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Original Article

Pd(II) and Zn(II) Complexes with 9-Anthraldehyde 3-tetramethyleneiminylthiosemicarbazone

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Abstract: Two Pd(II) and Zn(II) complexes with an anthracene-based thiosemicarbazone (H-5cATSC) have been conveniently prepared. Reaction of the ligand with relevant metal precursors yields the complexes Pd-5cATSC, and Zn-5cATSC which have been then structurally determined by X-ray crystallography. The results reveals that the complexes are of mononuclear structure, adopts square-planar, and tetrahedral geometries around the central metal ions.

Keywords: Anthracene, palladium, zinc, thiosemicarbazone, X-ray structure.

1. Introduction

Anthracene, a simple polycyclic aromatic hydrocarbon, has been recognized for its unique absorption, and emission behaviors. The compound also adopts a rigid geometrical structure, making it useful in constructing many supramolecular architectures [1,2]. Extensive intramolecular and intermolecular π–π stackings between anthracenyl cores have been observed due to its extended π-conjugated system [3,4]. Recently, a number of chemosensors that contain anthracene have been developed in order to detect cations, and anions based on emission turning on mechanism such as CHEF, ESIPT [5,6]. Thiosemicarbazone is long known as a simple ligand with diverse coordination [7,8]. Therefore, combining thiosemicarbazone, and anthracene moieties into a ligand might bring forth many intriguing structural and electronic properties upon complexation.

Pd(II), a d^8 metal, has strong preferences for square planar geometry thanks to a large crystal field stabilization energy. In view of steric effect of the ligands, most of Pd(II) complexes are expected to have *trans* configuration [9,10]. Meanwhile, Zn(II) complexes with d^{10} configuration gains no crystal field stabilization

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energy. Therefore, tetrahedral geometry which is more favourable in energy is normally seen in Zn(II) complexes [11].

In this work, we report the syntheses, crystal structures of Pd(II) and Zn(II) complexes with 9-anthraldehyde 3-tetramethyleneiminylthiosemicarbazone. Our results showed that the Pd(II), and Zn(II) complexes adopt square planar and tetrahedral geometries, respectively. In addition, extensive intermolecular π-π stackings among the complexes were detected.

2. Experimental

2.1. Materials and Instruments

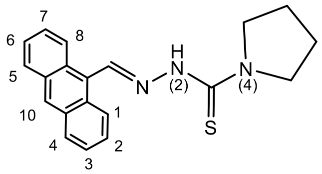
All the solvents used for synthesis and spectroscopic measurements were purified according to literature procedures. 9-Anthraldehyde, 3-tetramethyleneiminylthiosemicarbazide were used as received without further purification. $Pd(CH_3CN)_2Cl_2$ was synthesized according to reported method [12]. The synthesis of H-5cATSC has been previously reported [13].

The FT-IR spectra of the complexes were measured on a FT-IR 8700 infrared spectrophotometer (4000−400 cm^{-1}) in KBr pellets. The ^1H NMR spectra were recorded on an AVANCE Bruker-500MHz spectrometer in $CDCl_3$ solution at room temperature. ESI-MS spectra were recorded on an Agilent LC/MSD SL spectrometer.

The intensities for the X-ray determinations were collected on a Bruker D8 Quest instrument with Mo Kα radiation (λ = 0.71073 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with OLEX2 and SHELXT programs [14,15]. Hydrogen atom positions were calculated for idealized positions.

2.2. Synthesis of H-5cATSC

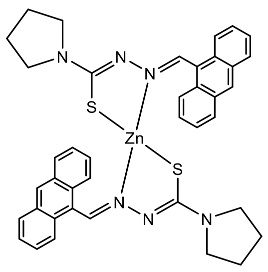
To a 10 mL ethanolic solution of 9-anthraldehyde (1.0 mmol) was added 10 mL acidified aqueous solution of 3-tetramethyleneiminylthiosemicarbazide (1.0 mmol). The resulting mixture was stirred for 4 h at 60°C to afford a pale-yellow solid. The product was washed by large amount of water and then air-dried. Yield: 73 %.



Spectroscopic Data for H-5cATSC. IR (KBr, cm^{-1}): 3177 (m), 3049 (m), 2963 (m), 1550 (s), 1475 (w), 1423 (s), 1338 (s), 1287 (s), 1223 (s), 876 (s), 723 (s), 685 (s). ^1H NMR (500 MHz, $CDCl_3$, δ ppm): 1.83; 1.92; 3.96 [m, 8H, $N(CH_2)_4$]; first set of signals: 7.56-7.60 (m, 4H, $H_{2,3,6,7}$); 7.95 (d, 2H, $H_{4,5}$); 8.09 (d, 2H, $H_{1,8}$); 8.32 (s, 1H, H_{10}); 8.42 (s, 1H, CH); 8.59 (s, 1H, N^2H); second set of signals: 7.47-7.54 (m, 4H, $H_{2,3,6,7}$); 8.04 (d, 2H, $H_{4,5}$); 8.43 (d, 2H, $H_{1,8}$); 8.51 (s, 1H, H_{10}); 8.78 (s, 1H, CH); 9.21 (s, 1H, N^2H).

2.3. Synthesis of Zn-5cATSC

An aqueous solution of $Zn(CH_3COO)_2.2H_2O$ (0.04 mmol) (5 ml) was added dropwise to a solution of H-5cATSC (0.08 mmol) in ethanol (15 ml) in the presence of excess NH_3. The mixture was heated to 60°C and stirred for 5 h in darkness, then filtered, washed with methanol, and last dried in vacuum to give product in good yields. Single crystals of Zn-5cATSC were harvested in about two weeks by recrystallization from chloroform/methanol (v/v = 1:1).

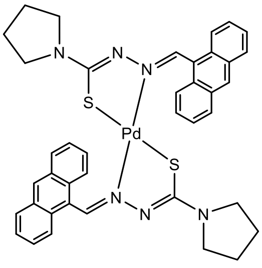


Spectroscopic Data for Zn-5cATSC. Yield: 70%. IR (KBr, cm^{-1}): 3049 (w), 2965 (w), 2943 (w), 2864 (s), 1587 (w), 1516 (w), 1485 (m), 1466 (s), 1447 (s), 1389 (s), 1360 (s), 1304 (s), 881 (s), 837 (s), 731 (s). ESI-MS: (100%) 729.1, $[M + H]^+$.

Crystal Data for Zn-5cATSC: triclinic, space group P-1 (no. 2), a = 10.3722(6) Å, b = 12.0225(6) Å, c = 15.1546(8) Å, α = 99.275(2), β = 108.169(2), γ = 100.984(3), V = 1712.66(16) Å^3, Z = 2, T = 100.0 K, μ(MoKα) = 0.879 mm^{-1}, $Dcalc$ = 1.416 g/cm^3, 6946 reflections measured (5.788° ≤ 2θ ≤ 56.512°), 5483 unique (R_{int} = 0.0248, R_{sigma} = 0.0627) which were used in all calculations. The final R_1 was 0.0593 (I > 2σ(I)) and wR_2 was 0.1566 (all data).

2.4. Synthesis of Pd-5cATSC

A solution of $Pd(CH_3CN)_2Cl_2$ (0.04 mmol) in acetone (5 mL) was added dropwise to a solution of H-5cATSC (0.08 mmol) in acetone (15 mL) in the presence of excess triethylamine. The mixture was heated to 60°C and stirred for 5 h in the absence of light, then filtered, washed with methanol, and last dried in vacuum to give product in good yields. Single crystals of Pd-5cATSC were harvested by recrystallization from chloroform/methanol (v/v=1:1). Yield: 78%.



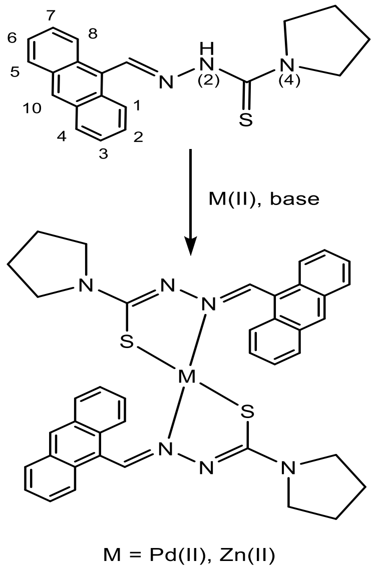
Spectroscopic Data for Pd-5cATSC. IR (KBr, cm^{-1}): 3048 (w), 2965 (w), 2855 (w), 1557 (m), 1497 (s), 1472 (s), 1454 (s), 1391 (s), 1350 (s), 1188 (m), 881 (m), 731 (s). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 1.69 (m, 8H, tetramethylene); 2.99 (m, 8H, tetramethylene); 7.36 (t, 4H, $H_{3,6}$, anthryl); 7.53 (t, 4H, $H_{2,7}$, anthryl); 7.97 (d, 4H, $H_{4,5}$, anthryl); 8.06 (d, 4H, $H_{1,8}$, anthryl); 8.59 (s, 2H, H_{10}, anthryl); 8.67 (s, 2H, CH=N). ESI-MS: m/z (100%) 771.1, [M + H]$^+$.

Crystal Data for Pd-5cATSC : orthorhombic, space group Pbca (no. 61), a = 8.4508(4) Å, b = 21.3357(10) Å, c = 37.9683(16) Å, V = 6845.8(5) Å^3, Z = 8, T = 100.0 K, μ(MoKα) = 0.704 mm^{-1}, $Dcalc$ = 1.497 g/cm^3, 122566 reflections measured (5.612° ≤ 2θ ≤ 55..°), 7845 unique (R_{int} = 0.0884, R_{sigma} = 0.0345) which were used in all calculations. The final R_1 was 0.1598 (I > 2σ(I)) and wR_2 was 0.3879 (all data).

3. Results and Discussion

3.1. Syntheses

The ligand H-5cATSC was easily achieved by condensation between 9-Anthraldehyde and acidified 3-tetramethyleneiminylthiosemicarbazide. Refluxing $Pd(CH_3CN)_2Cl_2$ with H-5cATSC in acetone in the presence of trimethylamine yielded bright orange solids of Pd-5cATSC. Meanwhile, Zn-5cATSC was obtained as pale-yellow solids from the reaction between $Zn(CH_3COO)_2$ and H-5cATSC with the aid of NH_3. The complexes are highly soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, and DMF. X-ray characterizations of Pd-5cATSC and Zn-5cATSC were feasible as the complexes could be recrystallized to give single crystals.



Scheme 1. Synthetic scheme of the complexes.

In order to characterize the complexes, conventional physical methods such as infrared spectroscopy, ^{1}H NMR spectroscopy, and mass spectrometry (ESI-MS) were utilized. The ESI mass spectra exhibit major cluster peaks assigned to molecular ions $[M + H]^+$, validating the correct formulation of the two complexes, which includes one central metal ion and two thiosemicarbazone ligands. The observed isotopic distributions in the cluster peaks and those calculated on the basis of the molecular formula are almost the same. Figure 1 depicts illustrates the cluster peak of the molecular ion $[Zn\text{-}5cATSC + H]^+$ (*m/z* = 729.1) and its calculated isotopic distribution.

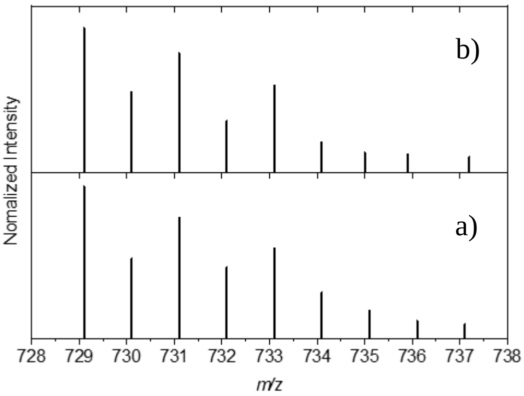


Figure 1. a) Simulated isotopic distribution for $[Zn\text{-}5cATSC + H]^+$; b) ESI-MS cluster peak for $[Zn\text{-}5cATSC + H]^+$.

The IR spectrum of H-5cATSC reveals intense absorptions attributable to *v*(C=N) at 1550 cm^{-1}. The absorptions are bathochromically shifted to 1497 and 1485 cm^{-1} in Pd-5cATSC and Zn-5cATSC, thus indicating that the nitrogen atom of the azomethine moiety is engaged in complexation. The bands assigned to *v*(C=S) at 839 and 837 cm^{-1} for Pd-5cATSC and Zn-5cATSC are lower than those for H-5cATSC by ~30 cm^{-1}. The frequency decrease implies that the thiolate sulfur atom is also involved in coordination mode. This is consistent with the accepted mechanism that the ligands are tautomerized into thiol form and then deprotonated [9,16].

The solution ^1H NMR spectra of Pd-5cATSC reveal proton signals ascribable to Anthracenyl moiety and Thiosemicarbazone fragments. In line with IR spectroscopy, the tautomerization of thiosemicarbazone moieties in H-5cATSC upon coordination is clearly evidenced by the disappearance of $N^{(2)}$–H signals in the spectra of Pd-5cATSC. The anthracenyl proton signals can be rather easily assigned by *peri* effect in which H_{10} and $H_{1,8}$ experience largest steric congestion to give the most downfield chemical shifts [17]. Also, the C_2 symmetry of symmetric Pd-5cATSC as well as local symmetry of anthracenyl rings are reflected in the number of aromatic proton signals. Namely, a set of five anthracenyl proton signals are observed including one singlet (H_{10}), two doublets ($H_{1,8}$ and $H_{4,5}$), and two triplets ($H_{2,3,6,7}$) (Figure 2). Similarly, one azomethine proton signal occurs at 8.67 ppm, respectively. Unfortunately, Zn-5cATSC was not obtained with sufficient purity, rendering its ^1H NMR data complicated.

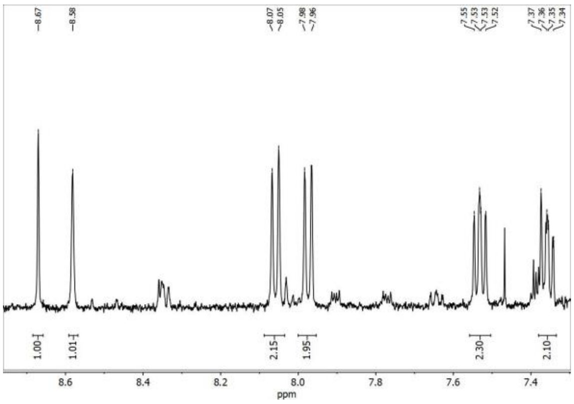
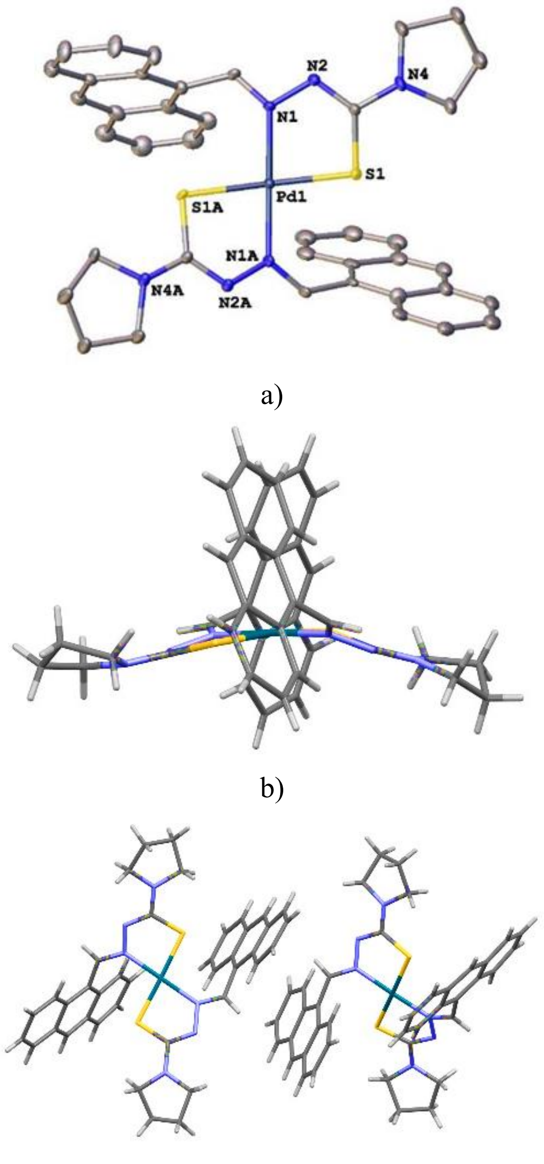


Figure 2. ^1H NMR spectrum of Pd-5cATSC.

3.2. Characterization of complexes by X-ray crystallography

The structures of the two complexes were determined by X-ray single crystal crystallography (Figure 3 and 4) [14]. Selected bond lengths and angles of the complexes are provided in Table 1. Pd-5cATSC reveal *trans* square planar configurations in which Pd(II) binds to two Thiosemicarbazone ligands through two nitrogen and two sulfur atoms from each (Figure 1 and Figure 2). Zn-5cATSC has similar binding mode with H-5cATSC, except that Zn(II) is in tetrahedral arrangement (Figure 3a and 4a).



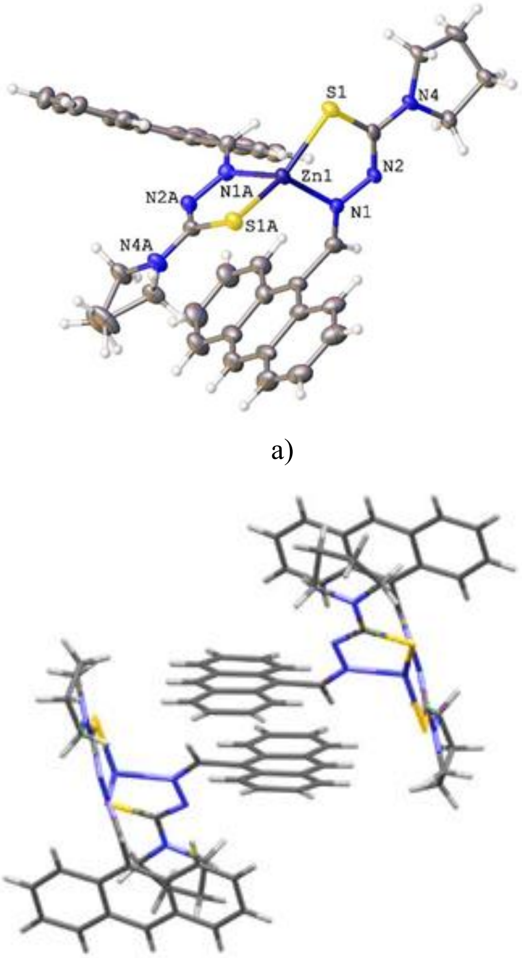
a)

b)

c)

Figure 3. a) X-ray structure of Pd-5cATSC; b) Butterfly geometry; c) Intermolecular π-π stackings.

For Pd-5cATSC and Zn-5cATSC, the Pd–S/Pd–N bond lengths (2.255–2.322/2.044–2.070 Å) and S–Pd–N angles (81.8–87.1°) are in the normal range for reported five-membered chelate ring of thiosemicarbazone ligands. In addition, C2–N2/C2A–N2A and C2–S1/C2A–S1A bonds in thiosemicarbazone moieties span between carbon-nitrogen and carbon-sulfur single and double bonds, respectively. This clearly indicate the delocalization of π-electrons in thiosemicarbazone moiety upon coordination with Pd(II) and Zn(II), which is fully in line with the IR results. Intriguingly, Pd-5cATSC display a greatly bent shape with Pd(II) being 0.092 Å from the S1–N1–S1A–N1A least square plane. The butterfly geometry of Pd-5cATSC is further demonstrated by a large dihedral angle (ca. 38°) between N1–N2–C2–S1 and N1A–N2A–C2A–S1A facets (Figure 3b). The distortion is similar but less severe to that observed in Pd-PhATSC [18].



a)

b)

Figure 4. a) X-ray structure of Zn-5cATSC; b) Intermolecular π-π stackings.

More intriguingly, the two complexes display extensive intermolecular π–π stackings in solid state structure. The ring separations in Zn-5cATSC are of 3.401 Å, normal to reported values. Especially, Zn-5cATSC displays significant overlap between the rings, up to 20% projected area (Figure 4c). Meanwhile, anthracenyl rings of Pd-5cATSC in solid state are not in perfect parallel arrangements despite the separation being ca. 3.5 Å. Instead, the rings form a small dihedral angle of 11^{o}. Notably, C-H···π interactions (2.748–2.862 Å) between imine proton (N=CH) and anthracenyl ring are also detected (Figure 3c).

Table1. Selected bond lengths (Å) and angles (^{o}) of the complexes

	Pd-5cATSC	Zn-5cATSC
M-S1A	2.322(4)	2.2552(12)
M-S1	2.308(4)	2.2739(12)
M-N1A	2.045(12)	2.048(4)
M-N1	2.044(12)	2.070(4)
S1A-C2A	1.749(15)	1.768(5)
S1-C2	1.718(15)	1.753(5)
N1A-N2A	1.386(16)	1.368(5)
N1A-C1A	1.303(19)	1.292(6)
N2-N1	1.405(17)	1.386(5)
N2-C2	1.320(19)	1.332(7)
N2A-C2A	1.303(19)	1.350(7)
N4A-C2A	1.342(18)	1.345(6)
N4-C2	1.395(18)	1.352(5)
N1-C1	1.279(19)	1.311(7)
S1A-M-S1	173.31(17)	138.36(6)
N1A-M-S1A	81.8(4)	87.10(11)
N1A-M-S1	96.7(4)	116.41(12)
N1-M-S1A	97.7(3)	123.40(12)
N1-M-S1	83.4(3)	87.10(11)
N1-M-N1A	177.1(6)	101.24(17)

4. Conclusion

In summary, the coordination chemistry of Pd(II) and Zn(II) complexes with 9-anthraldehyde 3-tetramethyleneiminylthiosemicarbazone was explored. X-ray structures of Pd(II) complex revealed square planar geometry with *trans* configuration. Zn(II) complex displayed a tetrahedral structure. Both complexes exhibited extensive π–π stackings in solid state.

Acknowledgments

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