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LETTERS TO THE EDITOR

Complex Formation Between Sulfur-Containing Dinaphthylmethanes and Pd and Nd Salts

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Compounds having in the molecule several aromatic rings functionalized with sulfur-containing groups are widely used as ligands in the metal complex catalysis [1–3]. Their ligand ability depends on the nature, number and mutual orientation of electron-donor fragments attached to an aromatic scaffold.

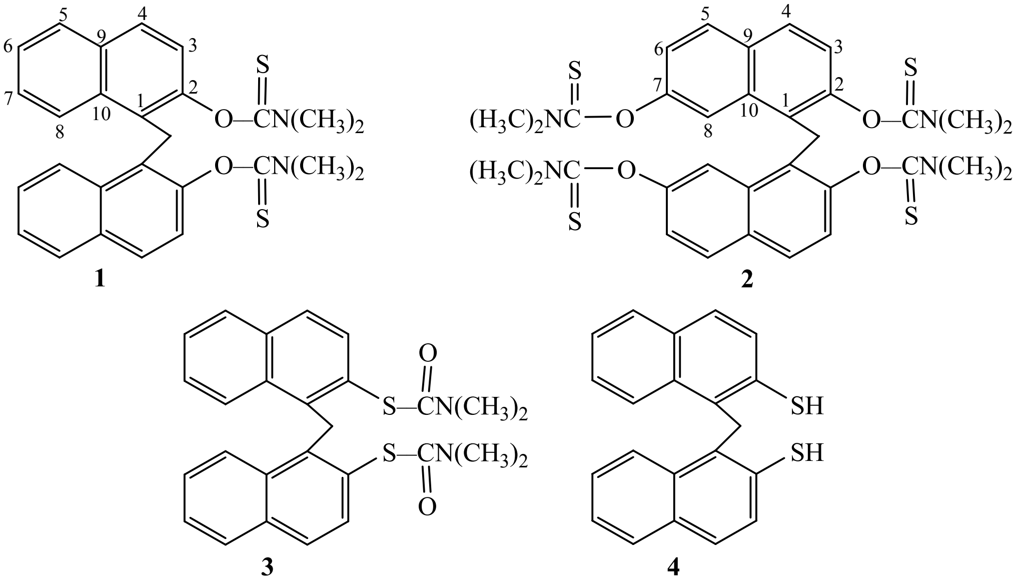
We have previously prepared new di- and tetradentate ligands **1**–**4** whose molecules contained thiocarbamoyl (**1**, **2**), carbamoylthiol (**3**), and mercapto (**4**) groups immobilized at dinaphthylmethane scaffold [4, 5] (Scheme 1).

This paper presents the first data on the interaction of sulfur-containing dinaphthylmethanes **1**–**4** with heavy metals salts like $PdCl_2$ and $Nd(NO_3)_3{\cdot}6H_2O$.

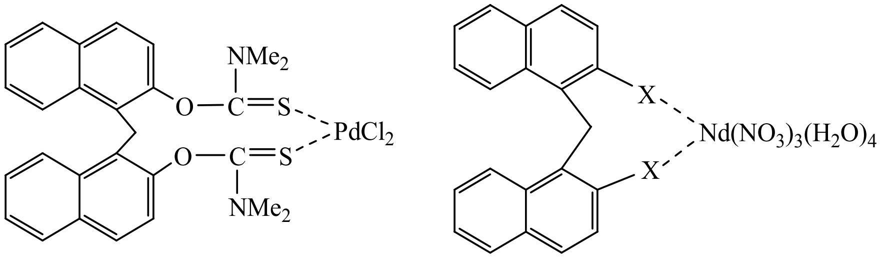
The complex formation was carried out in acetone at a ligand-to-metal ratio of 1 : 1.5 (**1**, **3**, **4**) and 1 : 3 (**2**). The reaction mixture was maintained at room temperature varying the processing time from 6 to 28 days depending on the ligand and the complexing agent.

Reactions of 2,2'-di(thiocarbamoyl)-2,2'-di(carbamoyltiol)- and 2,2'-dimercaptodinaphthylmethanes **1**,

Scheme 1.



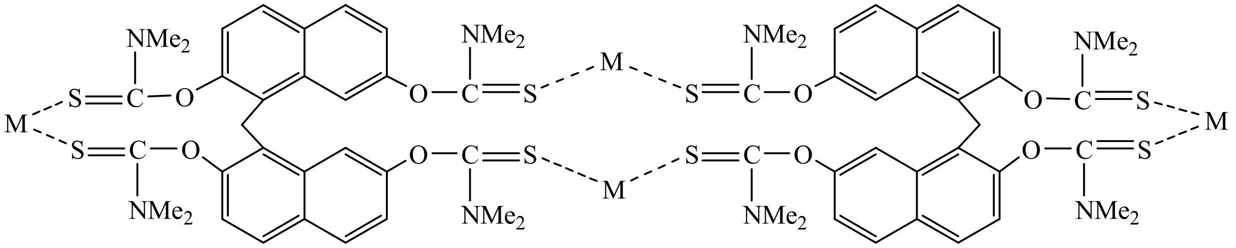
Scheme 2.



5 **6–8**

X = OC(S)NMe$_2$ (**6**), SC(O)NMe$_2$ (**7**), SH (**8**).

Scheme 3.



M = PdCl$_2$ (**9**), Nd(NO$_3$)$_3$(H$_2$O)$_4$ (**10**).

3, and **4**, in whose molecules the electron-donor group are closely-spaced, resulted in the formation of chelate complexes **5**–**8** with a ligand-to-metal ratio of 1 : 1 (Scheme 2).

2,2',7,7'-Tetra(thiocarbamoyl)dinaphthylmethane **2** containing closely (at positions 2,2') and widely (at positions 7,7') spaced thiocarbamoyl group formed dimeric complexes **9** and **10**, where dinaphthylmethane ligands were coordinated with the metal through 7,7'-thiocarbamate groups (Scheme 3).

Elemental analysis of the complexes **5**–**10** corresponded to their general formulas. The MALDI spectra of compounds **5**–**8** contained the peaks of molecular ions. In the IR spectra of the compounds obtained there were shifting and change in intensity of the absorption bands of C=S [1216, 1136 cm^{-1} (**5**), 1116 cm^{-1} (**6**), 1215, 1135 cm^{-1} (**9**), 1214, 1136 cm^{-1} (**10**)] and C=O groups [1662, 1601 cm^{-1} (**7**)] in comparison with the starting ligands [4, 5]. In addition, absorption bands in the region of 1453–1470 cm^{-1} characteristic of inorganic nitrate ions were observed in the spectra of complexes **6**–**8,** and **10**. The NMR spectral data of complexes **5**–**10** were similar to those of the free ligands **1**–**4** [4, 5].

Complex 5. To a solution of 2,2'-di(thiocarbamoyl)-dinaphthylmethane **1** (0.112 mmol) in acetone (12 mL) was added PdCl$_2$ (0.155 mmol). The reaction mixture was kept at 22–25°C for 25 days. After removing 8 mL of acetone to the residue was added 10 mL of hexane. The precipitate was filtered off, washed with hexane (5 mL) and dried at 20°C within 8 h (1 mmHg). Yield 20%, brown powder, mp 288–290°C. IR spectrum, ν, cm^{-1}: 1574, 1510, 1401, 1275, 1216, 1136, 1049, 989, 923, 854, 811, 747, 608, 529. ^{1}H NMR spectrum (DMSO-*d*$_6$), δ, ppm: 22.17 s (6H, NCH$_3$), 3.05 s (6H, NCH$_3$), 4.61 s (2H, CH$_2$), 7.05 d (2H, H^3, ^3J 8.7 Hz), 7.53 m (4H, H^7, H^6), 7.78 d (2H, H^4, ^3J 8.7 Hz), 7.94 d (2H, H^8, ^3J 7.8 Hz), 8.2 d (2H, H^5, ^3J 8.2 Hz). ^{13}C NMR spectrum (DMSO-*d*$_6$), δ$_C$, ppm: 24.75, 37.5, 42.92, 123.6, 124.41, 125.83, 126.67, 127.94, 128.63, 129.13, 132.31, 132.96, 150.03, 185.63. Mass spectrum, *m*/*z*: 651 [*M*]$^+$. Found, %: C 49.26; H 3.98; N 4.45. $C_{27}H_{26}Cl_2N_2O_2PdS_2$. Calculated, %: C 49.74; H 4.02; N 4.30.

Complex 8 was synthesized similarly from 0.094 mmol of 2,2'-dimercaptodinaphthylmethane **4** and 0.1 mmol of Nd(NO$_3$)$_3$·6H$_2$O; reaction time 6 days. Yield 50%, yellow powder, mp 126–130°C. IR spectrum, ν, cm^{-1}: 3206, 1628, 1471, 1263, 1022, 799, 732, 554, 536, 505. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.87 br.s (2H, SH), 5.76 s (2H, CH_2), 7.42 d (2H, H^3, ^3J 8.6 Hz), 7.51 d.d (2H, H^7, ^3J 7.3, 7.6 Hz), 7.62 d.d (2H, H^6, ^3J 7.3, 8.3 Hz), 7.69 d (2H, H^4, ^3J 8.6 Hz), 7.85 d (2H, H^8, ^3J 8.1 Hz), 8.41 d (2H, H^5, ^3J 8.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.17, 122.74, 125.28, 126.38, 126.62, 126.88, 128.60, 132.38, 133.24, 133.43, 135.19. Mass spectrum, *m*/*z*: 659 $[M]^+$. Found, %: C 38.03; H 2.87; N 5.87. $C_{21}H_{16}N_3O_9NdS_2$. Calculated, %: C 38.06; H 2.43; N 6.34.

Complex 9 was synthesized similarly from 0.013 mmol of 2,2'7,7'-tetra(thiocarbamoyl)dinaphthylmethane **2** and 0.389 mmol of $PdCl_2$; reaction time 8 days. Yield 26%, brown powder, mp 330–334°C. IR spectrum, ν, cm^{-1}: 2923, 2853, 1579, 1511, 1458, 1401, 1358, 1273, 1214, 1136, 1058, 841. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (6H, NCH_3), 3.12 s (6H, NCH_3), 3.37 s (6H, NCH_3), 3.45 s (6H, NCH_3), 4.46 br.s (2H, CH_2), 7.11 br.s (2H, H^3), 7.31 br.s (2H, H^6), 7.86 br.s (4H, H^4, H^5), 7.97 br.s (2H, H^8). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 24.96, 37.87, 39.05, 42.94, 43.38, 116.47, 122.23, 123.34, 127.21, 127.69, 129.44, 130.17, 133.88, 150.40, 152.48, 186.10, 187.60. Mass spectrum, *m*/*z*: 907 $[M^+ - 2Cl]$. Found, %: C 38.03; H 3.11; N 4.96. $C_{33}H_{36}Cl_4N_4O_4\cdot Pd_2S_4$. Calculated, %: C 38.27; H 3.50; N 5.41.

^{1}H and ^{13}C NMR spectra were recorded on a Jeol ECX-400 spectrometer operating at 400 and 100.5 MHz, respectively, internal reference TMS. Mass spectra (MALDI-TOF) were obtained on a Bruker Ultraflex TOF/TOF mass spectrometer (Bruker Daltonics GmbH) using 1,8,9-trihydroxyanthracene as a matrix. Elemental analysis was performed on a CHN analyzer Thermo Flash EA112. IR spectra were recorded on a Nicolet 380 Thermo instrument in reflection mode in the range of 4000–500 cm^{-1} using ZnSe glass.

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