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Synthesis and structural characterization of binuclear palladium(II) complexes of salicylaldimine dithiosemicarbazones

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A B S T R A C T

A series of binuclear palladium(II) salicylaldiminato dithiosemicarbazone complexes have been synthesized and characterized. The palladium complexes were obtained by the reaction of various ethylene- and phenylene-bridged dithiosemicarbazones with $Pd(PPh_3)_2Cl_2$. The free salicylaldimine ligands and their palladium complexes were characterized by NMR and IR spectroscopies, ESI-mass spectrometry, elemental analyses and for two representative complexes also by X-ray diffraction. In both metal complexes, the solid-state structures show the two palladium centers to be coordinated in a slightly distorted square-planar geometry, which gives rise in each case to five- and six-membered chelate rings. The salicylaldimine thiosemicarbazone ligands coordinate to palladium in a tridentate manner, through the phenolic oxygen, imine nitrogen and thiolate sulfur atoms.

Keywords:
Palladium, Binuclear, Dithiosemicarbazone, Salicylaldehyde

1. Introduction

In view of the wide spectrum of biological applications of thiosemicarbazones [1–4], including activity against diseases such as TB [5], leprosy [6], malaria [7,8], as well as a range of bacterial infections [9–13], the chemistry of thiosemicarbazones and their metal complexes has attracted prolific attention over the past decade [2,14–16]. Thiosemicarbazones belong to a class of compounds, grouped together with Schiff bases, containing sulfur and nitrogen donor atoms that can bond to electron-deficient metals. Selected metal complexes of thiosemicarbazones were found to display enhanced biological activity over the uncomplexed thiosemicarbazones [17,18].

Dithiosemicarbazones and bis(thiosemicarbazones) are dimeric structures generally containing two thiosemicarbazone moieties. Dithiosemicarbazones, a term used by Swearingen and West [19] to differentiate between bis(thiosemicarbazones) and dithiosemicarbazones, consist of two mono-thiosemicarbazone moieties connected by their amide nitrogen atoms to an aliphatic or aromatic spacer (Fig. 1). Bis(thiosemicarbazones) also consist of two monomeric thiosemicarbazone moieties, however, linked through their imine nitrogen atoms to a hydrocarbon spacer (Fig. 1).

There are few reports available on transition metal complexes of dithiosemicarbazones. Wiles et al. synthesized one of the first transition metal-containing dithiosemicarbazones, linked by an ethylene bridge [20]. The biological properties of these copper complexes were investigated and displayed antifungal activity against the cellulolytic microorganism, *Chaetomium globosum*. Examples of analogous dithiosemicarbazones have been successfully synthesized containing ethylene, phenylene and piperazine bridges. These dithiosemicarbazones have incorporated transition metals from group 4 (Ti, Zr) [21], group 9 (Co) [19], group 10 (Ni) [19,22], group 11 (Cu) [19,20], group 12 (Zn) elements [23], and the lanthanides (La, Pr) [24]. It is noteworthy that platinum group metal complexes of dithiosemicarbazones are sparse, given that platinum and palladium complexes of heterocyclic thiosemicarbazones show significant anticancer activity [25]. As part of our continuing interest in the synthesis of transition metal complexes of biological molecules, we have investigated the coordination behaviour of dithiosemicarbazones towards palladium(II), with a view to develop new transition metal pharmaceuticals. This paper describes the synthesis, structural characterization and preliminary biological activity of salicylaldimine dithiosemicarbazone ligands and their complexation with palladium(II) to form binuclear complexes.

2. Experimental

2.1. General experimental procedures

All reagents and solvents were purchased from commercial sources (Sigma–Aldrich, Fluka, Merck, Kimix) and used as received.

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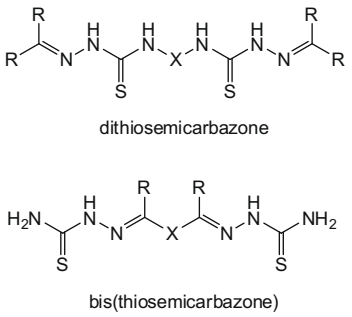


Fig. 1. Example of a dithiosemicarbazone and a bis(thiosemicarbazone) (X = aliphatic or aromatic spacer).

Palladium dichloride was received as a donation from Anglo Platinum. Ethane-1,2-dithiosemicarbazide [26], benzene-1,4-dithiosemicarbazide [23], and $Pd(PPh_3)_2Cl_2$ [27] were prepared following reported literature procedures. Solvents were freshly distilled and dried over the appropriate drying agents.

2.2. Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on either a Varian Mercury XR300 MHz spectrometer (^{1}H at 300.08 MHz, ^{13}C at 75.46 MHz, ^{31}P at 121.47 MHz) or a Varian Unity XR400 MHz spectrometer (^{1}H at 399.95 MHz, ^{13}C at 100.58 MHz, ^{31}P at 161.90 MHz). ^{1}H and $^{13}C\{^1H\}$ NMR chemical shifts are reported using tetramethylsilane (TMS) as the internal standard and $^{31}P\{^1H\}$ spectra were measured relative to H_3PO_4 as the external standard. Infrared (IR) spectra were determined using a Perkin–Elmer Spectrum One FT-IR spectrometer and were recorded using KBr pellets. Elemental analyses (C, H and N) were recorded on a Thermo Flash 1112 Series CHNS-O Analyser. Mass spectrometry was carried out at the University of Stellenbosch on a Waters API Quattro Micro triple quadrupole mass spectrometer. Data were recorded using Electrospray Ionisation (ESI) mass spectrometry in the negative or positive modes. Melting points are corrected and were determined on a Reichert Thermovar hot stage microscope.

*2.3. Synthesis of ethylene- (**1**–**3**) and phenylene-bridged (**4**–**6**) dithiosemicarbazone ligands*

General procedure: Either ethane-1,2-dithiosemicarbazide or benzene-1,4-dithiosemicarbazide (1 equiv.) was dissolved in *N,N*-dimethylformamide (20 mL) at 120 °C. Upon complete dissolution, the appropriate salicylaldehyde (2 equiv.), dissolved in DMF (5 mL), was then added dropwise to the solution. The mixture was stirred at 120 °C for 5 h. Cold water was added to induce precipitation of the product in all cases. The resulting precipitate was collected by filtration and washed with cold water. The products were dried in the oven at 110 °C.

Compound **1** was prepared from ethane-1,2-dithiosemicarbazide (0.205 g, 0.985 mmol) and salicylaldehyde (0.210 mL, 1.97 mmol). Compound **1** was isolated as a light yellow powder. Yield 0.307 g (74.7%). M.p. 223–227 °C. *Anal.* Calc. for $C_{18}H_{20}N_6S_2O_2$: C, 51.90; H, 4.84; N, 20.17; S, 15.40. Found: C, 51.58; H, 5.11; N, 20.30; S, 16.06%. ν_{max}/cm^{-1} 1618 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 3.83 (4H, s, CH_2), 6.77 (2H, t, J = 7.72, Ar), 6.85 (2H, d, J = 8.17, Ar), 7.19 (2H, t, J = 7.53, Ar), 7.96 (2H, d, J = 7.73, Ar), 8.39 (2H, s, CH=N), 8.57 (2H, s, $NHCH_2$), 9.86 (2H, s, OH), 11.47 (2H, s, C=NNH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ = 43.32, 115.85, 118.99, 120.22, 126.61, 130.78, 139.64, 156.22, 177.23 ppm. MS ESI: m/z 415 (100%, $[M-H]^+$).

Compound **2** was prepared from ethane-1,2-dithiosemicarbazide (0.205 g, 0.986 mmol) and 2-hydroxy-3-methoxy-benzaldehyde (0.300 g, 1.97 mmol). The product was isolated as a pale yellow powder. Yield 0.441 g (93.7%). M.p. 245–249 °C. *Anal.* Calc. for $C_{20}H_{24}N_6S_2O_4$: C, 50.40; H, 5.08; N, 17.63; S, 13.46. Found: C, 49.99; H, 5.34; N, 17.36; S, 12.92%. ν_{max}/cm^{-1} 1671 (CN). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 3.80 (6H, s, OMe), 3.83 (4H, s, CH_2), 6.73 (2H, t, J = 7.98, Ar), 6.94 (2H, d, J = 7.03, Ar), 7.58 (2H, d, J = 7.86, Ar), 8.41 (2H, s, CH=N), 8.56 (2H, s, $NHCH_2$), 9.12 (2H, s, OH), 11.5 (2H, s, CH=NNH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ = 43.32, 55.79, 112.84, 118.14, 118.74, 120.68, 139.44, 145.8, 147.78, 177.23 ppm. MS ESI: m/z 475 (100%, $[M-H]^+$).

Compound **3** was prepared from ethane-1,2-dithiosemicarbazide (0.204 g, 0.979 mmol) and 3-*tert*-butyl-salicylaldehyde (0.340 mL 1.96 mmol). Compound **3** was isolated as a pale yellow powder. Yield 0.365 g (73.9%). M.p. 226–230 °C. *Anal.* Calc. for $C_{24}H_{36}N_6S_2O_2$: C, 57.11; H, 7.19; N, 16.65; S, 12.71. Found: C, 57.55; H, 6.88; N, 16.44; S, 12.80%. ν_{max}/cm^{-1} 1599 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 1.39 (18H, s, ^{t}Bu), 3.84 (4H, s, CH_2), 6.84 (2H, t, J = 7.67, Ar), 7.24 (4H, m, Ar), 8.29 (2H, s, CH=N), 8.60 (2H, s, $NHCH_2$), 9.96 (2H, s, OH), 11.41 (2H, s, CH=N–NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C): δ = 30.06, 35.15, 44.33, 119.52, 120.02, 129.14, 129.99, 137.49, 147.66, 156.00, 177.88 ppm. MS ESI: m/z 529 (100%, $[M+Na]^+$).

Compound **4** was synthesized from benzene-1,4-dithiosemicarbazide (0.205 g, 0.800 mmol) and salicylaldehyde (0.171 mL, 1.60 mmol). The precipitate was isolated as a pale yellow powder. Yield 0.323 g (86.9%). M.p. 233–241 °C. *Anal.* Calc. for $C_{22}H_{20}N_6S_2O_2$: C, 56.88; H, 4.34; N, 18.09; S, 13.80. Found: C, 56.32; H, 4.36; N, 17.63; S, 13.41%. ν_{max}/cm^{-1} 1622 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 6.85 (4H, m, Ar), 7.23 (2H, t, J = 8.46, Ar), 7.55 (4H, s, Ph), 8.02 (2H, d, J = 7.78, Ar), 8.49 (2H, s, CH=N), 9.89 (2H, s, OH), 9.93 (2H, s, S=CNHPh), 11.64 (2H, s, CH=NNH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ = 116.03, 119.16, 120.15, 124.88, 127.15, 131.16, 136.02, 140.45, 156.47, 175.72 ppm. MS ESI: m/z 465 (100%, $[M+H]^+$).

Compound **5** was prepared using benzene-1,4-dithiosemicarbazide (0.206 g, 0.800 mmol) and 2-hydroxy-3-methoxy-benzaldehyde (0.245 g, 1.60 mmol). Compound **5** was isolated as a pale yellow powder. Yield 0.273 g (65.1%). M.p. 233–236 °C. *Anal.* Calc. for $C_{24}H_{24}N_6S_2O_4$: C, 54.95; H, 4.61; N, 16.02; S, 12.22. Found: C, 54.10; H, 4.65; N, 16.84; S, 12.94%. ν_{max}/cm^{-1} 1659 (CN). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 3.83 (6H, s, OMe), 6.81 (2H, t, J = 7.96, Ar), 6.99 (2H, d, J = 8.06, Ar), 7.48–7.66 (2H, m, Ar), 7.57 (4H, s, Ph), 8.52 (2H, s, CH=N), 9.82 (2H, m, OH), 9.93 (2H, m, S=CNHPh), 11.66 (2H, s, CH=NNH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ = 55.89, 113.16, 118.58, 118.86, 120.58, 124.99, 135.99, 140.18, 146.15, 147.88, 175.70 ppm. MS ESI: m/z 525 (10%, $[M+H]^+$); 391 (100%, $[M-C_8H_6O_2]^+$).

Compound **6** was prepared using benzene-1,4-dithiosemicarbazide (0.153 g, 0.596 mmol) and 3-*tert*-butyl-salicylaldehyde (0.204 mL, 1.19 mmol) in a DMF/EtOH solution. Compound **6** was isolated as a pale yellow powder. Yield 0.098 g (28.5%). M.p. 288–292 °C. *Anal.* Calc. for $C_{30}H_{36}N_6S_2O_2$: C, 62.47; H, 6.29; N, 14.57; S, 11.12. Found: C, 62.19; H, 6.57; N, 14.55; S, 11.05%. ν_{max}/cm^{-1} 1667 (CN). ^{1}H NMR (300 MHz, DMSO-d_6; 25 °C): δ = 1.33 (18H, m, ^{t}Bu), 6.95 (2H, m, Ar), 7.75–7.21 (8H, m, Ar/Ph), 8.39 (2H, s, CH=N), 10.07 (4H, m, OH/NHPh), 11.58 (2H, m, CH=NNH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6; 25 °C): δ = 29.17, 34.42, 118.75, 119.24, 121.09, 125.10, 128.50, 129.43, 136.857, 147.47, 155.42, 176.40 ppm. MS ESI: m/z 577 (100%, $[M+H]^+$).

2.4. Synthesis of binuclear palladium complexes (**7**–**12**)

2.4.1. General procedure

A heated solution (50 °C) of either ethane-1,2-dithiosemicarbazone or benzene-1,4-dithiosemicarbazone (1 equiv.) in ethanol (50 mL) was stirred under nitrogen. To the mixture was added, 1 equiv. of triethylamine. Upon dissolution of the dithiosemicarbazone, $Pd(PPh_3)_2Cl_2$ (2 equiv.) was added resulting in an orange reaction mixture. The reaction mixture was refluxed for 6 h and then cooled to room temperature. The resulting orange precipitate was filtered, washed with ethanol and dried *in vacuo*.

2.4.2. Compound **7**

Compound **1** (0.103 g, 0.247 mmol), triethylamine (0.035 mL) and $Pd(PPh_3)_2Cl_2$ (0.347 g, 0.494 mmol) were refluxed in ethanol. The product was obtained as a light orange powder. Yield 0.213 g (74.9%). M.p. 274–283 °C (with decomposition). *Anal.* Calc. for $C_{54}H_{46}N_6S_2P_2O_2Pd_2$: C, 56.40; H, 4.03; N, 7.31; S, 5.58. Found: C, 56.08; H, 4.04; N, 7.02; S, 5.09%. ν_{max}/cm^{-1} 1599 (C=N). ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 3.36 (4H, s, CH_2), 6.55 (4H, m, Ar), 6.98 (2H, s, N*H*CH_2), 7.18 (2H, t, J = 8.78, Ar), 7.38 (2H, d, J = 7.80, Ar), 7.39–7.68 (30H, m, PPh_3), 8.33 (2H, d, J = 13.98, CH=N) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ = 44.99, 114.31, 117.77, 119.81, 128.38–134.02, 148.82, 161.47, 169.16 ppm. ^{31}P NMR (120 MHz, DMSO-d_6, 25 °C): δ = 25.58 (2P, s, PPh_3) ppm. MS ESI: m/z 1151 (100%, $[M+H]^+$).

2.4.3. Compound **8**

Compound **2** (0.119 g, 0.249 mmol), triethylamine (0.035 mL) and $Pd(PPh_3)_2Cl_2$ (0.350 g, 0.498 mmol) were refluxed in ethanol. The product was isolated as an orange powder. Yield 0.286 g (94.9%). M.p. 264–271 °C (with decomposition). *Anal.* Calc. for $C_{56}H_{50}N_6S_2P_2O_4Pd_2$: C, 55.58; H, 4.17; N, 6.90; S, 5.30. Found: C, 56.00; H, 4.49; N, 6.36; S, 5.30%. ν_{max}/cm^{-1} 1598 (C=N). ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = (OMe signal suppressed by H_2O), 3.59 (4H, s, CH_2), 5.72 (2H, s, N*H*CH_2), 6.52 (2H, t, J = 7.41, Ar), 6.86 (2H, m, Ar), 7.10 (2H, d, J = 7.41, Ar), 7.20–7.88 (30H, m, PPh_3), 8.27 (2H, d, J = 14.01, CH=N) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ = 44.97, 55.87, 113.52, 114.24, 117.42, 125.85, 128.13–134.14, 149.04, 150.68 152.87, 168.83 ppm. ^{31}P NMR (120 MHz, DMSO-d_6, 25 °C): δ = 19.61 (2P, s, PPh_3) ppm. MS ESI: m/z 1210 (20%, $[M+H]^+$); 279 (100%, $[M-C_8H_6N_2SO_2Pd(PPh_3)_2]^+$).

2.4.4. Compound **9**

Compound **3** (0.122 g, 0.243 mmol), triethylamine (0.034 mL) and $Pd(PPh_3)_2Cl_2$ (0.341 g, 0.485 mmol) were refluxed in ethanol. This yielded the product **9** as an orange powder. Yield 0.221 g (72.1%). M.p. 258–262 °C (with decomposition). *Anal.* Calc. for $C_{62}H_{62}N_6S_2P_2O_2Pd_2$: C, 59.00; H, 4.95; N, 6.66; S, 5.08. Found: C, 60.21; H, 5.32; N, 5.89; S, 4.94%. ν_{max}/cm^{-1} 1593 (C=N). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.75 (18H, s, ^{t}Bu), 3.38 (2H, s, CH_2), 5.08 (2H, s, N*H*CH_2), 6.56 (2H, t, J = 7.57, Ar), 7.19–7.79 (34H, m, PPh_3, Ar), 8.28 (2H, d, J = 14.19, CH=N) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ = 30.08, 34.95, 45.91, 114.39, 118.88, 128–135, 139.92, 151.07, 161.95 ppm. ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C): δ = 24.35 (2P, s, PPh_3) ppm. MS ESI: m/z 1263 (50%, $[M+H]^+$); 675 (100%, $[M-C_{11}H_{13}N_2SOPdPPh_3]^+$).

2.4.5. Compound **10**

Compound **4** (0.100 g, 0.210 mmol), triethylamine (0.031 mL) and $Pd(PPh_3)_2Cl_2$ (0.312 g, 0.430 mmol) were refluxed in dry ethanol. Compound **10** was isolated as an orange powder. Yield 0.239 g (95.1%). M.p.: does not melt below 300 °C. *Anal.* Calc. for $C_{58}H_{46}N_6S_2P_2O_2Pd_2$: C, 58.15; H, 3.87; N, 7.02; S, 5.35. Found: C, 57.45; H, 3.83; N, 6.96; S, 5.50%. ν_{max}/cm^{-1} 1598 (CN). ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 6.60 (4H, m, Ar), 7.21 (4H, m, Ar), 7.57–7.71 (34H, m, PPh_3, Ph), 8.63 (2H, d, J = 13.78, CH=N), 9.26 (2H, s, N*H*Ph) ppm. ^{31}P NMR (120 MHz, DMSO-d_6, 25 °C): δ = 25.61 (2P, s, PPh_3) ppm.

2.4.6. Compound **11**

Compound **5** 0.113 g, 0.210 mmol), triethylamine (0.030 mL) and $Pd(PPh_3)_2Cl_2$ (0.301 g, 0.430 mmol) were refluxed in ethanol. A dark orange powder (**11**) was isolated. Yield 0.241 g (91.3%). M.p.: does not melt below 300 °C. *Anal.* Calc. for $C_{60}H_{50}N_6S_2P_2O_4Pd_2$: C, 57.28; H, 4.01; N, 6.68; S, 5.10. Found: C, 57.62; H, 3.84; N, 6.84; S, 5.21%. ν_{max}/cm^{-1} 1589 (C=N). ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 3.63 (6H, s, OMe), 6.56 (2H, t, J = 7.81, Ar), 6.91 (2H, d, J = 7.70, Ar), 7.16 (2H, d, J = 8.24, Ar), 7.76–7.49 (34H, m, PPh_3, Ar), 8.61 (2H, d, J = 13.85, CH=N), 9.23 (2H, s, N*H*Ph) ppm. ^{31}P NMR (120 MHz, DMSO-d_6, 25 °C): δ = 19.73 (2P, s, PPh_3) ppm.

2.4.7. Compound **12**

Compound **6** (0.126 g, 0.219 mmol), triethylamine (0.031 mL) and $Pd(PPh_3)_2Cl_2$ (0.307 g, 0.438 mmol) were refluxed in ethanol. A dark orange powder was isolated. Yield 0.227 g (79.12%). M.p.: does not melt below 300 °C. *Anal.* Calc. for $C_{66}H_{62}N_6S_2P_2O_2Pd_2$: C, 60.50; H, 4.77; N, 6.42; S, 4.89. Found: C, 60.45; H, 4.91; N, 6.88; S, 4.95%. ν_{max}/cm^{-1} 1593 (C=N). ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 0.69 (18H, s, ^{t}Bu), 6.53 (2H, t, J = 7.56, Ar), 7.08–7.86 (38H, m, Ar/Ph), 8.59 (2H, d, J = 14.05, CH=N), 9.12 (2H, s, N*H*Ph) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*, 25 C): δ = 29.4, 34.8, 114.1, 118.1, 119.4, 128.4–134.8, 140.3, 153.2, 162.4, 164.8 ppm. ^{31}P NMR (120 MHz, DMSO-d_6, 25 °C): δ = 25.67 (2P, s, PPh_3) ppm. MS ESI: m/z 1311 (10%, $[M+H]^+$).

2.5. X-ray crystallography

Crystals suitable for X-ray diffraction study for **7**·2 DMSO and **11**·4 DMSO were grown from concentrated DMSO solutions of complexes **7** and **11**, respectively. An orange crystal of **7**·2 DMSO was mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°, increment of 1.2°, $D_{max} - D_{min}$ = 12.45–0.81 Å. Whereas a yellow crystal of **11**·4 DMSO was mounted on a Nonius Kappa-CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å), equipped with an Oxford Cryostream cooling system. Data were evaluated using the Bruker Nonius "Collect" program and was scaled and reduced using DENZO-SMN software. Both structures were solved by direct methods using the program SHELXS-97 [28]. The refinement and all further calculations were carried out using SHELXL-97 (see Table 1) [29]. The hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. All non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Figs. 2 and 3 were drawn with ORTEP [30]. Packing diagram (Fig. 4) was produced using the program PovRay [31] and the graphic interface X-seed [32].

2.6. Cytotoxic assay

The dithiosemicarbazone ligands were evaluated for their *in vitro* anticancer activity against three oesophageal cancer cell lines, WHCO1, WHCO5 and WHCO6, derived from biopsies of primary oesophageal squamous cell carcinomas [33] and kindly provided by Professor Rob Veale (University of Witwatersrand, South Africa). IC_{50} determinations were carried out using the MTT assay. Briefly, 3000 cells were seeded per well in 96-well plates. Cells were incubated at 37 °C under 5% CO_2 (24 h), after which aqueous DMSO solu-

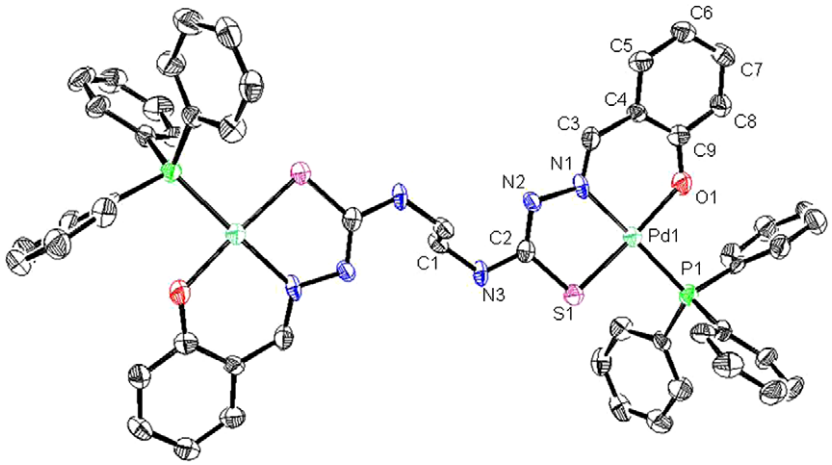


Fig. 2. Molecular structure of complex **7** showing ellipsoids at the 50% probability level with hydrogen atoms and solvent molecules omitted for clarity.

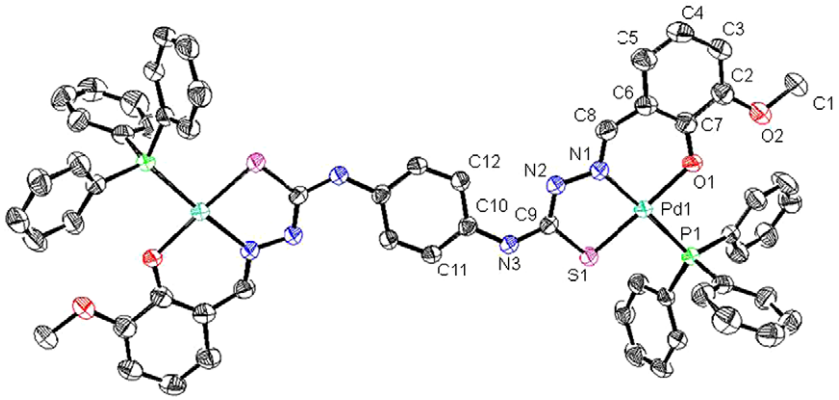


Fig. 3. Molecular structure of complex **11** showing ellipsoids at the 50% probability level with hydrogen atoms and solvent molecules omitted for clarity.

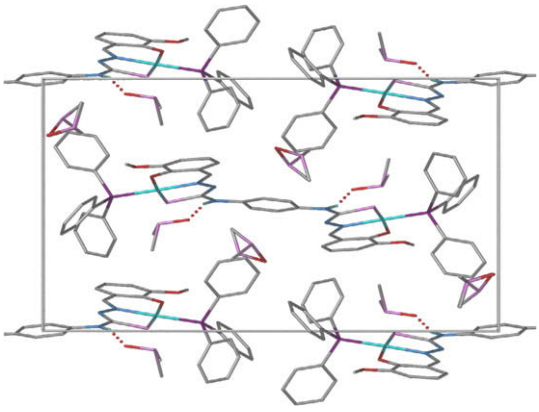


Fig. 4. Crystal packing arrangement of compound **11**·4 DMSO.

tions of each compound (10 μL, with a constant final concentration of DMSO = 0.2%) were plated at various concentrations. After 48 h incubation, observations were made, and MTT (10 μL) solution added to each well. After a further 4 h incubation, solubilization solution (100 μL) was added to each well, and plates were incubated overnight. Plates were read at 595 nm on a BioTek microplate reader.

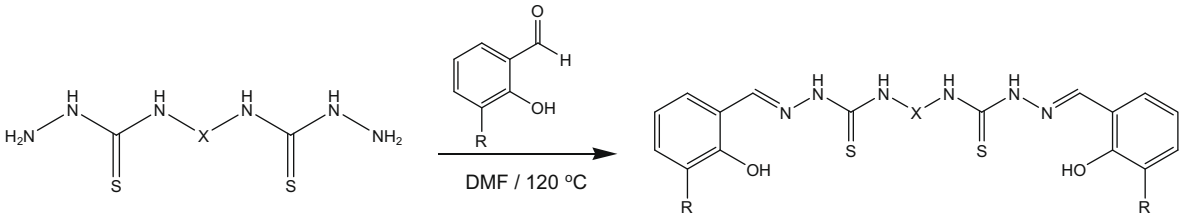
3. Results and discussion

*3.1. Synthesis and characterization of dithiosemicarbazone ligands (**1**–**6**)*

A series of ethylene- and phenylene-bridged salicylaldimine dithiosemicarbazones were synthesized using a procedure similar to that previously reported by Scovill [26] and Dilworth et al. [23]. Our initial attempts at preparing dithiosemicarbazones via amination reactions of the appropriate aryl thiosemicarbazide with either ethylenediamine or phenylenediamine proved to be unsuccessful, despite refluxing for extended periods or using microwave-assisted techniques.

Two different routes were followed to prepare the bridged dithiosemicarbazone ligands. The synthesis of the ethylene-bridged dithiosemicarbazone ligands via the known reaction of hydrazine with a diacid precursor produced ethane-1,2-dithiosemicarbazide [26]. Benzene-1,4-dithiosemicarbazide was obtained using a simple one-step procedure via the reaction of hydrazine with phenylene diisothiocyanate as the starting precursor [23]. Subsequent Schiff-base condensation of either ethane-1,2-dithiosemicarbazide or benzene-1,4-dithiosemicarbazide with salicylaldehyde, 2-hydroxy-3-methoxy benzaldehyde or 3-*tert*-butyl salicylaldehyde afforded the ethylene-bridged (**1–3**) and phenylene-bridged (**4**–**6**) dithiosemicarbazones (Scheme 1).

The ethylene- and phenylene-linked dithiosemicarbazone ligands (**1**–**6**) were isolated by precipitation in water, as pale yellow



Scheme 1. Synthetic route to dithiosemicarbazones **1–6**.

powders in varying yields (65–94%) and the proposed structures are supported by analytical and spectroscopic data.

The structures of dithiosemicarbazone ligands **1–6** were confirmed by ^{1}H, ^{13}C, COSY and HSQC NMR spectroscopy. The ^{1}H NMR spectra of the products show a singlet in the range δ 8.3–8.5 ppm, assigned to the imine protons. A characteristic singlet is observed for the ethylene (**1–3**) and phenylene protons (**4–6**) at about δ 3.83 ppm and δ 7.55 ppm respectively, due to the symmetrical nature of the dithiosemicarbazone compounds. Generally, the phenylene-bridged thiosemicarbazone ligands (**4–6**) show similar trends in the NMR spectra to those of the ethylene-bridged ligands (**1–3**). $^{13}C\{^{1}H\}$ NMR spectral assignments were made with the aid of 2D Heteronuclear Single Quantum Coherence (HSQC) spectroscopy. Peaks assigned to the carbons of the aromatic groups are observed in the region of δ 115–156 ppm. A peak assigned to the imine carbon is observed around δ 140 ppm.

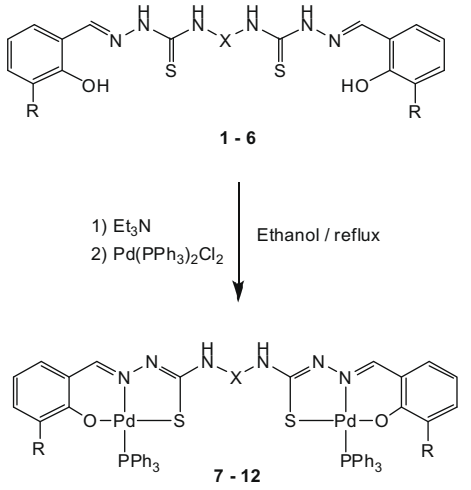
Further information on the integrity of the ligands was gleaned from infrared spectroscopic techniques. The IR spectra of the Schiff base dithiosemicarbazone ligands showed a strong absorption band for the imine functionality at around 1622–1598 cm^{-1}. The absorption band at 850–820 cm^{-1} in the free ligand may be assigned to the thioamide vibration $\nu_{(C=S)}$, indicating that the ligands exist in the thione form.

The ESI mass spectra for compounds **1–2**, **4–6** recorded in the negative mode generally showed a 100% relative intensity peak (base peak) due to the $[M-H]^{+}$ ion. For compound **3**, however, a base peak at m/z 527 is observed in the ESI spectrum, attributed to the presence of a sodium adduct, $[M+Na]^{+}$.

*3.2. Binuclear dithiosemicarbazone salicylaldiminato palladium(II) complexes (**7–12**)*

For polydentate ligands such as compounds **1–6**, various bonding modes are possible depending on the ligand to metal ratio. In an attempt to prepare binuclear palladium dithiosemicarbazones, the palladium(II) complexes (**7–12**) were selectively prepared by reacting the corresponding dithiosemicarbazone ligands (**1–6**) with $Pd(PPh_3)_2Cl_2$ in a 1:2 stoichiometric ratio (ligand:metal), giving rise to binuclear palladium complexes (Scheme 2). The synthesis of the complexes was performed using methodologies similar to those reported previously by Halder et al. [34].

The palladium complexes (**7–12)** are isolated as orange powders in high yields (75–95%). They are air-stable as solids and in solution. The ethylene-bridged palladium(II) complexes (**7–9**) are readily soluble in polar solvents such as DMSO, chlorinated solvents (CH_2Cl_2), and are sparingly soluble in alcoholic solvents. The phenylene-bridged palladium(II) complexes (**10, 11**), however, are found to be far less soluble than their ethylene-bridged counterparts. Surprisingly, complex **12** shows greater solubility than the analogous phenylene-bridged palladium complexes. The bimetallic complexes (**7–12**) have been characterized by elemental analyses, ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopies, and ESI-MS.



Scheme 2. General synthetic pathway to complexes **7–12**.

3.2.1. NMR spectroscopy

The ethylene- and phenylene-bridged palladium complexes display in the ^{1}H NMR spectra the expected singlet for the ethylene and phenylene protons at around δ 3.38 ppm and δ 7.47–7.71 ppm, respectively, due to the symmetrical nature of the compounds. Evidence for the formation of palladium complexes is seen by the notable shift of the signal for the imine proton, suggesting coordination of palladium to the imine nitrogen. Splitting of the imine signal into a doublet in the region at around δ 8.33 ppm is observed and is attributed to coupling of the imine proton to the nucleus of the phosphorus atom ($^{4}J_{P-H}$ = 13.98 Hz). The disappearance of the signal for the hydroxyl proton, together with the observed shift of the imine proton observed in the ^{1}H NMR spectrum, provides good evidence of coordination of palladium, resulting in a six-membered ring with N,O donor atoms. In addition to this, the disappearance of the signal assigned to the hydrazinic proton adjacent to the imine group, confirms the formation of a second imine bond upon coordination of palladium, suggesting that the sulfur atom coordinates in the thiolate form rather than the thione form, thus forming a five-membered chelate ring (N, S donor atoms). The phenylene-bridged complexes (**10, 11**) were difficult to characterize using NMR spectroscopic techniques due to their low solubility in most deuterated solvents, including DMSO-d_6. The ^{1}H NMR spectrum of compound **10**, specifically, was not well-resolved, but a trend similar to that of the ethylene-bridged complex **7** was discernible and assignments made on that basis.

All the expected peaks are observed in the $^{13}C\{^1H\}$ NMR spectra for compounds **7–12**. It was not possible to obtain ^{13}C NMR spectral data for the phenylene-bridged complexes (**10, 11**), even at elevated temperatures, due to the poor solubility of these complexes. A sharp singlet is observed in the $^{31}P\{^1H\}$ NMR spectra for each palladium-PPh_3 complex in the region around δ 25.6 ppm.

3.2.2. Infrared spectroscopy

Infrared spectroscopy is a useful diagnostic tool to confirm coordination of palladium. The IR spectra of the palladium complexes **7–12** show a band of medium to strong intensity within 1599–1589 cm^{-1}, attributed to the C=N–N=C fragment of the coordinated dithiosemicarbazone ligand. The shift of the imine absorption band (ν_{C-N}) in the free ligand (1600–1671 cm^{-1}) to lower wavenumbers in the metal complexes, is indicative of the coordination of palladium to the imine nitrogen. The IR spectra of the [Pd(L)(PPh_3)] (L = dithiosemicarbazone) complexes (**7–12**) generally show many vibrations of different intensities in the 1600–400 cm^{-1} region and are qualitatively very similar. Three diagnostic bands for the PPh_3 ligands near 533, 694 and 743 cm^{-1} are observed for all the complexes. The characteristic bands due to the $\nu_{(P-C)}$ vibration are also observed in the region 1098–1095 cm^{-1}, indicative of the presence of coordinated PPh_3 in the complexes [35–37]. Bands involving the C=S functional group are often difficult to assign. Coordination by sulfur induces changes in position and intensity of the bands and the proximity of the phenyl ring bands (triphenylphosphine ligand) makes it difficult to clearly assign the vibration modes. The disappearance of the C=S band observed in the free ligand, correlates with the loss of double-bond character upon deprotonation of the NH group. This supports the lengthening of the C–S bond which we observe in representative molecular structures. For thiosemicarbazones bonding in the thiolate form, the C=S band generally shifts to lower energy in the region 820–790 cm^{-1}. However, no definite assignment of each individual band to a specific vibration could be made.

3.2.3. Mass spectrometry

ESI-mass spectrometry further confirmed the integrity of the binuclear complexes. The ESI spectrum of compound **7** displays a base peak for the complex in its protonated form $[M+H]^+$ at *m/z* 1151. The spectrum of compound **8** reveals a peak at *m/z* 1210 for the $[M+H]^+$ ion of 20% intensity. A base peak at *m/z* 279, accounts for the fragment, $[M-C_8H_6N_2SO_2Pd(PPh_3)_2]^+$. The spectrum of compound **9** displays a peak of 50% intensity for the protonated complex at *m/z* 1263. In addition to this, a base peak at *m/z* 675, corresponds to the fragment, $[M-C_{11}H_{13}N_2SOPdPPh_3]^+$. The poor solubility of complexes **10** and **11** precluded an accurate determination by ESI-mass spectrometry.

*3.3. Solid-state structures of complexes **7** and **11***

To further confirm the mode of coordination of these palladium dithiosemicarbazone complexes, molecular structures of one member of each group (ethylene- and phenylene-bridged) have been determined using single-crystal X-ray crystallography. Single crystals of compounds **7** and **11** were obtained from concentrated dimethyl sulfoxide solutions. Figs. 2 and 3 show the molecular structures of **7** and **11**, respectively, while Table 2 gives selected bond lengths and angles.

The crystal structures show that the dithiosemicarbazone ligands coordinate to each palladium center *via* the phenolic oxygen, imine nitrogen and sulfur atoms in a square-planar geometry, as the spectroscopic data suggests. These two structures confirm that the fourth coordination site is occupied by a triphenylphosphine ligand. Both complexes show that the dithiosemicarbazone ligands (**1** and **5**) are coordinated to palladium in the expected tridentate (O–N–S) fashion on either side of the dithiosemicarbazone. The structures show the formation of six- and five-membered chelate rings upon coordination, thus imposing distortion around the square-planar metal centers. Indeed, the structures display O(1)–Pd(1)–N(1) and N(1)–Pd(1)–S(1) bite angles of 93.1(2)° and 84.55(17)° in **7** and of 92.15(12)° and 84.03(10)° in **11**. In both, a triphenylphosphine ligand is found trans to the nitrogen atom with Pd–P distances of 2.273(2) and 2.284(1) Å, respectively and with O(1)–Pd(1)–P(1) and S(1)–Pd(1)–P(1) bite angles of 88.53(14) and 93.91(7)° in **7** and of 91.28(8) and 92.44(4)° in **11**. These parameters are comparable to those in other trans P–N, S–O square-planar palladium complexes [16]. In addition to this, it can be seen that coordination of the dithiosemicarbazone sulfur atoms occur *via* the thiolate form, rather than the thione form (Figs. 2 and 3) due to the formation of a second imine bond

Table 1
Crystallographic data and structure refinement parameters for complexes **7**·2 DMSO and **11**·4 DMSO

	7·2 DMSO	**11**·4 DMSO
Chemical formula	$C_{58}H_{56}N_6O_4P_2Pd_2S_4$	$C_{68}H_{74}N_6O_8P_2Pd_2S_6$
Formula weight	1304.07	1570.43
Crystal system	monoclinic	monoclinic
Space group	*C* 2/*c*	*P* $2_1/n$
Crystal colour and shape	orange rod	yellow needle
Crystal size	0.12 × 0.07 × 0.06	0.24 × 0.11 × 0.11
a (Å)	30.436(3)	10.4372(3)
b (Å)	10.0175(9)	14.8288(4)
c (Å)	18.732(2)	22.7294(5)
α (°)	90	90
β (°)	100.57(1)	100.526(1)
γ (°)	90	90
V (Å^3)	5614.3(9)	3458.7(2)
Z	4	2
T (K)	173(2)	173(2)
D_c (g cm^{-3})	1.543	1.508
μ (mm^{-1})	0.899	0.806
Scan range (°)	4.28 < 2θ < 52.42	3.30 < 2θ < 50.84
Unique reflections	5553	6344
Reflections used [$I > 2\sigma(I)$]	1533	5063
R_{int}	0.1920	0.0685
Final *R* indices [$I > 2\sigma(I)$][a]	0.0336, wR_2 0.0488	0.0444, wR_2 0.1096
R indices (all data)	0.1786, wR_2 0.0734	0.0611, wR_2 0.1194
Goodness-of-fit (GOF)	0.478	1.051
Maximum, minimum $\Delta\rho$ (e Å^{-3})	0.524, −1.125	1.073, −0.906

[a] Structures were refined on F_o^2: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$

Table 2
Selected bond lengths (Å) and angles (°) for complexes **7** and **11**.

	7		**11**
Pd(1)–P(1)	2.273(2)	Pd(1)–P(1)	2.284(1)
Pd(1)–S(1)	2.238(2)	Pd(1)–S(1)	2.244(1)
Pd(1)–N(1)	2.028(5)	Pd(1)–N(1)	2.018(3)
Pd(1)–O(1)	2.019(4)	Pd(1)–O(1)	2.062(3)
N(1)–C(3)	1.284(8)	N(1)–C(8)	1.296(5)
N(1)–N(2)	1.403(7)	N(1)–N(2)	1.405(4)
N(2)–C(2)	1.311(7)	N(2)–C(9)	1.300(5)
N(3)–C(2)	1.354(7)	N(3)–C(9)	1.352(5)
N(3)–C(1)	1.455(8)	N(3)–C(10)	1.413(5)
S(1)–C(2)	1.781(6)	S(1)–C(9)	1.769(4)
P(1)–Pd(1)–S(1)	93.91(7)	P(1)–Pd(1)–S(1)	92.44(4)
P(1)–Pd(1)–O(1)	88.53(14)	P(1)–Pd(1)–O(1)	91.28(8)
P(1)–Pd(1)–N(1)	177.82(17)	P(1)–Pd(1)–N(1)	175.64(10)
S(1)–Pd(1)–N(1)	84.55(17)	S(1)–Pd(1)–N(1)	84.03(10)
S(1)–Pd(1)–O(1)	176.59(14)	S(1)–Pd(1)–O(1)	175.68(8)
N(1)–Pd(1)–O(1)	93.1(2)	N(1)–Pd(1)–O(1)	92.15(12)
C(1)–N(3)–C(2)	120.9(6)	C(8)–N(1)–N(2)	114.1(3)
C(3)–N(1)–N(2)	115.8(5)	N(1)–N(2)–C(9)	113.4(3)
N(1)–N(2)–C(2)	113.3(5)	N(2)–C(9)–N(3)	121.8(3)
N(2)–C(2)–N(3)	121.4(6)	C(9)–N(3)–C(10)	129.4(3)

Table 3
IC_{50} values (μM) of dithiosemicarbazone ligands (**1**–**3**, **5**, **6**) in various oesophageal cancer cells.

Compound	IC_{50} values in μM (95% CI)		
	WHCO1	WHCO5	WHCO6
1	8.62 (7.06–10.54)	5.63 (4.72–6.72)	10.36 (9.34–11.49)
2	2.53 (1.78–3.58)	5.88 (5.57–6.21)	3.56 (2.92–4.36)
3	6.38 (5.42–7.52)	3.26 (2.39–4.45)	11.70 (10.62–12.89)
5	2.67 (2.08–3.43)	1.64 (1.14–2.35)	12.37 (9.59–15.94)
6	1.28 (0.97–1.69)	1.24 (0.93–1.66)	30.97 (12.81–74.91)

between C(2) and N(2) in **7** and between C(9) and N(2) in **11**: Values of 1.311(7) and 1.300(5) Å being found for these bonds. This further supports that these C–N bonds tend towards double-bond character upon coordination. Comparison of these distances to the C(2)–N(3) and C(9)–N(3) bond lengths, shows that the latter are slightly longer (1.354(7) and 1.352(5) Å) and therefore tend towards single-bond character. The C–S bond lengths are also found to be consistent with coordination of sulfur in the thiolate form, with values of 1.781(6) and 1.769(4) Å, respectively. A previous study by Halder et al. [34] based on similar monomeric complexes, reported C–S values of approximately 1.75 Å. In simple systems it would be expected that a single C–S bond length would be approximately 1.82 Å and a double C═S bond would exhibit a length of 1.56 Å. The length obtained in this study, therefore appears to be close to the nature of a single C–S bond.

Further analysis of compound **11** reveals that the packing arrangement displays four solvent molecules (DMSO) of crystallisation per complex. This can be seen in the crystal lattice (Fig. 4). Closer inspection of the packing arrangement of compound **11** reveals hydrogen bonding of two oxygen atoms of two of the DMSO molecules to the secondary amine groups on either side of the complex. This bonding is depicted by N(3)–H(3)N···O(1X) on the right-hand side of the molecule. The same phenomenon is observed on the adjacent end of the complex. In **7**, in which two symmetry related molecules of DMSO crystallized per complex, the oxygen atom of the solvent interacts with two adjacent hydrogen atoms of the dithiosemicarbazone phenyl groups. The H···O distances are 2.686 and 2.691 Å and the C–H···O angles 122.9° and 124.4°, respectively.

The information obtained herein therefore allowed us to further confirm the integrity of these molecules, in addition to their spectral properties. We were therefore able to rationalize the modes of coordination upon complexation of the metals.

3.4. Preliminary biological evaluation

The dithiosemicarbazone ligands were evaluated for their *in vitro* anticancer activity against three oesophageal cancer cell lines (WHCO1, WHCO5, WHCO6). All the dithiosemicarbazone ligands, with the exception of ligand **4**, were cytotoxic in the cell lines evaluated, showing IC_{50} values in the range 1.2–35 μM. The fact that ligand **4** did not show any biological activity is ascribed to the poor solubility of the ligand. The IC_{50} values calculated from the dose-survival curves obtained after 48 h drug treatment from the MTT assay, are shown in Table 3. Unfortunately, the cytotoxicity of the palladium complexes could not be determined due to the poor solubility of these complexes. Detailed studies are currently underway to prepare more soluble palladium(II) salicylaldiminato dithiosemicarbazone complexes.

4. Conclusions

In summary, we have shown that palladium(II) complexes of salicylaldimine dithiosemicarbazones containing ethylene or phenylene spacers may be prepared by the reaction of the new salicylaldehyde-derived dithiosemicarbazone ligands (**1–6**) with $Pd(PPh_3)_2Cl_2$. This involved the preparation of ethylene- and phenylene-bridged dithiosemicarbazides, that were condensed with the appropriate salicylaldehydes, and thereafter metallated to give rise to the new binuclear palladium complexes (**7–12**). For each binuclear complex, it was found that in their solid-state structures, both palladium centers coordinate in a tridentate (O–N–S) manner. The expected square-planar geometry of the metal was also observed. Preliminary *in vitro* antitumour activity of the dithiosemicarbazone ligands showed a moderate to good cytotoxicity for the indicated cell lines. Biological activity of the palladium(II) complexes of the dithiosemicarbazones could not be determined due to poor solubility. Further investigations are underway to increase the solubility of the palladium complexes and to explore their anticancer activity.

Supplementary data

CCDC 723512 and 719351 contain the supplementary crystallographic data for **7**·2 DMSO and **11**·4 DMSO. These data can be obtained free of charge via http://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; or e-mail: deposit@ccdc.cam.ac.uk.

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