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Syntheses, Crystal Structures, and Photoluminescent Properties of Pd$^{\mathrm{II}}$ Complexes Containing a Disulfanenitrile Ligand

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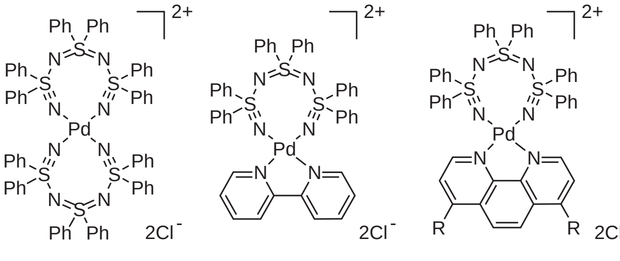
The bidendate ligand $\mathrm{Ph_2S(=N–(Ph_2)S\equiv N)_2}$ (ndsdsd) was used to prepare new Pd$^{\mathrm{II}}$ complexes. The homoleptic complex, $\mathrm{[Pd(ndsdsd)_2]Cl_2}$ (**1**) and the heteroleptic complexes, $\mathrm{[Pd(diimine)(ndsdsd)]Cl_2}$ (diimine: 2,2′-bipyridine (**2**), 1,10-phenanthroline (**3a**), and 4,7-diphenyl-1,10-phenanthroline (**3b**)) were prepared, and the molecular structures of **1**–**3** were characterized. The complexes **2** and **3** are not emissive at ambient temperature in the solid state, but the homoleptic complex **1** shows an unstructured emission bond ($\lambda_{\max} = 690$ nm).

Luminescent transition-metal complexes have received considerable attention in recent years, mostly because of their potential applications in organic light-emitting devices (OLEDs).[1] Among them, luminescent Pd$^{\mathrm{II}}$ complexes are exceedingly rare, and with very few exceptions,[2] most systems emit only at low temperatures.[3] Nevertheless, several photoactive Pd$^{\mathrm{II}}$ complexes have been recently designed to be potential candidates for luminescent materials.[4,5]

Recently, we have succeeded in synthesizing a new type of λ^6-sulfanenitrile with an SN triple bond at both ends, *N*,*N*-bis[(nitrilo(diphenyl)-λ^6-sulfanyl)](diphenyl)-λ^6-sulfanediimide $\mathrm{Ph_2S(=N–(Ph_2)S\equiv N)_2}$ (ndsdsd), and found that its terminal nitrogen atoms chelate to the Co$^{\mathrm{II}}$, Ni$^{\mathrm{II}}$, and Cu$^{\mathrm{II}}$ centers as a bidentate ligand.[6,7] With our recent interest in the exploration of the coordination chemistry of λ^6-sulfanenitrile ligands,[7,8] we become interested in extending the work to investigate luminescent complexes bearing our new ligands. We now describe the synthesis, structure, and luminescent properties of a new Pd$^{\mathrm{II}}$ complex containing the ndsdsd ligand, $\mathrm{[Pd(ndsdsd)_2]Cl_2}$ (**1**, Figure 1). For comparative purposes, we also prepared the heteroleptic complexes, $\mathrm{[Pd(diimine)(ndsdsd)]Cl_2}$ (**2** and **3**, Figure 1) (diimine: 2,2′-bipyridine (bpy) (**2**), 1,10-phenanthroline (phen) (**3a**), and 4,7-diphenyl-1,10-phenanthroline (bathophen) (**3b**)) and examined their structural and luminescent characteristics.



1

2

3a (R = H)
3b (R = Ph)

Figure 1. Complexes of **1**–**3**.

Homoleptic Pd$^{\mathrm{II}}$ complex, $\mathrm{[Pd(ndsdsd)_2]Cl_2}$ (**1**), was prepared by reacting $\mathrm{[PdCl_2(MeCN)_2]}$ with ndsdsd[6] in the ratio 1:2 in MeOH at ambient temperature. Heteroleptic Pd$^{\mathrm{II}}$ complexes, $\mathrm{[Pd(diimine)(ndsdsd)]Cl_2}$, were obtained from the treatment of the corresponding $\mathrm{[PdCl_2(diimine)]}$[9] with ndsdsd in the ratio 1:1 in MeOH under reflux conditions. These complexes, separated in good yields (82–94%) from MeOH/Et$_2$O, are air-stable solids (but hygroscopic); their elemental analyses and spectroscopic data (UV–vis, IR, and NMR) confirmed the expected stoichiometry.[10]

The crystal structures of complexes **1**–**3** were determined by X-ray crystallographic analysis.[10] ORTEP drawings of **1**, **2** (one of two independent molecules), and **3a** (as a representative) are depicted in Figures 2–4. Crystals of **1**–**3** contain MeOH, MeCN, and/or water molecules. The palladium atom in $\mathrm{[Pd(ndsdsd)_2]Cl_2}$ (**1**) and $\mathrm{[Pd(diimine)(ndsdsd)]Cl_2}$ (**2** and **3**) is surrounded by four nitrogen atoms originating from two-coordinated ndsdsd ligands or from corresponding diimine and ndsdsd ligand, respectively. The geometry around the palladium center in **1** adopts an essentially flat structure, while the heteroleptic complexes **2** and **3** exhibit distorted square-planar geometries (dihedral angle between N–Pd–N planes: **2**, 9.92°; **3a**, 2.94°; **3b**, 4.92°). The average $\mathrm{Pd–N_{ndsdsd}}$ bond length in **1** is 2.036(2) Å, and they are 2.007(3), 2.004(5), and 2.014 Å in **2**, **3a**, and **3b**, respectively. The $\mathrm{Pd–N_{diimine}}$ bond lengths in **2** (av 2.016 Å) and **3** (**a**, av 2.029(5) Å; **b**, av. 2.031(3) Å) are shorter than those in bischelated $\mathrm{[Pd(bpy)_2]^{2+}}$ (av 2.035 Å)[11] and $\mathrm{[Pd(phen)_2]^{2+}}$ (av 2.041 Å)[11b,11d,12] species in which steric interactions are observed between bpy and phen ligands, respectively. The dihedral angles between the pyridine planes

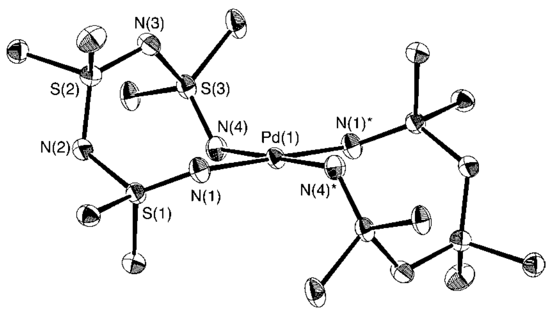


Figure 2. ORTEP drawing of **1** [50% probability thermal ellipsoids; H, C atoms (apart from the Cα atoms of the phenyl rings), chloride anions, and methanol molecules have been omitted for clarity]. Selected bond lengths (Å) and angles (°); Pd(1)–N(1) 2.034(2), Pd(1)–N(4) 2.037(2), S(1)–N(1) 1.481(2), S(1)–N(2) 1.669(2), S(2)–N(2) 1.554(2), S(2)–N(3) 1.559(2), S(3)–N(3) 1.647(2), S(3)–N(4) 1.476(2), N(1)–Pd(1)–N(4) 91.18(9), N(1)–Pd(1)–N(4)* 88.82(9).

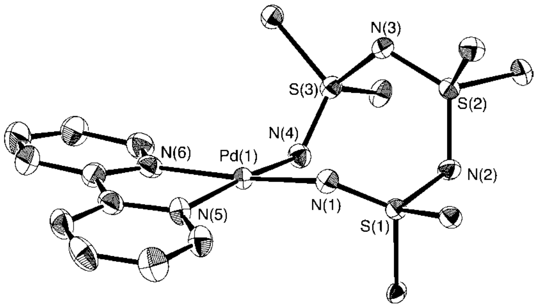


Figure 3. ORTEP drawing of **2** [50% probability thermal ellipsoids; H, C atoms (apart from the Cα atoms of the phenyl rings of ndsdsd ligand), chloride anions, acetonitrile, and water molecules have been omitted for clarity]. Selected bond lengths (Å) and angles (°); Pd(1)–N(1) 2.009(3), Pd(1)–N(4) 2.004(3), Pd(1)–N(5) 2.017(3), Pd(1)–N(6) 2.015(3), S(1)–N(1) 1.482(3), S(1)–N(2) 1.665(3), S(2)–N(2) 1.559(4), S(2)–N(3) 1.563(3), S(3)–N(3) 1.675(3), S(3)–N(4) 1.481(4), N(1)–Pd(1)–N(4) 92.60(13), N(1)–Pd(1)–N(5) 92.37(15), N(1)–Pd(1)–N(6) 169.71(14), N(4)–Pd(1)–N(5) 172.14(15), N(4)–Pd(1)–N(6) 95.16(14), N(5)–Pd(1)–N(6) 80.66(14).

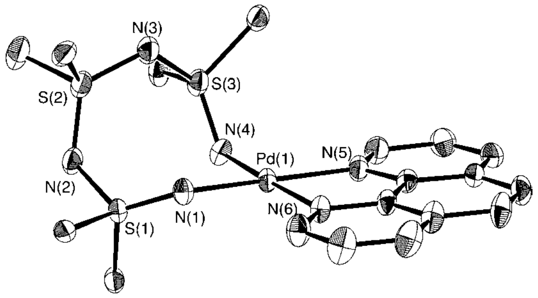


Figure 4. ORTEP drawing of **3a** [50% probability thermal ellipsoids; H, C atoms (apart from the Cα atoms of the phenyl rings of ndsdsd ligand), chloride anions, methanol, and water molecules have been omitted for clarity]. Selected bond lengths (Å) and angles (°); Pd(1)–N(1) 2.006(5), Pd(1)–N(4) 2.011(5), Pd(1)–N(5) 2.028(5), Pd(1)–N(6) 2.030(5), S(1)–N(1) 1.495(5), S(1)–N(2) 1.652(5), S(2)–N(2) 1.567(5), S(2)–N(3) 1.560(5), S(3)–N(3) 1.656(5), S(3)–N(4) 1.485(5), N(1)–Pd(1)–N(4) 94.10(19), N(1)–Pd(1)–N(5) 171.5(2), N(1)–Pd(1)–N(6) 90.35(19), N(4)–Pd(1)–N(5) 94.0(2), N(4)–Pd(1)–N(6) 175.46(19), N(5)–Pd(1)–N(6) 81.6(2).

in **2** and **3** are 9.58, 2.35, and 1.38°, respectively. The eight-membered Pd(NSN)$_2$S rings in **1**–**3** adopt a boat-twist conformation, and the coordinated and internal S–N bond lengths of ndsdsd ligands are very similar. The coordinated and internal S–N bond lengths in **1**–**3** (S–N$_{\text{coordinated}}$, 1.476–1.495 Å; S–N$_{\text{internal}}$, 1.554(2)–1.675(3) Å) are close to the corresponding S–N bond lengths of the free ligand (S–N$_{\text{terminal}}$, 1.457(2) Å; S–N$_{\text{internal}}$, 1.550(2)–1.656(2) Å) and to those exhibited by [M(ndsdsd)$_2$]Cl$_2$ bearing square-planar Ni$^{\text{II}}$ and Cu$^{\text{II}}$ centers (M = Ni and Cu; S–N$_{\text{coordinated}}$, 1.468(3)–1.4792(14) Å; S–N$_{\text{internal}}$, 1.551(3)–1.6676(14) Å).[6,7] These results also indicated that the bond order in the N≡S–N=S=N–S≡N backbone of ndsdsd was maintained.[7]

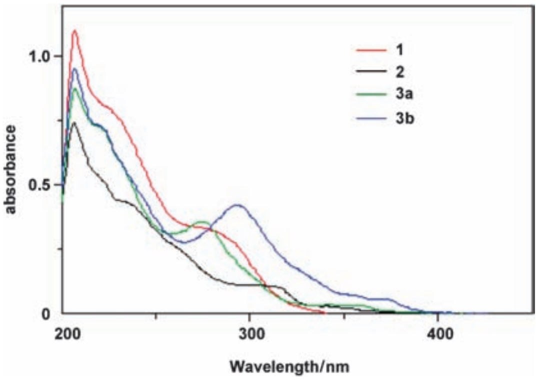


Figure 5. UV–vis absorption spectra of **1**–**3** (MeOH, 10^{-5} M) at rt.

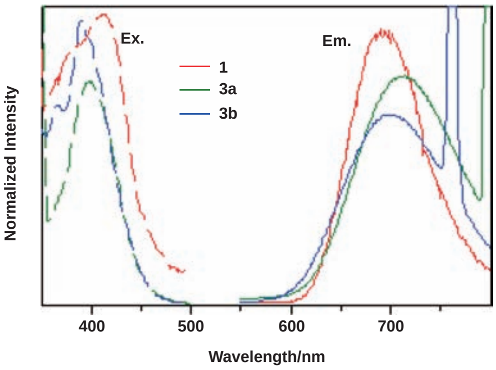


Figure 6. Emission (solid line) and excitation (broken line) spectra of **1**, **3a**, and **3b** in 1:4 MeOH/EtOH (10^{-2} M) at 77 K.

In the absorption spectra of complexes **1**–**3** in MeOH (Figure 5, <10^{-5} M),[13] according to the literature[14] and comparing the spectra for free ndsdsd ligand, we attribute the high-energy intense bands at ca. 207 nm with a series of shoulders at ca. 250 nm to spin-allowed ligand-centered (LC) transitions. At longer wavelengths absorbances in the range of 250–380 nm are tentatively ascribed to a mixture of spin-allowed metal-to-ligand charge-transfer (MLCT) and LC transitions. It is worthy of notice that the MLCT or/and ligand-to-ligand charge-transfer (LLCT) transitions are observed at the lowest-energy bands (380–450 nm) while increasing the concentration of the complexes **1**–**3**.

At ambient temperature, complexes **1**–**3** have no luminescence. Upon cooling the solutions (10^{-2} M) to a glassy state (77 K), red emission bands at $\lambda_{\max} = 690$–715 nm from **1** and **3** are observed, as shown in Figure 6, while the complex **2** is not emissive.[15] Interestingly, although the heteroleptic complexes **2** and **3** are not emissive at ambient temperature in the solid state, the homoleptic complex **1** shows an unstructured emission band ($\lambda_{\max} = 690$ nm, $\Phi_{\text{em}} = 0.01$) whose excitation spectra appear in the absorption spectra in the lowest-energy region (Figure 7). As mentioned above, room-temperature luminescence of Pd$^{\text{II}}$ complexes in solution is very rare.[2] The solid-state luminescence at room temperature has also been reported for SCS,[4a,4d] NCN,[4e] and NNC[4f,4j] pincer-type palladacycles, which is ascribed to an excimeric emission, but its luminescence efficiency is relatively low ($\Phi_{\text{em}} < 0.01$). Curiously, the emission maximum of **1** appears red-shifted by ca. 10 nm upon cooling the solid sample to 77 K, and its excitation spectrum ($\lambda_{\text{em}} = 700$ nm) is similar to

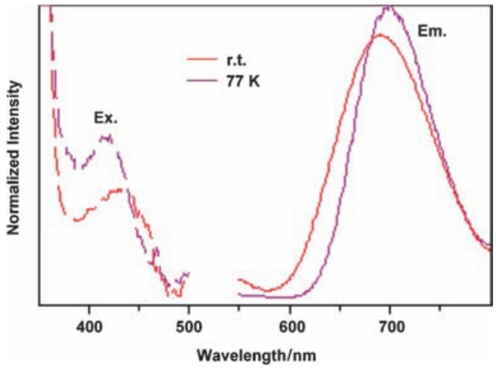


Figure 7. Emission (solid line) and excitation (broken line) spectra of **1** in solid state at rt and 77 K.

those seen in the solid state at ambient temperature and the glassy state at 77 K (Figures 6 and 7). Furthermore, the intensity of the emission band of **1** in the glassy state band decreases with the concentration, being essentially undetectable at 10^{-5} M. This behavior seems to indicate that these emissions are due to emissive ground-state aggregates generated by MMLC and/or π–π interactions.[16] However, the shortest Pd⋯Pd and C⋯C separation distances of 10.458 and 3.704 Å, respectively, in **1** are too large to allow the MMLC and π–π interactions. The red shift to lower energies observed at 77 K relative to room temperature can be attributed to a lattice compression of the solid sample at low temperature.[17]

These results demonstrate that the ndsdsd ligand with SN triple bond binds readily to Pd^{II} metal centers to form luminescent complexes, thus providing a new avenue of investigation for luminescent transition-metal compounds.

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13 Complexes **1**–**3** show low solubility in common organic solvents (hexane, Et_2O, THF, $CHCl_3$, CH_2Cl_2, CH_3CN, and acetone), except in MeOH, in which the electronic absorption spectra were measured (Figure 5, 10^{-5} M).

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17 The effect of the counter anions (Br^- (**1b**), I^- (**1c**), and AcO^- (**1d**)) on emission spectra has been investigated. In the solid state at ambient temperature, **1b** is slightly emissive, whereas the emission spectra in **1c** and **d** are essentially not detectable.