

A multiprotic indole-based thiocarbohydrazone in the formation of mono-, di- and hexa-nuclear metal complexes



Abeer A. Ibrahim^{a,b}, Hamid Khaledi^{a,*}, Hapipah Mohd Ali^a

^a Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

^b Presidency of Sulaimani Polytechnic University, Kurdistan Region, Iraq

ARTICLE INFO

Article history:

Received 30 April 2014

Accepted 24 June 2014

Available online 9 July 2014

Keywords:

Ditopic ligand

Bridging ligand

Schiff base

Coinage metal

Polynuclear complex

ABSTRACT

A new thiocarbohydrazone (LH₄) derived from indole-7-carbaldehyde was synthesized and reacted with Ni^{II}, Pd^{II}, Pt^{II}, Cu^I and Ag^I salts to bind the metals in various coordination fashions, forming complexes with different nuclearities. The reaction with CuCl in the presence of PPh₃ produced a dinuclear Cu^I complex with the formula [Cu₂Cl₂(LH₄)₂(PPh₃)₂], in which LH₄ binds the metals as a neutral μ₂-S-donor ligand. The reaction of the thiosemicarbazone with Ag^I resulted in the formation of a hexanuclear complex featuring an Ag₆S₆ core. The ligand in this complex is monoanionic and uses the sulfur and a hydrazinic nitrogen atom in binding to the metals. The reaction of LH₄ with [MCl₂(PPh₃)₂] (M = Ni^{II}, Pd^{II} and Pt^{II}) at room temperature yielded complexes of the type [M(LH₂)(PPh₃)]. The thiocarbohydrazone in these complexes takes advantage of one indole N atom donor to act as a dianionic NNS tridentate ligand. A modification of the conditions of the reaction with the Pd^{II} salt led to the formation of the dinuclear complex [Pd₂Cl(LH)(PPh₃)₃]. In this molecule, the thiocarbohydrazone is triply deprotonated and chelates one metal center by its dianionic NNS pocket, while coordinating the second metal ion through a hydrazinic N atom. The structure of the molecules was studied by X-ray crystallography and NMR spectroscopy.

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1. Introduction

In the past decade, there has been growing interest in the coordination chemistry of thiocarbohydrazones. Depending on the substituents and the reaction conditions, they have been shown to assume a variety of coordination modes to form mononuclear [1–8], dinuclear [9] or tetranuclear metal complexes [10–18]. In this context, particular attention has been devoted to the substitution patterns which confer the thiocarbohydrazone ligand ditopic character such that molecular rectangles are created [10–17]. Moreover, a special example has shown the formation of an octanuclear-Cu^{II} complex from four fully deprotonated bis(salicylaldehyde)thiocarbohydrazones, where the ligand used its maximal donor capacity [19].

We have recently been exploring ligands derived from indole-7-carbaldehyde. The structure of indole-7-carbaldimines resembles those of the analogous salicylaldimines: both contain a potential donor atom linked to an iminic carbon via two intervening C atoms; however, the donor atom in indole-7-carbaldimines is the

softer and less electronegative N atom versus the O atom in salicylaldimines (Scheme 1).

In our previous articles we showed that indole-7-carbaldimines can coordinate to metal ions in various modes to produce complexes incorporating the biologically important indole nucleus [20,21]. In continuation of our program to develop new indole-based complexes with biological significance, bis(indole-7-carbaldehyde)thiocarbohydrazone was prepared and reacted with Ni^{II}, Pd^{II}, Pt^{II}, Cu^I and Ag^I ions. In order to prevent the formation of high order aggregates and enhance the solubility of the products, which is essential for pharmacological applications, the reactions were conducted in the presence of triphenylphosphine. This article discusses the coordination chemistry and the structures of the obtained complexes.

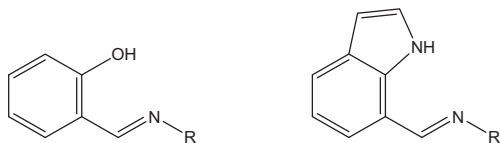
2. Experimental

2.1. Materials and measurements

Indole-7-carbaldehyde was purchased from the Sigma–Aldrich Company. Elemental microanalyses (C, H, N) were carried out on a Perkin-Elmer 2400 elemental analyzer. The NMR spectra were recorded on a 400 MHz Bruker spectrometer. The IR spectra were taken on a Perkin-Elmer Spectrum 400 ATR-FT-IR spectrometer.

* Corresponding author. Tel.: +60 3 79674246; fax: +60 3 79674193.

E-mail addresses: grdenia_77m@yahoo.com (A.A. Ibrahim), khaledi@um.edu.my, hamid.khaledi@gmail.com (H. Khaledi), hapipah@um.edu.my (H.M. Ali).



Scheme 1. Indole-7-carbaldimines vs. salicylaldimines.

2.2. Synthesis of LH_4

A mixture of indole-7-carbaldehyde (2.9 g, 20 mmol) and thio-carbohydrazide (1.06 g, 10 mmol) in methanol (40 mL) containing a few drops of HCl (37%) was stirred for 3 h. The solution was then partially evaporated, followed by addition of distilled water to precipitate the yellowish product. It was filtered, washed with 40% aqueous methanol and dried over silica gel. Yield: 3.0 g, 83%. *Anal.* Calc. for $C_{19}H_{16}N_6S$: C, 63.31; H, 4.47; N, 23.32. Found: C, 63.75; H, 4.17; N, 23.28%. 1H NMR (DMSO- d_6) δ (ppm): 6.63 (2H, br.s, Ar-H); 7.17 (2H, t, $J = 7.4$ Hz, Ar-H); 7.35 (1H, br.s, Ar-H); 7.43 (1H, br.s, Ar-H); 7.58 (2H, br.s, Ar-H); 7.75 (2H, d, $J = 7.8$ Hz, Ar-H); 8.52 (1H, s, HCNN); 8.83 (1H, s, HCNN); 11.29 (1H, s, indole-NH); 11.55 (1H, s, indole-NH); 12.11 (1H, s, NNH); 12.15 (1H, s, NNH). ^{13}C NMR (DMSO- d_6) δ (ppm): 102.66, 119.70, 123.38, 124.15, 126.50, 126.99, 128.56, 129.22 (Ar); 147.65, 147.94 (HCNN); 175.25 (CS).

2.3. Synthesis of $[Cu_2Cl_2(LH_4)_2(PPh_3)_2]$

A solution of PPh_3 (0.262 g, 1 mmol) in methanol (5 ml) was added to a solution of $CuCl$ (0.13 g, 1.3 mmol) in the same solvent (5 ml). The mixture was stirred for 15 min, followed by slow addition of a solution of LH_4 (0.36 g, 1 mmol) in 15 mL methanol-acetonitrile (50:50) at room temperature. The resulting brownish solution was kept at 4 °C for five days, upon which olive crystals of $[Cu_2Cl_2(LH_4)_2(PPh_3)_2] \cdot 6MeOH$ were formed. After determination of the structure by X-ray crystallography, the crystals were ground and dried at 50 °C for other analytical purposes. Yield 0.38 g, 53%. *Anal.* Calc. for $C_{74}H_{62}Cl_2Cu_2N_{12}P_2S_2$: C, 61.57; H, 4.33; N, 11.64. Found: C, 61.44; H, 4.08; N, 11.98%. 1H NMR (DMSO- d_6) δ (ppm): 6.59 (2H, br.s, Ar-H); 6.65 (2H, br.s, Ar-H); 6.99 (2H, br.s, Ar-H); 7.16 (2H, t, $J = 6.8$ Hz, Ar-H); 7.24–7.48 (34H, Ar-H); 7.58 (2H, br.s, Ar-H); 7.69 (4H, m, Ar-H); 7.77 (2H, d, $J = 7.7$ Hz, Ar-H); 8.55 (2H, br.s, HCNN); 8.94 (2H, br.s, HCNN); 11.30 (2H, s, indole-NH); 11.33 (2H, s, indole-NH); 12.32 (2H, s, NNH); 12.55 (2H, s, NNH). ^{13}C NMR (DMSO- d_6) δ (ppm): 102.86, 116.82, 117.92, 119.75, 119.84, 123.96, 124.14, 124.70, 126.44, 126.96, 127.14, 128.75–129.37, 130.48, 131.57, 133.71–133.96 (Ar); 149.89, 150.29 (HCNN); 172.43 (CS).

2.4. Synthesis of $[Ag_6(LH_3)_6]$

To a solution of $AgNO_3$ (0.17 g, 1 mmol) in methanol (5 ml) was added a solution of PPh_3 (0.262 g, 1 mmol) in the same solvent (5 ml). The mixture was stirred for 15 min, followed by slow addition of a solution of LH_4 (0.36 g, 1 mmol) in 15 mL methanol-acetonitrile (50:50). The mixture was stirred at room temperature for 30 min and the resulting clear yellow solution was kept at 4 °C for a week to give a yellow precipitate. The solid was filtered, washed with methanol and dried over silica-gel. Yield: 0.23 g. *Anal.* Found: C, 48.94; H, 3.69; N, 17.32%. Recrystallization from DMF at room temperature afforded X-ray quality crystals of $[Ag_6(LH_3)_6] \cdot 6DMF$. For elemental analysis and IR spectroscopy, the crystals were ground and dried at 50 °C to remove the solvate molecules. Yield: 0.183 g, 39%. *Anal.* Calc. for $C_{114}H_{90}Ag_6N_{36}S_6$: C, 48.83; H, 3.24; N, 17.98. Found: C, 48.61; H, 3.09; N, 17.76%.

2.5. Synthesis of $[Ni(LH_2)(PPh_3)]$

A solution of $[Ni(PPh_3)_2Cl_2]$ (0.65 g, 1 mmol) in methanol (10 mL) was added to a solution of LH_4 (0.36 g, 1 mmol) in 20 mL methanol-acetonitrile (50:50), followed by the addition of a few drops of triethylamine. The mixture was stirred at room temperature for 3 h and then kept at 4 °C for a week to give brownish crystals of $[Ni(LH_2)(PPh_3)] \cdot 2CH_3CN$. After determination of the structure by X-ray crystallography, the crystals were ground and dried at 50 °C for other analytical purposes. Yield: 0.49 g, 72%. *Anal.* Calc. for $C_{37}H_{29}N_6NiPS$: C, 65.41; H, 4.30; N, 12.37. Found: C, 65.38; H, 4.11; N, 12.24%.

2.6. Synthesis of $[Pd(LH_2)(PPh_3)]$

A solution of *trans*- $[Pd(PPh_3)_2Cl_2]$ (0.70 g, 1 mmol) in methanol (10 mL) was added to a solution of LH_4 (0.36 g, 1 mmol) in 10 mL methanol-acetonitrile (50:50), followed by the addition of a few drops of triethylamine. The mixture was stirred at room temperature for 3 h to yield an orange precipitate. The solid was washed with 50% aqueous methanol and dried at 50 °C. Yield: 0.57 g, 79%. *Anal.* Calc. for $C_{37}H_{29}N_6PdS$: C, 61.12; H, 4.02; N, 11.56. Found: C, 61.47; H, 3.99; N, 11.33%. 1H NMR (DMSO- d_6) δ (ppm): 6.10 (1H, br.s, Ar-H); 6.51 (2H, br.s, Ar-H); 7.00–7.07 (2H, m, Ar-H); 7.13 (1H, d, $J = 6.8$ Hz, Ar-H); 7.24 (1H, br.s, Ar-H); 7.41–7.62 (11H, Ar-H); 7.67–7.84 (7H, Ar-H); 8.16 (1H, s, HCNN); 8.80 (1H, d, $J = 11.8$ Hz, HCNN); 10.04 (1H, br.s, indole-NH); 11.68 (1H, s, NNH). ^{13}C NMR (DMSO- d_6) δ (ppm): 102.42, 102.59, 116.97, 117.51, 118.61, 119.90, 122.34, 123.35, 126.09, 126.30, 127.64, 128.35 (Ar); 129.21–129.45; 130.11, 130.52, 131.94, 132.43, 134.17 (Ar); 135.25 (d, J [^{31}P - ^{13}C] = 10.8 Hz, Ar), 139.70 (d, J [^{31}P - ^{13}C] = 8.4 Hz, Ar); 142.71, 151.45 (HCNN); 168.80 (CS).

X-ray quality crystals of $[Pd(LH_2)(PPh_3)] \cdot DMSO$ were obtained from a DMSO solution of the complex on standing for two days at room temperature.

2.7. Synthesis of $[Pt(LH_2)(PPh_3)]$

A solution of *cis*- $[Pt(PPh_3)_2Cl_2]$ (0.79 g, 1 mmol) in methanol (10 mL) was added to a solution of LH_4 (0.36 g, 1 mmol) in 20 mL methanol-acetonitrile (50:50), followed by the addition of a few drops of triethylamine. The mixture was stirred at room temperature for 3 h and then kept at 4 °C for a month to give red-orange crystals of $[Pt(LH_2)(PPh_3)] \cdot 2CH_3CN$. After determination of the structure by X-ray crystallography, the crystals were ground and dried at 50 °C for other analytical purposes. Yield: 0.73 g, 89%. *Anal.* Calc. for $C_{37}H_{29}N_6PtS$: C, 54.47; H, 3.58; N, 10.3. Found: C, 54.29; H, 3.44; N, 10.17%. 1H NMR (DMSO- d_6) δ (ppm): 6.21 (1H, br.s, Ar-H); 6.57 (1H, br.s, Ar-H); 6.83 (1H, br.s, Ar-H); 7.08 (1H, t, $J = 7.6$ Hz, Ar-H); 7.18 (2H, t, $J = 7.6$ Hz, Ar-H); 7.36 (1H, m, Ar-H); 7.47–7.62 (11H, Ar-H); 7.73–7.90 (7H, Ar-H); 8.24 (1H, s, HCNN); 9.10 (1H, d, $J = 10.7$ Hz, HCNN); 10.00 (1H, br.s, indole-NH); 11.87 (1H, s, NNH). ^{13}C NMR (DMSO- d_6) δ (ppm): 102.66, 103.23, 116.96, 117.82, 118.58, 119.93, 122.36, 123.56, 126.31, 126.69, 128.22, 128.36, 128.94–129.37, 130.05, 130.66, 132.17–132.63 (Ar); 135.29 (d, J [^{31}P - ^{13}C] = 11.44 Hz, Ar); 140.12 (d, J [^{31}P - ^{13}C] = 6.7 Hz, Ar); 142.85, 149.92 (HCNN); 170.32 (CS).

2.8. Synthesis of $[Pd_2Cl(LH)(PPh_3)_3]$

A solution of *trans*- $[Pd(PPh_3)_2Cl_2]$ (0.70 g, 1 mmol) in methanol (10 mL) was added to a hot solution of LH_4 (0.36 g, 1 mmol) in 10 mL methanol-acetonitrile (50:50), followed by the addition of a few drops of triethylamine. The mixture was refluxed for 3 h and then evaporated to half of its original volume. The orange solid of the product was precipitated by addition of a small amount of

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