 2 and 3. Selected distances and angles are given in Table II.

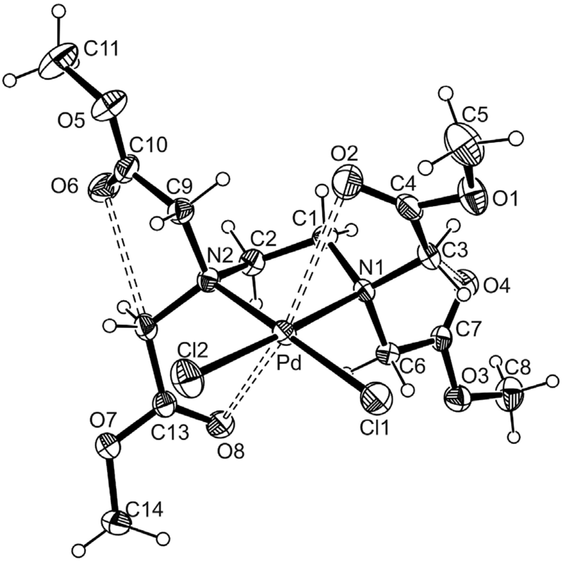

FIG. 2
ORTEP representation of complex **2a** in crystals of **2a**·$CDCl_3$. Displacement ellipsoids are plotted at the 30% probability level and H atoms are shown as small spheres of arbitrary radii

The Pd atoms in both complexes have a square-planar geometry with one EDTA tetraalkyl ester ligand coordinated through the two nitrogen atoms ($\kappa^2 N,N'$ coordination). The remaining two coordination sites are occupied by chloro ligands.

The Pd–N distances (2.098(4)–2.106(7) Å) are within the typical range for palladium complexes with EDTA[14,15] and ethylenediamine ligands (2.03–2.09 Å)[16], but longer than those with amino acid ligands (2.00–2.03 Å)[17]. The Pd–Cl bond distances (2.287(2)–2.298(2) Å) are in the same range as those in $[PdCl_2(EDTA)]\cdot xH_2O$, $x = 5, 6$ (2.30(1) Å)[15]. The Pd atoms adopt approximately square-planar coordination; the Pd, Cl, N atoms lie nearly in plane (greatest deviation from the mean plane: 0.052(5) Å for N2 in **2a** and 0.033(7) Å for N1 in **2b**). The largest deviations from a right angle was found for the N1–Pd–N2 angles (**2a**: 85.9(2), **2b**: 85.6(3)°) due to the chelate binding of the R_4EDTA ligands, as found also for $[PdCl_2(EDTA)]\cdot xH_2O$ (x = 5, 6) complexes (85.1°)[15].

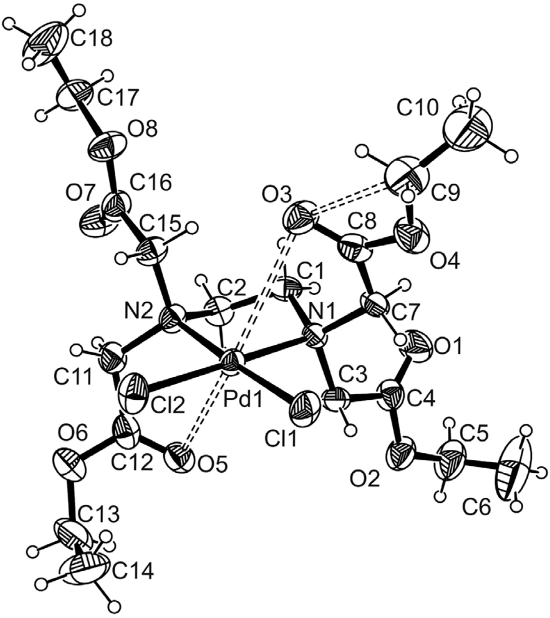

FIG. 3
ORTEP representation of complex **2b**. Displacement ellipsoids are plotted at the 30% probability level and H atoms are shown as small spheres of arbitrary radii

TABLE II
Selected bond lengths (in Å), bond and torsion angles (in °) and contact distances (in Å) for complexes **2a**·$CDCl_3$ and **2b**

Atoms	**2a**·$CDCl_3$	**2b**	
	Bond lengths		
Pd–Cl1	2.295(2)	2.287(2)	
Pd–Cl2	2.298(2)	2.289(3)	
Pd–N1	2.098(4)	2.101(7)	
Pd–N2	2.106(4)	2.106(7)	
	Bond angles		
Cl1–Pd–Cl2	91.37(6)	91.1(1)	
Cl1–Pd–N1	90.7(1)	92.0(2)	
Cl1–Pd–N2	174.9(1)	177.2(2)	
Cl2–Pd–N1	177.8(1)	176.5(2)	
Cl2–Pd–N2	92.0(1)	91.3(2)	
N1–Pd–N2	85.9(2)	85.6(3)	
Pd–N1–C1	105.4(3)	105.5(6)	
Pd–N1–C2	105.0(3)	105.2(2)	
	Torsion angles		
N1–C3–C4–O2	–18.9(8)	N1–C7–C8–O3	–16(2)
N1–C6–C7–O4	–3.3(8)	N1–C3–C4–O1	–2(2)
N2–C9–C10–O6	3.9(8)	N2–C15–C16–O7	7(2)
N2–C12–C13–O8	–30.3(8)	N2–C11–C12–O5	–22(2)
	Contact distances		
Pd···O2	2.984(5)	Pd···O3	3.124(9)
Pd···O8	3.172(5)	Pd···O5	3.065(7)
C3···O4	2.990(8)	C9···O3	2.68(2)
C12···O6	2.873(8)		

The Pd(ethylenediamine) five-membered rings adopt a half-chair conformation twisted about the C1–C2 part[18]. It is evident from the N–C–C–O torsion angles that two of the four glycine moieties of the ligand are nearly synperiplanar (–2(2)...7(2)°) and the other two are in between of *synperiplanar* and *gauche* conformations (–16(2)...–30.3(8)°).

The solid-state structures of **2a** and **2b** seem to be stabilized by weak Pd···O interactions between two of the four carbonyl O atoms (**2a**: O2, O8; **2b**: O3, O5) which are oriented towards the Pd atom (Pd···O, **2a**: 2.984(5)/3.172(5); **2b**: 3.065(7)/3.124(9) Å; sum of van der Waals radii: 3.15 Å[19]). Furthermore, structure **2a**·$CDCl_3$ appears to be stabilized by two weak intramolecular C–H···O interactions (C3···O4 2.990(8), C12···O6 2.873(8) Å). The short C9···O3 contact (2.68(2) Å) in **2b** also indicates a weak intramolecular C–H···O interaction.

2a·$CDCl_3$ and **2b** are the first examples of palladium(II) complexes with R_4EDTA ligands that have been structurally characterized by X-ray structural analysis.

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