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Synthesis, Structural and Theoretical Studies of Dithiodiglycolamide Compounds of Palladium (II)

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The reaction of palladium (II) halide with dithiodiglycolamide ligands yielded compounds of the type $[\text{PdX}_2\text{L}]$ (where $\text{X} = \text{Cl}$, $\text{L} = (\text{CH}_2\text{SCH}_2\text{CON}^i\text{Pr}_2)_2$ (**1**); $\text{L} = (\text{CH}_2\text{SCH}_2\text{CON}^i\text{Bu}_2)_2$ (**2**); $\text{L} = (\text{CH}_2\text{SCH}_2\text{CONBu}_2)_2$ (**3**); $\text{L} = \text{C}_7\text{H}_6(\text{SCH}_2\text{CON}^i\text{Bu}_2)_2$ (**4**); $\text{X} = \text{Br}$, $\text{L} = (\text{CH}_2\text{SCH}_2\text{CON}^i\text{Bu}_2)_2$ (**5**); $\text{X} = \text{I}$, $\text{L} = (\text{CH}_2\text{SCH}_2\text{CON}^i\text{Bu}_2)_2$ (**6**)), whereas palladium (II) nitrate yielded compounds of the type $[\text{PdL}_2](\text{NO}_3)_2$ (where $\text{L} = (\text{CH}_2\text{SCH}_2\text{CON}^i\text{Pr}_2)_2$ (**7**); $\text{L} = (\text{CH}_2\text{SCH}_2\text{CON}^i\text{Bu}_2)_2$ (**8**)). All compounds were characterized by using, IR, ¹H NMR spectral techniques and CHN analyses. The structures for the compounds **4**, **5** and **7** have been determined by using X-ray diffraction methods. The structures show that the ligands bond through the thioether group to the metal centre in all compounds. They show further that the palladium (II) ion is surrounded by four atoms (two halogens and two thio groups in **4** and **5** and four thiogroups in **7**) in a square planar arrangement. The dithiodiglycolamide ligand acts as a bidentate chelating ligand and bonds through both the thioether groups to metal centre and leaving the carbamoyl groups uncoordinated. Theoretical studies reveal that the 1:2 compound is energetically more stable and nicely correlates with the IR carbamoyl stretching frequencies as compared to the 1:1 compound in which the ligand acts as a tetradentate ligand.

1. Introduction

The separation of platinum group metals (PGM) from spent catalysts obtained from automotive petroleum industries and high level liquid waste (HLW) from nuclear processes is of recent interest and offers an opportunity for hydro metallurgist and separation scientists due to the value of the metals and their application in various fields.¹⁻⁴ Various new extractants containing soft sulphur and nitrogen atoms have been explored for this purpose in recent years.⁵

Among them, extractants based on dithiodiglycolamide (Figure 1) and thiodiglycolamide have shown excellent extraction and kinetic properties as compared to other extractants reported such as tertiary and quaternary amine, oximes and sulphides.^{4, 6} These ligands having one or two thioether groups with two carbamoyl groups attached to sulphur have been explored extensively for the separation of palladium from HLW.^{3, 6-8} Solvent extraction data have revealed that the dithiodiglycolamide forms a 1:1 compound with palladium nitrate and also palladium chloride,^{3, 6-8} whereas the thiodiglycolamide ligand forms a 2:1 compound with palladium chloride⁶.

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Electronic Supplementary Information (ESI) available: [The CCDC 1000037, 1000038 and 1000039 contain the supplementary crystallographic data for the compounds **4**, **5** and **7**. Copies of this information may be obtained free of charge from The Cambridge Crystallographic Data Centre via [www: http://www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)]

Recent studies using Extended X-ray Absorption Fine Structure (EXAFS)⁹ and theoretical studies of a palladium nitrate compound with dithiodiglycolamide show that the ligand form a 1:1 compound by bonding to the metal through both the thioether and carbamoyl groups in a tetradentate fashion (chelate binding mode).¹⁰ However, there is no spectroscopic evidence provided to support that conclusion. Indeed, if there is bonding between the metal and the carbamoyl group, then it should be reflected in the IR spectrum by showing a frequency difference ($\Delta\nu$) of 40- 80 cm^{-1} for the carbamoyl group with respect to the free ligand.^{11a} The slight difference observed in the reported spectrum¹⁰ has been explained recently as being

due to the protonation of the carbamoyl group during contact with HNO_3 ¹². The observed Pd-O distance of 2.04 ($\pm 5\%$) Å in the EXAFS study may be due to the oxygen atom from water, nitrate or carbamoyl groups. The X-ray structures of the compounds [*trans*[Pd(NO₃)₂(Pyrolidone)₂]^{11a} and *trans*-[Pd(NO₃)₂(H₂O)₂]^{11b,c} show Pd-O distances of 1.999 (5) and 2.011 (5) Å for Pd-O(NO₃), 2.009(11) Å for Pd-O(C=O)^{11a} and 2.021 (4) , 2.030 (5) Å for Pd-H₂O. Furthermore it was reported that Pd-O (NO₃) distances lie in the range 1.995–2.030 Å^{11d} in M₂[Pd(NO₃)₄] (M = Na, K, Rb, Cs) compounds and Pd-O(H₂O) distances lie in the range^{11e} of 2.097–2.220 Å depending upon the groups *trans* to H₂O. Thus, under these conditions and without any spectroscopic evidence, the pre-assumption of coordination of carbamoyl groups to palladium ion is inconclusive from the EXAFS study alone. We have recently reported the complexation chemistry of thiodiglycolamide and dithiodiglycolamide based ligands^{13,14} with lanthanide and actinide ions. However, no systematic structural study on the complexation chemistry of these technologically important ligands with palladium(II) ion is reported in the literature. We report herein the synthesis, characterization, structural studies of palladium chloride, bromide and nitrate with dithiodiglycolamide ligands (L1 to L5, Figure 1). In conjunction to the experimental data, quantum chemical calculations are carried out to understand the feasibility for the formation of 1:1 and 1:2 (palladium to ligand) complexes.

2. Experimental

All reagents and solvents were of analytical grade and used as received. IR spectra were recorded as nujol mulls using a JASCO- 610 FITR spectrometer. ¹H NMR spectra were recorded using a Bruker AMX-300 spectrometer or Varian 500MHz instruments. The chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz. Electrospray ionization mass spectrometric (ESI-MS) detection of positive ions in CH₃CN was recorded using a MicrOTOF Q-II instrument. The samples were introduced into the source with the syringe pump. Nitrogen was employed as both the drying and spraying gas, with a source temperature of 180 °C. The cone voltage was set to 45 V, the voltage applied on the capillary was 1162 kV and sample solution flow rate was 5 $\mu\text{L min}^{-1}$. Dithiodiglycolamide (L1-L5) ligands were prepared according to reported methods.¹³

2.1 General synthesis for complexes of palladium chloride

PdCl₂ (1 mmol) was suspended in acetonitrile and heated to get a clear solution to which an appropriate ligand (1mmol) was added and stirred for 5 hours. This solution on evaporation yielded an orange colored product which was filtered and washed with hexane, dried and recrystallized from CH₂Cl₂/MeOH mixture as an orange colored crystalline solid in good yield.

2.2 Synthesis of [PdCl₂(CH₂SCH₂CON(^{iso}Pr)₂)₂] (1)

Yield : 85 % ; ¹H NMR (25 °C, CDCl₃): δ = 1.260 (d, 12H, CH₃, ^{iso}Pr), 1.391 (d, 12H, CH₃, ^{iso}Pr), 3.016 (d, 2H, -CH₂S-), 3.590 (d, 2H, -CH₂S-), 3.511 (d, 2H, -SCH₂CO-), 4.557 (d, 2H, -SCH₂CO-), 3.511 (m, 2H, CH, ^{iso}Pr), 4.115 (m, 2H, CH, ^{iso}Pr). IR (cm⁻¹): ν = 1633 (C=O). Analysis (%): Calcd. for PdCl₂C₁₈H₃₆O₂N₂S₂: C, 39.0; H, 6.5; N, 5.1; S, 11.6; Found: C, 39.1; H, 6.8; N, 4.9; S, 11.5.

2.3 Synthesis of [PdCl₂(CH₂SCH₂CON(^{iso}Bu)₂)₂] (2)

Yield :90%; ¹H NMR (25 °C, CDCl₃): δ = 0.878 (d, 12H, CH₃, ^{iso}Bu), 0.960 (d, 12H, CH₃, ^{iso}Bu), 1.977 (m, 4H, CH^{iso}Bu), 3.075 (d, 2H, -CH₂S-), 3.575 (d, 2H, -CH₂S-), 3.149 (d, 4H, NCH₂^{iso}Bu), 3.205 (d, 4H, NCH₂, ^{iso}Bu), 4.164 (d, 2H, -SCH₂CO-), 4.594 (d, 2H, -SCH₂CO-). IR (cm⁻¹): ν = 1633(C=O). Analysis (%): Calcd. for PdCl₂C₂₂H₄₄O₂N₂S₂: C, 43.3; H, 7.2; N, 4.6; S, 10.5; Found: C, 43.5; H, 7.1; N, 4.3; S, 10.7.

2.4 Synthesis of [PdCl₂(CH₂SCH₂CON(*n*-Bu)₂)₂] (3)

Yield : 84% ; ¹H NMR (25 °C, CDCl₃): δ = 0.929 (m, 12H, CH₃, Bu), 1.302 (m, 4H, NCCCH₂, Bu), 1.357 (m, 4H, NCCCH₂, Bu), 1.502 (m, 4H, NCCH₂, Bu), 1.572 (m, 4H, NCCH₂, Bu), 3.138 (d, 2H, -CH₂S-), 3.580 (d, 2H, -CH₂S-), 3.319 (m, 8H, NCH₂, Bu), 4.228 (d, 2H, -SCH₂CO-), 4.535 (d, 2H, -SCH₂CO-). IR (cm⁻¹): ν =1633 (C=O). Analysis (%): Calcd. for PdCl₂C₂₂H₄₄O₂N₂S₂: C, 43.3; H, 7.2; N, 4.6; S, 10.5; Found: C, 43.8; H, 7.1; N, 4.3; S, 10.8.

2.5 Synthesis of [PdCl₂(C₇H₆SCH₂CON(^{iso}Bu)₂)₂] (4)

Yield : 85%; ¹H NMR (25 °C, CDCl₃): δ = 0.899 (m, 24H, CH₃, ^{iso}Bu), 1.886 (br, 2H, CH, ^{iso}Bu), 2.014 (br, 2H, CH, ^{iso}Bu), 2.385 (s, 3H, -CH₃(tolyl)), 3.212 (m, 8H, NCH₂, ^{iso}Bu), 4.507 (m, 2H, -SCH₂CO-), 4.703 (m, 2H, -SCH₂CO-), 7.276 - 7.810 (3H, aromatic H). IR (cm⁻¹): ν =1650 (C=O). Analysis (%): Calcd for PdCl₂C₂₇H₄₆O₂N₂S₂: C, 48.3; H, 6.8; N, 4.2; S, 9.5; Found: C, 48.4; H, 6.9; N, 4.0; S, 9.8.

2.6 Synthesis of [PdBr₂(CH₂SCH₂CON(^{iso}Bu)₂)₂] (5)

To a solution of **2** (0.5 mmol, 304 mg) in acetone, potassium bromide (1mmol, 119 mg) was added and stirred for 2 hours. The solution was filtered to remove an insoluble white precipitate and the filtrate on evaporation yielded an orange coloured product. This powder was crystallized from CH₂Cl₂/MeOH mixture to yield an orange colored crystalline solid. Yield (80 %). ¹H NMR (25 °C, CDCl₃): δ = 0.889 (d, 12H, CH₃, ^{iso}Bu), 0.963 (d, 12H, CH₃, ^{iso}Bu), 1.967 (m, br, 4H, CH^{iso}Bu), 3.537 (d, 2H, -CH₂S-), ~3.1 (merged with -NCH₂, 2H, -CH₂S-), 3.218 (m, 8H, NCH₂, ^{iso}Bu), 4.155 (d, 2H, -SCH₂CO-), 4.614 (d, 2H, -SCH₂CO-). IR (cm⁻¹): ν = 1626(C=O). Analysis (%): Calcd for PdBr₂C₂₂H₄₄O₂N₂S₂: C, 37.8; H, 6.3; N, 4.0; S, 9.2; Found: C, 37.9; H, 6.0; N, 3.9; S, 9.5

2.7 Synthesis of [PdI₂(CH₂SCH₂CON(^{iso}Bu)₂)₂] (6)

This was prepared similarly to **5** by using KI. Yield (90 %). ¹H NMR (25 °C, CDCl₃): δ = 0.901 (d, 12H, CH₃, ^{iso}Bu), 0.972 (d,

12H, CH₃, ¹Bu), 1.993 (m, br, 4H, CH¹Bu), 3.8-4.6 (br, 4H, -CH₂S- and 4H, -SCH₂CO-), 3.2 (br, 8H, NCH₂¹Bu), IR (cm⁻¹): ν = 1633(C=O). Analysis (%): Calcd for PdI₂C₂₂H₄₄O₂N₂S₂: C, 33.3; H, 5.6; N, 3.5; S, 8.1; Found: C, 33.4; H, 5.7; N, 3.3; S, 8.5.

2.8 Synthesis of [Pd{(CH₂SCH₂CON(¹⁵⁰Pr)₂)₂}]₂(NO₃)₂ (7).

To a solution of Pd(NO₃)₂·2H₂O (1 mmol) in acetonitrile, ligand L1 (2 mmol) was added and stirred for 5 hours. This solution was evaporated to dryness and the resultant residue was washed with hexane and dried. The orange coloured product thus obtained was recrystallized from CH₂Cl₂ / 1, 2-dichloroethane as an orange coloured crystalline solid. Yield :70%; ¹H NMR (25 °C, CDCl₃): δ = 1.245 (d, 24H, CH₃, ¹Pr), 1.360 (d, 24H, CH₃, ¹Pr), 2.268 – 5.188 (d and m for -CH₂S- and -SCH₂CO-), 3.447 (m, 4H, CH, ¹Pr), 4.046 (m, 4H, CH, ¹Pr). IR (cm⁻¹): ν = 1642 (C=O). Analysis (%): Calcd for PdC₃₆H₇₂O₁₀N₆S₄: C, 43.9; H, 7.3; N, 8.6; S, 13.0; Found: C, 44.2; H, 7.3; N, 8.4; S, 13.5.

2.9 Synthesis of [Pd{(CH₂SCH₂CON(¹⁵⁰Bu)₂)₂}]₂(NO₃)₂ (8).

This was prepared similarly to 7 by using L2. Yield :80%; ¹H NMR (25 °C, CDCl₃): δ = 0.866 (d, 24H, CH₃, ¹Bu), 0.941 (d, 24H, CH₃, ¹Bu), 1.976 (m, br, 8H, CH¹Bu), 3.104 - 4.924 (d and m 8H, -CH₂S- and 8H, -SCH₂CO-), 3.194 (br, 16H, NCH₂¹Bu); IR (cm⁻¹): ν = 1637 (C=O). Analysis (%): Calcd for PdC₄₄H₈₈O₁₀N₆S₄: C, 48.2; H, 8.0; N, 7.7; S, 11.7; Found: C, 48.3; H, 7.7; N, 7.6; S, 11.9

2.10 Crystal structure determinations

Crystal data for 4 and 5 were measured on a Oxford Diffraction X-Calibur CCD System at 150(2)K with MoK_α radiation (λ = 0.71073 Å). The crystals were positioned at 50 mm from the CCD. 321 frames were measured for both the crystals with a counting time of 10 s. For compound 7 the data was collected on a Agilent SuperNova system equipped with Titan CCD detector at 293(2) K using CuK_α radiation (λ = 1.5418 Å). The crystals were positioned at 101 mm from the CCD. 925 were measured with a counting time of 1s. Data analyses were carried out with the CrysAlis program^{15a} for all compounds. The structures were solved using direct methods with the Shelxs97 program.^{15b} All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in the geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they attached. Empirical absorption corrections were carried out using the ABSPACK program^{15c} for all compounds. The structures were refined to convergence on F² using Shelxl97.^{15b} Selected crystallographic data for 4, 5 and 7 are summarized in Table 1.

2.11 Computational Details

To gauge our experimental data and to provide insights on the formation of favourable 1:2 PdL₂ complexes as compared to 1:1 complexes, we have carried out density functional theory (DFT) based calculations. For comparison with di-thio ligand,

we have also carried out DFT calculations of monothiodiglycolamide Pd complexes as proposed found by Ruhela et al.¹⁰ All geometries are completely optimized and verified as minima by performing harmonic frequency calculations using BP86 functional.^{16,17} An effective pseudopotential (def-ECP)¹⁸ is employed to treat the core electrons of Pd (28 electrons in core), whereas the valence electrons of Pd is treated using def-TZVP basis set.¹⁹ The ligand electrons are treated using TZVP basis set.²⁰ For the computation of energetics, a B3LYP functional^{21,22} is used in conjunction with a more accurate segmented All electron relativistically Contracted (SARC) basis set²³(def2-TZVP basis set²⁴ for all atoms), scalar relativistic effects (using zeroth order regular approximation, ZORA²⁵) and solvent effects (using the dielectric constant of water) are incorporated with the COSMO continuum solvation model.²⁶ The resolution of the identity (Split-RJ),²⁷ and chain of spheres (COSX),²⁸⁻³¹ approximations were used in combination with the appropriate auxiliary basis sets and integration grids. It should be noted that such computational strategy have been successfully used by us in the past for several transition metal^{32,33} and actinide complexes.³⁴⁻³⁶ All calculations are carried out with TURBOMOLE V6.0.3³⁷ and ORCA 3.0 packages.³⁸ For computational efficiency, we have truncated the R-groups of the ligand to methyl groups. The starting structures for 1:1 and 1:2 Pd-complexes are built from the X-ray structures reported here.

Further energy decomposition analysis (EDA) is carried out for some Pd-complexes to gain insights on the nature of interactions present between Pd and the ligands with ADF program³⁹ based on the methods pioneered by Morokuma⁴⁰ and Ziegler⁴¹ at B3LYP/TZP with ZORA. The total interaction energy (ΔE_{int}) between the two fragments is calculated using the following equation,

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{pauli}} + \Delta E_{\text{orb}} \quad (1)$$

and the percentage covalency have been calculated using the equation 2,

$$[\Delta E_{\text{orb}} / (\Delta E_{\text{elstat}} + \Delta E_{\text{orb}})] \times 100 \quad (2)$$

where, ΔE_{elstat} and ΔE_{pauli} represents the electrostatic and repulsive interaction energy contributions between the fragments respectively. ΔE_{orb} is the stabilizing energy arises from orbital contributions; thus represents the strength of covalent bonding between the fragments. We have chosen Pd and ligands (both thiodiglycolamide and dithiodiglycolamide) as two fragments.

3. Results and Discussion

3.1 Compounds of dithiodiglycolamide with palladium (II) chloride, bromide and iodide.

The 1:1 reaction of ligands L1, L2, L3 and L5 with palladium (II) chloride yielded the compounds 1- 4. (Scheme 1). The reaction of compound 2 with KBr and KI in acetone yielded the

corresponding bromo (**5**) and iodo (**6**) compounds respectively (Scheme 1). The CHN analyses revealed that the ligands form 1:1 compounds with the palladium chloride, bromide and iodide. The IR spectra of all compounds show that the carbamoyl groups (see the ESI) are free and uncoordinated. The ¹H NMR spectra of all compounds show the expected peaks and multiplicities.

When the thioether sulphur is bonded to a metal centre, it becomes a stereogenic centre and forms different stereoisomers. In the dithiodiglycolamide ligand, there are two thioetheric sulphur groups, so it can form four different stereoisomers when it bonds to a metal centre in a chelating mode as shown in Figure 2.

When a ligand has C₂ symmetry (in the case of L1, L2 and L3) and the R groups on both the sulphur atoms are the same, than only two stereo isomers are possible for these compounds, namely RS or SR and RR or SS.^{4, 42} These two diastereomers henceforth will be called as A (*anti*) and B (*syn*) of which the A isomer has been established experimentally to be more favoured than B.^{4, 42} If the ligand has C_s symmetry (as in the case of L4) then the number of isomers will remain four from which RS/SR and RR/SS form pairs of enantiomers which are not resolvable in a simple NMR spectrum. One or more diastereomeric forms may be more stable in solid state and solution.^{4, 42} The ¹H NMR spectra of complexes **1-3** and **5** clearly show that both isomeric forms (*syn* and *anti*) are present in the solution for ethylene based dithiodiglycolamide (L1-L3) ligands. In complexes **1**, **2**, **3** and **5**, the -CH₂S- and -SCH₂CO groups show four doublets for each isomer A and B with different intensities.⁴³ In complex **1**, for the -SCH₂CO- group, two doublets appeared at δ = 4.557 and 4.251 for one isomer A, while for the other isomer B, they appeared at δ = 4.417 and 4.283 with an intensity ratio of 3:2. Hence, it can be concluded that in complex **1**, the diastereomers (A and B) are present in solution in the ratio of 3:2. For other 1:1 complexes, details of diastereomers present are given in Table 2.

In complex **4**, the C_s symmetry in the ligand ensures that the -SCH₂CO- protons on the arms are non-equivalent. Hence, for one diastereomer, four doublets are expected and if there are two diastereomers, eight doublets are expected. The ¹H NMR spectrum of **4** shows three multiplets in the range of 4.1-4.8 due to overlapping of different doublets making it difficult to quantify the ratio of stereoisomers. The structures for complexes **4** and **5** were determined by single crystal X-ray diffraction analysis and are consistent with the spectral and elemental analysis results.

3.2 Molecular Structure of 4

The X-ray structure of **4** which contains two molecules in the asymmetric unit called A and B, is shown in figure 3 and selected interatomic bond distances and angles are given in table 3. The space group is centrosymmetric therefore the unit cell contains equal numbers of RR and SS isomers. Molecules A and B have equivalent structures in which the palladium (II)

is surrounded by two dithioether sulphur and two chlorides in a square planar geometry.

In both molecules the carbamoyl arms of the two ligands are opposite to each other thus taking up the *anti* configuration. The Pd-S bond distances range from 2.243(2)-2.255 (2) Å and Pd-Cl bond distances from 2.316(2)-2.326(2) Å in both molecules and are in agreement with the reported values.⁴¹ There are two short weak interactions (2.971(4) Å and 3.190(4) Å) from the two amidic C=O groups to palladium (II) ion in both the molecules. This type of weak interaction between palladium and oxygen atoms has been reported previously for many palladium compounds in the literature.⁴⁵⁻⁵⁰

3.3 Molecular structure of 5

The molecular structure of **5** is shown in Figure 4 and selected interatomic bond distances and angles are given in Table 3. The structure shows that the palladium (II) ion is surrounded by two thioether sulphur atoms and two bromide ions in a square planar geometry. The Pd-Br (2.436 (1) Å and 2.428 (1) Å) and Pd-S (2.271 (2) Å and 2.272(2) Å) distances agree well with previously reported values.⁵¹ The space group is centrosymmetric so the structures contain equal numbers of RS and SR configurations with *syn* geometry (i.e. in *meso* form).

3.4 Palladium nitrate–dithiodiglycolamide compounds

The reaction of palladium (II) nitrate with ligands L1 and L2 in acetonitrile yielded compounds **7** and **8**. The CHN analysis shows that the ligands form a 2:1 compound with palladium (II) nitrate. The IR spectra of compounds show that the carbamoyl group is uncoordinated (free). In general the ¹H NMR spectra for both compounds **7** and **8** are more complex compared to those of corresponding 1:1 compounds (1-3, 5-6) because of the generation of four stereogenic sulphur centres after compound formation. This leads to a large number of stereoisomers and hence a complex ¹H NMR spectrum is observed (see the ESI). If a 1:1 complex is formed in which the ligand bonds through both the sulphur and C=O groups as reported¹⁰ than there will be only one species present in solution due to bonding restrictions and hence the expected ¹H-NMR spectrum should be simpler. However, our observed NMR spectra of complexes **7** and **8** confirm the presence of a 2:1 rather than a 1:1 complex.¹⁰ The structure for the complex **7** is determined by X-ray diffraction, and is consistent with elemental analysis and spectral results.

3.5. Molecular structure of 7

Molecular structure of **7** is shown in Figure 5 and the selected interatomic bond distances and angles are given in Table 3. The metal atom is positioned on a crystallographic centre of symmetry and bonded to four sulphur atoms in a square planar arrangement. The carbamoyl groups are uncoordinated as indeed are nitrate groups which are outside the primary coordination sphere. The structure shows that both the arms of one of the ligands are directed above the PdS₄ plane, while those of the other are directed below the plane leading to an RSRS/SRSR configuration in the solid state. The observed Pd-

S distances (2.328 (1) Å and 2.313 (1) Å) are within the accepted values.⁴⁴

In recent structural studies on complexes of palladium with dithiodiglycolamide in solution by EXAFS and theoretical methods, it has been shown that the ligand forms a 1:1 complex with palladium (II) nitrate and bonds through both the sulphur and carbamoyl groups to form a square planar cationic complex¹⁰. Several attempts to prepare the 1:1 compound as reported above always yielded the 2:1 compound **7** and hygroscopic palladium nitrate salts.

To determine the C=O coordination in solution, 0.1 M palladium nitrate solution in 3M HNO₃ was extracted with 0.1 M L5 ligand in dodecane. The IR spectrum of dodecane solution after extraction shows a shift of ca 4 cm⁻¹ with respect to the free ligand (see the ESI), indicating clearly that there is no C=O coordination with the metal centre.¹²

The ESI MS spectrum of the dodecane solution after contacting with palladium nitrate solution shows the peak at 1419.9 [Pd (L5)₂ +H], indicating the presence of 2:1 complex. Similarly, the complex **7**, also shows the peak at 858.0 [Pd (L1)₂], confirming the presence of a 2:1 complex in solution.

4. Theoretical studies

To understand the differential binding of the two thio ligands, the structures and Pd-complex formation energies are computed at the DFT level. Prior to ligand binding, the optimized structures of *cis* and *trans* isomers of palladium-nitrates are discussed. As palladium prefers *tetra*-coordinate square planar arrangement, the nitrates are bonded in *mono*-dentate binding motif, whereas the two water molecules saturates the coordination around the Pd plane (figure 6). As expected the bond lengths of Pd to O_{NO3} are shorter as compared to P-O_{H2O} in both isomeric forms. Within the two isomers, the *trans*-isomer is somewhat more stable (~8.7kcal mol⁻¹) as compared to the *cis*-isomer.

It should be remembered that 1:1 complex can only arise from *cis*-isomer and not from *trans*-isomer due to steric effect. Indeed, our experimental data (species 5) show that two bromine atoms are in *cis* isomer in the 1:1 complex. However, the formation of chelate binding mode and the 1:2 complexes can be formed with the most stable *trans*-palladium nitrate isomer. Our optimized Pd-L and Pd-Br bond lengths are slightly overestimated by 0.05Å as compared to X-ray data (figure 7). Furthermore, the computed C=O stretching frequency (1635cm⁻¹ vs 1626 cm⁻¹) of the bare di-thio ligand and for the mono-thio ligand (1639cm⁻¹) is excellently reproduced within 10 cm⁻¹ of the experimental data which convinces the BP86 functional used here.

4.1 Structure and Vibrational frequencies

We have identified five possible 1:1 and one 1:2 Pd-dithiodiglycolamide complexes (figure 7). For the Ruhela's thiodiglycolamide ligand,¹⁰ we have identified five 1:2 Pd-

complexes in which some of the species are already reported by Ruhela et al¹⁰ (figure 8).

We have optimized the 1:1 tetra-coordinated Pd-complex (denoted as [PdL₁(Che)]²⁺), where the four ligand atoms (two sulfurs of thio-ether groups and two oxygen atoms of carbamoyl) directly bonded to Pd. The Pd-O bond lengths are shorter (by 0.2 Å) as compared to Pd-S bond lengths. As the carbamoyl oxygens are involved with bonding with Pd, the C=O bonds are elongated by more than 0.04 Å which is not surprising. Our optimized structural parameters are very close to those of Ruhela et al.¹⁰ The weakening of this bond is indeed reflected in the computed C=O stretching frequencies. We find that the C=O stretching frequency (1598 cm⁻¹ and 1606 cm⁻¹) is red-shifted by ~70 cm⁻¹ as compared to the free ligand (1668 cm⁻¹).

Apart from the chelate mode, we have also found four other minimum energy species (species 7) in which two coordination sites are saturated by the ligand, whereas the other two coordination are saturated by either two water molecules (denoted as [PdL₁(H₂O)₂]²⁺ or one nitrate (in bi-dentate motif, denoted as [PdL₁(NO₃)]¹⁺ or with two nitrates (denoted as [PdL₁(NO₃)₂]) or with one nitrate and a water molecule (denoted as [PdL₁(NO₃)H₂O]¹⁺). In all these four complexes, the Pd-S bond length is somewhat longer (by ~0.04 Å) as compared to those of the tetradentate chelate mode. Furthermore, the two water molecules are somewhat loosely bound (~2.2 Å) as compared to those nitrate binding (by ~2.1 Å) to the central metal centre.

Further, unlike the tetradentate chelate binding motif, the computed C=O stretching frequencies of all three complexes are slightly red shifted (by 20-30 cm⁻¹) as compared to the free ligand. Thus, a red shift of ~70 cm⁻¹ in the C=O stretching frequencies of the Pd complex may well be used as a *vibrational marker* to distinguish direct coordination of carbamoyl oxygen to the Pd centre.

We have also optimized the 1:2 complexes with di-thio and mono-thio diglycolamides, where X-ray structure is reported here for the di-thio ligand (figure 7). The computed Pd-S bond lengths are slightly over-estimated (by ~0.08 Å) as compared to those of experimental estimates. Furthermore, the computed C=O stretching frequency (1632 cm⁻¹, 1633 cm⁻¹, 1639 and 1640cm⁻¹) is very close to the experimental value (1642 cm⁻¹).

For comparison with our di-thioglycolamide Pd complexes, we have optimized thio-diglycolamides with Pd (figure 8). Our optimized *cis* and *trans*-PdL₂ complexes are very similar to those found by Ruhela et al, where the Pd-S bond length in the *cis* isomer is shorter as compared to the *trans* isomer. Conversely, the Pd-O bond is longer in the *cis*-isomer than the *trans*-isomer. These variations in structures are similar to those of Ruhela et al.¹⁰

In addition to the ligand binding to Pd, we have also considered other possibilities such as nitrates and water

molecules coordinating to the metal centre whose optimized structures are shown in figure 8. Similar to the di-thio species, the Pd-S bond length is longer for the water or nitrate coordinating to Pd as compared to pure ligand coordination to Pd.

As expected whenever the C=O functional group is involved in bonding with Pd, a red-shifting ($\sim 70\text{ cm}^{-1}$) is noted in the computed vibrational frequencies (for *cis*- and *trans*-[PdL₂]²⁺) as compared to bare thio-diglycolamides, whereas such large red shift is not found for the other three species in which the C=O group is free from coordination.

4.2 Binding Free energies

For thio-diglycolamides Pd complexes, we can clearly see that the formation both *cis* and *trans*-PdL₂ species are more favorable (by $> 25\text{ kcal mol}^{-1}$) as compared to water or nitrate coordination systems. In fact, these are the two most stable species are studied by Ruhela et al.¹⁰

However, for di-thio-diglycolamides we find that we find that 1:2 PdL₂ binding free energies are somewhat larger (by 7 kcal mol⁻¹ as compared to 1:1 tetradentate chelate binding mode). Of the several 1:1 Pd-species, we note that tetradentate chelate binding free energies are strongest as compared to other four complexes. However, it should be note that strain of the ligand (energy difference between the ligand in complexed and uncomplexed form) in tetradentate chelate mode is very high in [PdL₁(Che)]²⁺ complex ($\sim 23\text{ kcal mol}^{-1}$) as compared to [PdL₁(NO₃)₂] complexes. For the latter complex, the ligand strain is very less (less than 2 kcal mol⁻¹).

Thus, the observed IR spectra of the complexes in solution as well as in solid state clearly ruled out the possibility of complex ([PdL₁(H₂O)₂]²⁺) as no peak corresponding to the presence of H₂O group (see the ESI). The possibility of complex [PdL₁(Che)]²⁺ is also ruled out, since there is no change in the position of ν_{CO} group with respect to free ligand for both solution and solid state complexes (see the ESI). Thus, within the several proposed (1:1 Pd to ligand) complexes, we propose [PdL₁(NO₃)₂] species have large formation energy ($\sim 38\text{ kcal mol}^{-1}$) and the structural parameters correlate nicely with the experimental EXAFS and IR data.¹⁰ It is clearly evident from the theoretical studies that the 1:2 complex [PdL₂]²⁺ is most stable species.

4.3 Energy Decomposition Analysis

To gain insights on the bonding nature of the metal ion with two ligands, EDA was carried out (table 5). For the 1:1 complexes of nitrate coordinated thio- and dithio-Pd complexes, the electrostatic interaction (ΔE_{elstat}) is dominant as compared to Pauli repulsion (ΔE_{Pauli}) largely due to the presence of negatively charged nitrates. The orbital interaction is also found to be significant, but overall the electrostatic term is dominant.

However, a different type of bonding interaction is found when only the thio- and dithio-ligands are coordinated (i.e.

nitrates or waters are not coordinated to Pd). For the [PdL₁(Che)]²⁺ complex of di-thio complex and for the 1:2 *cis* and *trans* isomers of thio [PdL₂]²⁺ complexes, a somewhat larger covalent character is noticed ($\sim 60\%$). The electrostatic and Pauli repulsion almost cancel each other particularly for the [PdL₁(Che)]²⁺ complex. For our experimentally observed 1:2 dithio-complex [PdL₂]²⁺, maximum covalent character is clearly seen ($\sim 66\%$). Further, we have also computed the $\Delta E_{\text{elstat}}/\Delta E_{\text{orb}}$ ratio of 1:1 [PdL₁(NO₃)₂]⁰, [PdL₁(Che)]²⁺, and 1:2 [PdL₂]²⁺ species which reveal about the nature of the coordination bond.⁵² We find the ratios are 1.16, 0.67 and 0.51. Thus, within the three complexes, the 1:2 crystallographically observed species is more covalent as compared to the other two species.

5. Conclusions

The structures of dithiodiglycolamide ligand with palladium chloride and bromide show that the ligands form 1:1 complexes and bond through the thioether sulphur atoms to metal centres in a bidentate mode. The structure of palladium nitrate dithiodiglycolamide shows that the ligand forms a 2:1 compound with palladium nitrate leaving both the nitrate groups outside the coordination sphere. Structures of all complexes clearly show that there is no bonding between carbonyl oxygen and palladium (II) ion, thus supporting the IR spectral results. Theoretical studies clearly reveal the 2:1 complex is more energetically stable than that of all other possible 1:1 complexes. Thus, our experimental and theoretical calculations clearly predict that carbonyl functional groups cannot be direct bonded to Pd, although with AgOTf or Ag(BF₄) in anhydrous non-coordinating media such as CH₂Cl₂, a different coordination environment may be possible.

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TOC Graphic

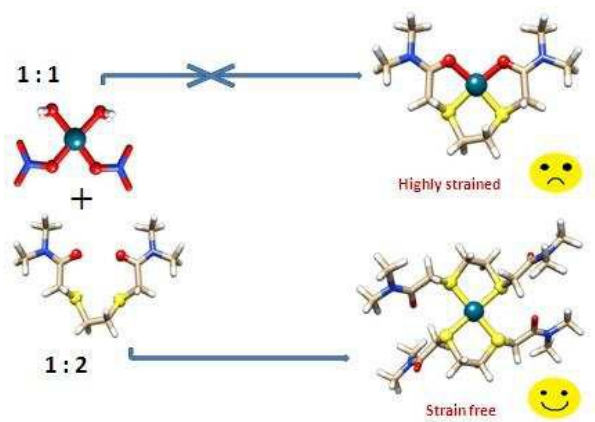


Table 1 : Crystal and structure refinement details for **4**, **5** and **7**

Empirical Formula	C ₂₇ H ₄₆ S ₂ N ₂ O ₂ Cl ₂ Pd	C ₂₂ H ₄₄ S ₂ N ₂ O ₂ Br ₂ Pd	C ₃₆ H ₇₂ S ₄ N ₆ O ₁₀ Pd
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P -1	P -1
a (Å)	13.7993(7)	10.9113(11)	7.3801(7)
b (Å)	16.2142(9)	11.2873(10)	11.9176(13)
c (Å)	16.6779(9)	12.6881(16)	14.8102(14)
α (°)	77.074(5)	93.601(9)	107.383(9)
β (°)	65.654(4)	106.481(10)	90.550(8)
γ (°)	89.887(4)	92.090(8)	90.063(8)
V (cm ³)	3296.4(3)	1493.1(3)	1243.0(2)
Z	4	2	1
ρ _{calcd} [g cm ⁻³]	1.354	1.555	1.314
μ [mm ⁻¹]	0.877	3.457	5.023
Reflections/unique	18353/10601	8328/4689	4525/3984
Data/restraints/Parameters	10601/18/666	4689/0/288	3984/0/267
Goodness of fit on F ²	1.034	0.952	1.075
Final R ₁ indices [I > 2σ(I)]	0.0971	0.0699	0.0813
wR ₁ indices(all data)	0.2618	0.1974	0.2306

$w = 1/[\sigma^2(\text{Fo}^2)+(0.0944\text{P})^2]$ for **4**, $w = 1/[\sigma^2(\text{Fo}^2)+(0.0794\text{P})^2]$ for **5** and $w = 1/[\sigma^2(\text{Fo}^2)+(0.1888\text{P})^2]$ for **7**

Table 2: Ratio of diastereomers (A and B) for compounds **1**, **2**, **3**, **5** in solution

Complex	Diastereomers	-SCH ₂ CO-	Intensity ratio
1	A	(d, 4.557); (d, 4.251)	3:2
	B	(d, 4.417); (d, 4.283)	
2	A	(d, 4.595); (d, 4.166)	3:2
	B	(d, 4.277); (d, 4.192)	
3	A	(d, 4.535); (d, 4.228)	3:2
	B	(d, 4.298); (d, 4.228)	
5	A	(d, 4.614); (d, 3.914)	1:1
	B	(d, 4.346); (d, 4.157)	

Table 3: Important bond lengths (Å) and angles (°) for **4**, **5** and **7**

4			
Pd1 – S11A	2.247(2)	S11A – Pd1 – S14A	89.63(6)
Pd1 – S14A	2.255(2)	S11A – Pd1 – Cl2A	87.50(6)
Pd1 – Cl1A	2.317(2)	S14A – Pd1 – Cl1A	87.02(7)
Pd1 – Cl2A	2.323(2)	Cl1A – Pd1 – Cl2A	95.96(7)
Pd2 – S11B	2.244(2)	S11B – Pd2 – S14B	89.66(6)
Pd2 – S14B	2.243(2)	S11B – Pd2 – Cl2B	87.09(7)
Pd2 – Cl1B	2.326(2)	S14B – Pd2 – Cl1B	87.65(6)
Pd2 – Cl2B	2.319(2)	Cl1B – Pd2 – Cl2B	95.73(7)
		S11A – Pd1 – Cl1A	175.81(8)
		S14A – Pd1 – Cl2A	176.11(6)
		S14B – Pd2 – Cl2B	175.62(8)
		S11B – Pd2 – Cl1B	176.12(6)
5			
Pd1 – S11	2.272(2)	S11 – Pd1 – S14	89.59(6)
Pd1 – S14	2.272(2)	S11 – Pd1 – Br2	89.76(5)
Pd1 – Br1	2.436(1)	S14 – Pd1 – Br1	87.87(5)
Pd1 – Br2	2.428(1)	Br1 – Pd1 – Br2	92.78(3)
		S14 – Pd1 – Br2	178.57(5)
		S11 – Pd1 – Br1	177.45(5)
7			
Pd1 – S1	2.3278(1)	S1 – Pd1 – S2	88.78(5)
Pd1 – S2	2.317(1)		

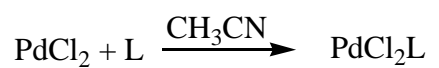
Table 4. Computed binding free energies (ΔG , in kcal mol⁻¹) for the formation of various Pd-complexes.

Reaction	ΔG
Complexes with dithiodiglycolamide ligand	
$trans\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + \text{L} \rightarrow [\text{PdL}_1(\text{Che})]^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O}$	-38.91
$cis\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + \text{L} \rightarrow [(\text{PdL}_1(\text{H}_2\text{O})_2)]^{2+} + 2\text{NO}_3^-$	-23.33
$cis\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + \text{L} \rightarrow [(\text{PdL}_1(\text{NO}_3))]^{1+} + \text{NO}_3^- + 2\text{H}_2\text{O}$	-40.34
$cis\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + \text{L} \rightarrow [(\text{PdL}_1(\text{NO}_3)_2)]^0 + 2\text{H}_2\text{O}$	-38.02
$cis\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + \text{L} \rightarrow [(\text{PdL}_1(\text{NO}_3)(\text{H}_2\text{O}))]^{1+} + \text{H}_2\text{O} + \text{NO}_3^-$	-36.10
$trans\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + 2\text{L} \rightarrow [\text{PdL}_2]^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O}$	-46.31
Complexes with thiodiglycolamide ligand	
$trans\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + 2\text{L} \rightarrow cis\text{-}[\text{PdL}_2]^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O}$	-40.21
$trans\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + 2\text{L} \rightarrow trans\text{-}[\text{PdL}_2]^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O}$	-34.77
$trans\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + 2\text{L} \rightarrow trans\text{-}[\text{PdL}_2(\text{H}_2\text{O})_2]^{2+} + 2\text{NO}_3^-$	-11.48
$trans\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + 2\text{L} \rightarrow trans\text{-}[\text{PdL}_2(\text{NO}_3)_2]^0 + 2\text{H}_2\text{O}$	-8.54
$trans\text{-}[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^0 + 2\text{L} \rightarrow trans\text{-}[\text{PdL}_2(\text{NO}_3)(\text{H}_2\text{O})]^{1+} + \text{H}_2\text{O} + \text{NO}_3^-$	-8.66

Table 5. Energy decomposition analysis of Pd complexes with mono and di-thio ligands at B3LYP/TZP level with ZORA (all energies are in kcal mol⁻¹)

Pd-complexes	Pauli repulsion ΔE_{pauli}	Electrostatic interaction ΔE_{elstat}	Total steric interaction ΔE°	Orbital interactions ΔE_{orb}	Total bonding energy
<i>L= dithiodiglycolamide</i>					
<i>cis</i> -[PdL ₁ (NO ₃) ₂] ⁰	293.58	-584.71 (53.8%)	-291.13	-500.29 (46.2%)	-791.42
[PdL ₁ (Che)] ²⁺	340.18	-332.86 (40.1%)	7.33	-498.31 (59.9%)	-490.99
[PdL ₂] ²⁺	285.67	-280.05 (33.9%)	5.62	-546.82 (66.1%)	-541.21
<i>L=thiodiglycolamide</i>					
<i>trans</i> -[PdL ₂ (NO ₃) ₂] ⁰	271.34	-571.19 (54.0%)	-299.85	-487.14 (46.0%)	-786.99
<i>trans</i> -[PdL ₂] ²⁺	301.93	-332.29 (40.2%)	-30.35	-494.87 (59.8%)	-525.23
<i>cis</i> -[PdL ₂] ²⁺	307.70	-335.95 (40.2%)	-28.25	-500.48 (59.8%)	-528.73

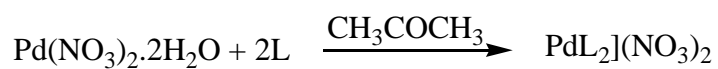
Scheme – 1: The syntheses of palladium (II) complexes



L=L1(1); L2(2); L3 (3); L5 (4)



X=Br (5); X=I (6)



L=L1 (7); L2 (8)

Figure 1. Structures of dithiodiglycolamide ligands used in this work.

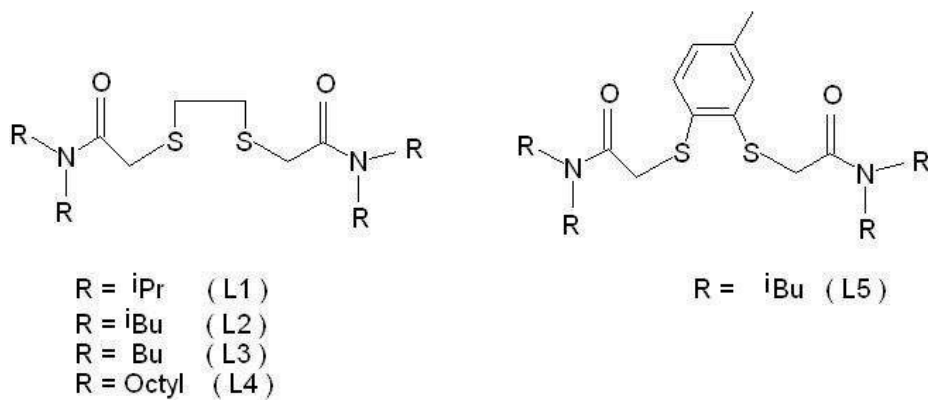


Figure 2: Stereogenic sulphur centres showing SYN and ANTI isomerism

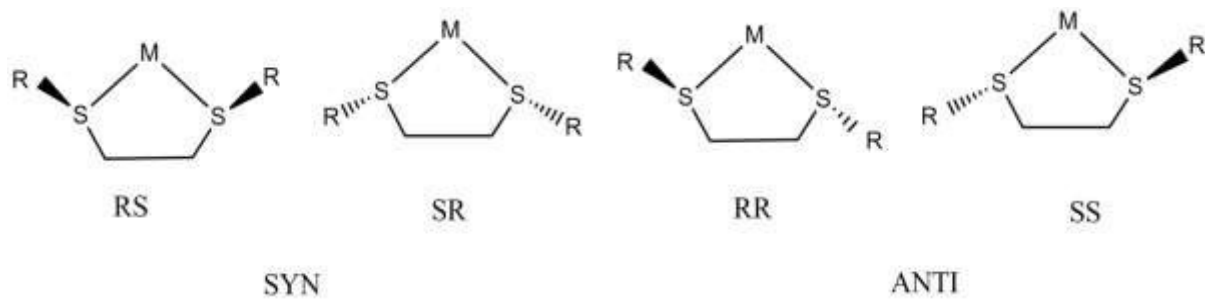


Figure 3. The Molecular structure of 4

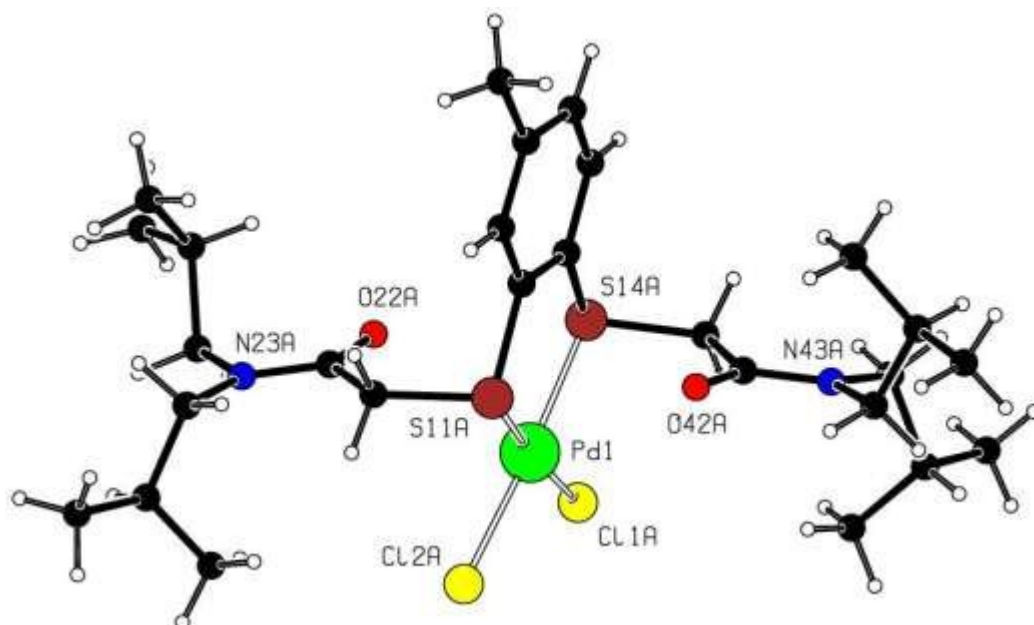


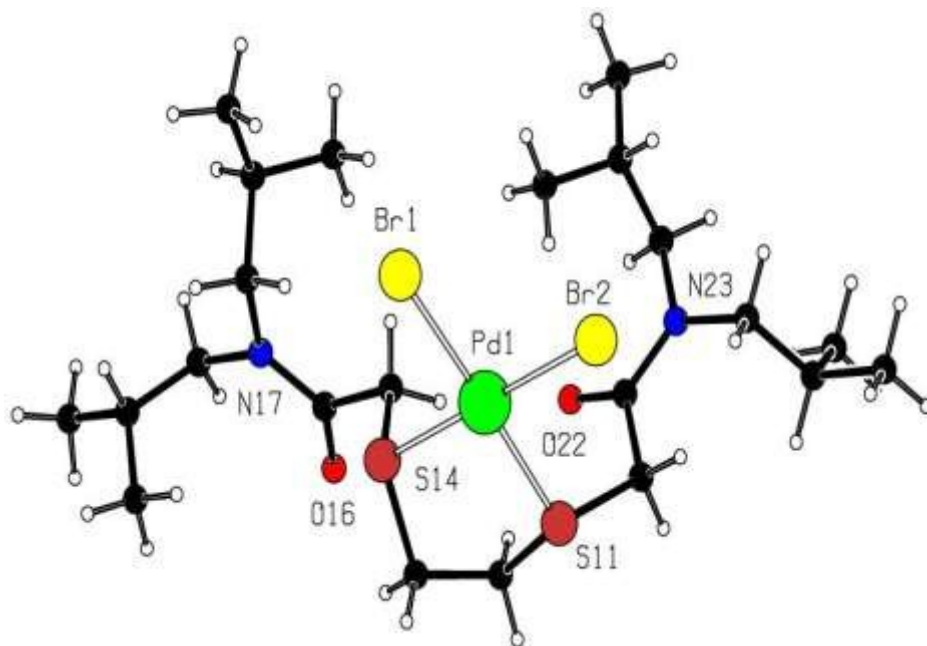
Figure 4: Structure of **5**

Figure 5: The centrosymmetric structure of **7**. The nitrate ions are omitted for clarity.

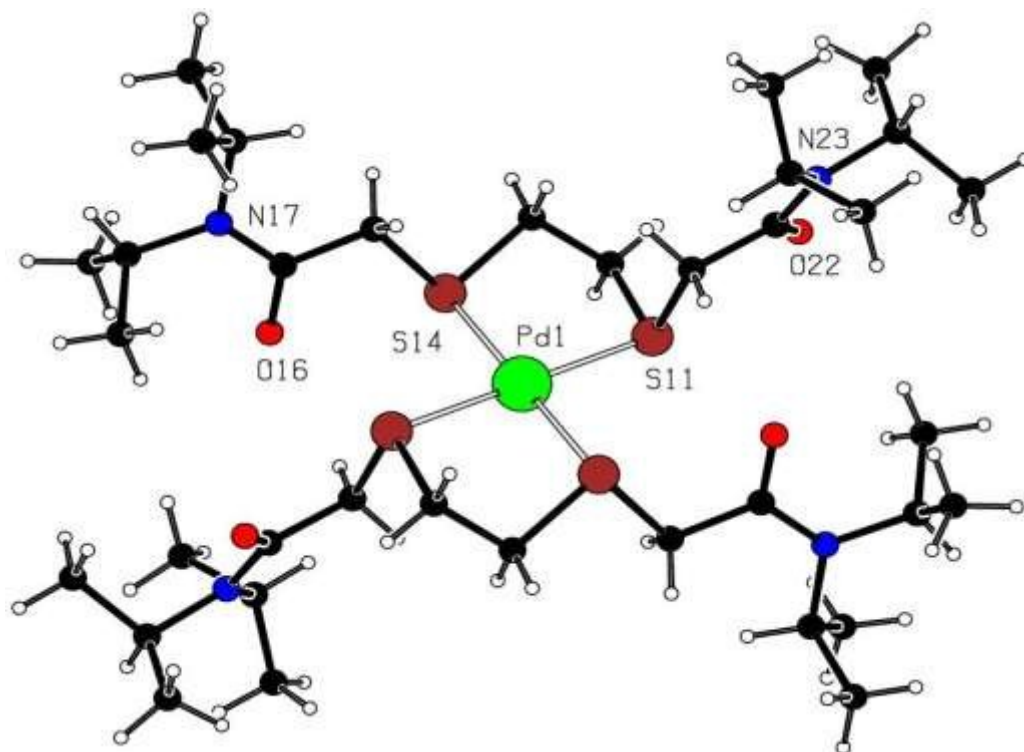


Figure 6. Optimized structure (in Å) of (a) *cis* and (b) *trans*-Pd-nitrates

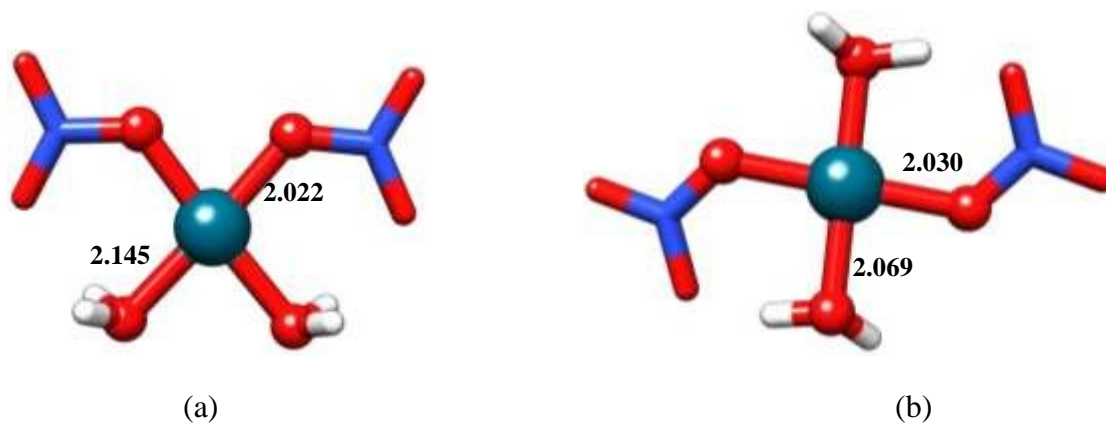


Figure 7. Optimized structures (in Å) of various 1:1 and 1:2 complexes with dithiodiglycolamide ligand.^a

$[\text{PdL}_1\cdot\text{Br}_2]^0$	
$[\text{PdL}_1(\text{Che})]^{2+}$	$[(\text{PdL}_1(\text{H}_2\text{O})_2)]^{2+}$
$[\text{PdL}_1(\text{NO}_3)]^{1+}$	$[(\text{PdL}_1(\text{NO}_3)_2)]^0$
$[\text{PdL}_1(\text{NO}_3)(\text{H}_2\text{O})]^{1+}$	$[\text{PdL}_2]^{2+}$

^a Values in brackets are for the corresponding X-ray structure.

Figure 8. Optimized structures (in Å) of various 1:1 and 1:2 Pd complexes thiodiglycolamide.^a

