



Syntheses, crystal structures and properties of sterically congested heteroleptic complexes of group 10 metal ions with p-tolylsulfonyl dithiocarbamate and 1,2-bis (diphenylphosphino) ethane

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ABSTRACT

Three novel heteroleptic complexes of the type *cis*-[ML(dppe)] [M = Ni(II), Pd(II), Pt(II); L = p-tolylsulfonyl dithiocarbamate; dppe = 1,2-bis(diphenylphosphino)ethane] have been prepared and characterized. X-ray crystallography revealed the close proximity of one of the ortho phenyl protons of the dppe ligand to the metal in the Ni(II) complex showing existence of the less common C–H···Ni anagostic interactions observed for the first time in the dithio-phosphine mixed-ligand systems. The platinum complex showed a strong photoluminescence emission near visible region in CH₂Cl₂ solution.

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Group 10 metal complexes of dianionic dithiocarbamates are of current interest because of their resemblance to unianionic dithiocarbamates and related dianionic dithioligands such as isomaleonitrile dithiolate (i-mnt²⁻), maleonitriledithiolate (mnt²⁻) and 1,3-dithiole-2-thione-4,5-dithiolate (dmit²⁻) which have exhibited interesting physical and spectroscopic properties [1–9]. The importance of ternary complexes of platinum(II) with dithioligands containing polypyridyl and less often phosphine ligands as luminescent materials and photocatalysts has been known for some time [10–12]. The phosphine ligands because of their σ -donor and π -acceptor properties, larger steric demands, electronic and energetic factors have been useful components in the metal complexes which provide interesting chemical reactivity and physical properties, such as the conversion of light to chemical energy, and acting as chemical sensors and probes in biological imaging [10,13–16]. Therefore, the synthesis, structure and luminescent properties of the analogous complexes with a chelating phosphine–dithioligand combination are a worthy subject for active investigation.

Compared to the rich coordination chemistry of the dithiocarbamate ligand, studies of those with the dithiocarbamate ligands are extremely limited [17–19]. Complexes of the ligand aromaticsulfonyl dithiocarbamate and their possible applications have however been exploited recently [20–22]. This ligand has two important features (i)

it may exhibit greater electron delocalization through C–S, C–N and N–SO₂–Ar bonds and (ii) upon S, S coordination to a metal center it forms a more strained four-membered chelate ring in comparison with the five-membered ring formed with the mnt²⁻ complexes which in turn can influence intra and inter ligand S···S and M···S dimensions. These features make huge differences in the structures and properties of their complexes.

In this communication we report the syntheses, structures and photoluminescent properties of three novel sterically crowded heteroleptic complexes of the form *cis*-M(dppe)L [M = Ni(II), Pd(II), Pt(II); L = p-tolylsulfonyl dithiocarbamate (p-CH₃C₆H₄SO₂N = CS₂²⁻), dppe = 1,2-bis(diphenylphosphino)ethane].

The heteroleptic complexes M(dppe)L were obtained in similar conditions by the reaction of NiCl₂·6H₂O or K₂[MCl₄] [M = Pd(II), Pt(II)] with the ligand L, and dppe, (one equivalent of each) in CH₃OH/CH₂Cl₂ according to Scheme 1.

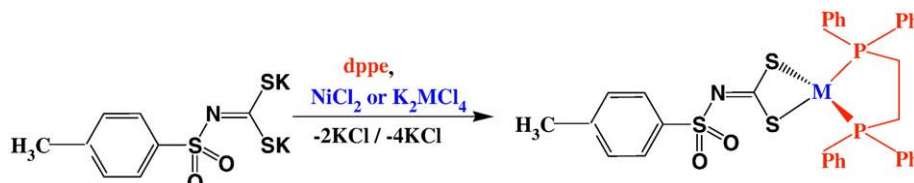
In the IR spectra all the three complexes display absorptions near 1435, 1216–1292, 1120 and 900 cm⁻¹ characteristic of ν (C=N), $\nu_{\text{asym}}(\text{SO}_2)$, $\nu_{\text{sym}}(\text{SO}_2)$ and $\nu_{\text{asym}}(\text{CS}_2)$ vibrations respectively indicating S, S coordination of the ligand dithiocarbamate with increasing importance of the canonical form I (Scheme S1 in the ESI) [20–22].

Apart from the characteristic ¹H and ¹³C NMR signals, the ³¹P spectrum of **1** displays a singlet at δ 58.1 ppm whereas **2** and **3** show two singlets at δ 52.6 and δ 4.4 ppm and δ 42.1 ppm flanked with platinum satellites with ¹J (¹⁹⁵Pt–³¹P) = 2983 Hz and δ 4.4 ppm respectively due to P, P coordination mode of the ligand dppe; the signal at δ 4.4 ppm shows more complex solution behavior of **2** and **3**.

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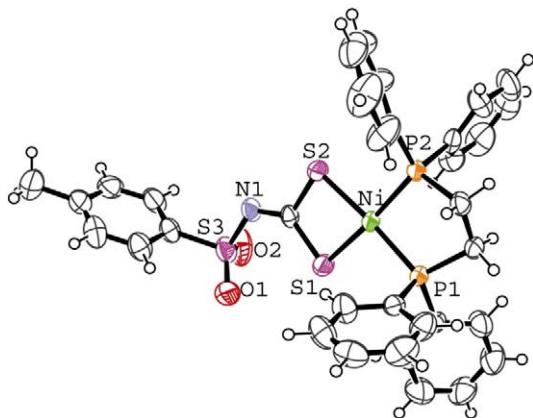
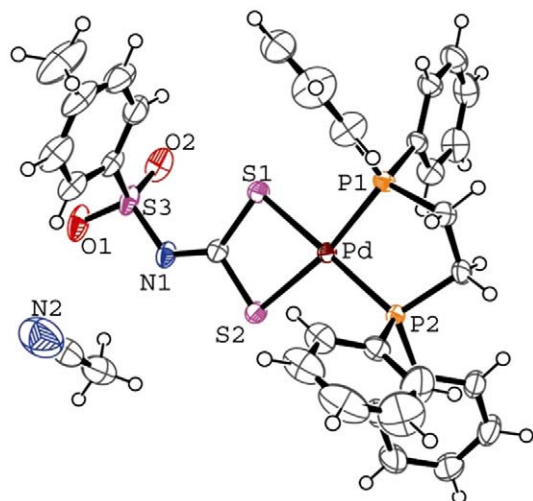
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Scheme 1. Synthesis of Complexes.

A perceptible lowfield shift observed for the palladium and platinum complexes indicates the greater strengths of Pt–P and Pd–P bonds compared to Ni–P bonds. The expected downfield shift in the phenyl proton of the dppe ligand involved in the C–H⋯Ni rare anagostic interactions as revealed by X-ray crystallography (vide infra) could not be detected because of the presence of the phenyl proton signals of the ligand *p*-tolylsulfonyl dithiocarbamate in the same region. Hence, the persistence of the anagostic interactions in solution cannot be unequivocally confirmed.

The immediate coordination geometry about the metal atom in Ni(dppe)L **1**, Pd(dppe)L **2** and Pt(dppe)L **3** are defined by the two phosphorus atoms of dppe and the two sulfur atoms S(1) and S(2) of L in which the metal atom lies at the center of a distorted square planar

Fig. 1. ORTEP diagram of **1** with 30% probability, together with the atom numbering.Fig. 2. ORTEP diagram of **2** with 30% probability, together with the atom numbering.

coordination geometry [23] (Figs. 1, 2 and S1 in the ESI). The bond lengths and angles are listed in Table 1. In **1**, the P(1)–Ni–S(1) angle at 98.57(7)° is more distorted from ideal than the P(2)–Ni–S(2) angle at 95.47(7)° but in **2** and **3** the reverse is the case with P(1)–M–S(1) angles of 94.98(2) and 95.24(6)° and P(2)–M–S(2) angles of 103.82(2) and 103.47(6)°. The P(1)–M–P(2) angles, part of a five-membered chelate ring are as expected much closer to the ideal 90° [87.01(6), 85.75(2), and 86.17(6)°] than the S(1)–M–S(2) angles part of a four-membered chelate ring [79.19(6), 75.42(2), and 75.11(6)°] in the three complexes **1**, **2** and **3** respectively. The root mean square (r.m.s.) deviations of M, S(1), S(2), P(1) and P(2) from the least square planes are 0.0656, 0.0424, and 0.046 Å in **1**, **2** and **3** respectively, thus showing very little deviation from planarity. The M–S(1) and M–S(2) distances 2.1836(15) and 2.2040(16) Å differ significantly in **1**, but are more similar in **2** and **3** at 2.3229(5); 2.3379(6) Å and 2.3395(18); 2.3454(18) Å respectively. On the contrary, no significant differences are observed in the M–P(1) and M–P(2) distances of 2.1684(16); 2.1728(15) Å in **1**. M–P distances in **2** at 2.2567(5); 2.2803(5) Å and **3** at 2.2433(17); 2.2585(18) Å also show barely significant differences. Another feature showing the difference between **1** on one hand and **2** and **3** on the other is the trans angles. In **1**, the P(2)–Ni–S(1) and P(1)–Ni–S(2) angles are similar at 173.95(7) and 174.43(8)° while in **2** and **3** the former angle at 179.22(2) and 178.59(2)° is far larger than the latter at 169.42(2) and 169.30(2)°. As will be discussed later the difference can be related to the Ni–H interactions. In all three structures the S(1)–C(1)–N(1)–S(3) torsion angles are close to zero (–1.6(8), 4.3(4), and 3.0(10)°) showing significant planarity. The average C–S and C–N bond lengths in **1**, **2** and **3** respectively are well in the range of carbon–sulfur single bond and carbon–nitrogen double bond length in [20–22] accordance with the importance of the resonance form I in the complexes (Scheme 1 in the ESI). A comparison of the structural data shows the trend Ni < Pd < Pt for M–S and Ni < Pd < Pt for M–P bond distances. The bite angles S(1)–M–S(2) and P(1)–M–P(2) are observed in the order Ni > Pd > Pt. As expected the

Table 1
Selected bond lengths [Å] and angles [°] in complexes **1**, **2** and **3**.

	1	2	3
<i>Bond lengths/Å</i>			
M–S(1)	2.1837(16)	2.3229(6)	2.3375(18)
M–S(2)	2.2043(16)	2.3377(6)	2.3465(18)
M–P(1)	2.1680(16)	2.2568(6)	2.2437(17)
M–P(2)	2.1728(16)	2.2803(6)	2.2564(18)
C(1)–S(1)	1.734(5)	1.731(2)	1.769(6)
C(1)–S(2)	1.735(6)	1.747(2)	1.740(8)
C(1)–N(1)	1.305(6)	1.292(3)	1.262(9)
<i>Bond angles/°</i>			
S(1)–M–S(2)	79.19(6)	75.42(2)	75.11(6)
P(1)–M–P(2)	87.01(6)	85.75(2)	86.17(6)
P(2)–M–S(2)	95.47(7)	103.82(2)	103.47(6)
P(1)–M–S(1)	98.57(7)	94.98(2)	95.24(6)
P(2)–M–S(1)	173.95(7)	179.22(2)	178.59(6)
P(1)–M–S(2)	174.43(8)	169.42(2)	169.30(6)

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