Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 623

www.rsc.org/dalton

PAPER

Unprecedented coordination of dithiocarbimate in multinuclear and heteroleptic complexes†

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Received 1st June 2010, Accepted 14th October 2010
DOI: 10.1039/c0dt00582g

An uncommon coordination protocol induced by the *p*-tolylsulfonyl dithiocarbimate ligand (L) [L = p-$CH_3C_6H_4SO_2N{=}CS_2^{2-}$] in conjunction with PPh_3 allowed the formation of novel homodimetallic, $Cu_2(PPh_3)_4L$ (**1**), trinuclear heterometallic $Cu_2Ni(L)_2(PPh_3)_4$ (**2**) and heteroleptic complexes of general formula *cis*-[$M(PPh_3)_2L$] [M = Pd(II) (**3**), Pt(II) (**4**)]. The complexes have been characterized by microanalysis, mass spectrometry, IR, ^1H, ^{13}C and ^{31}P NMR and electronic absorption spectra and single-crystal X-ray crystallography. **2** uniquely consists of square planar, trigonal planar and tetrahedral coordination spheres within the same molecule. In both heteroleptic complexes **3** and **4** the orientation of aromatic protons of PPh_3 ligand towards the Pd(II) and Pt(II) center reveals C–H···Pd and C–H···Pt rare intramolecular anagostic or preagostic interactions. These complexes exhibit photoluminescent properties in solution at room temperature arising mainly from intraligand charge transfer (ILCT) transitions. The assignment of electronic absorption bands has been corroborated by time dependent density functional theory (TD-DFT) calculations. Complexes **1** and **2** with σ_{rt} values ~ 10^{-6} S cm^{-1} show semi-conductor properties in the temperature range 313–403 K whereas **3** and **4** exhibit insulating behaviour.

Introduction

The coordination chemistry of transition metal complexes with dithioligands represents a very active area of research because of their exciting conducting, magnetic, photophysical, properties and industrial applications.[1] The majority of studies on the homo- and heterometallic complexes of 1,1- and 1,2-dithioligands including dithiocarbimates showed that coordination to metals usually occurred solely through thiolate sulfur atoms with the nitrogen rarely bonded, leaving the remaining donor atoms uncoordinated.[1,2] The construction of mono- and multi-metallic Cu(I), Ni(II), Pd(II) and Pt(II) complexes that support metal fragments in distinct coordination environments achieved by multifunctional ligands and sterically demanding phosphines as ancillary ligands have received much attention owing to their significant luminescence properties with possible applications in solar energy conversion, electrochemical responses, luminescent based sensors, biological imaging probes and catalytic activities.[1–3] The dianionic dithiocarbimates are virtually akin to dithiocarbamates, except for a variation in anionic charge. To the best of our knowledge the multi-metallic complexes of the aromatic sulfonyldithiocarbimate ligands are still unexplored. Furthermore, this ligand has three important features (i) it shows greater electron delocalization beyond the MS_2 bonds through the C–S, C═N bonds and aromatic SO_2 group (ii) it possesses multiple coordination sites such as (S,S), N and O atoms and (iii) it is similar in some respects to both monoanionic dithiocarbamate and dianionic 1,1-dithioligands such as i-mnt^{2-} (i-mnt^{2-} = isomaleonitriledithiolate) which places it as intermediate between these two types of ligand, which make huge differences in the structure, binding and properties of its complexes.

Surprisingly, despite their synthetic versatility and practical utility as compared to the dithiocarbamates and related dithio ligand complexes, complexes with dithiocarbimates have gained less attention.[2] Recently, the coordination chemistry and possible applications of transition metal aromatic sulfonyl dithiocarbimate complexes have been exploited.[4,5] Inspired by these observations and considering the steric and energetic restrictions caused by the ligand triphenylphosphine and aromatic sulfonyldithiocarbimate, we have studied the unusual coordinative abilities of the dithiocarbimates in the organization of new multi-metallic and heteroleptic complexes of Cu(I), Ni(II), Pd(II) and Pt(II) and their photoluminescent and conducting properties and report the results here.

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† Electronic supplementary information (ESI) available: Molecular packing and weak interaction diagrams. CCDC reference numbers 745652 (**1**), 745653(**2**), 745654 (**3**) and 745655 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00582g

‡ For crystallographic correspondence.

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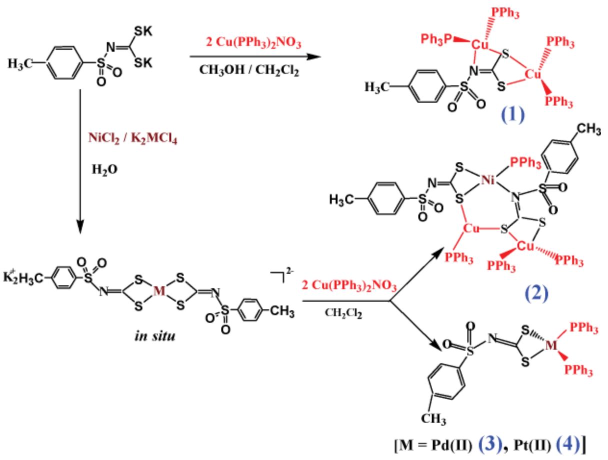
Results and discussion

General aspects

The homodimetallic complex $Cu_2(PPh_3)_4L$ (**1**) was prepared by treating a methanolic solution of the ligand K_2L and dichloromethane solution of $Cu(PPh_3)_2NO_3$ in 1 : 2 molar ratio. Attempts to synthesise the trinuclear heterometallic complexes $Cu_2M(L)_2(PPh_3)_4$ [M = Ni(II), Pd(II), Pt(II)] by treating two equivalent of CH_2Cl_2 solution of $Cu(PPh_3)_2NO_3$ with an *in situ* generated aqueous solution of $K_2[M(L)_2]$ [M = Ni(II), Pd(II), Pt(II)] were only successful for M = Ni(II) **2**. With M = Pd(II) **3** and Pt(II) **4** are formed due to PPh_3 ligand transfer from $Cu(PPh_3)_2NO_3$ to palladium(II) or platinum(II) meeting the steric and geometric requirements of the system. Alternatively, **3** and **4** could also be prepared by the reaction of an aqueous-methanolic solution of K_2MCl_4 with K_2L and the ligand PPh_3 in appropriate molar ratio (Scheme 1).

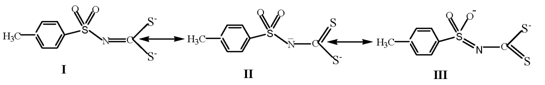


Scheme 1 Synthesis of the complexes.

All four complexes are air stable solids and melt with decomposition in the temperature range of 114–195 °C. They have been characterized by mass spectrometry, IR, UV-vis, ^1H, ^{13}C and ^{31}P NMR and single crystal X-ray analyses and their solid phase conducting and solution photoluminescence properties studied. The electronic absorption bands have been assigned by employing time dependent density functional theory.

Spectroscopy

In the ESI-MS spectra, the intense peaks at m/z 875.8 and 965 for **3** and **4** are consistent with the expected molecular ion peaks at 876.33 and 964.99 respectively. The IR spectra of compounds **1–4** show diagnostic absorptions [4,5] near 1384–1473, 1300, 1145 and 990 cm^{-1} arising from $\upsilon(C{=}N)$, $\upsilon_{asym}(SO_2)$, $\upsilon_{sym}(SO_2)$, and $\upsilon_{asym}(CS_2)$ modes, respectively; the appearance of $\upsilon(C{=}N)$ at higher stretching frequency compared to the free ligand L is consistent with the domination of the resonance form **I** (Scheme 2).



Scheme 2 Resonance structures of the ligand *p*-tolylsulfonyl dithiocarbimate.

The absorptions below 400 cm^{-1} are assigned to υ(M–S) vibrations in the complexes.

All the complexes display ^1H and ^{13}C NMR signals characteristic of the functional groups of the coordinated ligands and integrate well to the corresponding hydrogens. The anticipated downfield shift in the ^1H NMR spectra for the *ortho*-proton of the phenyl groups of the ligand PPh_3 involved in the intramolecular C–H···M [Pd(II), Pt(II)] anagostic or preagostic interactions as revealed by X- ray crystallography (*vide supra*) could not be confirmed unambiguously as being retained in solution because of the overlapping of observed aromatic signals of the *p*-tolylsulfonyl dithiocarbimate ligand in the same region. However, upon cooling the samples down to –60 °C in $CDCl_3$, the resonances in the range δ 7.22–7.36 ppm begin to merge and eventually two to three broad peaks are observed which may in part, be attributed to the presence of weak anagostic interactions in solution. A noticeable shift of δ 10–13 ppm for the NCS_2 carbon in the ^{13}C NMR spectra of all complexes compared to the uncoordinated dithiocarbimate ligand indicates M–S bonding in the complexes. The ^{31}P NMR spectrum of **1** in $CDCl_3$ displays a single resonance at δ –1.29 ppm due to the fluxional behaviour of the ligand PPh_3 which causes signal overlap at room temperature. On cooling the sample down to 0 °C it shows two distinct signals at δ –1.13 and 5.28 ppm associated with the Cu(1) and Cu(2) centers, respectively. On further cooling up to –60 °C the signal at δ –1.13 ppm starts broadening and splits into two broad peaks at δ –0.04 and –0.88 ppm corresponding to two PPh_3 ligands because of the change in the environment *i.e.* N,S coordination of dithiocarbimate ligand about the Cu(1) center. A single strong peak observed at δ 9 ppm is due to identical S,S coordination of the dithiocarbimate about the Cu(2) center. The compound, **2** displays three distinct ^{31}P NMR signals at δ 21.57, 4.61 and –0.11 ppm due to the square planar nickel(II), tetrahedral copper(I) and trigonal planar copper(I) centers, respectively, thus showing that the structure is retained in solution. In the $^{31}P\ \{^1H\}$ NMR spectra of complex **3** a single resonance at δ 30.94 ppm and in **4** a well defined sharp singlet at δ18.97 ppm flanked by ^{195}Pt satellites [$J(^{195}Pt–^{31}P)$ = 3112.10 Hz] are in the range of analogous dithiocomplexes.[2g] An appreciable low-field shift observed for the palladium complex suggests greater strength of the Pt–P bond compared to Pd–P bonds.

Crystal structure

Single crystals of complexes **1** and **2** were obtained by slow diffusion of CH_3OH in CH_2Cl_2 and ether in CH_2Cl_2 solution, respectively, those of **3** and **4** were grown by slow evaporation of $CH_2Cl_2 : CH_3CN$ solvent. The crystallographic details are provided in Table 1. The structures of **1**, **2**, **3** and **4** are presented in Fig. 1–4 and selected bond distances and angles are listed in Tables 2, 3 and 4.

The structure of **1** contains the $Cu_2(PPh_3)_4L$ complex together with five solvent methanol molecules (Fig. 1). $Cu_2(PPh_3)_4L$ is a dinuclear complex in which ligand L, *p*-tolylsulfonyl dithiocarbimate, acts as a bridging ligand between two $Cu(PPh_3)_2$ units. Both copper atoms have distorted tetrahedral environments, Cu(2) is bonded to two triphenylphosphine ligands and both sulfur atoms of the ligand, (p-$CH_3C_6H_4SO_2N{=}CS_2$) in a chelating manner. The nitrogen atom N(1) of the ligand and one of the chelating sulfur atoms, S(2) is linked to the second metal Cu(1) the latter atom

Table 1 Crystallographic data and structure refinements for complexes

Compound	**1**·5CH$_3$OH	**2**·CH$_2$Cl$_2$	**3**	**4**
Empirical formula	$C_{85}H_{87}Cu_2NO_7P_4S_3$	$C_{91}H_{80}Cl_6Cu_2N_2NiO_4P_4S_6$	$PdC_{44}H_{37}NO_2P_2S_3$	$PtC_{44}H_{37}NO_2P_2S_3$
Formula weight	1581.80	1980.30	876.27	964.96
T/K	293(2)	100(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$Pbca$	$Pbca$
Crystal size/mm	0.23 × 0.22 × 0.18	0.18 × 0.12 × 0.08	0.25 × 0.25 × 0.12	0.40 × 0.15 × 0.10
a/Å	19.785(2)	13.144(5)	16.3447(2)	16.3309(10)
b/Å	16.651(2)	13.801(5)	18.3512(2)	18.3563(2)
c/Å	24.213(3)	25.209(5)	25.5480(3)	25.5226(2)
α/°	90	85.998(5)	90	90
β/°	94.18(2)	83.325(5)	90	90
γ/°	90	81.990(5)	90	90
V/Å^3, Z	7955.6(16), 4	4491(3), 2	7662.99(15), 8	7651.09(11), 8
D_{calcd}/Mg M^{-3}	1.321	1.464	1.519	1.675
Reflection collected	51 499	29 778	114 928	117 355
Independent reflections [R_{int}]	19 704[0.0715]	21 371[0.0441]	8754 [0.0919]	8720 [0.0854]
F(000)	1724	2032	3584	3840
μ/mm^{-1}	0.748	1.118	0.771	3.955
GOF on F^2	1.072	1.092	1.020	1.031
Final indices [$I > 2\sigma(I)$]	$R_1 = 0.0709$, w$R_2 = 0.1691$	$R_1 = 0.0883$, w$R_2 = 0.2294$	$R_1 = 0.0399$, w$R_2 = 0.0952$	$R_1 = 0.0289$, w$R_2 = 0.0601$
R indices (all data)	$R_1 = 0.1319$, w$R_2 = 0.2209$	$R_1 = 0.1531$, w$R_2 = 0.3193$	$R_1 = 0.0685$, w$R_2 = 0.1095$	$R_1 = 0.0521$, w$R_2 = 0.0679$
Largest diffraction peak and hole/e Å^{-3}	1.344 and −0.908	2.343 and −1.394	0.898 and −0.639	0.957 and −1.268

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Bond lengths/Å			
Cu(1)–N(1)	2.154(4)	Cu(2)–P(3)	2.244(12)
Cu(1)–S(2)	2.447(12)	Cu(2)–P(4)	2.241(12)
Cu(1)–P(1)	2.239(13)	C(8)–N(1)	1.346(5)
Cu(1)–P(2)	2.239(13)	C(8)–S(1)	1.703(4)
Cu(2)–S(1)	2.389(12)	C(8)–S(2)	1.718(5)
Cu(2)–S(2)	2.442(12)		
Bond angles/°			
P(1)–Cu(1)–N(1)	118.50(11)	S(1)–Cu(2)–S(2)	74.74(4)
P(2)–Cu(1)–N(1)	111.48(11)	P(1)–Cu(1)–P(2)	123.36(5)
P(1)–Cu(1)–S(2)	110.63(4)	P(3)–Cu(2)–P(4)	121.30(5)
P(2)–Cu(1)–S(2)	111.92(4)	S(3)–N(1)–Cu(1)	136.2(2)
P(3)–Cu(2)–S(1)	111.33(5)	S(1)–C(8)–S(2)	118.0(3)
P(3)–Cu(2)–S(2)	113.01(4)	O(1)–S(3)–O(2)	116.8(2)
P(4)–Cu(2)–S(2)	108.06(4)	O(1)–S(3)–N(1)	104.8(2)
P(4)–Cu(2)–S(1)	118.79(4)	O(2)–S(3)–N(1)	111.8(2)
N(1)–Cu(1)–S(2)	67.27(10)		

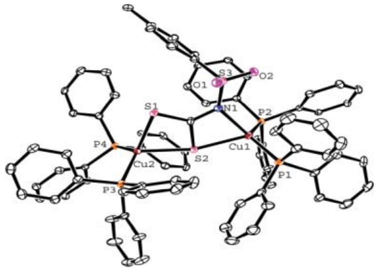


Fig. 1 ORTEP diagram of **1** with thermal ellipsoids set to 30% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

thus bridging Cu(1) and Cu(2). Two triphenylphosphine ligands are also attached to Cu(1) to complete the tetrahedral coordination sphere. The Cu–P distances are in the range 2.239(13)–2.244(12) Å. The bond lengths to the bridging sulfur atom S(2) are longer at 2.447(12) Å than that to the chelating S(1) at 2.389(12) Å. The Cu(1)–N(1) bond length at 2.154(4) Å is as expected for a Cu(1)–N bond.

The structure of **2** contains the complex $Cu_2NiL_2(PPh_3)_4$ together with 3 molecules of dichloromethane (Fig. 2). $Cu_2NiL_2(PPh_3)_4$ contains one Ni(II) and two Cu(I) centers in different coordination environments *i.e.* square planar for Ni(II), tetrahedral for Cu(1), and the rare three-coordinate trigonal planar for Cu(2). Here, one of the dithiocarbimates chelates Cu(1) through S(1), S(2) and additionally bridges Ni(1) *via* its free nitrogen donor N(2) and Cu(2) *via* the coordinated sulfur S(1) while the other dithiocarbimate chelates Ni(1) *via* S(3), S(4) and one of its chelated sulfur atoms, S(3) bridges Cu(2) overall constructing a strained six-membered ring composed of nickel, copper, carbon, nitrogen and two sulfur atoms. Thus, this unusual heterometallic complex has one dithiocarbimate ligand acting as

Table 3 Selected bond lengths (Å) and angles (°) in **2**

Bond lengths/Å			
Ni(1)–N(2)	1.959(5)	Cu(2)–S(3)	2.260(2)
Ni(1)–P(3)	2.213(2)	Cu(2)–P(4)	2.204(2)
Ni(1)–S(4)	2.174(2)	C(44)–N(2)	1.356(9)
Ni(1)–S(3)	2.234(2)	C(63)–N(1)	1.275(9)
Cu(1)–P(1)	2.256(2)	C(44)–S(1)	1.757(7)
Cu(1)–P(2)	2.259(2)	C(44)–S(2)	1.691(7)
Cu(1)–S(1)	2.430(19)	C(63)–S(3)	1.765(7)
Cu(1)–S(2)	2.396(2)	C(63)–S(4)	1.748(8)
Cu(2)–S(1)	2.219(2)		
Bond angles/°			
S(4)–Ni(1)–S(3)	78.34(8)	P(1)–Cu(1)–S(1)	115.29(7)
S(4) –Ni(1)–P(3)	89.17(8)	P(2)–Cu(1)–S(1)	110.44(7)
P(3)–Ni(1)–N(2)	97.6(2)	P(4)–Cu(2)–S(1)	119.05(8)
S(3) –Ni(1)–N(2)	95.2(2)	P(4)–Cu(2)–S(3)	130.65(8)
S(4)–Ni(1)–P(3)	89.17(8)	S(1)–Cu(2)–S(3)	110.08(7)
S(3) –Ni(1)–P(3)	166.41(8)	O(1)–S(5)–O(2)	119.5(4)
S(4)–Ni(1)–N(2)	172.5(2)	O(1)–S(5)–N(1)	113.1(3)
S(2)–Cu(1)–S(1)	73.53(6)	O(2)–S(5)–N(1)	104.1(3)
P(1)–Cu(1)–P(2)	124.51(7)	O(3)–S(6)–O(4)	119.3(3)
P(2)–Cu(1)–S(2)	109.31(7)	O(3)–S(6)–N(2)	111.5(3)
P(1)–Cu(1)–S(2)	112.36(8)	O(4)–S(6)–N(2)	101.6(3)

Table 4 Selected bond lengths (Å) and angles (°) in complex **3** and **4**

Complex **3**			
Bond lengths/Å		**Bond angles/°**	
Pd–S(1)	2.306(8)	S(1)–Pd–S(2)	75.20(3)
Pd–S(2)	2.347(8)	P(1)–Pd–P(2)	97.88(3)
Pd–P(1)	2.309(8)	S(1)–Pd–P(1)	92.30(3)
Pd–P(2)	2.326(9)	S(1)–Pd–P(2)	168.85(3)
C(1)–N	1.298(4)	S(2)–Pd–P(1)	166.00(3)
C(1)–S(1)	1.746(3)	S(2)–Pd–P(2)	95.13(3)
C(1)–S(2)	1.747(3)	O(1)–S(3)–O(2)	117.89(15)
S(3)–O(1)	1.437(2)	O(1)–S(3)–N	104.62(14)
S(3)–O(2)	1.439(2)	O(2)–S(3)–N	111.20(14)
Complex **4**			
Bond lengths/Å		**Bond angles/°**	
Pt–S(1)	2.321(9)	S(1)–Pt–S(2)	74.85(3)
Pt–S(2)	2.354(9)	P(1)–Pt–P(2)	97.82(3)
Pt–P(1)	2.283(9)	S(1)–Pt–P(1)	92.90(3)
Pt–P(2)	2.295(9)	S(1)–Pt–P(2)	168.47(3)
C(1)–N	1.301(4)	S(2)–Pt–P(1)	166.35(3)
C(1)–S(1)	1.747(4)	S(2)–Pt–P(2)	94.89(3)
C(1)–S(2)	1.751(4)	O(1)–S(3)–O(2)	117.98(17)
S(3)–O(1)	1.436(3)	O(1)–S(3)–N	104.69(16)
S(3)–O(2)	1.439(3)	O(2)–S(3)–N	111.03(16)

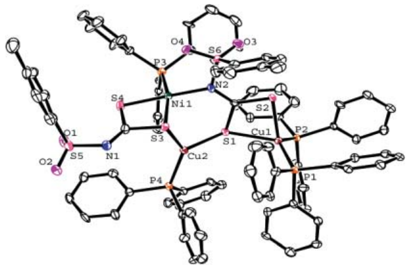


Fig. 2 ORTEP diagram of **2** with thermal ellipsoids set to 30% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

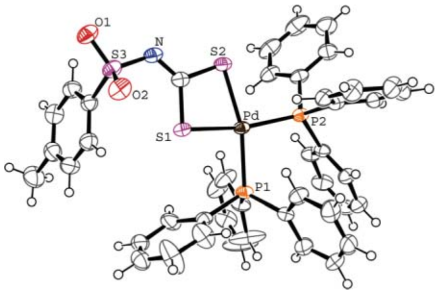


Fig. 3 ORTEP diagram of **3** with 30% probability, together with the atom numbering scheme. Only one component of the disordered phenyl group attached to P1 is also shown for clarity.

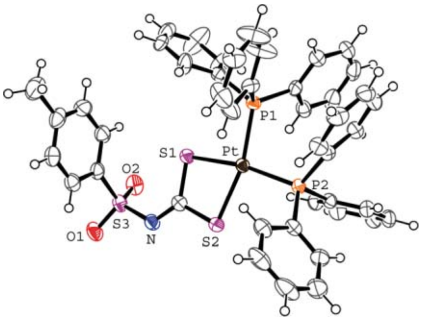


Fig. 4 ORTEP diagram of **4** with 30% probability, together with the atom numbering. Only one component of the disordered phenyl group attached to P1 is also shown for clarity.

μ-(κ^3N,S,S) and the other as μ_3-(κ^3S,S). As far as we are aware these variations in the ligating mode of the dithioligands and resulting formation of the multi-metallic complexes are unique; indeed **2** is the first crystallographically established system in the area of dithiolate chemistry featuring three distinct geometries. The bonds around the trigonal planar Cu(2), namely Cu(2)–S(1) 2.219(2), Cu(2)–S(3) 2.260(2), Cu(2)–P(4) 2.204(2) Å are shorter than those around the tetrahedral Cu(1), Cu(2)–P 2.256(2), 2.259(2) Å, Cu(1)–S(1) 2.430(2), Cu(1)–S(2) 2.396(2) Å. The distances around Cu(1) are equivalent to those found in **1** for Cu(2) which has an equivalent environment. In **2** the bridging sulfur atom around both Cu(2) and Cu(1) shows an increased bond length when compared to the Cu–S bonds to the terminal sulfur, by 0.041 and 0.034 Å, respectively. The nickel atom Ni(1) has a four-coordinate square planar environment with bond lengths Ni(1)–N(2) 1.959(5), Ni(1)–P(3) 2.213(2), Ni(1)–S(3) 2.234(2), Ni(1)–S(4) 2.174(2) Å. As in the two copper coordination spheres, the bond to the bridging sulfur is longer than that to the terminal sulfur, here by 0.060 Å. The four donor atoms are planar with a r. m. s. deviation of 0.081 Å with the nickel atom 0.015(1) Å from the plane. The intermetallic Ni(1)···Cu(2) distance of 2.879 Å is shorter than the sum of the van der Waals radii of Cu and Ni atom *i.e.* 3.03 Å. The remaining coordination sites around the metal ions are occupied by the triphenylphosphine ligand. The angles around the Cu(2) in **2** vary substantially (110.08(8)–130.65(8)°) but their sum is close to 360° (359.8°). This places the copper atom in the plane of the three donor atoms within experimental error. The main source of distortion from the ideal geometries around the three metals arises from the small bite of the dithiocarbimate.

The C–N bond distances 1.346(5) Å for **1** and 1.356(9) and 1.275(9) Å for **2**, respectively, clearly indicate that the former has approximately the same length reported for the complex anion $[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]^{2-}$ whereas the C–N bond length is intermediate between double and single bond lengths (1.27, 1.40 Å)[2c] showing sufficient delocalization of π-electrons over NCS_2 unit. In **2** one of the C–N bond lengths is close to that observed in complex **1** containing only Cu metal centres while the other associated with the nickel center is well in the range of C=N double bond lengths observed[2e] in the neutral bis-triphenylphosphine nickel(II) dithiocarbimate.

The structures of **3** and **4** are presented in Fig. 3 and 4, respectively. For both complexes one of the phenyl ring carbon atoms C(10), C(11), C(13) and C(14) of the PPh_3 ligand are disordered over two positions with an occupancy ratio of 51 : 49. In both complexes, the central metal has a distorted square-planar *cis*-MP_2S_2 coordination sphere. In **3** and **4**, P(1)–M–S(1), P(2)–M–S(2), P(1)–M–P(2) angles are all near 90°, while the bite angle S(1)–M–S(2) deviates somewhat [74.85(3)°,75.20(3)°, respectively, atoms M, S(1), S(2), P(1) and P(2) are approximately planar showing a maximum deviation of 0.112 Å. The M–P and M–S distances in **3** and **4**, respectively, are compatible with analogous Pt(II) and Pd(II) dithiocomplexes.[2g,h,4] In both **3** the Pd–S(1) and Pd–S(2) distances are similar at [2.306(8), 2.347(8) Å] while in **4** the corresponding Pt–S distances are 2.321(9), 2.354(9) Å similar to values found in the reported[4] anionic complex $[Pt(C_6H_5SO_2N{=}CS_2)_2]^{2-}$. The two M–P(1) and M–P(2) bond lengths are identical within experimental error at 2.309(8), 2.326(9) for M=Pd in **3** and 2.283(9), 2.295(9) Å for M=Pt in **4**. The intraligand S···S separations 2.840 Å and 2.842 Å in **3** and **4** respectively are substantially shorter than the sum of the van der Waals radii of two sulfur atoms 3.60 Å suggesting significant non-bonding S···S interaction.

The C(1)–S(1,2) bond length [1.746(3)–1.751(4) Å] are slightly shorter than the typical C–S single bond length (1.81 Å) due to the partial π-conjugation in the S–C–S group. The C(1)–N bond length 1.298(4) Å for **3** and 1.301(4) Å for **4** exhibit significant amounts of double bond character.

The most important feature in the crystal structures of **3** and **4** is that one phenyl group each from two different PPh_3 in **4** and one phenyl group of one PPh_3 ligand in **3** are oriented such that the *ortho* proton of the phenyl rings are directed towards the metal(II) [**3**: C(16)–H(16)···Pd 2.79 Å; ∠C–H–Pd: 124°; **4**: C(16)–H(16)···Pt: 2.82; C(38)–H(38)···Pt 2.89 Å; ∠C–H–Pt: 122, 123°] resulting in unusual anagostic or preagostic interactions.[6] These interactions are illustrated in Fig. 5 and show that the hydrogen atoms are directed towards approximately vacant axial positions in the metal coordination spheres. It appears that such interactions in these complexes are favored due to the steric and electronic demands of the bulky ligand PPh_3 and *p*-tolylsulfonyl substituent of the dithiocarbimate moiety and the d^8 configuration of the metal ions. Such type of interactions *via ortho* protons of the phenyl rings are unusual but have been reported in a $[Ni(L_2)]$ [L = dithiolate] moiety present in a heteronuclear cluster[7] $[\{Ni(L)_2\}_2(CuI)_6]$. To the best of our knowledge this is the first example of anagostic interactions in bis-triphenylphosphine metal dithiocarbimate complexes.

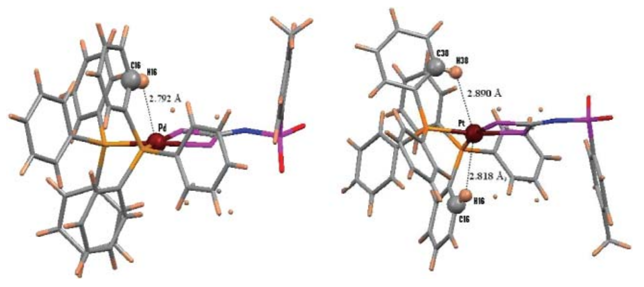


Fig. 5 View of the C–H···Pd (left) and C–H···Pt (right) anagostic interactions in complex **3** and **4**.

A closer inspection of the crystal structures of all complexes reveals a number of weaker intermolecular non-covalent C–H···O, C–H···S, C–H···N and C–H···Cl interactions (Table S1 see ESI).† Molecular packing diagrams for **1** and **2** are given in (Fig. S1 see ESI).† The lattice solvent molecules, methanol in **1** and dichloromethane in **2**, are located in cavities of **1** but form a channel-like motif in **2** thus generating three dimensional supramolecular networks.

Electronic absorption and photoluminescence spectra

The electronic absorption and emission spectra of all complexes **1–4** in CH_2Cl_2 solution are presented in Fig. 6.

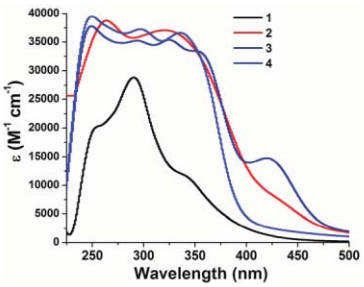


Fig. 6 Electronic absorption of complexes **1–4** in CH_2Cl_2 solution at room temperature.

The observed electronic absorption bands of **1**, **3** and **4** have been interpreted with the help of TD-DFT calculations. The electronic absorption spectra of the complexes show some common bands between 250–350 nm due to multiple ligand centered transitions.[3,4] Calculations indicate that in **1** the lower energy band calculated at 349 nm with oscillator strength (*f*) 0.0087 is due to the charge transfer transition from sulfur atom coordinated to only one copper center to the aromatic ring of the triphenylphosphine group with some admixture of d-orbitals of both copper atoms (Fig. 7). The next higher energy band at 305 nm having oscillator strength (*f*) 0.0421 is also attributed to ligand to ligand charge transfer (LLCT) from the sulfur atom coordinated to both the metal center to another aromatic ring of the triphenylphosphine group (Fig. 7). The other transitions are also of the LLCT type. Calculated excitation energies, wavelength, oscillator strength and major contribution are given in Table 5.

Additionally, **2** exhibits a very weak band at 440 nm due to Ni ← S (dithiocarbimate) MLCT transition; an absorption band at 560 nm in the solid as Nujol mull (Fig. S2 see ESI)† of this compound is ascribed to d-d transition for square planar geometry about nickel(II).[4]

Table 5 Calculated wavelength λ/nm, excitation energies E/eV and oscillator strength (f) for **1**, **3** and **4**

Complex	λ/nm	E/eV	f	Transition type
1	355	3.4890	0.0730	$n^a \rightarrow \pi^*$
	349	3.5550	0.0087	$n^a \rightarrow \pi^*$
	347	3.5779	0.0420	$n^a \rightarrow \pi^*$
	305	4.0594	0.0421	$n^a \rightarrow \pi^*$
	304	4.0744	0.0183	$n^a \rightarrow \pi^*$
3	430	2.8857	0.0026	$n \rightarrow$ P atom
	368	3.3714	0.0068	$n \rightarrow \pi^*$
	332	3.7345	0.0200	$n \rightarrow \pi^*$
	294	4.2188	0.1388	LMCT
	249	4.9793	0.0125	$n \rightarrow \pi^*$
4	332	3.7345	0.0015	$n \rightarrow \pi^*$
	302	4.1114	0.0225	$\pi \rightarrow \pi^*$
	248	4.9932	0.0177	$\pi \rightarrow \pi^*$

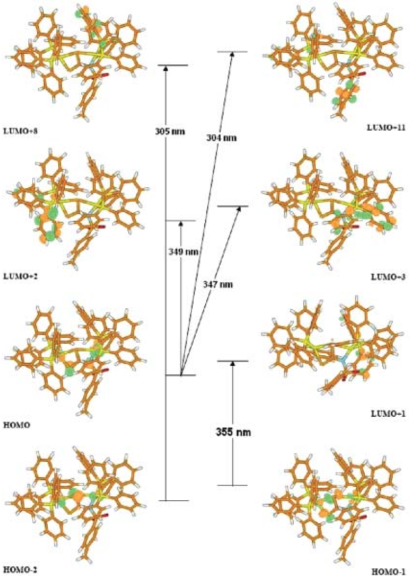


Fig. 7 Selected orbital transitions for the complex (orbital contour value 0.05).

The palladium complex **3** exhibits five bands at 419, 351, 325, 294 and 248 nm. TD-DFT calculations indicate that the low energy band (calculated at 430 nm with oscillator strength (f) 0.0026) is due to HOMO → LUMO electron excitation and is attributed to electron transfer from the coordinated sulfur atom of the ligand to the phosphorus atom with slight intermixing of the metal d-orbital (Fig. 8). The next two bands calculated at 368 nm and 332 nm with oscillator strengths (f) 0.0068 and 0.0200, respectively, are assigned to the charge transfer transitions from the coordinated sulfur atoms and π-electron clouds of the aromatic ring of the sulfonamide ring to the phosphorus and metal d-orbital. Additionally, the absorptions calculated at 294 and 249 nm with oscillator strengths (f) 0.1338 and 0.0125, respectively, are ascribed to ligand to-metal (LMCT) and intraligand (ILCT) charge transfer transitions (Fig. 8).

Likewise, in the case of platinum complex **4** the electronic absorption spectrum recorded in CH_2Cl_2 solution displayed three bands at 335, 296 and 248 nm. Quantum chemical calculations reveal that the first lower energy band calculated at 332 nm with oscillator strength (f) 0.0015 can be assigned to the HOMO → LUMO + 2 electron transfer from the coordinated sulfur atoms of the dithiocarbimate ligand with slight intermingling of the metal d-electrons to the aromatic ring of the triphenylphosphine. The rest of the lower energy bands calculated at 302 and 248 nm having oscillator strengths (f) 0.225 and 0.0177, respectively, arise from ligand to ligand (LLCT) and intraligand (ILCT) charge transfers (Fig. 9). The calculated and observed bands are in good agreement for both the complexes.

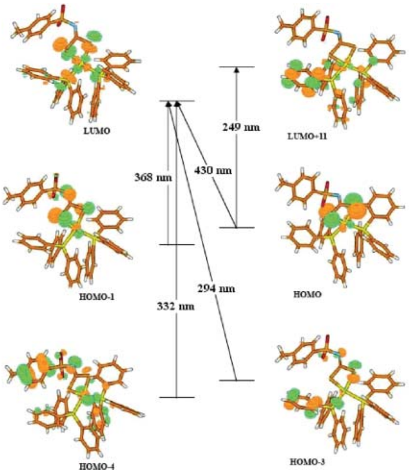


Fig. 8 Selected orbital transitions for palladium complex **3** (orbital contour value is 0.05).

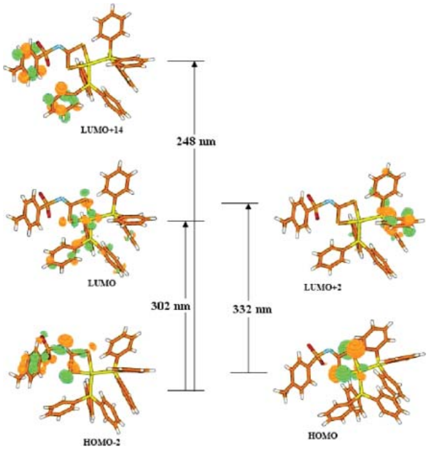


Fig. 9 Selected orbital transitions for platinum complex **4** (orbital contour value is 0.05).

When excited at 262 nm, **1** shows luminescence emission at around 475 nm whereas upon excitation at 250 nm the emission intensity of **2** is significantly decreased. In the light of previous reports on the copper(I) phosphine complexes the emissive states for the observed emissions may be ascribed principally to the perturbed ligand centered π–π* transitions together with some admixture of copper d-orbitals.[3] The decrease in the luminescence intensity of **2** is due to the presence of a nickel(II) centre, d^8 electronic configuration which exhibits low energy absorptions in the visible region and acts as a quencher. Upon excitation at 242 and 298 nm, **3** shows an intense emission band at 360 nm which arises from intraligand (ILCT) and ligand to metal (MLCT) charge transfer transitions. Likewise upon excitation at 235 and 302 nm, **4** displays a strong luminescent emission near visible region at 350 nm arising from the π → π* (ILCT) intraligand transitions (Fig. 10).[7,8]

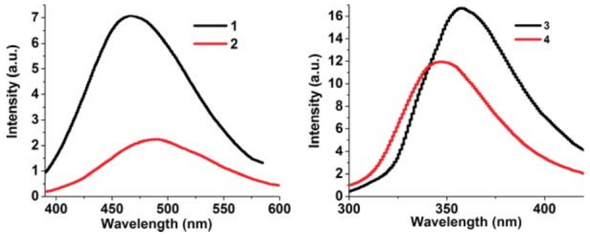


Fig. 10 Fluorescence spectra of **1–4** in CH_2Cl_2 solution at room temperature.

Upon coordination to a metal, the phosphine ligands do not give rise to a dramatic spectral wavelength shift[8] as compared to nitrogen ligands because the phosphorus lone pairs are relatively less involved in π- conjugation when compared to nitrogen lone pairs.[9,10]

Conductivity

Pressed pellet conductivity, $\sigma_{rt} \sim 10^{-6}$ S cm^{-1} for both **1** and **2** (Fig. 11) shows their weakly conducting property because of the very weak S···S/M···S intermolecular stacking. They exhibit semiconductor behaviour as their conductivity progressively increases with temperature and decreases ideally with temperature in the range 403 K to 313 K with a band gap of 0.183–0.186 eV. The heteroleptic complexes **3** and **4** show insulating behaviour because of, the absence of S···S/M···S intermolecular stacking.

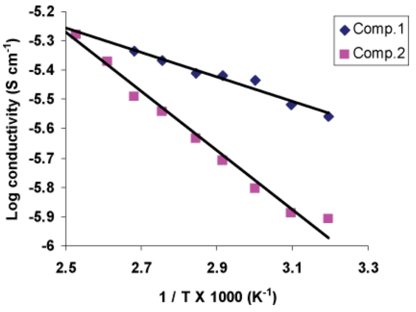


Fig. 11 Temperature dependent electrical conductivities of **1** and **2**.

Experimental

General procedure

All reactions were carried out in open atmosphere at ambient temperature. The solvents such as dichloromethane, diethyl ether, methanol, dimethylformamide (DMF) and carbon disulfide were purchased from Merck and where necessary were purified by standard procedures prior to their use. $NiCl_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ both SDS, *p*-methylphenylsulfonamide (Spectrochem), K_2PtCl_4, K_2PdCl_4, KOH and triphenylphosphine (all Sigma–Aldrich) were used as received. The dipotassium salt of *p*-tolylsulfonyl dithiocarbimate (*p*-$CH_3C_6H_4SO_2N{=}CS_2K_2{\cdot}2H_2O$) ligand was prepared by reaction of *p*-tolylsulfonamide, KOH and carbon disulfide according to literature procedure[11] and characterized by IR, ^{1}H and ^{13}C NMR spectra. The precursor $Cu(PPh_3)_2NO_3$ was prepared by a method reported elsewhere.[12]

The melting point of the complexes were determined in an open capillary using a Gallenkamps apparatus. Elemental analyses (C, H, N, S) were performed on a Model CE–440 CHN analyzer. IR as KBr pellet and ^{1}H, ^{13}C and ^{31}P NMR spectra in $CDCl_3$ were recorded on a Varian 3100 FTIR and JEOL AL 300 FTNMR spectrophotometers respectively. Chemical shifts were reported in parts per million using TMS as internal standard for ^{1}H and ^{13}C NMR and PCl_3 as external standard (δ 220 ppm) for ^{31}P NMR spectra. The electronic absorption and emission spectra were obtained in CH_2Cl_2 solution at room temperature from Shimadzu UV–1700 Pharma Spec UV-Vis and Varian Cary Eclipse Fluorescence spectrophotometers, respectively. Compressed pellet electrical conductivities of the complexes were measured on a Keithley 236 Source Measure Unit employing conventional two-probe technique in the 313–403 K temperature range. The pellet surfaces were coated with silver paint to make the electrical contact. The electrospray ionization-mass spectra (ESI-MS) were obtained in CH_3OH on a Micromass Quattro II spectrometer.

Synthesis of $Cu_2(PPh_3)_4L$ (1)

To a stirred 25 mL CH_2Cl_2 solution of $Cu(PPh_3)_2(NO_3)$ (1.3 g, 2 mmol) was added gradually 15 mL methanolic solution of the ligand $K_2L{\cdot}2H_2O$ (0.360 g, 1 mmol). The yellow solid formed by stirring the reaction mixture for about 4 h was filtered off and washed with water followed by methanol and dried *in vacuo* over $CaCl_2$.

Yield: (1.04 g, 66%), m.p. 114–116° (dec.). Calcd for $C_{85}H_{87}Cu_2NO_7P_4S_3$. C 64.54, H 5.54, N 0.89, S 6.08, Cu 8.03%. Found: C 64.40, H 5.46, N 0.86, S 6.00, Cu 8.00%. IR (KBr, cm^{-1}): 1384 ν(C=N), 1301 ν_{asym} (SO_2), 1143 ν_{sym}(SO_2), 995 ν_{asym}(CS_2). ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 7.47 (d, J = 9.0 Hz, 2 H, H2 and H6), 6.86 (d, J = 9.0 Hz, 2 H, H3 and H5), 2.33 (s, 3 H, CH_3), 7.25 (m, 60 H, PPh_3). ^{13}C (75.45 MHz,, $CDCl_3$, ppm): δ 208.24 (N=CS_2), 142.76 (C4), 132.33 (C1), 132.02 (C3 and C5), 128.56 (C2 and C6), 21.46 (CH_3). Triphenylphosphine signals: 133.93 (C1′), 132.16 (C2′ and C6′), 129.15 (C3′ and C5′), 128.29 (C4′). ^{31}P NMR (121.50 MHz, $CDCl_3$): δ –1.29 ppm. UV-vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1}cm^{-1}): 351 (1.2×10^4), 305 (2.9×10^4), 253 (2.04×10^4). $\sigma_{rt} = 2.76 \times 10^{-6}$ S cm^{-1}, E_a = 0.183 eV.

Synthesis of $Cu_2Ni(L)_2(PPh_3)_4$ (2)

To a 15 mL aqueous solution of the ligand $K_2L{\cdot}2H_2O$ (0.720 g, 2 mmol) was added solid $NiCl_2{\cdot}6H_2O$ (0.237 g, 1 mmol), which after stirring generated a clear green solution of complex salt $K_2[NiL_2]$. Reaction of 20 mL CH_2Cl_2 solution of $Cu(PPh_3)_2NO_3$ (1.3 g, 2 mmol) with one equivalent of *in situ* generated complex salt $K_2[Ni(L)_2]$ resulted in the formation of dark brown colored solution after overnight stirring. The dark brown solid was collected by the removal of the solvent and dried *in vacuo* over $CaCl_2$.

Yield: (1.34 g, 68%), m.p. 155–158° (dec.). Calcd for $C_{91}H_{80}Cl_6Cu_2N_2NiO_4P_4S_6$: C 55.19, H 4.07, N 1.41, S 9.71, Ni 2.96, Cu 6.42%. Found: C 55.10, H 4.03, N 1.32, S 9.38, Ni 2.89, Cu 6.35%. IR (KBr, cm^{-1}): 1473 ν(C=N); 1306 ν_{asym}(SO_2); 1149 ν_{sym}(SO_2); 987 ν_{asym}(CS_2). ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 7.98 (d, J = 6.0 Hz, 4 H, H2 and H6), 6.82 (d, J = 6.0 Hz, 4 H, H3 and H5), 2.26 (s, 6 H, CH_3), 7.58 (m, 60 H, PPh_3). ^{13}C (75.45 MHz, $CDCl_3$, ppm): δ 208.10 (N═CS_2); 142.04 (C4), 133.88 (C1), 132.16 (C3 and C5), 128.56 (C2 and C6), 21.47 (CH_3). Triphenylphosphine signals: 135.01 (C1′), 133.81(C2′ and C6′), 129.80 (C3′ and C5′), 127.81(C4′). ^{31}P NMR (121.50 MHz, $CDCl_3$): δ 21.57, 4.61 and –0.11 ppm. UV-vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1}cm^{-1}): 440 (5.5×10^3), 350 (3.7×10^4), 263 (3.9×10^4). $\sigma_{rt} = 1.24 \times 10^{-6}$ (S cm^{-1}), $E_a = 0.186$ eV.

Synthesis of $Pd(PPh_3)_2L$ (3)

Reaction of 20 mL CH_2Cl_2 solution of $Cu(PPh_3)_2NO_3$ (1.3 g, 2 mmol) with one equivalent of *in situ* generated complex salt $[K_2Pd(L)_2]$ adopting exactly the same procedure as for **2** but using K_2PdCl_4 (0.326 g, 1 mmol) led to the formation of yellowish-brown powder. The dissolution of the powdered compound in CH_2Cl_2 yielded yellow crystals in good yield.

Alternatively, **3** could be prepared by the reaction of methanol solution (25 mL) of triphenylphosphine (0.524 g, 2 mmol) with an aqueous-methanol (40 : 60) solution (15 mL) of $K_2L{\cdot}2H_2O$ (0.360 g, 1 mmol) producing a clear solution. Solid K_2PdCl_4 (0.326 g, 1 mmol) was added to the above reaction mixture which resulted in the formation of yellow solid product after continuous stirring for about 24 h. The compound thus formed was filtered off, washed twice with water, followed by diethyl ether and dried *in vacuo* over anhydrous calcium chloride.

Yield (0.727 g, 83%), m.p. 190–192° (dec.), Anal. calcd for: $C_{44}H_{37}NO_2P_2PdS_3$: C 60.31, H 4.26, N 1.60, S 10.98%. Found: C 60.29, H 4.20, N 1.54, S 10.92%. IR (KBr, cm^{-1}): 1438 ν(C═N), 1301 $\nu_{asym}(SO_2)$, 1142 $\nu_{sym}(SO_2)$, 919 $\nu_{sym}(CS_2)$, 381 ν(Pd–S).^{1}H NMR (300.40 MH$_z$, $CDCl_3$, ppm): δ 7.78 (d, J = 6.0 Hz, 2 H, H2 and H6), 7.36–7.11 (m, 32 H, H3, H5, and PPh_3), 2.36 (s, 3 H, CH_3). ^{13}C (75.45 MH$_z$, $CDCl_3$, ppm): δ 205.38 (N═CS_2); 141.80 (C4); 134.32 (C1), 130.86 (C3 and C5); 128.61 (C2 and C6); 21.53 (CH_3). Triphenylphosphine signals: 134.24 (C1′), 134.16 (C2′ and C6′), 128.50 (C3′ and C5′), 127.87(C4′) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$, 20 °C): δ 30.94 ppm. UV-vis. (CH_2Cl_2, λ_{max}/nm, ε/M^{-1}cm^{-1}): 419 (1.4×10^4), 351(3.35×10^4), 325 (3.55×10^4), 294 (3.53×10^4), 248 (3.8×10^4). ES-MS: m/z = 875.8 [M$^+$].

Synthesis of $Pt(PPh_3)_2(L)$ (4)

This colourless complex was prepared in good yield adopting exactly similar procedures for **3** using K_2PtCl_4 (0.415 g, 1 mmol).

Yield (0.753 g, 78%), m.p. 192–195° (dec.), Anal. calcd for $C_{44}H_{37}NO_2P_2PtS_3$: C 54.77, H 3.86, N 1.45, S 9.97%. Found: C 54.65, H 3.80, N 1.43, S 9.94%. IR (KBr, cm^{-1}): 1453 ν(C═N); 1305 $\nu_{asym}(SO_2)$; 1145 $\nu_{sym}(SO_2)$; 997 $\nu_{asym}(CS_2)$; 348 ν(Pt–S).^{1}H NMR (340.40 MH$_z$, $CDCl_3$, ppm): δ 7.76 (d, J = 9.0 Hz, 2 H, H2 and H6), 7.38–7.11 (m, 32 H, H3, H5 and PPh_3), 2.37 (s, 3 H, CH_3). ^{13}C (75.45 MH$_z$, $CDCl_3$, ppm): δ 210.67 (N═CS_2); 141.94 (C4); 134.38 (C1), 130.98 (C3 and C5); 128.65 (C2 and C6); 21.54 (CH_3). Triphenylphosphine signals: 134.36 (C1′); 134.23 (C2′ and C6′); 128.60 (C3′ and C5′); 127.86 (C4′) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$, 20 °C): δ 18.97 ppm, $J^{195_{Pt}-31_P}$ = 3112.10 Hz. UV-vis. (CH_2Cl_2, λ_{max}/nm): 335 (3.67×10^4), 296 (3.74×10^4), 248 (3.98×10^4). ESI-MS: m/z = 965 [M$^+$].

Crystallography

Single-crystal X-ray data and the space group, unit cell dimensions and intensity data for the complexes were collected on Bruker Smart Apex (**1**, **2**) and Nonius Kappa CCD (**3**, **4**) diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å for **1**, **3**, **4** and 0.71069 for **2**). The crystals were mounted on a glass fiber. The structures were solved by the direct method using SHELXS-97[13] for **1** and SHELXTL[14] for **2** and refined anisotropically for non-hydrogen atoms by full matrix least-squares technique using SHELXL–97[15] programme package. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding, Ref U and constr model. PLATON[16] was used for analyzing the weak interactions, bond distances and angles. Figure for **1**, **2**, **3** and **4** were prepared using ORTEP[17] In complex **3** and **4**, which are isomorphous one phenyl ring was found to be disordered. Refinement of the disorder showed it to be 49 : 51, so final refinements were carried out with 1 : 1 disorder.

Computational details

Optimized molecular geometries were calculated using the B3LYP[18] exchange–correlation functional. The spin restricted DFT method was employed to model the closed-shell species. The LANL2DZ (d, p) basis set for Pd and Pt atoms, 6-31G** for C, H, O, N, S and P atoms while 3-21G** for all atoms for **1** was used. The optimized structures of the complex were used for molecular orbital analyses and time-dependent DFT (TD-DFT) calculations at the same level of theory with polarized continuum model (PCM).[19] The solvent parameters were those of the dichloromethane. The energies and intensities of 40 for **1** and 60 for **3** and **4**, lowest-energy spin allowed electronic excitations respectively were calculated using the TD-DFT. All the calculations were performed using the Gaussian 03 programme.[20] The molecular orbital plots were constructed with the MOLDEN program.[21]

Conclusion

In conclusion, we have shown three different modes of coordination of the ligand *p*-tolylsufonyl dithiocarbimate in combination with PPh_3 within the same molecule which resulted in the formation of unique homodi-, trinuclear heterometallic and heteroleptic complexes. The trinuclear heterometallic complex **2** has three distinct-geometries in a single entity. Preparation of the analogous trinuclear heterometallic complexes with soft metal ions palladium(II) and platinum(II), instead yielded the mononuclear complex $M(PPh_3)_2$(dithiocarbimate) *via* PPh_3 transfer because of the greater propensity of these metals to adopt square planarity compared to nickel(II). In the heteroleptic complexes of palladium(II) and platinum(II) rare intramolecular C–H···M, anagostic interactions were identified in the crystal structures. These are unique examples with MP_2S_2 chromophore involving *ortho* phenyl protons of the PPh_3 ligand. All complexes exhibit photoluminescence emission in solution at room temperature. The TD-DFT calculations show that the intra ligand charge transfer transitions are primarily responsible for their photoluminescent emissions. The di- and trinuclear heterometallic complexes show semiconductor behaviour whereas the heteroleptic complexes are insulators.

Acknowledgements

We acknowledge the council of scientific and industrial research (CSIR) for funding (project no. 01(2290)/09/EMR-II, New Delhi), Dr A. Mishra, for fluorescence spectra and Dr Abhinav Kumar, Lucknow University for theoretical calculation assistance. We thank EPSRC (UK) and the University of Reading for funds for the diffractometer.

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