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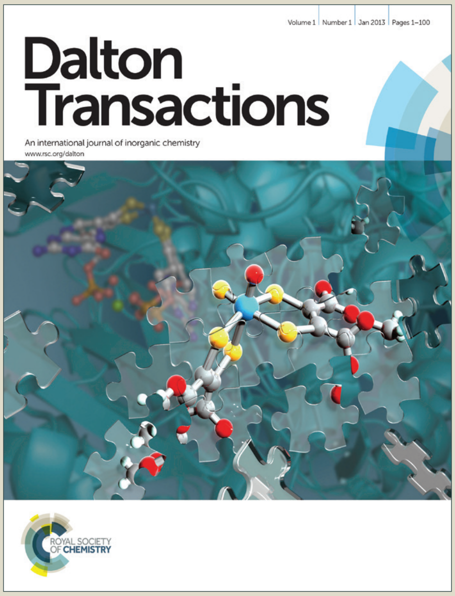

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Intermolecular Tl…H-C anagostic interactions in luminescent pyridyl functionalized thallium (I) dithiocarbamates

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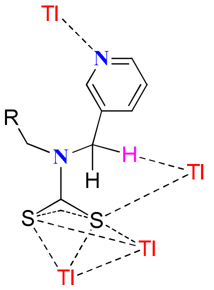
Crystal structures of novel pyridyl functionalised $[Tl(L)]_{\infty}$ (L = (N-benzyl-N-methylpyridyl) dithiocarbamate(L1) 1, bis(N-methylpyridyl) dithiocarbamate(L2) 2, (N-methylpiperonyl-N-methylpyridyl) dithiocarbamate(L3) 3, (N ferrocenyl-N-methylpyridyl) dithiocarbamate(L4) 4) complexes revealed rare intermolecular C–H···Tl anagostic and C-S...Tl interactions forming a six-membered chelate ring about the metal center which have been assessed by DFT calculations. The strong thallophilic bonding is responsible for the strong luminescent characteristics of the complexes in the solid phase.

Introduction

In the past few years there has been a phenomenal growth of interest in the general field of metal dithiolate chemistry.[1-8] Yet compared to transition metal dithiocarbamates, the main group counter parts including those of thallium (I) have not gained much attention because of the complexity of coordination numbers and geometries influenced by the relativistic effect of the stereochemically active $6s^2$ lone pair on metal centers.[9]
Considerable efforts have been focussed on the less common bonding interactions involving the transition metals (M) and a C-H bond on the ligand fragments[10] in organometallic and occasionally in dithio complexes[11] due to their possible implications in organic synthesis via C-H bond activation[12] and supramolecular synthons.[10e] Based on the geometrical dimensions and structural features these C-H…M interactions have been broadly classified into (i) agostic, (ii) anagostic and (iii) hydrogen bonding interactions.[10-12] The agostic bonds are formed by electron deficient early transition metal ions whereas the anagostic and hydrogen bonding interactions are stabilised by electron rich late group 10, d^8 or even d^9 complexes. By contrast, reports on the existence of C-H…Tl interactions are rare,[13] and therefore a subject of intense investigation. Given these facts and in order to gain more insights into the structure and bonding of such complexes it was considered worthwhile to investigate the nature of Tl...H-C interactions in novel Tl(I) pyridyl functionalised dithiocarbamate complexes (**1-4**). The pyridyl functionalised dithiocarbamate ligands used in the present study can exhibit a variety of coordination modes in these compounds.



The judicious choice of these metal-ligand systems is due to the following considerations: (i) the pyridyl functionalised dithiocarbamate ligands have both distinctly soft sulphur and hard Py(N) donor atoms which may facilitate the formation of mono- and polynuclear complexes with Tl(I) having preferences for both the hard and soft donors: (ii) the steric bulk of the substituents on the dithiocarbamate unit and pronounced relativistic effects of Tl(I) with a closed subshell, $6s^2$, thereby contracting the 6s- orbital which makes the metal ion more electronegative and therefore more likely to induce metal assisted Tl...H-C interactions: (iii) the significant Tl...Tl interactions may enhance luminescent characteristic of the complexes (iv) also the conformational rigidity due to interactions of Tl with the Py(N) may modify the luminescent properties of the complexes and (v) different donor atoms on the ligand substituents may be involved in the formation of non-covalent interactions organising supramolecular structures. The anagostic and thallophilic interactions observed in complexes **1-4** have been assessed by theoretical calculations and described here. The correlation between structure and luminescent properties has been established.

Experimental section

Materials and General Methods

All reactions were carried out in the open at ambient temperature. The solvents were purified by standard procedures. $TlNO_3$ and 3-pyridine carboxaldehyde, 3-picolyl amine, piperonal, ferrocenealdehyde (all Sigma-Aldrich) were used as received. The secondary amines required for the synthesis of ligands were obtained by the condensation of pyridine functionalized amines and different aldehyde separately to give the corresponding imines, followed by their subsequent reduction with $NaBH_4$. The potassium salt of the ligands (Fig. 1), (N-benzyl-N-methylpyridyl) dithiocarbamate (K**L1**), bis (N-methylpyridyl) dithiocarbamate (K**L2**), and (N-ferrocenyl-N-methylpyridyl) dithiocarbamate(K**L4**) were obtainedas solids and (N-methylpiperonyl-N-methylpyridyl) dithiocarbamate(K**L3**), in solution were synthesised by the reaction of the appropriate secondary amine with CS_2 and KOH and characterized spectroscopically. The experimental details pertaining to the elemental (C, H, N) analysis and recording of IR (KBr), ^{1}H and ^{13}CNMR, UV-Vis. and photoluminescent spectra are the same as described elsewhere.[14a, b]

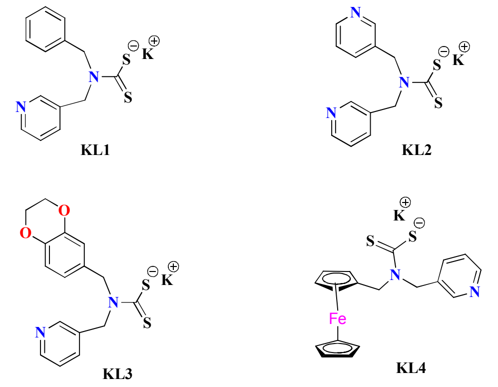


Fig. 1 Structures of the potassium salts of the dithiocarbamate ligands used in this work.

Synthesis and characterization of complexes

[Tl(L)] (L = L1 (**1**), L2 (**2**), L3 (**3**) and L4 (**4**))

Complexes **1-4** were prepared adopting following this general procedure. To a 15 ml stirred methanol/water(80/20v/v) solution of the ligands, KL1(0.312 g, 1 mmol), KL2(0.313 g, 1 mmol), KL3(0.370g, 1.0 mmol) or KL4(0.450 g, 1.0 mmol) was added slowly to a 5 ml solutionof $TlNO_3$ (0.266 g, 1.00 mmol) in the same solvent mixture. In each case the reaction mixture was stirred for an additional 6 h yielding precipates with colours ranging from cream to yellow .The solid products thus formed were filtered off and washed with the same solvent mixture followed by diethyl ether. The compounds were recrystallized in dichloromethane/methanol.

Characterization data

1. Yield: (0.41g, 86%). m.p. 270-273^{0}C, Anal. Calcd for $C_{14}H_{13}N_2S_2Tl$ (478.03): C 35.41, H 3.01, N 6.07. Found: C 34.85, H 3.15, N 5.75.IR (KBr, cm^{-1}): 1385 υ(C=N), 993 υ(C-S). ^{1}H NMR (300.40 MHz, DMSO $d_{6,}$ δ ppm): 8.427-8.426 (m, 2H, C_5H_5N), 7.74-7.72 (m, 5 H, -C_6H_5), 7.31 (m, 2H, C_5H_4N), 5.2 (s, 4H,-$CH_2C_5H_4N$, -CH_2Ar). ^{13}C NMR (75.45 MHz DMSO, DMSO d_6 δ ppm): 210 (CS_2), 148.93, 148.14, 137.20, 135.25, 132.92 (NC_5H_4), 128.30, 127.60, 126.99, 123.35 (-C_6H_5), 59.67 (-$CH_2C_5H_4N$), 57.69 (-CH_2Ar).UV-Vis. nujol (CH_2Cl_2 : Methanol) λ max, nm: 305, 370 (270, 315).

2. Yield: (0.426 g, 89%). m.p. 281-285^{0}C, Anal. Calcd for $C_{13}H_{12}N_3S_2Tl$ (478.75): C 32.85, H 2.79, N 8.93. Found: C 32.45, H 2.75, N 8.55. IR (KBr, cm^{-1}): 1385ν(C=N), 992ν(C–S). ^{1}H NMR (300.40 MHz, DMSO d^6, δ ppm): 8.50-8.41 (m, 4H, C_5H_4N), 7.74-7.72 (m, 4H, -C_5H_5N), 5.22 (s, 4H, -$CH_2C_5H_5N$), ^{13}C{^{1}H} NMR (75.45 MHz, DMSO $d_{6,}$ δ ppm): 211.50 (CS_2), 148.99, 148.27, 135.35, 132.76,123.39 (NC_5H_4), 51.69(-CH_2C_5H). UV-Vis. nujol (CH_2Cl_2:Methanol) λ max, nm : 290, 346, 375 (272, 316).

3. Yield: (0.42g, 81%). m.p. 274-276^{0}C, Anal. Calcd for $C_{15}H_{13}N_2O_2S_2Tl$ (521.76): C 34.53, H 2.51, N 5.37. Found: C 34.23, H 2.56, N 5.15. IR(KBr, cm^{-1}): 1388ν(C=N), 1002ν(C-S). ^{1}H NMR (300.40 MHz, DMSO d_6, δ ppm): 8.46 (2H, m, –C_5H_5N), 7.68-7.31 (m, 3H, C_5H_5N), 6.85-6.78 (m, 3H, $C_6H_3CH_2CH_2O_2$), 5.13 (m, 2H, -$CH_2C_5H_4N$), 5.06 (m, 2H, -$CH_2C_6H_3CH_2CH_2O_2$), 4.19 (m, 4H, -$C_2H_4C_6H_3O_2$). ^{13}C NMR (75.45 MHz, DMSO d_6, δ ppm) 210.61 (CS_2), 148.86-142.58 (NC_5H_4), 135.25-116.42 (-$C_6H_3CH_2CH_2$O2), 64.04 (-$C_4H_4O_2C_6H_3$), 53.00 (-$CH_2C_5H_4N$) and 50.87(-$CH_2C_7H_5O_2$). UV-Vis. nujol (CH_2Cl_2:Methanol) λ max, nm: 275, 320, 375 (273, 320).

4. Yield: (0.468 g, 80%). m.p. 271-273^{0}C, Anal. Calcd for $C_{18}H_{17}FeN_2S_2Tl$ (585.68): C 36.91, H 2.93, N 4.78. Found: C 36.34, H 2.98, N 4.54. IR(KBr, cm^{-1}): 1386ν(C=N), 992 ν(C-S). ^{1}H NMR (300.40 MHz, DMSO d^6, δ ppm): 8.54-8.50 (2H, m, -C_5H_5N), 7.65-7.63 (3H, m,-C_5H_5N), 5.25 (2H, m, -$CH_2C_6H_5N$), 4.99 (2H, m,-CH_2Fc), 4.36 (4H, m, C_5H_5), 4.15 (s, 5H, Fc). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm) 205.5 (CS_2), 149.1-132.2 (-C_5H_5N), 123.5 (C_5H_5), 51.8 (-$CH_2NC_5H_5$), 49.7 (-CH_2Fc). UV-Vis. nujol (CH_2Cl_2:Methanol) λ max, nm: 295, 340, 465 (270, 315).

Results and discussion

Treatment of a methanol/water solution of the $TlNO_3$ with potassium salt of the ligands KL1- KL4, (Fig. 1) in equimolar ratio yielded the homoleptic complexes **1-4**, in good yield. The compounds are air and moisture stable and melt in the 270-287 °C temperature range. These complexes have been characterized by microanalysis and their structures have been investigated by X-ray crystallography. The ligand framework and crystal packing effect facilitating metal assisted intermolecular, C-H···Tl anagostic, Tl…S, Tl…N and Tl…Tl interactions have been investigated. DFT calculations have been performed to support the observed bonding in the complexes. Their solid phase and solution luminescent properties have been studied and correlated with their structures.

Spectroscopy

All the complexes showed diagnostic, υ(C-N) and υ(C-S) vibrations in the IR spectra for the dithiocarbamate ligands. ^1H and ^{13}C NMR spectra of the complexes display characteristic resonances for different functionalities of the ligands; the ^1H resonances integrate well to the corresponding protons. A somewhat low downfield shift δ of 0.008-0.124 ppm in the ^1H NMR spectra for the methylene proton in the complexes **1**, **2** and **4** than the C-H proton of uncoordinated ligands showed that the anagostic interactions as elucidated by X-ray crystallography (vide infra) are only partially retained in DMSO- d_6 solution at room temperature. In the ^{13}C NMR spectra, a perceptible downfield shift of δ 6-12 ppm for the NCS_2 carbon in the complexes as compared to the potassium salts of the ligands indicates M-S bonding.

Crystallography

Single crystals of **1-4** were obtained from dichloromethane-methanol solution within 15-20 days. Intensity data for **1-3** were collected at 293 K and data for**4** at 150 Kon an Oxford Diffraction X-calibur CCD diffractometer. Data analyses were carried out with the CrysAlisprogram.[15] The structures were solved by direct methods using SHELXS-97 and refined on F^2 by full matrix least squares technique using SHELXL-97.[16] 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, Mercury and Diamond software.[17] The cif files have been deposited at the Cambridge Crystallographic Data Centre with reference numbers CCDC No. 1031503, 1031504, 1031505 and 1031506 for **1, 2, 3** and **4** respectively.

Theoretical calculations

All calculations were carried out using the Gaussian 03 program.[18] Structures were optimized using the B3LYP density functional together with basis sets LANL2DZ for Tl, 6-31+G* for S and 6-31G for the remaining atoms. Starting models were taken from the crystal structures but with hydrogen atoms given theoretical positions. Single point calculations were primarily carried out but geometry optimisation was used for selected models.

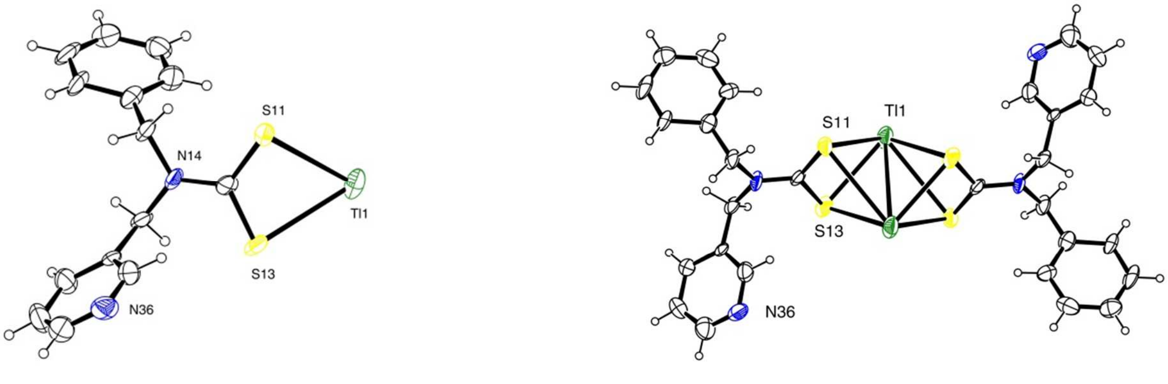
Crystal structures

Single crystals of **1-4** were obtained by slow evaporation of a solution of compound inCH_2Cl_2/methanol. The crystallographic details and selected bond lengths and angles are listed in Table 1 and Table S1 respectively.

1 and **2** are isomorphous. While **3** and **4** are not, their essential structural features are virtually similar but differ subtly with regard to crystal packing arrangements and supramolecular topologies. In the isomorphous complexes Tl(1)-S(13), Tl(1)-S(11) contacts are 2.961(4)Å, 3.051(3) Å in **1** and 2.976(4), 3.054(3)Å in **2,** values which are in good agreement with distances found in structures of previously determined thallium (I) dithio complexes.[19] The chelating S(11)-Tl(1)-S(13) angles are 58.75(9), 58.83(8)°.

In all four structures, the asymmetric unit contains only one formula unit of TlL in which the Tl atom is chelated by the dithiocarbamate group with metal-sulphur distances in the range 2.961(4)-3.072(2)Å Å and bite angles of 57.98(5)-58.92(16)°. **1** and **2** are isomorphous and form a dimer over a centre of symmetry so that the metal is bonded to an additional chelate ring via S(11) and S(13) (1-x, -y, 1-z) at distances of 3.333(3), 3.218(4) Å in **1** and 3.387(3), 3.212(4) Å in **2**. Here the bite angle is somewhat smaller at 53.50(8), 53.27(8)° concomitant with the longer bond lengths. Because the two sulphur atoms are essentially simultaneously chelating two Tl(1) atoms both four membered TlS_2C rings are folded so that Tl(1) is 1.618(1), 1.623(2) Å and Tl(1)(1-x, -y, 1-z) 2.152(1), 2.191(2) Å from the S_2C plane. There is also a Tl(1)…Tl(1) (1-x, -y, 1-z) interaction at 3.771(2), 3.817(1)Å.[20] The structures of the monomer and dimer for **1** are shown in Figure 2 (a) and (b) respectively. The dimers are then linked by further bonds to form a two-dimensional polymeric structure. Each independent Tl(1) is bonded to three atoms from two different adjacent molecules, a pyridine nitrogen atom N(36) (1/2-x, 1/2+y, z) at 2.980(12), 2.921(13) Å; a further sulphur atom S(13) (1/2+x, 1/2-y,1-z) at 3.500(4), 3.478(3) Å and a methylene hydrogen atom H(31A) (1/2+x, 1/2-y, 1-z) from the same molecule at 3.06, 3.07 Å. The bonding of this hydrogen atom merits further discussion.

In previous work we have identified M…H interactions in structures of $M(bidentate)_2$[11b-e] where M = Ni, Pd, Pt and the bidentate ligand is dithiocarbamate. In those examples the hydrogen atoms from methylene groups occupy axial positions with the two bidentate ligands in the equatorial plane. However in the present case the arrangement is more complicated as the hydrogen atom is directed towards the metal atom with C-H-Tl angles of 149, 153° in **1** and **2**. However the H-Tl-CG angle (CG = centre of gravity of the four membered TlS_2C ring) is 152.2, 148.0° to the ring at x, y, z but 79.6, 77.6° to the second and more weakly bound ring (1-x, -y, 1-z) across the centre of symmetry. It is clear that the hydrogen atom occupies a coordination site as the closest donor atom is the S(13) atom from the same molecule at 2.54, 2.52 Å from the metal with S-Tl-H angles of 45.2, 44.6^{o}. Indeed these two interactions between Tl(1) and S(13), H(31A) could well be described as involving a six-membered chelate ring involving S(13)-C(12)-N(14)-C(31)-H(31A) bonding to the metal (Fig. 3).



(a) **(b)**

Fig. 2 (a) Asymmetric unit in the structure of **1** and (b) The centrosymmetric dimer in **1**. The structure of **2** is isomorphous.

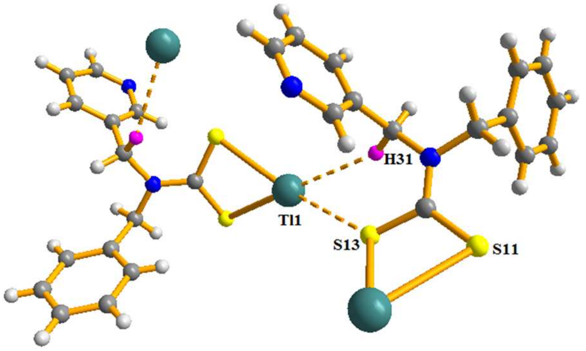


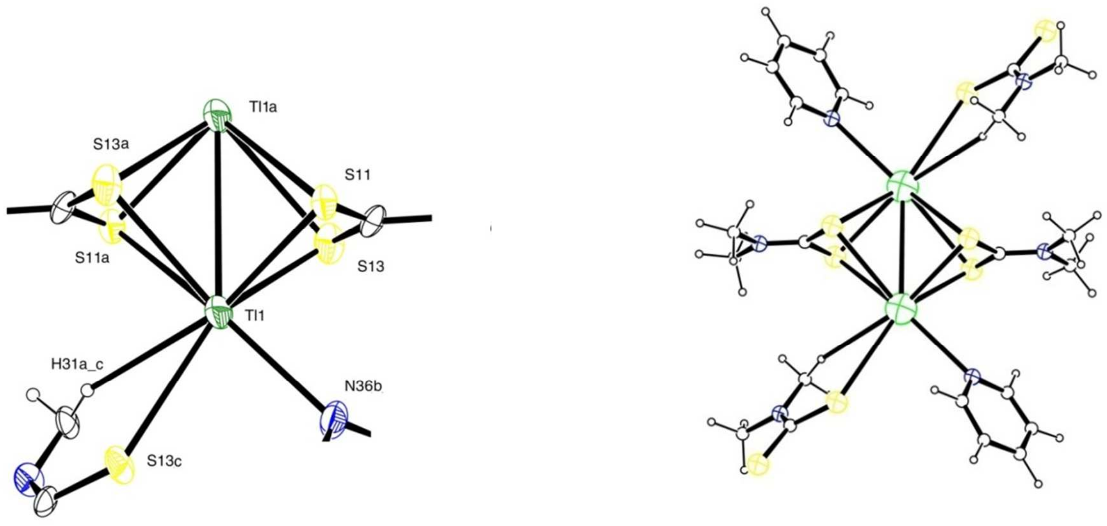
Fig. 3 The formation of the chelate ring around the metal in **1** with H and S donor atoms thus showing the anagostic interaction.

It is to be noted that Tl···H–C distances in the range 3.06-3.34 Å observed in these complexes are somewhat longer than values found in previous work with d^{8}, Ni^{+2}, Pd^{+2} and Pt^{+2} metal ions[11b-e] in the range 2.61-2.89 Å but this can be attributed to the larger size of the Tl(I) ion. These values are close to the sum of the van der Walls radii 3.05 Å for the former and 2.72-2.81 Å for the later complexes. It seems likely for **1** and **2** that the electronic and steric requirements of the pyridine substituent on the nitrogen atom of the dithiocarbamate unit, and crystal packing effects enable the orientation of the methylene protons on the adjacent molecules into the close proximity of the metal coordination environment to provide these unprecedented intermolecular, anagostic C–H···Tl interactions. In addition the formation of this bond is surely facilitated by the formation of the chelating six-membered ring with the sulphur atom. The importance of packing effects is confirmed by the fact that these interactions do not persist in solution (vide supra), but this fact does not negate the importance of the Tl…H-C interaction. Figure 3 clearly shows that other orientations of the N-CH$_2$-C$_5$H$_4$N moiety are possible that would not lead to a short Tl…H-C interaction.

With these additional bonds, the metal can best be considered as eight-co-ordinate as shown in Figure 4. The geometry can be defined as of a 1:4:3 Tl: (S,S), (S,S): N,(S,H) type by considering Tl-Tl bond as the axis. Passing down this axis from the apical Tl atom, the four sulphur atoms from two bidentate ligands form an plane. It will be noted that the Tl-Tl-S angles in both structures fall in the range 49.2(1)-57.8(1)^{o}. Then follows the central metal and finally the three monodentate donor atoms N(36), S(13) and H(31a) in a tripod shape. It seems likely that any active stereochemical lone pair would be located at this end of the molecule to complete a 1:4:4 geometry (Fig. 4).

These bonds from the metal ions in the [Tl$_2$L$_2$] dimer to nitrogen, hydrogen and sulphur lead to the formation of a two-dimensional polymer as shown in Figure S3.

While **3** and **4** are not isomorphous with **1** and **2**, their structures are similar. The bond lengths to sulphur are very similar to those found in **1** and **2** as indeed are those to the nitrogen (Fig. S4).



(a) (b)

Fig. 4 (a) The coordination sphere around Tl(1) in **1** showing eight-co-ordination with a 1:4:3 Tl: (S,S),(S,S): N,(S,H) configuration. Symmetry elements are denoted by a: 1-x, -y, 1-z; b: 1/2-x, 1/2+y, z; c: 1/2+x, 1/2-y, 1-z. The coordination spheres in **2**, **3** and **4** are similar. (b) The model used for theoretical calculations.

The dimensions of the chelate ring involving H(31A) and S(13) are however of interest. The Tl-H anagostic interactions are slightly longer than in **1** and **2** but the concomitant Tl-S and Tl-Tl distances are slightly shorter. Thus in **3** the Tl-H distance is 3.24Å and the Tl-H-C angle 148^{o} while values in **4** are 3.34Å and 152^{o}. The Tl-S(13) distances are 3.431(2), 3.356(2) Å compared to 3.500(4), 3.478(3) Å in **1** and **2**.

It is possible that these anagostic interactions in **3** and **4** are rather weaker than in **1** and **2,** due to steric restrictions of bulky piperonyl and ferrocenyl groups which might hinder appropiate orientation of the methylene protons towards the metal. To the best of our knowledge structures **1-4** are the first examples presenting intermolecular anagostic interactions in the thallium(I) complexes.

The supramolecular structures are sustained through C-H...π in **1**, C-H…N(Py) in **2,** C-H…S and C-H…O in **3** and C-H...π and C-H…S interactions in **4** (Fig. S5)**.**

Theoretical Calculations

The fact that all four complexes have the same complicated polymeric structure despite only **1** and **2** being isomorphous was remarkable. Clearly the formation of the [Tl$_2$L$_2$] dimer and then the subsequent formation of a polymer via the formation of Tl-N bonds and an additional chelate ring involving S and H donor atoms was a particularly stable arrangement. Single point DFT calculations were carried out to investigate how the various interactions around the Tl atom stabilised the overall structure. Complex **1** was considered. The energy difference for 2*monomer-dimer was calculated as -33.10 kcalmol^{1} showing considerable stabilisation for dimer formation. Next was calculated the energy of two dimers connected via one Tl-N bond and the energy of stabilisation compared to the energy of 2*dimer was -6.78 kcalmol^{-1}. A similar calculation was then carried out with two molecules connected via the H, S chelation and the energy of stabilisation was -6.70 kcalmol^{-1}. Next, geometry optimisation was carried out on the Tl$_2$L$_2$ dimer in Figure 2b and the structure proved to be stable with a Tl-Tl distance of 3.864Å and the eight Tl-S distances in the range 3.18 to 3.21Å. A further geometry optimisation was then carried out on the model shown in Figure 4b which includes the pyridine bond and the (H, S) chelating ring but in this case, while the Tl-N bond remained, the (H,S) ring part of the model became displaced from the Tl coordination sphere. This result suggests that the (H,S) chelating ring is formed as a result of crystal packing and is not likely to persist in solution.

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

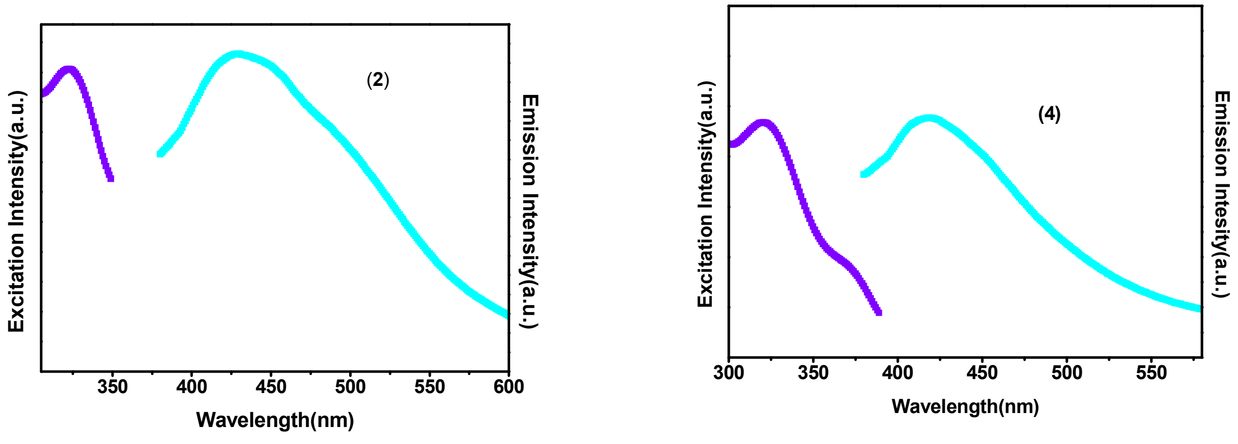
	1	2	3	4
Empirical Formula	$C_{14}H_{13}N_2S_2Tl$	$C_{13}H_{12}N_3S_2Tl$	$C_{15}H_{13}N_2O_2S_2Tl$	$C_{18}H_{17}FeN_2S_2Tl$
M(g mol^{-1})	477.75	478.75	521.76	585.68
crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
spacegroup	Pbca	Pbca	$P2_1/c$	Pbca
a (Å)	10.929(3)	10.8429(14)	15.7835(8)	9.6634(8)
b (Å)	9.981(4)	9.9762(17)	10.7720(5)	10.5339(14)
c (Å)	27.219(7)	27.222(3)	9.8639(4)	37.350(4)
β (deg)	(90)	(90)	101.993(4)	(90)
V (Å3)	2968.9(14)	2944.6(7)	1640.45(13)	3802.0(7)
Z	8	8	4	8
Dcalc (gcm^{-3})	2.138	2.160	2.113	2.046
F(000)	1792	1792	984	2224
Reflns collected	8946	8799	7538	25154
Independent reflections	3314	3266	3614	5537
Reflections with I>2σ(I)	1739	2108	2562	3740
Final *R* indices [*I* >2*r*(*I*)] R1^a, wR2^b	0.0809,0.1891	0.0724,0.1697	0.0506,0.0958	0.0523,0.1137
R indices(all data) R1^a, wR2^b	0.1387,0.2278	0.1160,0.1902	0.0816,0.1069	0.0876,0.1275
GoF	0.951	1.079	0.996	1.006
Residual electron density e/Å^3	1.863, -3.054	1.472, -1.999	1.948, -1.669	2.437, 2.308

$R1 = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$. $R_2 = \{[\Sigma w (F_0^2 - Fc^2)/ \Sigma w (F_0^2)^2]\}1/2$, $w = 1/ [\sigma2 (F_0^2) + (xP)^2]$, where $P = (F_0^2 + 2Fc^2)/3$

Absorption and emission spectra

The electronic absorption spectra of **1-4** inCH_2Cl_2display quite similar bands near 320, and 270 nm; **4** additionally shows a broad absorption at 450 nm (Fig. S6) characteristic of the ferrocene moiety.[14c, d] The first two absorption bands in all the complexes are assigned to Tl(I)-centered ligand to metal and intraligand charge transfer (ILCT) transitions respectively.[21a, b, d, 22] Spectra obtained from solids in nujol **1-4** (Fig. S7) show absorption bands with slight variations in the intensity and peak positions near 275-320, 340-375 and at 465 nm. A comparison of their absorption features in these two media reveals that the bands at 340-375 nm in the solid state which are not observed in solution most likely arise from the significant Tl...Tl interactions which are not retained.

In comparison to other metals, the photoluminescent properties of homoleptic thallium (I) compounds are rather less explored. The intriguing luminescent properties of the complexes with prominent metallophilic interactions including those with closed subshell electron configuration, are now well established.[21] In the homo- and heterometallic complexes, Tl…Tl/M...Tl intermetallic interactions have played an important role towards their rich photoluminescence behaviour.[21] In the solid state when excited at 320 nm (Fig. 5 and Fig. S8), complexes **1-4** all display a strong broad emission at 440-465 nm which emanates from the metal perturbed ILCT transition population of the metal based orbitals. The larger red shifted emissions with significant Stokes shift of 120-145 nm in the solid phase may be attributed to the prominent Tl…Tl intra- and Tl…N(Py) intermolecular interactions providing conformational rigidity in the polymeric chain structures and significant contribution of the lone pairs on the Py(N) of the dithiocarbamate ligands with enhanced delocalisation over the molecular framework. Upon excitation at 300 nm in CH_2Cl_2, **1-4** display an unstructured broad emission band near 335-350 nm (Fig S9) which clearly shows that the Tl…Tl interactions do not persist in solution. The excitation spectra for **2** and **4** collected at room temperature (Fig. 5) show λ_{ex} at 320 nm which almost matches their UV-Vis. spectra. It is to be noted that in both media the lowest emission intensity of **4** is due to the presence of the ferrocenyl group acting as a quencher.



(a) **(b)**

Fig. 5 Excitation and emission spectra of **2** and **4**in solid state at λ_{ex} = 320 nm.

The features of the excitation and emission bands of **1-4** are almost similar which suggest similar fluorophores in these complexes. A comparison of the luminescent wavelengths both in solution and solid phase suggests that the extended polymeric chains of Tl…Tl and Tl…N present in the solid play a crucial role in their luminescent behaviour and thus there is a good correlation between structure and luminescent properties.

Conclusions

Crystal structures of complexes **1-4** revealed unprecedented Tl...H-C intermolecular anagostic interactions via the formation of a chelating ring with accompanying sulphur bonding constructing 1-D polymeric structures; the interactions are stronger in **1** and **2** than in **3** and **4**. Complexes **1-4** are the first examples of main group metal dithiolates exhibiting anagostic interactions and have been assessed by DFT calculations. **1-4** are strongly luminescent in the solid state due to pronounced Tl...Tl interactions and conformational rigidity together with enhanced conjugation due to the lone pairs on the Py(N) in the delocalized polymeric structures. This study spurs further investigations of this lesser studied but important anagostic interactions for the main group element complexes with functionalised dithio ligands for their possible applications for C-H bond activations and supramolecular synthon.

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Notes and references

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Electronic Supplementary Information (ESI) available: Selected bond lengths (Å) and angles (°) for complexes, ORTEP views of **3** and **4**, packing views of complexes, Electronic absorption and Photoluminescence spectra of complexes. See DOI: 10.1039/b000000x/

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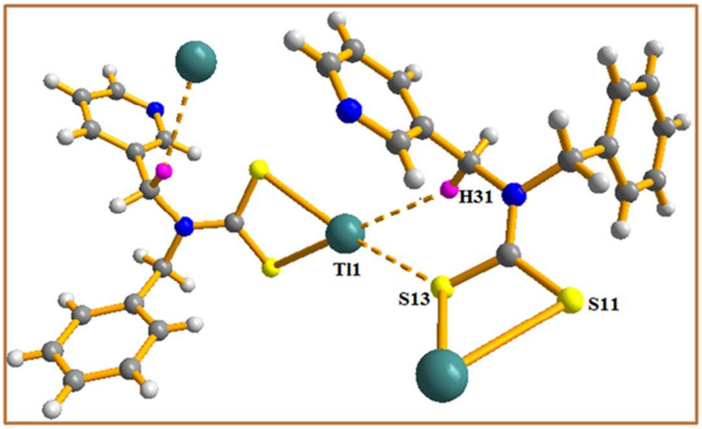

Rare Intermolecular C–H···Tl Anagostic and C-S...Tl Interactions Forming A Six-Membered Chelate Ring

254x190mm (96 x 96 DPI)