

# Structure and electrospray mass spectrometry studies on dithia-cyclooctan-3-ol-containing palladium(II) complex of *trans*-[Pd-(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO

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The structure of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO, in which dtco-3-OH is dithiacyclooctan-3-ol and DMSO is dimethyl sulfoxide, was determined by X-ray crystallographic analysis. The crystal data: space group  $P\bar{1}$ ,  $a = 0.7077(2)$  nm,  $b = 1.0788(1)$  nm,  $c = 1.1111(1)$  nm,  $\alpha = 67.710(8)^\circ$ ,  $\beta = 73.59(2)^\circ$ ,  $\gamma = 85.39(2)^\circ$ ,  $R_1 = 0.0368$  and  $R_w = 0.0998$ . The palladium(II) is coordinated by four sulfur atoms with a regular square planar configuration. The Pd—S distances are 0.2314(1) and 0.2317(1) nm, respectively. Both dtco-3-OH ligands are in the boat-chair configuration and two hydroxyl groups are on the opposite sites of the PdS<sub>4</sub> coordination plane and are towards Pd(II). The Pd—O distance is 0.285 nm, indicating a weak interaction between them. A typical hydrogen bond between the hydroxyl group of dtco-3-OH ligand and DMSO was observed in the crystal structure. An aqueous solution prepared with the crystals of the complex was used for the investigation of electrospray mass spectrometry (ESMS). Besides *trans*-[Pd(dtco-3-OH)<sub>2</sub>]<sup>2+</sup>·2DMSO observed, in the full scan spectrum of ESMS, all relative species of it, which were probably produced during electrospray ionization process, were also detected. From these experiments, it reveals that ESMS is a powerful tool for studying noncovalent interaction present in solution between inorganic complexes and solvents.

**Keywords**    Palladium(II) complex, dithiacyclooctan-3-ol, crystal structure, electrospray mass spectrometry

## Introduction

Electrospray mass spectrometry (ESMS) introduced

by Fenn and co-workers<sup>1-4</sup> has been shown to be a powerful technique for analyzing multiply-charged ions, and has been applied primarily to large biomolecules, such as proteins, peptides, nucleic acids, carbohydrates, glycoproteins, drug metabolites, and other biologically active species.<sup>1-8</sup> Because ESMS of most materials of high or low molecular weight gives primarily molecular ions, and few, if any, fragment ions, it is possible to detect noncovalently bound protein-protein or protein-ligand complexes, and to deduce information about the structures of these ions in solution.<sup>5,9-11</sup> In recent years, the technique has been used to elucidate the structural and solution properties of inorganic complexes in solution.<sup>12-21</sup> Although electrospray mass spectrometry is a gentle method for transferring ions (positive or negative) from solution into the gas phases, when the technique is used to inorganic complexes in solution, the interesting questions arise. How tightly must a ligand bind to metal ions to be seen? Is it possible to detect noncovalent bond, such as hydrogen bond, present in solution? Can the  $m/z$  or isotope distribution pattern of these gaseous ions be used to deduce information about the structures of these ions in solution? Which ions observed by ESMS are present in solution and which ions are produced during electrospray ionization process? In order to better understand these questions, in this article, we report the determination of the molecular structure of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO (dtco-3-OH = dithiacy-

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clooctan-3-ol) and using it as "standard sample" for ESMS studies. By precise determination of  $m/z$  of every species and simulation of their isotope distribution patterns, the comparison has been made between two techniques.

## Experimental

### Chemicals

Double-distilled water was used for preparation of aqueous solution. PdCl<sub>2</sub>, AgClO<sub>4</sub> and dithiacyclooctan-3-ol (dtco-3-OH) were obtained from Aldrich Chemical Co. All other chemicals were of reagent grade.

*Trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was prepared as follows. The dtco-3-OH (0.34 mmol) was added to a solution of 0.17 mmol of PdCl<sub>2</sub> in 6 mL of DMSO at 100°C under stirring. The color changed from red to yellow immediately. A solution of 0.34 mmol of AgClO<sub>4</sub> in 2 mL of DMSO was added and AgCl was removed by filtration. Partial removal of the solvent DMSO by distillation in vacuum produced a more concentrated filtrate from which the complex crystallized upon cooling. The product was filtered, washed with acetone and dried in vacuum. Diffusion of acetone into the nearly saturated solution of the solid in DMSO produced the bright yellow single crystals suitable for the crystallographic analysis. The single crystals were dissolved in small volume of DMSO and the solution was diluted with water for ESMS measurements.

### Measurements

A single crystal of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO was mounted on a glass fiber and intensity data were measured on a Siemens P4 four-circle diffractometer with monochromatic Mo K<sub>α</sub> ( $\lambda = 0.071073$  nm) radiation using  $\theta/2\theta$  scan mode with variable scan speed of 4.0–60.0°/min in  $\omega$ . The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.<sup>22</sup>

The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were found in the difference Fourier map and refined isotropically. All computations were carried out on a PC-586 using the SHELXTL-PC program package.<sup>23</sup>

An LCQ electrospray mass spectrometer (ESMS, Finnigan) was employed for  $m/z$  determination of the crystal sample of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO. The sample was diluted with water to a concentration of 100  $\mu\text{mol/L}$ . 1.0  $\mu\text{L}$  of such solution was loaded into the injection valve of the LCQ unit and then injected into the mobile phase solution (50% aqueous methanol), and was carried through the electrospray interface into the mass analyzer at a rate of 200  $\mu\text{L}/\text{min}$ . The employed voltage at the electrospray needles was 5 kV and the capillary was heated to 200°C. A maximum ion injection time of 200 msec along with 10 scans was set. Positive ion mass spectra were obtained. Zoom scan was used in these experiments. Predicted isotope distribution patterns for each species detected were calculated using the IsoPro 3.0 program.

## Results and discussion

### Molecular structure of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO

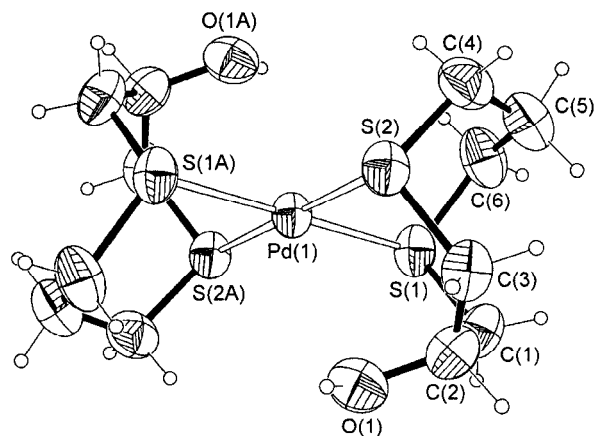
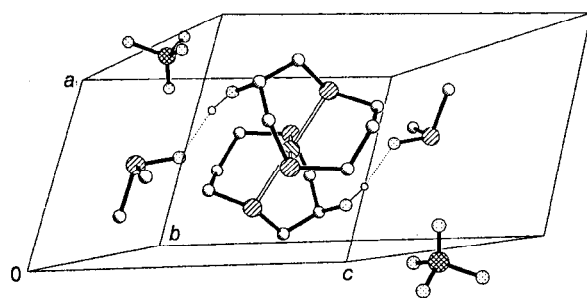
The crystallographic results were given in Tables 1 and 2. Fig. 1 demonstrates the planar arrangement of the four sulfur atoms around the palladium(II) which is

**Table 1** Crystal data for *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO

Formula	C <sub>16</sub> H <sub>36</sub> Cl <sub>2</sub> O <sub>12</sub> PdS <sub>6</sub>
Formula weight	790.11
Color	Yellow
Cryst. Syst.	Triclinic
Space group	$P\bar{1}$
<i>a</i> (nm)	0.7077(2)
<i>b</i> (nm)	1.0788(1)
<i>c</i> (nm)	1.1111(1)
$\alpha$ (deg)	67.710(8)
$\beta$ (deg)	73.59(2)
$\gamma$ (deg)	85.39(2)
<i>V</i> (nm) <sup>3</sup>	0.7526(2)
<i>Z</i>	1
Density (g/cm <sup>3</sup> )	1.743
<i>F</i> <sub>(000)</sub>	404
$\mu$ (Mo K <sub>α</sub> ) (cm <sup>-1</sup> )	12.63
Mo K <sub>α</sub> ( $\lambda$ /(nm))	0.071073
<i>T</i> (K)	293(2)
$2\theta$	4.08–49.98
<i>R</i> <sub>1</sub>	0.0368
<i>R</i> <sub>w</sub>	0.0998

**Table 2** Selected bond lengths (nm) and bond angles ( $^{\circ}$ ) in *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO

Pd(1)—S(2)	0.2314(1)	Pd(1)—S(1)	0.2317(1)
S(1)—C(6)	0.1818(5)	S(1)—C(1)	0.1819(5)
S(2)—C(3)	0.1813(5)	S(2)—C(4)	0.1818(5)
O(1)—C(2)	0.1418(6)		
S(2) # 1-Pd(1)-S(2)	180.0	S(2)-Pd(1)-S(1) # 1	89.71(4)
S(2)-Pd(1)-S(1)	90.29(4)	S(1) # 1-Pd(1)-S(1)	180.0
C(6)-S(1)-C(1)	104.5(3)	C(6)-S(1)-Pd(1)	106.4(2)
C(1)-S(1)-Pd(1)	105.3(2)	C(3)-S(2)-C(4)	103.2(2)
C(3)-S(2)-Pd(1)	106.25(14)	C(4)-S(2)-Pd(1)	105.8(2)
C(2)-C(1)-S(1)	116.9(3)	O(1)-C(2)-C(1)	106.8(4)
O(1)-C(2)-C(3)	112.9(4)		
Hydrogen bond			
O(1)⋯O(DMSO)	0.2673(7)	O(1)—H⋯O(DMSO)	166.26(6.46)

**Fig. 1** ORTEP representation of *trans*-[Pd(dtco-3-OH)<sub>2</sub>]<sup>2+</sup>.**Fig. 2** View of the unit cell of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO.

located at the crystallographically imposed symmetry center of the molecule. The Pd—S(1) and Pd—S(2) distances are 0.2314(1) and 0.2317(1) nm, respectively. Both dtco-3-OH ligands are in the boat-chair conforma-

tion, with two cycles folding in a butterfly-like fashion in such a way that C(2) and C(2A) (symmetry code A:  $1-x, 1-y, 1-z$ ) are pointing toward the metal, whereas C(5) and C(5A) are pointing away from it. Two hydroxyl groups are on the opposite sides of the PdS<sub>4</sub> coordination plane (called as *trans*-configuration) and are towards Pd(II). The Pd—O distance is 0.285 nm, less than 0.32 nm, the sum of van der Waals radii of palladium(II) and oxygen atom. In other words, a weak interaction exists between Pd(II) and the oxygen. There are two DMSO molecules involved in a unit cell (see Fig. 2). Each DMSO links with hydroxyl group of dtco-3-OH through a typical hydrogen bond, as shown in Table 2.

#### Electrospray mass spectrometry of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO

An aqueous solution of the single crystals of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO was subjected to ESMS measurement in order to understand what is happening for a well-known structural complex during the electrospray mass ionization process. A full scan spectrum and the zoom scan spectra for six groups of peaks with calculated isotopic distribution patterns inserted are given in Figs. 3 and 4. As seen in Figs. 3 and 4(d), the observed peaks with  $m/z = 293.9-296.9$  separated by 0.5  $m/z$  fit well to those calculated for *trans*-[Pd(dtco-3-OH)<sub>2</sub>]<sup>2+</sup>·2DMSO in which, as indicated by X-ray determination, each DMSO molecule is attached to *trans*-[Pd(dtco-3-OH)<sub>2</sub>]<sup>2+</sup> by means of a typical hydrogen bond between DMSO and hydroxyl group of dtco-3-

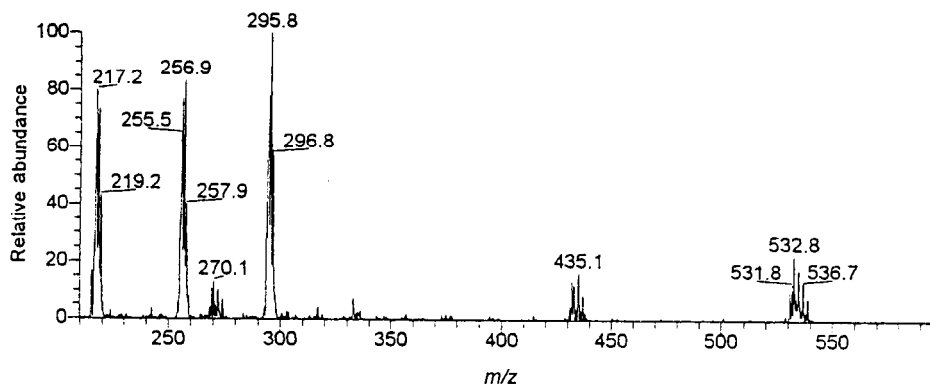


Fig. 3 ESMS spectrum of *trans*-[Pd(dtcO-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2DMSO.

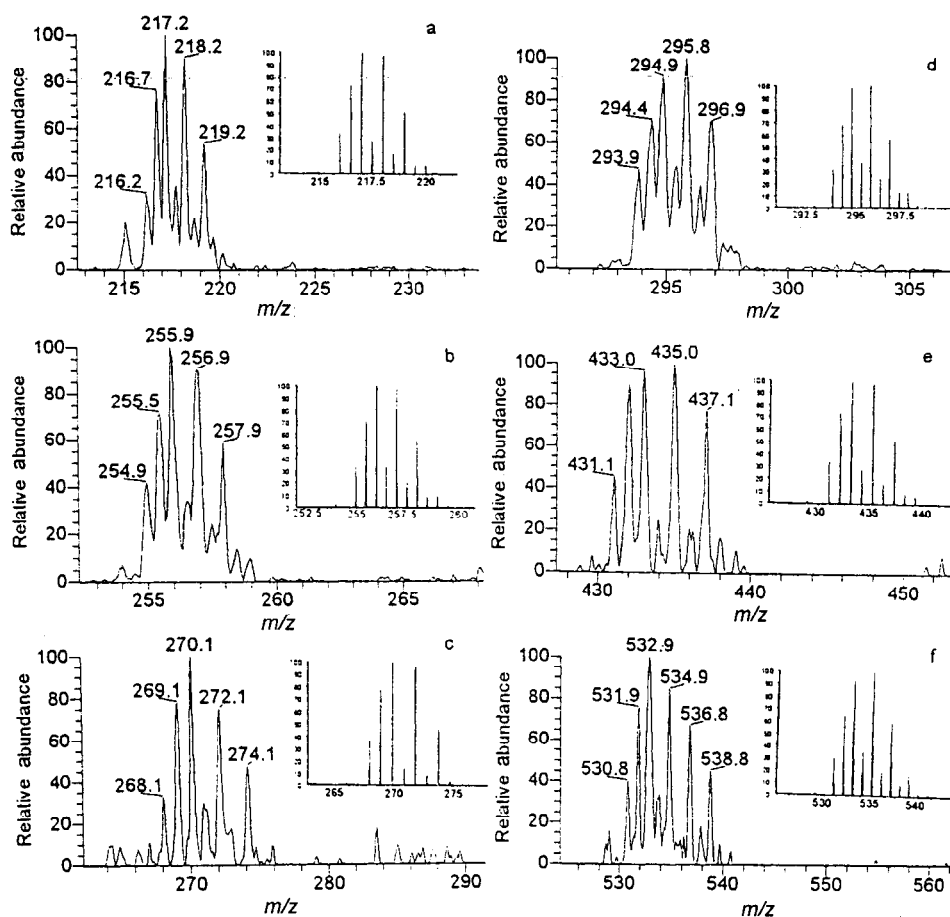


Fig. 4 Zoom scan spectra for each group of peaks with corresponding calculated isotope distribution patterns inserted. a: [Pd(dtcO-3-OH)<sub>2</sub>]<sup>2+</sup>; b: [Pd(dtcO-3-OH)<sub>2</sub>]<sup>2+</sup>·DMSO; c: [Pd<sup>(I)</sup>(dtcO-3-OH)]<sup>+</sup>; d: [Pd(dtcO-3-OH)<sub>2</sub>]<sup>2+</sup>·2DMSO; e: [Pd(dtcO-3-OH)<sub>2</sub>-H<sup>+</sup>]<sup>+</sup>; f: {[Pd(dtcO-3-OH)<sub>2</sub>](ClO<sub>4</sub>)}<sup>+</sup>.

OH ligand. The *trans*-[Pd(dtcO-3-OH)<sub>2</sub>]<sup>2+</sup>·2DMSO probably is a unique species present in solution. The

observed peaks, with *m/z* = 254.9–257.9 (Figs. 3 and 4(b)) and 216.2–219.2 (Figs. 3 and 4(a)),

separated by 0.5  $m/z$ , are attributed to double charged complexes of *trans*-[Pd(dtco-3-OH)<sub>2</sub>]<sup>2+</sup> · DMSO and *trans*-[Pd(dtco-3-OH)<sub>2</sub>]<sup>2+</sup>, respectively. These two species are produced during electrospray ionization process by breaking one or two hydrogen bonds in its precursor. Besides, the peaks with  $m/z = 530.8$ — $538.8$  (Figs. 3 and 4(f)) separated by 1.0  $m/z$  are due to the fragment of ion pair *trans*-[Pd(dtco-3-OH)<sub>2</sub>(ClO<sub>4</sub>)]<sup>+</sup>. During electrospray ionization process, two less abundance signals were created at  $m/z = 268.1$ — $274.1$  (Figs. 3 and 4(c)) and  $431.1$ — $437.1$  (Figs. 3 and 4(e)), both separated by 1.0  $m/z$ . The former is due to the fragment of *cis*-[Pd(dtco-3-OH)]<sup>+</sup> in which Pd(II) is reduced to Pd(I), and the latter is assigned to *trans*-[Pd(dtco-3-OH)<sub>2</sub> - H<sup>+</sup>]<sup>+</sup> that was obtained by deprotonation of hydroxyl group of one dtco-3-OH ligand. That both dtco-3-OH ligands in the *trans*-[Pd(dtco-3-OH)<sub>2</sub>]<sup>2+</sup> are deprotonated during electrospray ionization process seems to be possible, but the neutral species obtained can not be detected by ESMS. From these experiments, it further provides an example that the ESMS is also a powerful tool to give an insight into noncovalent interaction of metal complexes with solvents in solution. It is also indicated that although the ESMS is a gentle method, some species, associated with breaking hydrogen bond or deprotonation or reduction of Pd(II) and dissociation of ligand, are created during electrospray ionization process.

## Conclusion

This report provides an example of application of electrospray mass spectrometry to probe the solution structures of a well-known structural palladium(II) complexes of *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> · 2DMSO. The hydrogen bonds in *trans*-[Pd(dtco-3-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> · 2DMSO confirmed by crystal structure data are also confirmed by ESMS in solution. By combining the full scan and zoom scan spectra of ESMS as well as simulation of isotope distribution patterns, the information about which species are present in solution and which one is created by electrospray ionization process has been obtained successfully.

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