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Influence of ligand environment on the structure and properties of silver (I) dithiocarbamate cluster-based coordination polymers and dimers

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Luminescent silver(I) homo- and heteroleptic pyridyl functionalised dithiocarbamate(dtc) complexes of the form, $[\{Ag(L)\}_4]_\infty$ (L = N-benzyl-N-methylpyridyldtc(L1) **1**, bis-(N-methylpyridyl)dtc(L2) **2**) and $[Ag(L)PPh_3]_2$ (L = L1 (**3**), L2 (**4**)) have been synthesized and characterized by elemental analysis, TGA, spectroscopy (IR, ^1H, ^{13}C and ^{31}P NMR and UV–Vis.)and X-ray crystallography. Complexes **1** and **2** are isomorphous and have a tetranuclear cluster-based coordination polymeric structure. In these tetranuclear silver(I) cluster subunits the four Ag atoms form a distorted tetrahedron. Complexes **3** and **4** are also isostructural and have centrosymmetric structures in which each Ag atom forms a distorted tetrahedral coordination geometry. All complexes are weakly conducting and exhibit semiconductor behaviour. **1**-**4** are strongly luminescent in solid phase; a correlation between their structure and luminescent properties has been established.

1. Introduction

Transition metal dithiolates continue to attract the attention of chemists due to their intriguing molecular electrical conducting, magnetic and optical properties, used as precursors for the preparation of metal sulphides and multitude of applications in industries as rubber vulcanization accelerators, as flotation agents in metallurgy, fungicides, pesticides, petroleum additives and importance in biological processes.[1-4] There is a developing interest in the metal dithiocarbamate complexes in studying the functionalisation of substituents on the dithio backbone that may give rise to interesting molecular architectures and tuneable physical properties.[1,3] The distinctly soft silver(I) ion readily interacts with thiolato ligands, including the ubiquitious dithiocarbamate, forming a variety of complexes and clusters with varying nuclearities and architectures.[5-8] Many of these complexes have been found relevant for the structural elucidation of the metal-binding sites of metallothioneins[9] and are important in the area of advanced materials for the synthesis of monolayer–protected clusters[10] and nanostructured materials.[11] The dithiocarbamate ligands can coordinate to metal atoms via sulfur donor atoms, most commonly in a symmetrical or asymmetrical bidentate, bidentate-bridging and less commonly in a monodentate fashion. The presence of lone pairs on the coordinated sulfur atoms may facilitate the formation of hypervalent interactions or secondary interactions thereby constructing supramolecular architectures.

Luminescent d^{10} metal complexes including those of coinage metals have garnered much attention in recent years because of their possible applications as sensors, biological probes, in solar energy conversion processes and display devices.[12] By contrast the luminescent silver complexes have not gained as much attention as its congener copper (I) and gold(I) complexes because of their photosensitivity. However a few examples have been established where promising photoluminescent properties are promoted by Ag…Ag interactions.[13] The extent of metallophilic interactions, bridging capabilities and steric restrictions of substituents on the dithiocarbamate unit and auxiliary phosphine ligands have been found to play a crucial role in the construction of coordination frameworks and multinuclear aggregates.[5a,6] The HOMO-LUMO gap may be modified by the use of auxiliary phosphine ligands with strong σ- donor and π- acceptor properties as well as the formation of a rigid coordination environment and the incorporation of electron rich pyridine group on the dithiocarbamate substituents may also modify their luminescent properties. In comparison to classical metal dialkyl/diaryl dithiocarbamates[1,6,14] complexes bearing pyridine functionality have received little attention.[15] Despite their synthetic versatility and practical applications, studies on the luminescent properties of silver dithio and mixed dithio- phosphine complexes are extremely limited.[5a] In order to see the effect of the pyridine functionalized dithiocarbamates in conjunction with the triphenylphosphine ligands on the crystal structures, luminescent properties and molecular electrical conductivity in their homoleptic tetranuclear cluster- based coordination polymers and heteroleptic dinuclear silver (I) complexes. In order to assess the nature of the Ag….Ag interactions theoretical calculations have been performed. The results of these investigations are presented in this contribution.

2. Results and discussion

2.1. Synthesis of complexes and spectroscopy

Treatment of a methanol solution containing two equivalents of the ligand KL1 or KL2 with one equivalent of $AgClO_4$ yielded homoleptic dithiocarbamate complexes **1** and **2**. The heteroleptic complexes **3** and **4** were obtained by reacting a dichloromethane solution of the **1** or **2** with an equimolar amount of the PPh_3 ligand in the same solvent (Scheme 1). These complexes are air-stable and melt in the 195-220 ^{0}C temperature range. These have been characterised by elemental analysis, IR, NMR and UV-Vis. spectroscopy and their photoluminescent properties have been studied in solution and in the solid phase. The polymeric structures for **1** and **2** and dinuclear structures for **3** and **4** have been elucidated by X-ray crystallography. The impact of non-covalent C-H…S and C-H…π interactions in the organisation of supramolecular networks providing anti configuration in **3** and **4** have been investigated. The correlation between their structures and luminescent property has been examined.

$$AgClO_4 + KL \xrightarrow[-KClO_4]{\text{methanol, rt}} [\{Ag(L)\}_4]_\infty \xrightarrow{PPh_3\text{ / dichloromethane}} [Ag\,(L)PPh_3]_2$$

L =L1 **(1)**, L2 **(2)** L =L1 **(3)**, L =L2 **(4)**

Scheme 1 Synthetic methodology for the complexes (1-4).

The IR spectra of **1-4**, show the ν(C-N) and ν(C-S) frequencies at 1423-1437 and 983-1042 cm^{-1} respectively characteristic of the dithiocarbamate ligand coordination. The ^{1}H NMR spectra of the complexes show the presence of ligand functionalities and integrate well to the corresponding hydrogens. In the ^{13}C NMR spectra, all complexes show a single down field resonance at δ 208-217 ppm associated with the N-CS_2 unit. In the $^{31}P\{^1H\}$ NMR spectra, the complexes **3** and **4** show two resonances of unequal intensity at (δ 10.23, 29.13 ppm) and (δ 43.52, 24.43 ppm) respectively, arising from the mono- and bis-PPh_3 adducts are equilibrium in solution(Fig.S7).

2.2. Crystal structures

Single crystals of **1-4** were obtained by slow evaporation of a dichloromethane/ethanol solution of the complexes. ORTEP drawings of (**1-4**) are presented in Figures 1, 2 and S1. The selected bond lengths and angles are given in Table 1 and S1 and crystallographic details are given in Table 3. A comparison of important geometrical details of **1** and **2** with analogous dithio complexes is given in table 2.

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

Bond lengths(Å)	1	2
Ag(1)-S(11)\$1	2.590(5)	2.572(4)
Ag(1)-S(13)\$2	2.611(5)	2.578(5)
Ag(1)-S(11)	2.638(5)	2.646(5)
Ag(1)-S(13)\$3	2.645(5)	2.637(5)
Ag(1)-Ag(1)\$3	2.866(3)	2.845(3)
Bond Angles(°)		
S(11)\$1-Ag(1)-S(13)\$2	133.12(16)	132.41(15)
S(11)\$1-Ag(1)-S(11)	103.54(8)	103.07(8)
S(13)\$2-Ag(1)-S(11)	85.52(15)	83.49(12)
S(11)\$1-Ag(1)-S(13)\$3	83.22(14)	85.22(13)
S(13)\$2-Ag(1)-S(13)\$3	96.84(10)	97.28(8)
S(11)-Ag(1)-S(13)\$3	168.33(14)	168.62(13)
S(11)\$1-Ag(1)-Ag(1)\$3	113.88(12)	114.31(11)
S(13)\$2-Ag(1)-Ag(1)\$3	112.46(11)	112.89(10)
S(11)-Ag(1)-Ag(1)\$3	86.91(10)	86.76(9)
S(13)\$3-Ag(1)-Ag(1)\$3	81.62(10)	82.03(9)
C(12)-S(11)-Ag(1)\$4	106.9(4)	106.7(4)
C(12)-S(11)-Ag(1)	106.8(5)	106.9(4)
Ag(1)-S(11)-Ag(1)\$4	84.42(15)	84.38(13)
C(12)-S(13)-Ag(1)\$5	110.1(4)	110.7(4)
C(12)-S(13)-Ag(1)\$3	111.6(5)	110.1(4)
Ag(1)\$5-S(13)-Ag(1)\$3	90.72(14)	90.18(13)

Symmetry elements \$1 y, -x, 1-z; \$2 y,-x,-z: \$3 -x,-y,z \$4 -y, x, 1-z \$5 -y,x,-z

Complexes **1** and **2** are isostructural, the only difference being that ligand L1 contains one phenyl ring and one pyridine ring, while L2 has two pyridine rings. Each dithiocarbamate group acts as a tetradentate ligand being uniquely bonded to three Ag atoms in a μ^4, κ^4-S (11), S (11), S(13), S(13) chelating-bridging manner. The structures can be considered as containing Ag_4L_4 moieties surrounding a crystallographic -4 axis, as shown in Figure 1, which are then connected via bridging sulfur atoms along the unique c axis to form a 1-D polymeric ladder-like structure (Fig. 3). There is little difference between the Ag-S distances within the Ag_4L_4 moieties and those connecting them, with lengths of 2.572(5)-2.646(5) Å in **1** and **2.**

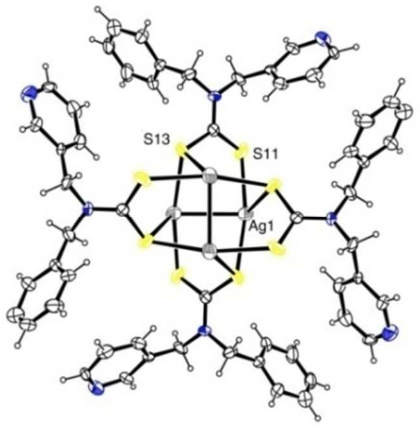

Fig. 1 Perspective view of the $Ag_4(\mu_4\text{-}S)_8$ core in 1 with ellipsoids at 20% probability. The structure of 2 is isomorphous.

The most significant feature of the Ag_4L_4 moieties is the existence of two very short Ag…Ag interactions at distances of (2.866(3), 2.845(3) Å**)** in **1** and **2** values even shorter than the Ag-Ag metallic bond distance of 2.88Å.[13a,16] These distances are comparable with the shortest Ag…Ag distances known,[17] as detailed in Table 1 and are indicative of dominant closed shell d^{10}-d^{10} argentophilic interactions. This contrasts the analogous $[Cu_4(\mu^2,\eta^1\text{-}S_2CNBu_2)_4]$ and $[Cu_4(\mu^2,\eta^1\text{-}S_2CNEt_2)_4]$ clusters which have a tetrahedral core containing five Cu-Cu interactions in the 2.6368-2.8119 Å range.[18] The longer Ag…Ag distances between silver atoms in the Ag_4L_4 moieties **1** and **2** are 3.513(5) and 3.509(5) Ǻ respectively, values which are only slightly longer than the sum of the van der Waals radii of two silver atoms (3.44 Å). Ag…Ag distances between the moieties along the polymeric chain are 3.740(6), 3.692(6) Å. The closest S...S seperations of 2.98(1)and 3.56(1)Ǻ for **1** and **2** respectively between the coordinated dithiocarbamate ligands show weak intermolecular associations in the solid state. Taking into account the four sulfur atoms and the adjacent silver atom, the geometry of the coordination sphere about each silver atom can be considered as highly distorted trigonal bipyramidal with $\boldsymbol{\tau}$ values of 0.58 and 0.60 respectively, ideal values being 0.0 for the square pyramid and 1.0 for the trigonal bipyramid[19] Notably the pyridyl groups on the dithiocarbamate unit are oriented away from the coordination sphere and not involved in bonding/bonding interactions probably due to the availability of lone pairs on the coordinated soft sulfur atoms in comparison to hard Py(N).

The dinuclear centrosymmetric complexes $[Ag(L)PPh_3]_2$ (L =L1(**3**), L2(**4**)) are isomorphous, in which the dithiocarbamate ligands L1 and L2 are bonded to each Ag atom in a μ^2,κ^3-S(13), S(13), S(11) chelating- bridging manner. The fourth coordination site on each silver atom is occupied by one PPh_3 ligand establishing a distorted tetrahedral coordination environment (Fig. 2). In (**3, 4)** the Ag-S distances of (2.619(1)-2.758(1), 2.628(1)-2.723(1)Å) and the Ag-P distances of(2.422(1), 2.413(1)Å) are as expected.[7e,f] The coordination sphere is a distorted tetrahedron with the major distortion coming from the small bite 67.02(3), 67.35(3)^o of the chelating ligand. The Ag···Ag distances of 2.983(1) and 3.004(1) Å in **3** and **4** respectively are shorter than the sum of the van der Waals radii, though significantly longer than values in **1** and **2**. The PPh_3 and dithiocarbamate ligands in **3** and **4** are in the anti configuration because of the existence of intermolecular C-H...S and C-H...π interactions (Fig. 4) which is rather different to the structure found in a similar dinuclear carboxylate complex,[20] $[(Cy_3P)Ag(O_2CCF_3)]_2$ where the phosphine and carboxalate ligands are in the syn- configuration.

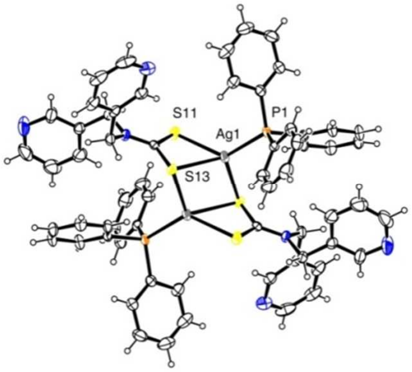

Fig. 2 The centrosymmetric structure of **4** with ellipsoids at 20% probability. The structure of **3** is isomorphous.

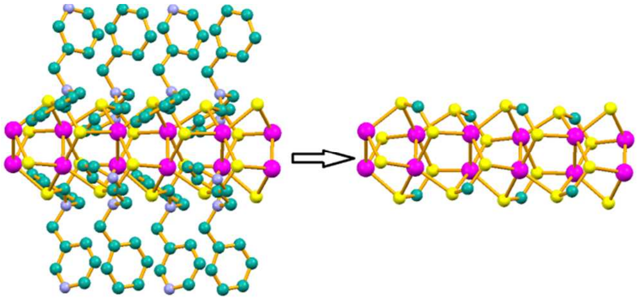

Fig. 3 Perspective views of **1** showing the formation of a polymeric structure through Ag...S ladder-like interactions between Ag_4S_8 cores along the c axis.Colour code: pink, silver; yellow, sulfur; blue, nitrogen; carbon, dark green

Table 2 A comparisons of selected geometrical details of **1** and **2** with those found in analogous dithio complexes.

Complexes	Ag-Ag(Å)	Ag-S(Å)	Geometry	Ref	Type of structure
[{Ag(N-benzyl-N- methylpyridyldtc)}$_4$]$_\infty$(**1**)	2.845-3.513	2.590-2.646	SP	*	Tetranuclear cluster based polymer
[{Ag(bis-(N-methylpyridyldtc)}$_4$]$_\infty$(**2**)	2.865-3.509	2.572-2.646	SP	*	Tetranuclear cluster based polymer
[Ag(dibenzyldtc)]$_\infty$	3.063	2.446-3.010	Td	5f	Polymer
[Ag(dipropyldtc)]$_6$	2.905-3.849	2.427-2.556	OCT	5b	Hexanuclear cluster
[Ag(diisopropyldtc)]$_6$	3.038-3.098	2.462-2.6123	Td	5c	Hexanuclear cluster
[{Ag(diethyldtc)}$_3$]$_\infty$	2.833, 3.463	2.491-2.620, 2.545-2.714	TG, Td	5d	Polymer
[Ag(ethylxant)]$_\infty$	3.054	2.507-2.837	TBP	5k	Polymer
[Ag(dipropyldithiophosphate)]$_6$	3.155-3.156	2.485-2.572	OCT	5h	Hexanuclear cluster
[{Ag(dithio-o-toluato)}$_4$]$_\infty$	2.944-3.216	2.392-3.007	Td	5j	Polymer
[{Ag$_6$(i-mnt)$_6$}]$^{6-}$	3.010-3.74	2.459-2.527	OCT	5g	Hexanuclear cluster
[Ag$_{12}${S$_2$Cd(*t*-Bu-fy)}$_6$]	2.874-3.280	2.382-2.427	Linear	8	Dodecanuclear cluster
[Ag(SC$_6$H$_2$Pr$^i_3$-2,4,6)]$_{10}$	2.899-4.313	2.389-3.236	Linear	5m	Decanuclear cluster

* This work

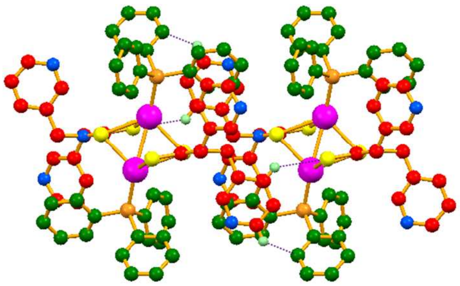

Fig. 4 View of C-H...S and C-H...π interactions in **4,** shown as dotted lines, stabilising the ligand (L3 red) and triphenyphosphine (green) in an anti configuration.

2.3. Electronic absorption and photoluminescent spectra

The optical properties, i.e absorption and emission, of **1-4** have been studied in dichloromethane solution and in nujol mull as solid and are displayed in Figures 5, 6 and S2-S5. In solution (**1**, **2**) and (**3**, **4**) show virtually similar absorptions near 280 nm and 260 nm respectively that can be assigned to π–π* intra ligand charge– transfer(ILCT)/ligand to ligand charge- transfer (LLCT) transitions.[5a,13] In the solid phase (**1**, **2**) show absorptions at (325, 354 nm) whereas (**3**, **4**) exhibit a medium broad absorption band at 320 nm which arise due to metal perturbed charge transfer transitions.[5a,13] The significant differences in the spectra of two set of complexes in solution and solid phase reveals that Ag….Ag interactions in the solid phase (vide infra in the crystal structures) are not retained in solution. Only a limited number of silver(I) complexes have been reported to exhibit luminescent properties at room temperature, the majority at low temperature.

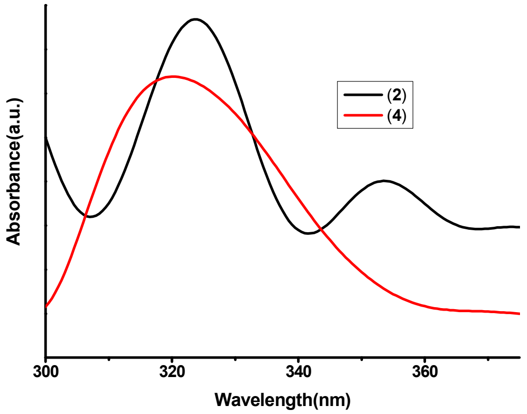

Fig. 5 Solid phase (nujol mull) UV-Vis. spectra of **2** and **4**.

Upon excitation at 300 nm in CH_2Cl_2 solution at room temperature, **1-4** show an emission band near 350 nm, (Fig. S4) arising from the metal perturbed charge transfer state of the dithiocarbamate ligands.[5a,13] Complex **3** and **4** show an additional emission band at 480 nm (Fig. S4b) which emanates from the metal perturbed ILCT state of the PPh_3 ligands.[21]

In the solid phase when (**1**, **3**) and (**2**, **4**) excited at 300 nm and 320 nm respectively show an unstructured emission band of comparable feature (Fig. 6 and S2) in between 410-480 nm. The significantly red shifted emissions with large Stokes shift of about 100 nm for the cluster complexes (**1**, **2**) in the solid phase can be ascribed to the silver cluster based centers with significant Ag…Ag interactions[5a,13] together with other factors like the rigid coordination environment and enhanced conjugation[13b] due to the lone pairs on the Py(N). It is worth mentioning that despite weaker Ag…Ag interactions, dinuclear heteroleptic complexes **3** and **4** also show larger Stokes shift influence by the metal perturbed charge transfer transitions together with bulky PPh_3 ligands providing rigid coordination environment about the metal centers. Furthermore somewhat stronger emission intensities of (**2**, **4**) may be ascribed to the presence of two pyridyl functionalities as compared to only one in (**1**, **3**). The excitation spectra recorded for **2** and **4** at room temperature (Fig. 6) show the λ_{ex} at 320 nm which match to the solid phase UV-Vis. spectra of the complexes.

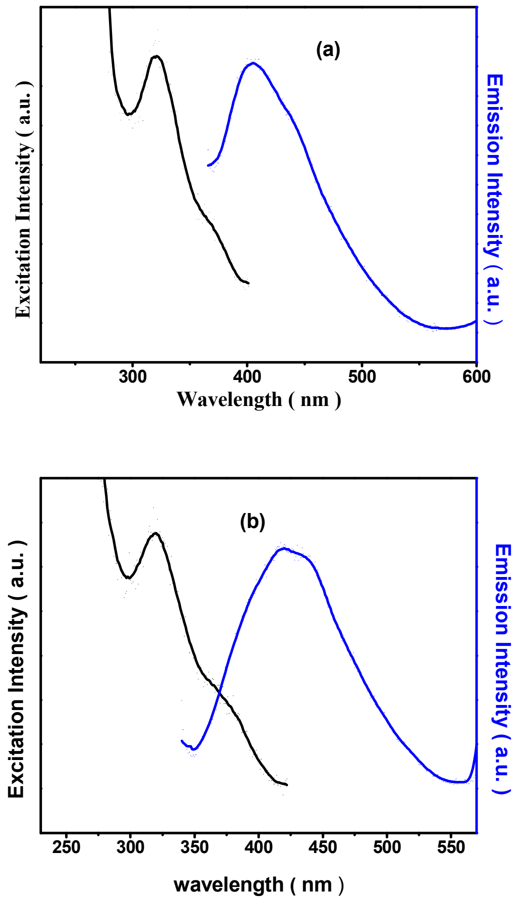

Fig. 6 Emission and excitation spectra of **2**(a) and **4** (b) in solid phase (λ_{ex} at 320 nm).

2.4. Pressed-pellet conductivity

The conducting properties of all the complexes have been measured using complex impedance spectroscopy with powdered samples as pressed pellets sandwiched by silver electrode (diameter: 10.5 mm for (**1**, **2**) and 10.2 mm for (**3**, **4**)); the pellet thickness of 1.6 mm (**1**), 1.6 mm (**2**), 0.95 mm (**3**) and 0.80 mm (**4**). The σ_{rt} value ~ 10^{-5} and 10^{-6} S cm^{-1} for (**1**, **2**) and (**3**, **4**) respectively (Fig.7) show their weakly conducting nature due to weaker S…S intermolecular stacking in the solid state (vide supra in the crystal structure). Somewhat higher conductivities of (**1**, **2**) as compared to (**3**, **4**) may be ascribed to relatively stronger Ag…Ag and S…S interactions in the former complexes. However their conductivities progressively increase with temperature and decreases ideally with temperature in the 303 K to 383 K temperature range with a band gap of 0.498, 0.516, 0.539 and 0.643 eV for **1-4** respectively showing their semiconducting behaviour.

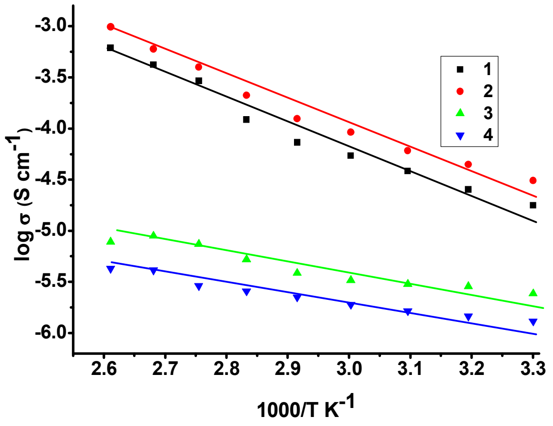

Fig. 7 Temperature dependent electrical conductivities of **1** - **4**.

2.5. Theoretical calculations

In order to investigate the structures of **1** and **2**, we considered the model in Figure 8 which is based on Figure 1 but with hydrogen atoms replacing the aromatic rings and the structure of **4**. Both structures were geometry optimised with the Gaussian03 program[22] using the hybrid B3LYP functional with the LANL2DZ basis set for silver, 6-31+G* for S, P and 6-31G for remaining atoms. The fragment from **1** optimised to convergence with Ag…Ag 2.948Å compared to 2.866(3) Å in **1**. The disparity may well be due to the omission of the bridging atoms that lead to the polymer formation shown in Figure 3. The nature of the HOMO orbitals is of significance. There are two of equivalent energy in which the two bonding pairs of silver atoms play a dominant part with 2s, 3s, 7d+1, 7d+2 having coefficients greater than 0.1 for two of the interacting silver atoms and 2s, 3s, 7d-1, 7d+2 for the other two silver atoms. The LUMO has large contributions all >0.45 from the 3s orbital of all four silver atoms. The HOMO-LUMO gap is 0.154 a.u.

Optimisation of structure **4** expanded the Ag…Ag distance to 3.148 Å. Examination of the frontier orbitals showed only one contribution from the silver atoms of greater than 0.1, namely from the 7d+1 orbital. The HOMO-LUMO gap is 0.148 a.u.

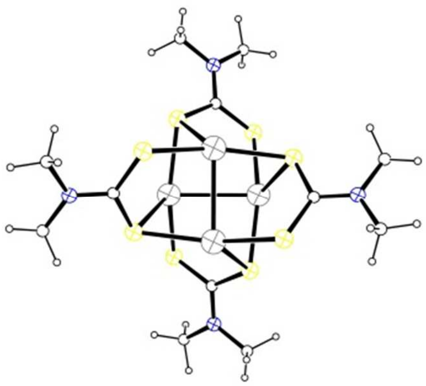

Fig. 8 DFT optimised structure of fragment from **1**.

2.6. Thermal degradation

TGA plots of (**2, 4**) and (**1, 3**) are shown in Figure 9 and Figures (S6, S7) respectively and the results are summarized in Table S2. TGA plot of compounds **2** and **4** is discussed here in detail. The homoleptic complexes (**1, 2**) show one-step decomposition in the temperature range 207-405 °C with weight loss of 66.6-67.5 % leaving the residue of Ag_2S. The heteroleptic complexes (**3**, **4**) show a two-step decomposition yielding a mass corresponding to Ag_2S. In the first step (150-330 °C) the weight left 34.5-29.2% corresponds to $Ag_2S_4P_2$ (calcd 31.5%). In the final step above 415 the weight of the residue 24.2-21.2% (calcd 19.16-19.17%) is consistent with Ag_2S. Thus the homoleptic (**1**, **2**) may serve as better single source precursor than the heteroleptic complexes (**3**, **4**).

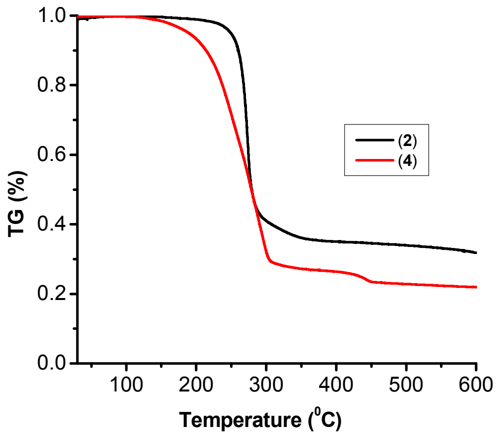

Fig. 9 Superimposed thermogravimetric (TG) trace of **2** and **4**.

3. Conclusions

Novel homoleptic silver(I) pyridine functionalized dithiocarbamate cluster based coordination polymers(**1**, **2**) featuring strong Ag-Ag contacts and heteroleptic dinuclear complexes (**3**, **4**) with weak Ag…Ag interactions have been synthesized and characterised by microanalysis and X-ray crystallography. All the complexes are weakly conducting and show semiconductor behaviour. All four compounds show luminescent properties with distinctive features in the solution and solid phase emanating from ILCT and metal perturbed charge transfer states. The red shifted emissions for **1** and **2** may be attributed to significant Ag-Ag bonding in the solid state. These complexes widen the scope of the underexplored pyridine functionalized ligands for the synthesis of multimetallic luminescent complexes of metal ions with closed shell d^{10}-d^{10} metallophilic interactions. TGA revealed that the homoleptic complexes with these systems may be potentially utilized for the preparation of metal sulphides.

4. Experimental section

4.1 Materials and methods

All experiments were carried out under aerobic conditions at ambient temperature and pressure. The solvents were purified by standard procedures and where necessary dried before use. The chemicals $AgClO_4$, 3-pyridine carboxaldehyde, 3-picolyl amine, benzyl amine, KOH and triphenylphosphine (all Sigma-Aldrich) were used as received. The secondary amines required for the yntheses of ligands were obtained by the condensation of aldehyde functionalized pyridine and different amines separately to give the corresponding imines, followed by their subsequent reduction by $NaBH_4$. The potassium salts of the ligands (Fig.10), (N-benzyl-N-methylpyridyl dithiocarbamate (KL1) and bis-(N-methylpyridyl) dithiocarbamate (KL2) were prepared by the reaction of secondary amines, CS_2 and KOH and characterized by IR, and NMR spectroscopy. The experimental details dealing with the elemental (C, H, and N) analysis and recording of IR (KBr), ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and UV-Vis. spectra are the same as described elsewhere.[4,15] Photoluminescent spectra in the solid phase and in dichloromethane solution were recorded on a Perkin-Elmer LS-45 spectrophotometer.

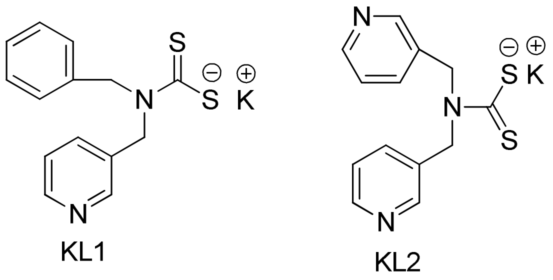

Fig. 10 Structures of dithiocarbamate ligands, as potassium salts, used in this work.

4.2. Synthesis of complexes

Ag (L)}$_4$]$_\infty$ (L = L1, (**1**), L2 (**2**))

To a stirred solution of KL1 (0.312 g, 1mmol) or KL2 (0.313 g, 1mmol) in methanol (15 ml) was added solid $AgClO_4$ (0.207g, 1mmol). In each case the reaction mixture was allowed to stir at room temperature for about 5 h. The solid products thus formed were filtered off and recrystallized from CH_2Cl_2/MeOH, and vacuum-dried over $CaCl_2$ to give light yellow crystals of the complexes **1** and **2**.

1. Yield: (312 mg, 82%). m.p. 205-208 °C. Anal.calcd for $C_{14}H_{13}AgN_2S_2$: C 44.10, H 3.44, N 7.35. Found: C 43.75, H 3.47, N 7.25. IR (KBr, cm^{-1}): 1034 *ν*(C-S), 1425 ν(C=N). ^{1}H NMR (300.40 MHz, $CDCl_3$, ***δ*** ppm): 8.49–8.44 (m, 4H, C_5H_4N), 7.85-7.32 (m, 5H, C_6H_5), 5.22 (s, 4H, $CH_2C_5H_4N$, $CH_2C_6H_5$. ^{13}C{1H} NMR (75.45 MHz, $CDCl_3$, ***δ*** ppm):212.56 (CS_2), 149.15, 148.67, 135.76, 134.05-133.83, 132.79-132.00 (C_5H_4N), 130.12, 128.85–128.63, 127.90–127.55, 123.49 (C_6H_5), 57.15 ($C_5H_5NCH_2$), 54.09 ($C_6H_5CH_2$). UV-Vis. (nujol/dichloromethane, λ max, nm, ε ($M^{-1}cm^{-1}$)): 325, 354, 280(0.230 × 10^5), 345(0.05 × 10^5). σ_{rt} = 7.90×10^{-5} S cm^{-1}, E_a = 0.498 eV.

2. Yield: (328 mg, 86%). m.p. 215-220°C. Anal.calcd for $C_{14}H_{13}AgN_3S_2$: C 42.54, H 3.31, N 10.63. Found: C 42.12, H 3.11, N 10.35. IR (KBr, cm^{-1}): 1020 *ν* (C-S), 1430 ν(C=N). ^{1}H NMR (300.40 MHz, $CDCl_3$, ***δ*** ppm): 8.50 (4H, C_5H_4N), 7.83-7.81 (m, 2H, C_6H_4N), 7.49– 7.35 (m, C5H4N), 5.24 (s, 4H, $CH_2C_5H_4N$). ^{13}C{1H} NMR (75.45 MHz, $CDCl_3$, ***δ*** ppm):212.59 (CS_2), 149.15,148.67, 135.76, 134.05-133.83, 132.79-132.00 (C_5H_4N), 54.73 ($C_5H_5NCH_2$).UV-Vis. (nujol/dichloromethane, λ max, nm, ε ($M^{-1}cm^{-1}$)): 325, 354, 280 (0.454 × 10^5), 345(0.073 × 10^5). σ_{rt} = 8.01×10^{-5} S cm^{-1}, E_a = 0.516eV.

[Ag (L) PPh_3]$_2$(L = L1, (**3**), L2 (**4**))

To a stirred 15 ml CH_2Cl_2 solution of complex **1**(0.190 g, 0.5 mmol) or **2** (0.191g, 0.5 mmol) was added slowly a 5ml solution of PPh_3 (0.132 g, 0.5 mmol) in the same solvent. The reaction mixture was further stirred for 5-6 h. The solvent was removed under vacuum and the residue was treated with ether (5 ml). The precipitate thus obtained was recrystallized from CH_2Cl_2/MeOH, and vacuum-dried to give yellow crystals of **3** and **4**.

3. Yield: (292 mg, 91%). m.p. 195-197 °C. Anal.calcd for $C_{32}H_{28}AgN_2PS_2$: C 59.72, H 4.39, N 4.35. Found: C 59.63, H 4.21, N 4.17. IR (KBr, cm^{-1}): 1074*ν* (C-S), 1419 ν(C=N).^{1}H NMR (300.40 MHz, $CDCl_3$, ***δ*** ppm): 8.491 (m, 4H, C_5H_4N), 7.85-7.83 (m, 5H, C_6H_5), 7.48-7.16 (s, 30H, C_6H_5), 5.22 (s, 4H, -$CH_2C_5H_4N$, $CH_2C_6H_5$). ^{13}C {1H} NMR (75.45 MHz, $CDCl_3$, ***δ*** ppm):212.56 (CS_2), 149.15, 148.67 (C_5H_4N), 135.76, 134.06, 133.83, 132.79, 132.44, 132.04, 130.13, 128.85, 128.72, 128.63, 127.91, 127.55, 123.50 (-C_5H_4N, -C_5H_5), 57815 (-$CH_2C_6H_4N$), 54.09 (-$CH_2C_6H_5$). ^{31}P{1H} (121.50 MHz, $CDCl_3$, ***δ*** ppm): 29.13, 10.23.UV-Vis. (nujol/dichloromethane, λ max, nm, ε ($M^{-1}cm^{-1}$)): 320, 260(0.59 × 10^5), 310(0.130 × 10^5). σ_{rt} = 2.4×10^{-5} S cm^{-1}, E_a = 0.539 eV.

4. Yield: (299 mg, 93%). m.p. 198-202 °C. Anal.calcd for $C_{31}H_{27}AgN_3PS_2$: C 57.77, H 4.22, N 6.52. Found: C 57.53, H 4.05, N 6.36. IR (KBr, cm^{-1}): 1089*ν* (C-S), 1420 ν(C=N). ^{1}H NMR (300.40 MHz, $CDCl_3$, ***δ*** ppm): 8.50 (m, 4H, C_5H_4N), 7.83-7.81 (m, 5H, C_6H_5), 7.49-7.18(s, 30H, C_6H_5), 5.24 (s, 4H, -$CH_2C_5H_4N$). ^{13}C{1H} NMR (75.45 MHz, $CDCl_3$, ***δ*** ppm):212.59 (CS_2), 149.09, 149.03 (C_5H_4N), 135.65, 133.97, 133.75, 132.37, 132.11, 131.98, 131.90, 131.87, 131.51, 130.25, 128.88, 128.76, 128.53, 128.37, 123.59 (-C_5H_4N, -C_6H_5), 54.73 (-$CH_2C_6H_4N$). ^{31}P{1H} (121.50 MHz, $CDCl_3$, ***δ*** ppm): 43.52, 24.43. UV-Vis. (nujol/dichloromethane, λ max, nm, ε ($M^{-1}cm^{-1}$)): 320, 260(0.53 × 10^5) 310(0.101 × 10^5). σ_{rt} = 1.3×10^{-5} S cm^{-1}, E_a = 0.643eV.

Table 3 Crystallographic parameters for the complexes **1-4**.

	1	**2**	**3**	**4**
Formula	$C_{14}H_{13}AgN_2S_2$	$C_{13}H_{12}AgN_3S_2$	$C_{32}H_{28}AgN_2P_1S_2$	$C_{31}H_{27}AgN_3P_1S_2$
Fw	381.25	382.25	643.52	644.52
crystal system	tetragonal	tetragonal	monoclinic	monoclinic
space group	I-4	I-4	$P2_1/c$	$P2_1/c$
a Å	22.126(4)	22.201(4)	9.3502(5)	9.3011(3)
b Å	22.126(4)	22.201(4)	17.4738(10)	17.7718(7)
c Å	6.012(2)	5.971(2)	17.3742(11)	17.3865(7)
β (deg)	(90)	(90)	90.395(5)	90.886(3)
V (Å^3)	2943.4(13)	2942.7(12)	2838.6(3)	2873.6(2)
Z	8	8	2	2
T (K)	293(2)	293(2)	150(2)	293(2)
ρcalcd(g cm-3)	1.721	1.726	1.506	1.490
F(000)	1520	1520	1312	1312
Reflectionsns collected	4178	4069	16299	22740
Independent reflections	2742	2835	7925	6479
Reflections with I>2σ(I)	1277	1421	6090	4208
Final *R* indices [*I* >2*r*(*I*)] R1^a, wR2^b	0.0921, 0.2430	0.0802, 0.1912	0.0461, 0.0846	0.0550, 0.0911
R indices all data) R1^a, wR2^b	0.1730, 0.3107	0.1559, 0.2383	0.0694, 0.0920	0.1006, 0.1023
GOF	0.867	1.009	1.016	1.014

R1 = Σ ‖F_0│-│F_c‖/ Σ │F_0│. R_2 = {[Σ*w* (F_0^2 – Fc^2)/ Σ*w* (F_0^2)^2] }1/2, *w* = 1/ [σ2 (F_0^2) + $(xP)^2$], where P = (F_0^2 + 2Fc^2)/3

4.3. X-ray crystallography

Intensity data for yellowish crystals of **1-4** were collected on Oxford Diffraction X-calibur CCD diffractometers using Mo-Kα radiation (λ = 0.71073 Å), **1, 2** and **4** at 293K and **3** at 150K. Data reduction for **1**–**4** was carried out by the

CrysAlisprogram.[23] The structures were solved by direct methods using SHELXS-97 and refined on F2 by full-matrix least-squares technique using SHELXL-97.[24] Non hydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically fixed with thermal parameters equivalent to 1.2 times that of the atom to which they were bonded. Diagrams for all complexes were prepared using ORTEP.[25]

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Notes and references

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†Electronic Supplementary Information (ESI) available: [ORTEP Diagram of **2** and **3**,^{31}P NMR Spectra of complexes **3** and **4**, Bond Lengths (Å) and Angles (°) for complexes **3** and **4**, Photophysical data of complexes, TGA results for the complexes (**2**, **4**)].

CCDC- 934751(**1**), 934752(**2**), 989805(**3**) and 934753(**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif

(1) (a) D. Coucouvanis, *Prog. Inorg. Chem*. 1979, **26**, 301-469; (b) G. Hogarth, *Prog. Inorg.Chem*. 2005, **53**, 71-561; (c) E. R. T. Tiekink and I. Haiduc, *Prog. Inorg. Chem*. 2005, **54**, 127-319; (d) P. J. Heard, *Prog.Inorg.Chem.* 2005, **53**, 268; (e) J. Cookson and P. D. Beer, *DaltonTrans*. 2007, 1459-1472; (f) Y. S. Tan, A. L. Sudlow,K. C. Molloy, Y. Morishima, K. Fujisawa, W. J. Jackson, W. Henderson, S. N. B. A. Halim and S. W. Ng, E. R.T. Tiekink, *Cryst.GrowthDes*. 2013, **13**, 3046–3056; (g) O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed. Engl.* 2000, **39**, 135; (h) M. E. Padilla-Tosta, O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed. Engl.* 2001, **40**, 4235 (i) Y. Yan, S. K. Kumar, H. Yu, S. Ramishetty, L. W. Deng, H. Leaf and D. Huang, *J. Am. Chem. Soc.*2013, **135**, 5312.

(2) (a) P. Cassoux and L.Valade, *Inorganic Materials*, 2nd ed: D. W. O' Hare Bruce Bruce, JohnWiley & Sons: Chichester U.K. 1996, 1;(b) A. T. Coomber, D. Beljonne, R. H. Friend, J. L. Bredas, A. Charlton, N. Robertson, A. E. Undrhill, M. Kurmoo and P. Day, Intermolecular interactions in the ferromagnetic $NH_4Ni(mnt)_2{\cdot}H_2O$. *Nature (London)*, 1996, **380**, 144.

(3) (a) D. Fan, M. Afzaal, M. A. Mallik, C. Q. Nguyen, P. O'Brien and P. J. Thomas, *Coord.Chem.Rev*. 2007, **251**, 1878; (b) Y. Zhao, W. Perez-Segarra, Q. Shi and A. Wei, *J. Am. Chem. Soc.*2005, **127**, 7328-7329; (c) S. Naeem, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Organometallics* 2010, **29**, 2547-2556; (d) J.-G. Kang, J.-S. Shin, D.-H. Cho, Y.-K. Jeong, C. Park, S.-F. Soh, C. S. Lai and E. R. T. Tiekink, *Cryst.GrowthDes*. 2010, **10,** 1247-1256.

(4) (a) A. Kumar, R. Chauhan, K. C. Molloy, G. K. Köhn, L. Bahadur and N. Singh, *Chem. Eur. J*. 2010, **16**, 4307-4314; (b) B. Singh, M. G. B. Drew, G. K.-Kohn, K. C. Molloy and N. Singh, *Dalton Trans.*, 2011, **40**, 623–631; (c)G. Rajput, V. Singh, S. K. Singh, L. B. Prasad, M. G. B. Drew and N. Singh, *Eur. J. Inorg. Chem.,* 2012, **24**, 3885; (d) V. Singh, R. Chauhan, A. N. Gupta, V. Kumar, M. G. B. Drew, L. Bahadur and N. Singh *Dalton Trans.*, 2014, **43**, 4752-4761.

(5) (a) F. Sabin, C. K. Ryu,P. C. Ford, and A. Vogler, *Inorg. Chem.*1992**,** **31**, 1941-1945; (*b*) R. Hesse and L. Nilson, *Acta Chem. Scand.*, 1969, **23**, 825–845; (*c*) X. Yin, M.-B. Xie, W.-G. Zhang, J. Fan and M. Zeller, *ActaCrystallogr. Sect. E: Struct. Rep. Online*, 2007, **63**, m2063–m2064; (*d*) Y.-W. Song, Z. Yu and Q. -F. Zhaang, *ActaCrystallogr. Sect. C:* 2006**, 62***,* m214-m216; (e) W.-G. Zhang, Y. Zhong, M.-Y. Tan, W.-S. Liu and Ch.-Y. Su, *Chin. J. Chem.*, 2002, **20**, 420–423; (*f*) X. Yin, M.-B. Xie, W.-G. Zhang and J. Fan. *ActaCrystallogr. Sect. E: Struct. Rep. Online*, 2007, **63**, m2273; (g) H. Dietrich, W. Storck and G. Manecke, *J. Chem. Soc., Chem. Commun.*1982, 1036–1037; (*h*) C. W. Liu, J. T. Pitts and J. P. Fackler Jr., *Polyhedron* 1997, **22**, 3899–3909; (i) M. C. Gimeno, P. G. Jones, A. Laguna and C. Sarroca, *Polyhedron* 1998, **17**, 3681-3688; (j) A. M. M. Lanfredi, F. Ugozzoli, A. Camus and N. Marsich, *J. Chem.Crystogr.* 1995*,* **25***,* 37-41; (k) I. Ara, F. E. Bahij and M. Lachkar, *ActaCryst.*2003**, C59,** m265-m267; (l) M. G. B. Drew, R. J. Hobson, P. P. E. Mumba and D. A.. Rice, *Inorg. Chim. Acta.*1988, **142**,301; (m) X. Jin, X. Xie, H. Qian, K. Tang, C. Liu, X. Wang and Q. Gong, *Chem. Commun.*2002, 600-601.

(6) E. J. Mensforth, M. R. Hill, S. R. Batten, *Inorg. Chim.Acta*, 2013**,** **403**, 9–24.

(7) (a) A. H. Othman, H.-K. Fun and K. Sivakumar, *ActaCrystallogr., Sect. C*1996, **52**, 843; (b) M. C. Gimeno, P. G. Jones, A. Laguna and C. Sarroca, *Polyhedron*1998, **17**, 3681;(c) C. D. Nicola, J.Ngoune, Effendy, C. Pettinari, B. W. Skelton and A. H. White, *Inorg. Chim.Acta*,2007,**360**, 2935–2943; (d) M. G. B. Drew, R. J. Hobson, P. P. E. M. Mumba andD.A.. Rice, *Chem. Soc., Dalton. Trans.*1987*,* 1569*;* (e)W. P. Su, M. C. Hong, R. Cao, J. T.Chen, D. X.Wu, H. Q. Liu, J. X. Lu, *Inorg. Chim. Acta*1998, **267**, 313; (f)C. W.Liu, B. J.Liaw, J. C.Wang, T. C. Keng, *Inorg. Chem.* 2000, ***39***, 1329.

(8) J. Vicente, P. G. lez-Herrero, Y. G. –S. Nchez and P. G. Jones, *Inorg. Chem.*2009, **48**, 2060-2071.

(9) (a) M. T. Salgado, K. L. Bacher, M. J. Stillman, *J. Biol. Inorg. Chem.* 2007, **12**, 294; (b) K. Fujisawa, S. Imai, S. Suzuki, Y. Moro-oka, Y. Miyashita,Y. Yamada, K. i. Okamoto, *J. Inorg. Biochem.* 2000, **82**, 229; (c) B. Krebs, G. Henkel, *Angew. Chem., Int. Ed.* 1991, **30**, 769.

(10) (a) M. R. Branham, A. D. Douglas, A. J. Mills, J. B. Tracy, P. S.White,R. W. Murray, *Langmuir,*2006, **22**, 11376; (b) D. Fenske, C. Persau, S. Dehnen, C. E. Anson, *Angew. Chem., Int. Ed.* 2004, **43**, 305.

(11) (a) Y.-B. Chen, L. Chen, L.-M. Wu, *Inorg. Chem.* 2005, **44**, 9817; (b) G. Viau, J.-Y. Piquemal, M. Esparrica, D. Ung, N. Chakroune, F. Warmont, F. Fievet, *Chem. Commun.* 2003, 2216.

(12) (a) C. A. Bignozzi, R. Argazzi and C. J. Kleverlaan, *Chem. Soc. Rev.*2000, **29**, 87; (b) D. R. McMillin and K. M. McNett, *Chem. Rev.*1998, **98**, 1201-1219; (c) C. Kutal, *Coord. Chem. Rev.*1990, **99**, 213-252; (d) E. Szlyk, R. Kucharek, I. Szymanska and L. Pazderski, *Polyhedron* 2003, **22**, 3389-3393; (e) E. Fournier, F. Lebrun, M. Drouin, A. Decken and P.D. Harvey, *Inorg. Chem.*2004, **43**, 3127-3135; (f) A. Kaltzoglou, P. J. Cox and P. Aslanidis, *Inorg. Chim. Acta* 2005, **358**, 3048-3056; (g) P. Aslanidis, P. J. Cox, S. Divanidis and P. Karagiannidis, *Inorg. Chim. Acta* 2005, **357**, 1063-1076.

(13) (a) J.-H. Yang, S. -L. Zheng, X. -L. Yu and X. -M. Chen, *Cryst. Growth Des.*2004**,** **4**, 831-836. (b) J. G. Haasnoot, *Coord. Chem. Rev.*2000, **131**, 200-202; (c) V. W.-W. Yam, *Acc. Chem. Res*. 2002, **35**, 555; (d) V. J. Catalano, H. M. Kar and J. Garmas, *Angew. Chem., Int. Ed.* 1999, **38**, 1979; (e) C. -M. Che, Z. Mao, V. M. Miskowski, M. -C. Tse, C.-K. Chan, K. -K. Cheung, D. L. Phillips and K. -H. Leung, *Angew. Chem., Int. Ed.* 2000, **39**, 4084; (f) M. -L. Tong, J. -X. Shi and X. -M. Chen, *New J. Chem.* 2002, **26**, 814; (g) A. Barbieri, G. Accorsi and N. Armaroli, Chem. Commun., 2008, 2185–2193; (h) E. Barreiro, J. S. Casas, M. D. Couce, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, A. Sánchez, J. Sordo, J. M. Varela and E. M. V. López, *Eur. J. Inorg. Chem.* 2011, 1322-1332.

(14) (a) M. A. Malik, M. Motevalli, T. Saeed and P. O'Brien, *Adv. Mater*, 1993, **5**, 653-654; (b) P. O'Brien, J. R. Walsh, I. M. Watson, M. Motevalli, L. Henriksen, J.Chem.Soc., Dalton Trans. 1996, 2491.

(15) (a) V. Singh, A. Kumar, A. Prasad, G. Rajput, M. G. B. Drew and N. Singh, *CrystEngComm*. 2011, **13**, 6817–6826; (b) G. Rajput, M. K. Yadav, T. S. Thakur, M. G.B. Drew and N. Singh. Polyhedron, 2014, **69***,* 225–233.

(16) (a) A. F. Wells, *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: London, 1990, 1015; (b) M. Jansen, *Angew. Chem., Int. Ed. Engl.*1987, **26**, 1098.

(17) (a) A. Bondi, *J. Phys. Chem.* 1964, ***68***, 441. (b) M. Jansen, *Angew. Chem., Int. Ed. Engl.* 1987, ***26*****,** 1098.

(18) (a) D. Cardell, G. Hogarth, S. Faulkner, *Inorg. Chim.Acta*, 2006**,** **359**, 1321-1324; (b) R. Hesse, Ark. Kemi, 1962, **20**, 481.

(19) A. W. Addison, T. N. Rao, J. Reedijk, j. van Rijn, G. C. Verschoor, J.Chem.Soc.Dalton Trans., 1984 1349-1356.

(20)C. -M. Che, M. -C. Tse, M. C. W. Chan, K. -K. Cheung, D. L. Phillips and K. -H. Leung, *J. Am. Chem. Soc.* 2000, **122***,* 2464-2468.

(21) B. Liaw, S**.** W. Orchard and C. Kutal, Inorg. *Chem.*1988**,** **27***,* 1311-1316.

(22) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J.Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J Austin, R. Cammi, C. Pomelli, J . W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D.Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A.Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, U. S. A. 2004**.**

(23) *CrysAlis RED program*, Oxford Diffraction, Abingdon, 2008.

(24) SHELXS97 and SHELXl97, Programs for Crystallographic Solution and Refinement: G. M. Sheldrick, *ActaCrystallogr.Sect. A,* 2008, **64**, 112.

(25) M. N. Burnett, C. K. Johnson, *ORTEP-III*, Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-6895, Oak Ridge National Laboratory, OakRidge, USA, 1996.

Table of Content

Four silver(I) homo- and heteroleptic pyridyl functionalised dithiocarbamate complexes have been synthesized and characterized by microanalysis. **1** and **2** are tetranuclear cluster-based coordination polymers whereas **3** and **4** are dinuclear. All complexes are weakly conducting and strongly luminish in solid phase.