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PALLADIUM(II) COMPLEXES BASED ON N,S-DONOR LIGANDS: SYNTHESIS AND MOLECULAR STRUCTURES

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Phenyl(chloro)dithioformate is treated with pyrazole derivatives and phenyl(Pz-1-carbodithioate) ligands (Pz = pyrazole (**1**), 3-methylpyrazole (**2**), and 3,5-dimethylpyrazole (**3**)) are obtained. These ligands are treated with $PdCl_2$ in acetonitrile and complexes of the general formula $Pd(L)Cl_2$ form in an essentially quantitative yield. The ligands are found to be N,S-bidentate linkers, and 5-membered palladacycles are obtained. Precursors **1-3** are oily materials and characterized by ^{1}H and ^{13}C NMR spectroscopy. Due to a partial solubility of Pd complexes, the complete set of NMR data cannot be collected. The structural elucidation is also accompanied by elemental and mass spectrometric analyses. Solid-state structures of complexes **5** and **6** are determined by X-ray diffraction. The data obtained for complexes **5** and **6** are also calculated by DFT using the *TURBOMOLE* program package. Experimental and calculated data sets are found to be in close agreement with each other.

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INTRODUCTION

The synthesis of dithocarbamic acid, its salts and esters is of great interest due to their wide potential as radicals, starting materials, and intermediates in the synthesis of many compounds [1-3]. They are used in Diels-Alder reactions [4] and have wide applications in the field of agriculture as pesticides [5] and polymerization reactions at the industrial scale [6]. Moreover, they are potent antioxidant, antifungal, antimicrobial, anticancer agents and possess the cytostatic activity [7-11].

The esters of dithiocarbamates are synthesized *via* different methods, i.e. treatment of dithiocarbamic acid salt with teraflouroborate salts [12], reactions of alkyl halide derivatives with dithiocarbamic acid salts [13], the Markovnikov addition reaction in the aqueous medium [14], regioselective thiolation [15], the reaction of alkyl halides with thiocarbamic salts [16], the Ullman reaction from phenyl diazonium tetrafluoroborate, carbon disulphide, and amines in water, and CuI-catalyzed coupling reactions [17].

The S and N donor ligands such as thioureas [18], thiocarbamates [19], and alkyl or aryl esters of thiocarbamates [9] are useful precursors in chemistry. Bidentate ligands are widely used in coordination chemistry with various metal centers to

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fix terminal ligands (halogens or organic groups) in the *cis* position for the specific reactivity, such as biological and catalytic applications. Better reactivity has been shown by d^8 metal centers (Ni(II), Pd(II), Pt(II)) with bidentate ligands. Considerable literature is available on Pd(II) complexes with bidentate neutral ligands with a residual MX moiety (where X can be halogen or an organic group coming from starting salt). The geometry around the metal center in normal cases is distorted square planar [20], a distortion being caused by bidentate chelating ligands.

In continuation of our previous work [21] here we report the synthesis of N,S ligands and their Pd(II) complexes. The final complexes contain the MCl_2 moiety, which can be used for secondary reactions. The NMR (^{1}H and ^{13}C) characterization and the X-ray structure of complexes **5** and **6** are discussed. The experimental data have also been reproduced theoretically by DFT.

EXPERIMENTAL

General considerations. Pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole, phenyldithioformate are commercial products (Sigma Aldrich) and were used without further purification. Triethylamine was distilled (bp 89.5 °C) prior to the use and dry toluene (sodium metal and benzophenone) was used throughout. Elemental analyses (CHN) were performed on a Vario EL III instrument. NMR spectra were recorded on Varian INOVA 300 (^{1}H 300 MHz; ^{13}C 75 MHz) at 23±1 °C. Chemical shifts are reported in ppm, proton NMR spectra were referenced to the chemical shifts of residual proton signals ($CHCl_3$ δ 7.27 and DMSO δ 2.50). The spectra of carbon were referenced to the ^{13}C resonance of the respective solvent ($CDCl_3$ δ 77.00 and DMSO δ 39.51). Mass spectra (EI, 70 eV) were measured using Finnigan MAT 8500 with a direct inlet system.

Synthesis of carbodithioate derivatives 1-3. To a solution of phenylchlorodithioformate (1.5 ml, 10 mmol) in toluene (30 ml) pyrazol was added (0.96 g, 10 mmol) followed by an equimolar amount of Et_3N (1.5 ml, 10 mmol). The mixture was left stirred for few hours, and after some time the $Et_3N{\cdot}HCl$ precipitate appeared, indicating the progress in the chemical reaction [22]. The reaction mixture was further stirred for 48 h. After the reaction was completed, the reaction mixture was filtered and the filtrate was washed with water and dried over Na_2SO_4. After the evaporation of the solvent and other volatiles, deep orange-red oil was collected and analyzed by NMR and elemental analyses. Compounds **2** and **3** were prepared in the same way.

1. Yield: 76%, $C_{10}H_8N_2S_2$. Elemental, found (Cal): C 55.16 (54.52); H 3.47 (3.66); N 11.53 (12.72). ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.62 (br, 2H, pz), 7.55-7.83 (m, aromatic protons, Ph/Pz), 6.51 (br, 1H, pz).^{13}C NMR ($CDCl_3$) δ (ppm) = 201.2, 145.0, 136.5, 130.9, 130.8, 130.5, 129.9, 111.0.

2. Yield: 77%, $C_{11}H_{10}N_2S_2$. Elemental, found (Cal): C 57.50 (56.38); H 4.71(4.30), N 11.20 (11.95). ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.52 (d, 1H, pz, $J(^1H,^1H)$ = 2.9 Hz), 7.53-7.73 (m, 5H, Ph), 6.31 (d, 1H, 4-pz, $J(^1H,^1H)$ = 2.9 Hz), 2.46 (s, 3H, 3-Me). ^{13}C NMR ($CDCl_3$) δ (ppm) = 200.2, 141.6, 136.4, 136.3, 131.2, 130.4, 129.4, 111.8, 14.1.

3. Yield: 89%, $C_{12}H_{12}N_2S_2$. Elemental, found (Cal): C 57.50 (58.03); H 4.49 (4.87), N 11.20 (11.28). ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.21-7.51 (m, 5H, Ph), 6.13 (s, 1H, pz), 2.64 (s, 3H, Me), 2.35 (s, 3H, Me). ^{13}C NMR ($CDCl_3$) δ (ppm) = 201.3, 152.6, 146.2, 136.9, 131.7, 130.6, 129.7, 113.8, 17.7, 14.0.

Synthesis of complexes 4-6. Palladium(II) chloride (0.177 g, 1 mmol) was dissolved in acetonitrile (20 ml). The solution was stirred overnight to afford the $[Pd(CH_3CN)_2Cl_2]$ adduct. The desired adduct was obtained as a yellow solution. A solution of compound **1** (0.2 g, 1 mmol) in acetonitrile (5 ml) was prepared in a separate flask and added to the Pd(II) solution. Immediately after the addition orange precipitates formed. The reaction was allowed to continue overnight. The precipitate was separated by filtration and washed with an excess amount of acetonitrile. Desired complex **4** was obtained in an essentially quantitative yield. The complex thus obtained was characterized by NMR (^{1}H and ^{13}C) spectroscopy, mass spectrometry, and elemental analysis. The same procedure was followed for the synthesis of complexes **5** and **6**. All complexes were obtained as yellow precipitates from their respective reaction mixtures.

4. Yield: 78%, $C_{10}H_8Cl_2N_2PdS_2$. Elemental analysis found (Cal.): C 30.42 (30.20), H 2.02 (2.03), N 7.22 (7.04). MS (EI-MS), *m*/*z* (%): 220(18), 111(80), 144(100). ^{1}H NMR (DMSO-d_6), ppm: 9.65 (br, 1H, Pz), 8.69, 8.23, 8.09 (m, m, m, 5H, Ph), 6.75 (m, 1H, Pz), 6.67 (d, 1H, Pz). ^{13}C NMR (DMSO-d_6), ppm: 173.5, 142.9, 129.8, 129.5, 129.5, 127.6, 127.2, 108.3.

5. Yield: 76%, $C_{11}H_{10}C_{l2}N_2PdS_2$. Elemental analysis found (Cal.): C 32.55 (32.09), H 2.45 (2.45), N 6.99 (6.80). MS (EI-MS), *m*/*z* (%): 234 (19), 125 (78), 158 (100).

6. Yield: 70%, $C_{12}H_{12}Cl_2N_2PdS_2$. Elemental analysis found (Cal.): C 33.77 (33.86), H 3.79 (2.84), N 6.60 (6.58). MS (EI-MS), *m*/*z* (%): 248 (20), 139 (70), 172 (100).

X-ray crystallography. Details pertinent to the crystal structure determination of Pd(II) complexes **5** and **6** are listed in Table 1. Crystals of the appropriate size were selected (in perfluorinated oil [23] at room temperature) and the data were collected at 133±2 K using a STOE IPDS II diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71069 Å). The system was equipped with an Oxford Cryostream low-temperature unit. Final refinement on F^2 was carried out by the full-matrix least-squares technique. Structure solutions and refinements were accomplished using SIR97 [24], SHELXL-97 [25], and WinGX [26].

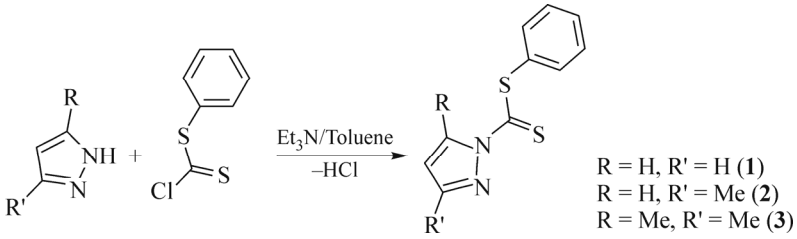
Computational methods. Density functional theory (DFT) calculations were performed with the *TURBOMOLE* program package [27]. The RI-DFT method [28] applying the B–P86 functional [29] with the default grid size m^3 was used for all calculations. The starting structure was obtained from the X-ray crystal structure of the corresponding molecule. The initial geometry optimization was performed with the split-valence basis set def2-SV(P) [30] for all atoms. The obtained geometry was optimized for the second time applying the triple zeta basis set def2-TZVP [30] for all atoms.

TABLE 1. Crystal Data and Structure Refinement Parameters for Complexes **5** and **6**

Empirical formula	$C_{11}H_{10}Cl_2N_2PdS_2{\cdot}CH_2Cl_2$ (**5**)	$C_{12}H_{12}Cl_2N_2PdS_2$ (**6**)
Formula weight	496.56	425.66
Temperature	133(2)	133(2)
Wavelength, Å	0.71069 (MoK_α)	
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*C*(2)/*c*
Unit cell dimensions *a*, *b*, *c*, Å	7.02(12), 9.08(13), 14.14(2)	25.70(14), 8.68(7), 16.10(12)
α, β, γ, deg.	71.62(12), 85.38(13), 88.32(13)	–, 111.29(7), –
Volume, Å^3	851.9 (2)	3349.2(4)
Z	2	8
Density, mg/m^3	1.936	1.688
Absorption coefficient, mm^{-1}	1.953	1.664
F(000)	488	1680
Crystal size, mm	0.11×0.07×0.06	0.17×0.15×0.09
θ range, deg.	1.52 to 27.32	1.70 to 27.38
Index ranges	h ±9; k ±11; l ±18	h ±33; k ±11; l ±20
Collected / independent reflections	13418 / 3823	25126 /3776
Completeness to θ	27.32, 99.8	27.38, 98.9
Data / restraints / parameters	3823 / 0 / 191	3776 / 0 / 174
Goodness-of-fit on F^2	0.839	1.059
Final *R* indices [$F^2 > 2\sigma(F^2)$]	0.0864	0.0470
R indices (all data)	0.1903	0.0588
Largest diff. peak and hole, e/Å^3	1.696 and –0.964	0.953 and –1.733

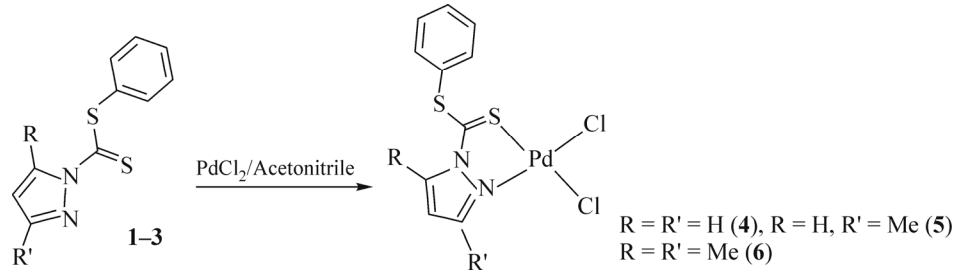
RESULTS AND DISCUSSION

Scheme 1 shows an overview of the synthetic route for compounds **1-3**. The reactions are straightforward, efficient and performed at ambient temperature adopting the literature procedure [22]. The coupling reactions between pyrazole derivatives and phenyl(chloro)dithioformate were carried out in the presence of an equimolar amount of trimethylamine. The $Et_3N{\cdot}HCl$ adduct can easily be removed by filtration from the solution, leaving behind the desired compounds. The reactions afforded the desired products in a reasonably pure form and an excellent quantity of the required compounds (yield 76-89%) was obtained. No side reactions/products were observed during the synthesis of compounds **1-3** (NMR analysis). All compounds of this series are air and moisture stable, viscous oil and can be stored under aerobic conditions for a reasonably long period of time. These compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy in the solution state (see EXPERIMENTAL). The structure of the compounds could easily be deduced from the consistent set of NMR parameters. Carbon CSS in ^{13}C NMR spectra in the range 200-201 ppm supports the formation of the products (**1-3**). All other ^{13}C signals corresponding to pyrazole and phenyl groups appear in their characteristic region of 111-155 ppm.



Scheme 1. Synthesis of N,S ligands derived from phenylchlorodithioformate and pyrazole derivatives **1-3**.

Ligands **1-3** show very good solubility in common organic solvents. They were dissolved in acetonitrile and treated with an equimolar amount of the $[PdCl_2(CH_3CN)_2]$ adduct (based on $PdCl_2$ contents) at room temperature (Scheme 2). The progress in the chemical reaction can easily be monitored by the physical appearance of orange-colored precipitates within few minutes (<5 min). The desired compound can easily be separated from the mother liquor by filtration. Palladium complexes **5** and **6** were insoluble in polar organic solvents such as DMSO, CH_2Cl_2, and CH_3Cl at room temperature, however, the solubility of complex **4** could be improved at high temperatures (30-40 °C) in DMSO. The structural elucidation of the complexes was carried out by the elemental analysis and mass spectrometry. The fragmentation pattern deduced from the MS data was quite supportive towards the expected structures. For complexes **4-6** molecular ion peaks were not observed and the peak with the highest *m/z* value corresponds to the respective free ligand. It indicates that ligands are loosely bound to metal and detached in the presence of 70 eV energy. After the dissociation of the complex the further fragmentation of ligands takes place (see EXPERIMENTAL).



Scheme 2. Five-membered palladacycles **4-6** derived from pyrazole-1-carbodithioate derivatives.

The extremely limited solubility of the synthesized complexes excludes the solution-state NMR characterization; only complex **4** is sparingly soluble in DMSO, which allowed for the required NMR data [31]. The data obtained for complex **4** shows a characteristic carbon signal at 173.47 ppm which could be assigned unambiguously to the **C**=S carbon atom. The **C**=S chemical shift is a good indication of the ligand coordination to metal through the S atom. Other carbon atoms and all protons appear in the expected region with slight changes in their chemical shifts.

The orange-colored powder material obtained for all three complexes containing Pd(II) as a central metal ion was dissolved in hot dichloromethane. Orange needle-like crystals were obtained for complexes **5** and **6** in 5 and 7 days, respectively. Such attempts were unsuccessful to get crystals of compound **4**.

Structural description of compound 5. The X-ray diffraction analysis of compound **5** (Fig. 1) reveals that it crystallizes in the triclinic crystal system with the space group *P*-1. The palladium metal ion is four-coordinated (S,N sites of ligand **2** and two chloro functions) and adopts a distorted square planar geometry with the sum of all bond angles around the metal ion being 360°. The distortion is obvious because of the ligand, making a five-membered metallacycle. The five-membered metallacycle contains an acute angle ∠N8–Pd1–S1 of 84.61°, as expected. Other angles around the Pd(II) ion were in the expected range, i.e. ∠Cl1–Pd1–Cl2 90.85°, ∠Cl2–Pd1–S1 85.05, except ∠N8–Pd1–Cl1 99.53° [32]. The methyl group attached to the ligand pyrazolyl moiety is predominantly involved to cause the change. Bond lengths around the metal center are within the expected limits: Pd–Cl1 233.4 pm, Pd1–Cl2 228.1 pm, and Pd1–N8 201.1 pm while the Pd1–S1 bond is shorter (223.4 pm) than the Pd–S (DTC) bond (227.9 pm, 229.7 pm) [33]. The elongation of the Pd1–Cl1 bond in the complex clearly reflects the greater *trans* effect of S compared with that of N. The C17 atom being sp^2-hybridized bears a trigonal planar geometry with bond lengths C17–S1 166.1, C17–S5 171.3, and C17–N9 134.7. The data show that the π electron pair is localized on S1 which causes an elongation in the CS bond (Table 2).

The $Pd(Ph(3\text{-}Me\text{–}Pz)CS_2)Cl_2$ building units of complex **5** are associated with each other *via* Cl2---S5 and Cl1---H22 interactions (316.3 pm and 261.6 pm), respectively, making a 1D supramolecular chain. The two adjacent chains are held together *via* CH_2Cl_2 molecules, as shown in Fig. 2.

Description of compound 6. The molecular structure of palladium complex **6** is shown in Fig. 3 and the data pertinent to the structure solution and refinements are summarized in Table 1. It crystallizes in the monoclinic crystal system with the space group *C*2/*c*. The coordination number of the palladium ion is four (S,N sites of ligand **3** and two chloro ions).

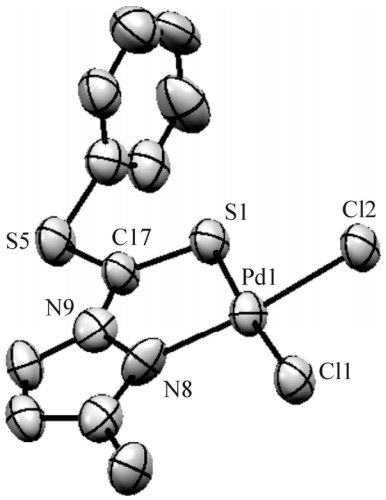


Fig. 1. Molecular structure of compound **5** with partial numbering scheme, thermal ellipsoids drawn at a 50% probability level, a CH_2Cl_2 solvent molecule and hydrogen atoms are omitted for clarity.

TABLE 2. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg.), Experimental and Calculated for Complexes **5** and **6**

Complex **5**	Experimental	Calculated	Complex **6**	Experimental	Calculated
Pd1–N8	2.011(13)	2.069	Pd1–N1	2.034(4)	2.071
Pd1–S1	2.234(4)	2.251	Pd1–S1	2.223(11)	2.233
Pd1–Cl2	2.281(4)	2.281	Pd1–Cl1	2.278(11)	2.285
Pd1–Cl1	2.335(3)	2.303	Pd1–Cl2	2.323(11)	2.311
S1–C17	1.662(12)	1.668	S2–C1	1.738(4)	1.763
S5–C17	1.713(12)	1.758	S1–C1	1.668(4)	1.672
N9–C17	1.346(17)	1.385	C1–N2	1.358(5)	1.389
N8–Pd1–Cl1	99.5(3)	97.8	N1–Pd1–S1	84.33(10)	84.2
Cl2–Pd1–Cl1	90.9(12)	90.6	S1–Pd1–Cl1	85.91(4)	86.3
S1–Pd1–Cl2	85.1(13)	86.6	N1–Pd1–Cl2	99.72(10)	99.3
N9–C17–S1	119.3(9)	119.8	Cl1–Pd1–Cl2	90.19(4)	90.2
N9–C17–S5	114.8(9)	114.2	N2–C1–S1	120.2(3)	120.0
S1–C17–S5	125.9(8)	126.0	N2–C1–S2	119.0(3)	117.6
			S1–C1–S2	120.8(2)	122.4

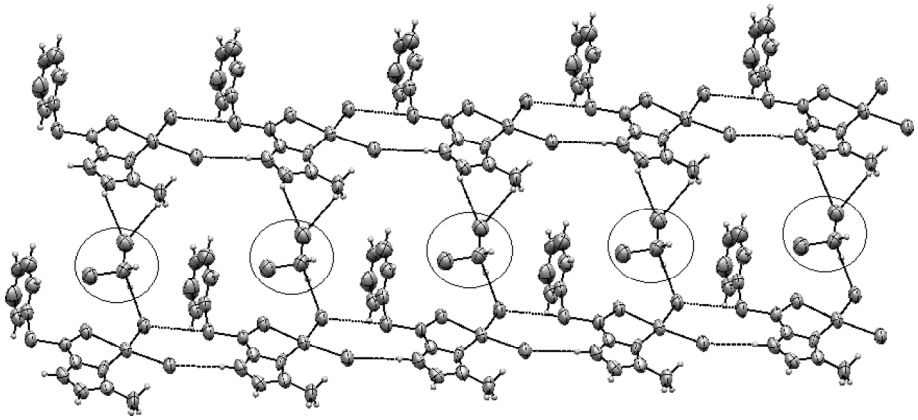


Fig. 2. 2D supramolecular network of compound **5** stabilized by Cl···S and Cl···H interactions. The adjacent chains are linked through solvent molecules; hanging contacts are omitted for clarity.

Palladium adopts a distorted square planar surrounding similar to that in complex **5**, with the sum of all bond angles of 360° (around the metal ion). The complex bears an endocyclic acute angle ∠N1–Pd1–S1 of 84.33°, as expected. Other angles around the Pd ion are within the permissible range ∠Cl1–Pd1–Cl2 90.19°, ∠Cl1–Pd1–S1 85.91°, and ∠N1–Pd1–Cl2 99.72° as observed for the complex discussed above. The Pd–Cl/S/N bond lengths are within the expected limits: Pd–Cl1 227.8 pm, Pd1–Cl2 232.3 pm, Pd1–N1 203.4 pm, and Pd1–S1 222.3 pm. The difference in Pd1–Cl1 and Pd1–Cl2 bonds is due to the presence of different donor atoms, i.e., N and S of the ligand in the *trans* position. Other structural features are very close to molecule **5**.

The solid-state structure of compound **6** shows that the molecules assemble into a layer structure through Cl---H(pz) non-bonding intermolecular interactions: Cl1–H5B 293.8 pm, Cl1–H12A 288.0 pm, Cl2–H3 272.2 pm, and Cl2–H7 280.6 pm (Fig. 4).

The secondary interactions in the molecules, as discussed above, are very useful to make the parent compound biologically active. These interactions make the molecule efficient to bind with polar biological macromolecules such as DNA and can be used for treatment of diseases such as cancer [34-36].

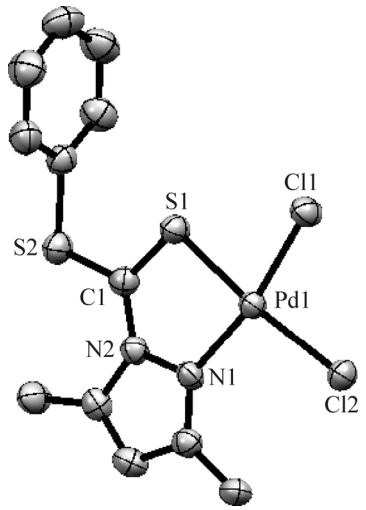


Fig. 3. Molecular structure of compound **6** with a partial numbering scheme, ellipsoids are drawn at a 50% probability level, all hydrogen atoms are omitted for clarity.

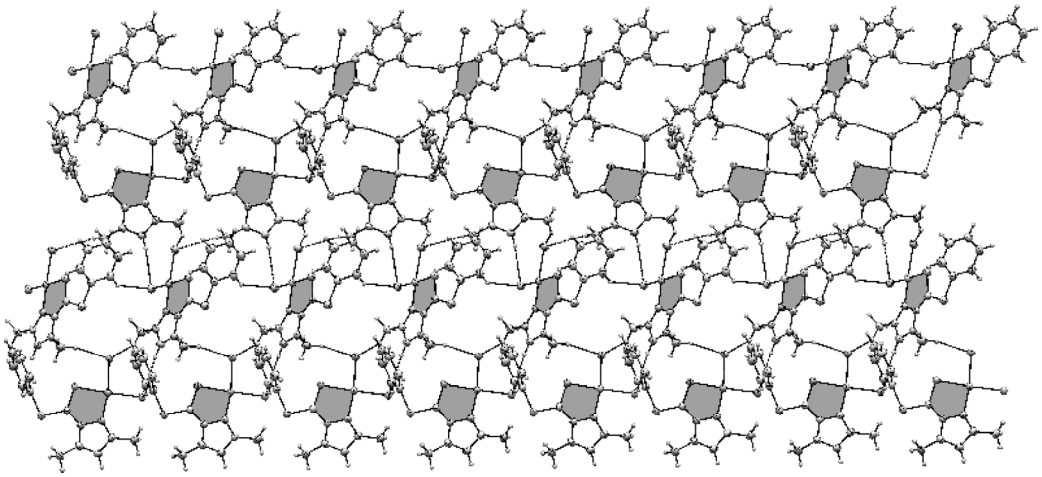


Fig. 4. 2D supramolecular layered network of compound **6** stabilized by Cl···H interactions. The five-membered ring containing Pd is shown shaded and hanging contacts are omitted for clarity.

The solid-state data for bond lengths and angles of complexes **5** and **6** were reproduced by DFT calculations using the *TURBOMOLE* program package. The data obtained were compared with the experiment and found to be in close agreement (Table 2).

CONCLUSIONS

Three ligands, namely phenyl-*1H*-pyrazole-1-carbodithioate, phenyl-3-methyl-1*H*-carbodithioate, and phenyl-3,5-dimethyl-1*H*-carbodithioate were prepared and treated with $PdCl_2$. All reactions were carried out at ambient temperature. The ligand derivatives showed the excellent reactivity towards Pd(II) metal. Three complexes containing the Pd(II) ion were isolated in a reasonably pure form. All complexes bear the $PdCl_2$ function, which can be used for secondary reactions. Complexes are mononuclear and exhibit poor solubility in CH_3Cl, CH_2Cl_2, and C_6H_6, which did not allow the full NMR

characterization, except complex **4**. To study the secondary reactivity and applications in the field of bio-inorganic chemistry these complexes are under investigation.

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The crystallographic data corresponding to compounds **5** and **6**, have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publications Nos. CCDC 1014352 and 1014353. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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