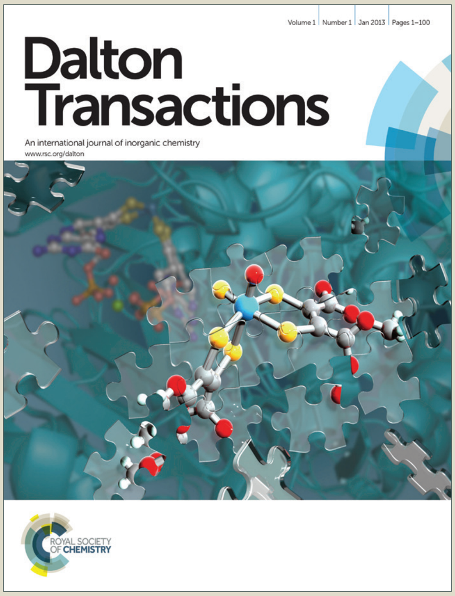
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/x0xx00000x

Synthesis, structural and photo-physical studies of bismuth(III) complexes with Janus scorpionate and co-ligands

Received 00th XXXX,
Accepted 00th XXXX

DOI: 10.1039/x0xx00000x

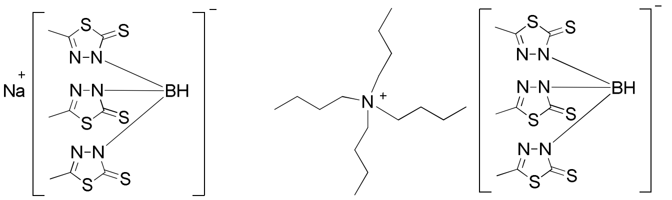
www.rsc.org/

Muhammad Imran,[a] Andreas Mix,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] Uwe Monkowius,[b] Petra Bleckenwegner[b] and Norbert W. Mitzel[a,*]

Some novel complexes of bismuth(III) with the Janus scorpionate ligand $[HB(mtda^{Me})_3]^-$ ($mtda^{Me}$ = 2-mercapto-5-methyl-1,3,4-thiadiazolyl) were synthesised. $Na[HB(mtda^{Me})_3]$ (**1**) was reacted with BiX_3 (X = Cl, I, NO_3) in molar ratio 2:1 to afford the bismuth complexes $\{HB(mtda^{Me})_3\}_2BiCl$ (**3**), $Na[\{HB(mtda^{Me})_3\}_2BiI_2]$ (**4**) and $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n$ (**5**). Two mixed complexes $\{HB(mtda^{Me})_3\}Bi(phen)Cl_2$ (**6**) and $\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2$ (**7**) were obtained using Janus scorpionate as primary ligand in the presence of 1,10-phenanthroline and 2,2′-bipyridyl, respectively, as co-ligands in 1:1 ratio. The obtained complexes were characterised by ^1H, ^{13}C and diffusion NMR (DOSY), elemental analyses and mass spectrometry. Structures of the compounds $NBu_4[HB(mtda^{Me})_3]$ (**2**), **3**, **4**, **5**, **6** and **7** were determined by single crystal X-ray diffraction. The molecular dynamic process in complex **3** was also studied by variable temperature NMR measurements. All bismuth complexes, except the polymeric **5**, are monomeric. Complexes **6** and **7** exhibit (B)H···Bi distances of 2.76(3) and 2.71(2) Å length, respectively. Compounds **2**, **6** and **7** were screened for their luminescence activity. At 77 Kin ethanol solution, complexes **6** and **7** exhibit phosphorescence from a ligand-to-ligand charge transfer (LLCT) and ligand-centred (LC) excited state, respectively.

Introduction

Since the first synthesis of soft scorpionate ligands namely (hydrotris(methimazolyl)borate (Tm)[1] a large number of contributions in this research area have appeared in the literature. This is because these soft ligands have been used successfully for stabilization of low-valent, electron-rich metal ions.[2-3] Such complexes also demonstrate susceptibility for oxidation and thus give access to unusual oxidation states. Furthermore such soft ligands also exert weaker field strengths compared to hard ligands as has been established for the examples $[Fe(Tm^{Me})_2]$[4] and $[Fe(Tp^{Me})_2]$.[5] Compared to their hard analogues, these ligands have twisting and flexibility capabilities to accommodate metal ions of larger ionic radii and show variable coordination behaviour including monodentate (κ^1-*S*), bidentate (κ^2-*S*,*S'*or κ^2-*S*,*H*) and tridentate (κ^3-*S*,*S'*,*S''*or κ^3-*S*,*S'*,*H*) binding modes.[6-7] Janus scorpionates are a subclass of soft scorpionate ligands with a simultaneous ability to coordinate through hard and soft donor sites; the term is borrowed from Roman mythology, where Janus, god of gates and doors, is a bifrons representing this disambiguation.[8-9] These ligands are known as hybrid of Trofimenko's tris(pyrazolyl)borates[10] and Reglinski's tris(mercaptoimidazolyl)borates[1] and are also closely related to Bailey's [11] and Marchiò's ambidentate thioxotriazolylborates.[12]



1

2

Scheme 1. Sodium and tetra-*n*-butyl ammonium derivatives of the Janus scorpionate ligand $[HB(mtda^{Me})_3]^-$ (**1** and **2**)

The anion $[HB(mtda^{Me})_3]^-$ ($mtda^{Me}$ = 2-mercapto-5-methyl-1,3,4-thiadiazolyl) is a typical Janus scorpionate ligand with conjoined (*N*,*N*,*N*-) and (*S*,*S*,*S*-) donor faces; it was first reported by Silva and co-workers in 2008 (Scheme 1).[9] They have described its polymeric alkali metal and monomeric iron complexes. The ligand is referred to as second generation Janus scorpionate ligand and differs from first generation ligands only by methyl substitution at position 5 of the heterocycle.

Recently we have reported a novel Janus scorpionate ligand along with its bismuth complexes.[13] In continuation of our growing interest in bismuth chemistry based on soft scorpionates, we present here bismuth complexes of $[HB(mtda^{Me})_3]^-$. For this purpose, we have utilised different bismuth sources such as $BiCl_3$, $Bi(NO_3)_3$ and BiI_3 to explore the effect of halide and halide free anions on the coordination geometry of the bismuth complexes. The idea was to see, whether these ions (with variable sizes and nature) permit Janus scorpionate ligands to adopt the κ^3-coordination mode, consequently resulting in cationic sandwich complexes of bismuth. Furthermore, the co-ligands (1,10-phenanthroline and 2,2′-bipyridyl) were employed to prepare mixed complexes of bismuth while keeping $[HB(mtda^{Me})_3]^-$ as primary ligand. Mixed complexes involving 2,2′-bipyridine and 1,10-phenanthroline have found considerable attention because of their favourable absorption and excited state properties.[14] However, such exploration towards bismuth has, despite strong spin-orbit coupling constant and less expensive nature, been less explored.[13,15] This contribution provides besides the structural and bonding aspects of several novel bismuth complexes also information on their photophysical properties.

Results and discussion

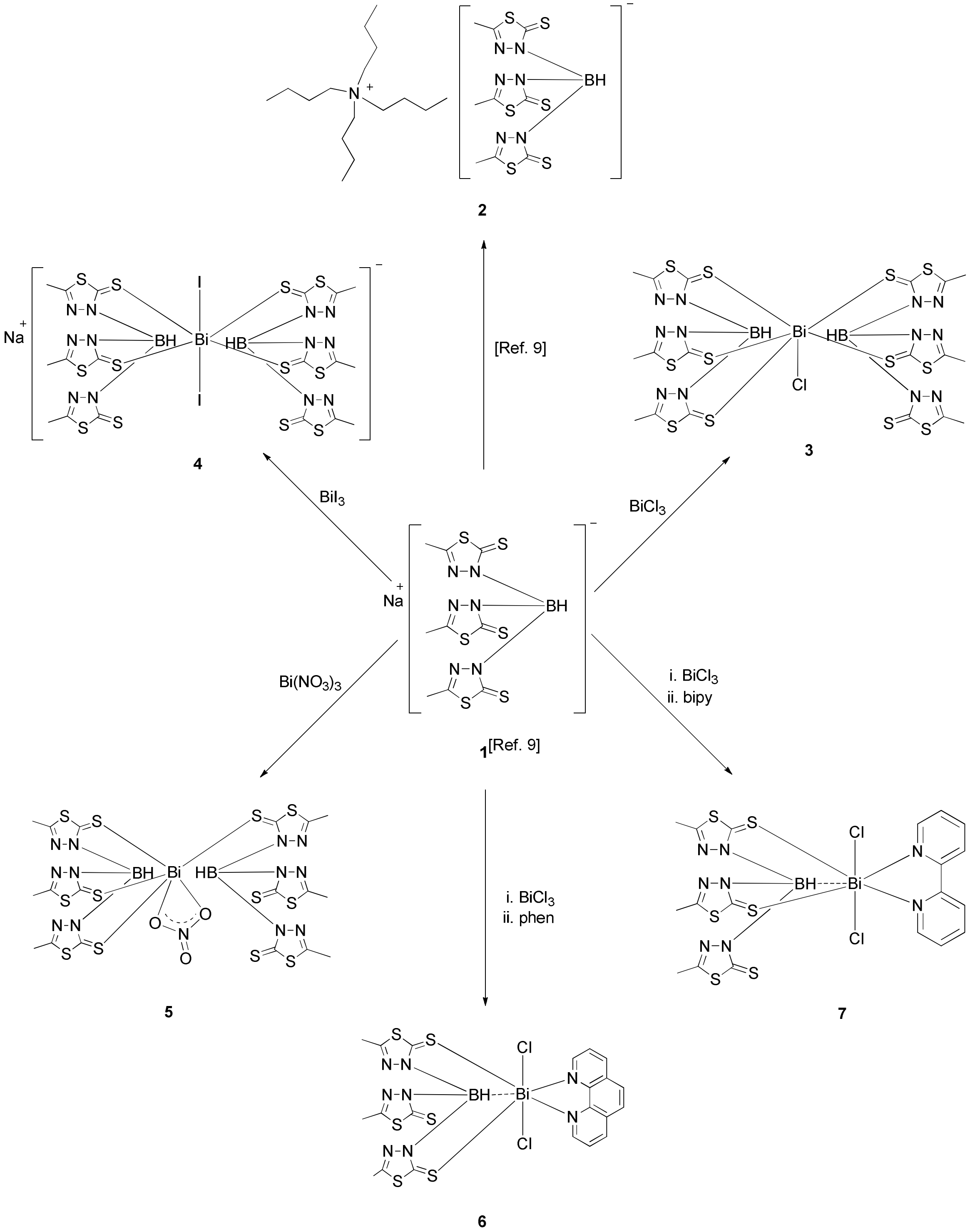
Recently we have reported bismuth complexes with a novel Janus scorpionate ligand namely $[Bi(Tr^{Me})Cl(\mu\text{-}Cl)_2]_2$ and $[Bi(Tr^{Me})Cl_2(\mu\text{-}Cl)]_n$ ($Tr^{Me} = [HBL_3]^-$ with L = 3-mercapto-4-methyl-1,2,4-triazole).[13] Extending the same methodology we present here the synthesis of some bismuth complexes with the known second generation Janus scorpionate ligand $[HB(mtda^{Me})_3]^-$ ($mtda^{Me}$ = 2-mercapto-5-methyl-1,3,4-thiadiazolyl). Syntheses of its sodium and tetrabutylammonium salts, $Na[HB(mtda^{Me})_3]$ (**1**) and $NBu_4[HB(mtda^{Me})_3]$ (**2**), were carried out according to literature protocols.[9] Additionally we report here the crystal structure of $NBu_4[HB(mtda^{Me})_3]$ (**2**). The tetrabutylammonium derivative was synthesised due to its favourable solubility and use during luminescence measurements. However, after various experiments $Na[HB(mtda^{Me})_3]$ (**1**) was found to be a more advantageous reagent for the synthesis of bismuth complexes (Scheme 2), because $NBu_4[HB(mtda^{Me})_3]$ (**2**) resulted in products which were difficult to purify and led to smaller yields. The same observation was made during the synthesis of $[Bi(Tr^{Me})Cl(\mu\text{-}Cl)_2]_2$.[13] Different bismuth salts such as $BiCl_3$, BiI_3 and the halide free $Bi(NO_3)_3$ were reacted in an M:L ratio of 1:2 with the intention to achieve octahedral geometry (Scheme 2).

Bismuth complexes **3** – **5** are coloured solids (**3** red, **4** orange, **5** red). Compared to bismuth complexes **4** and **5**, **3** is better soluble in dichloromethane, chloroform, acetonitrile, tetrahydrofuran and methanol. However, in highly polar solvents like dmf and dmso it dissociates. Compound **4** does not dissociate in dmf and dmso, while complex **5** dissociates in dmso but does not dissociate in dmf (see section "Solution NMR studies"). The synthetic chemistry was further extended with co-ligands such as 1,10-phenanthroline and 2,2'-bipyridyl (Scheme 2) to see the effect on (a) structural aspects of bismuth geometries upon introduction of these neutral bidentate ligands, (b) luminescence properties of these complexes due to their inherently conjugated nature. Complexes **6** and **7** were synthesised at room temperature and are also coloured (**6** yellow, **7** orange red) solids. They have poor solubilities in common organic solvents. In dmf and dmso, they lose their identity as mixed complexes, instead complexation occurs only between co-ligands and bismuth (see section "Solution NMR studies"). After workup, the yields of all complexes **3** – **7** range between 55 – 73 %.

Solid state characterization

Single crystal X-ray crystallography revealed molecular structures of the bismuth complexes with the compositions $\{HB(mtda^{Me})_3\}_2BiCl\cdot 2CH_3CN$ (**3**), $Na[\{HB(mtda^{Me})_3\}_2BiI_2]\cdot CH_3CN\cdot H_2O$ (**4**) $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n\cdot CH_3OH$ (**5**), $\{HB(mtda^{Me})_3\}Bi(phen)Cl_2\cdot 2.1CHCl_3$ and (**6**) $\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2\cdot CH_3CN$ (**7**). Selected bond lengths and angles are presented in Tables 1 – 3 and their molecular structures are shown in Figures 1 – 5.

The ionic molecular structure of **2** is shown in Figure S1 (supplymentary information). Important bond lengths and angles are listed in Table S1 and are within the normal range. The bond lengths and angles can be compared with the closely related salts $Na[HB(mtda^{Me})_3]$, $K[HB(mtda^{Me})_3]$ and $(K,Na)[HB(mtda^{Me})_3]$, whose molecular structures have been earlier reported.[9] The N–B–N angles range from 106.5(2) to 110.5(2)°, i.e. they slightly deviate from regular tetrahedral angles. Complex **3** crystallises in the orthorhombic space group $P2_12_12_1$. Its molecular structure is shown in Figure 1; selected structural parameters are listed in Table 1. Two acetonitrile molecules of the solvent required for crystallization are present in the crystal lattice. The central bismuth atom has a distorted octahedral geometry accomplished by two $[HB(mtda^{Me})_3]^-$ ligands with different coordination modes, (κ^3-*S,S',S''*) and (κ^2-*S,S'*). The sixth position is occupied by a chloro ligand. The Bi–S bond lengths for the (κ^3-*S,S',S''*) coordinate ligand cover the range between 2.717(2) and 2.905(2) Å, while for the (κ^2-*S,S'*) coordinate ligand the values are 2.907(2) and 2.978(2) Å. The chloride ligand is terminally bound to the bismuth atom with a distance of 2.586(1) Å and is in agreement with related literature Bi–Cl terminal distances.[13,16] One B–H units is oriented away from the bismuth, the other one is reasonably orientated toward the bismuth atom, but the resulting H(1)–Bi(1) distance is above 3 Å and not considered as a (B)H···Bi interaction. It is important to mention that the S–Bi–S bond angles involving the ligand with κ^3 mode are close to 90° (range: 85.4(2) – 89.1(2)°) while the S–Bi–S angle involving the κ^2-mode ligand deviates significantly at 117.9°. The Cl–Bi–S (*cis*) angles (Table 1) also show deviations from a regular octahedral arrangement of binding atoms. This distorted octahedral distribution of bond angles indicates the presence of a stereo-chemically active lone pair of electrons at bismuth. The binding situation in complex **3** is thus different to that in the closely related compound $[Bi(Tt)_2]Cl$ (Tt = hydrotris(thioxotriazolyl)borate),[11] where both ligands coordinate in a (κ^3-*S,S',S''*) mode resulting in a regular octahedral geometry. The structural parameters can also be compared with our recently reported $[Bi(Tr^{Me})Cl(\mu\text{-}Cl)_2]_2$ (Tr^{Me} is a soft scorpionate based on triazole) as well as with [Tm^{Me}BiCl(μ-Cl)$_2$]$_2$ [17] and [Tm$^{t\text{-}Bu}$BiCl(μ-Cl)$_2$]$_2$[18] (Tm^R is a soft scorpionate based on imidazole units). However, these complexes are dimeric and bridged by chloro ligands.



Scheme2. Synthesis of bismuth complexes **3 – 7**

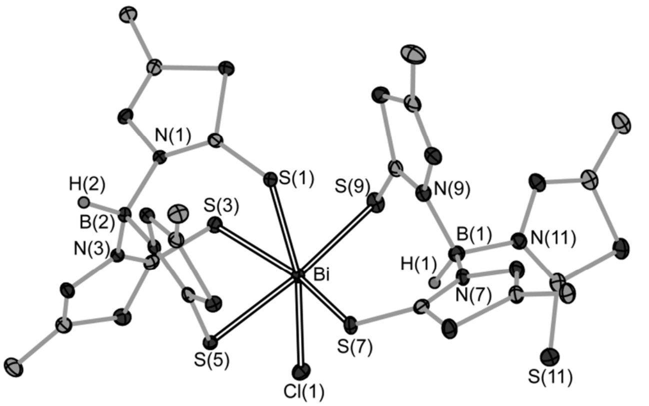


Figure 1. Molecular structure of {HB(mtda^{Me})$_3$}$_2$BiCl (**3**) in the crystal. Hydrogen atoms except B–H and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

The molecular structure of complex **4a** is shown in Figure 2. The asymmetric complex is arranged about a crystallographic centre of inversion. This leads to a situation that can coarsely be described as a disorder between a sodium ion and a water molecule. Because the sodium ion occupies only every second hard donor site of the otherwise crystallographically fully occupied ligand surrounding on both sides of the bismuth atom (left and right part in Figure 2) in an non-regular fashion, this leads necessarily to a 1:1 disorder of the sodium atom. For the 50% probability that there is a sodium atom, the left part of Figure 2 describes it, in the case that there is a void (instead of Na) acetonitrile and water molecules (some of them disordered and not at full crystallographic occupation) fill it. Then the water molecule makes hydrogen bonding contacts with N(4A) of the ligand at a distance of 2.23 Å and with acetonitrile N(7A) at a distance of 2.22 Å.

In contrast to complex **3** it displays only slight deviation from a regular octahedral geometry at bismuth. The bismuth atom binds to four sulphur atoms of two symmetric ligands with (κ^2-*S,S'*) coordination mode and iodo ligands placed *trans* to each other. Important bond lengths and angles are listed in Table 1. The Bi–S bond have lengths of 2.819(2) (S(1)) and 2.859(2) Å (S(3)) and are comparable to those in **3**. The monomeric as well as regular octahedral nature despite of halide presence is contrasting previous reports on [Bi(Tr^{Me})Cl(μ-Cl)$_2$]$_2$,[13] [Bi(Tr^{Me})Cl$_2$(μ-Cl)]$_n$[13] [Tm^{Me}BiCl(μ-Cl)$_2$]$_2$,[17] [Tm$^{t\text{-}Bu}$BiCl-(μ-Cl)$_2$]$_2$,[18] (where Tr^{Me} and Tm^{Me} are soft scorpionate ligands based on imidazole and triazole units). The (κ^2-*S,S'*) coordination mode of the ligand in complex **4a** also differs from that of the related bismuth complex [Bi(κ^3-Tm^{Me})(κ^1-Tm^{Me})I].[19] Spicer et al. reported that a regular S$_6$ coordination sphere would be unattainable in bismuth complexes in the presence of halide ions; they pointed out that by the presence of halide ions the balance of orbital energies is sufficiently changed to allow a directional lone pair to be observed.[19,20] Furthermore, the sodium ion is coordinated – as expected by the HSAB concept– to the three hard nitrogen donor sites of one ligand with coordination mode (κ^3-*N,N',N''*).

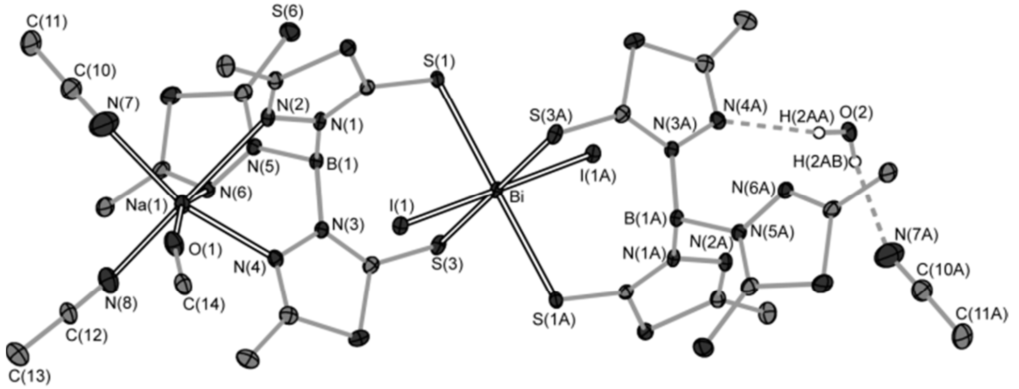


Figure 2. Molecular structure of [{[(CH$_3$CN)$_2$(CH$_3$OH)Na]μ-[Naκ^3-*N,N',N''*:Biκ^2-*S,S'*-{HB(mtda^{Me})$_3$]}$_2$BiI$_2$]·CH$_3$CN·H$_2$O (**4a**) in the crystal. Only one version of the disordered part is displayed (see text). Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 30% level. CH$_3$CN and H$_2$O are included to show H-bonding contacts.

Its octahedral coordination environment is completed by one methanol and two acetonitrile ligands. The Na–N distances to [HB(mtda^{Me})$_3$]$^-$ are in the range between 2.450(3) and 2.677(3) Å; this is in agreement with the related structure of Na[HB(mtda^{Me})$_3$].[9] So in essence the most salient features of the molecular structure of **4** in the light of previous results are the almost octahedral geometry at bismuth and the real Janus-type behaviour of the ligand [HB(mtda^{Me})$_3$]$^-$ towards Bi on the soft and Na on hard side. In this sense it is related to reports of Reglinski et al.[17] on the unusual salt [Tm$_2$Bi][Tp$_2$Na] (Tp = hydrotris(pyrazolyl)borate), with regular octahedral coordination geometry at bismuth, but with the difference that only one sort of ligand in **4** is capable of taking over the role of two different in this case.

Table 1. Selected bond lengths [Å] and angles [deg] of complexes **3** and **4**

3		**4**	
Bi–S(1)	2.905(2)	Bi–S(1)	2.819(2)
Bi–S(3)	2.749(2)	Bi–S(3)	2.859(2)
Bi–S(5)	2.717(2)	Bi–I(1)	3.002(1)
Bi–S(7)	2.907(2)	Na(1)–O(1)	2.309(4)
Bi–S(9)	2.978(2)	Na(1)–N(2)	2.677(3)
Bi–Cl(1)	2.586(1)	Na(1)–N(4)	2.450(3)
S–Bi–S (*cis*)	75.2(1)–117.5(2)	Na(1)–N(6)	2.599(3)
S–Bi–S (*trans*)	159.3(2)–167.1(2)	Na(1)–N(7)	2.440(4)
Cl–Bi–S (*cis*)	78.6(2) – 98.4(2)	Na(1)–N(8)	2.394(6)
Cl–Bi–S(1) (*trans*)	167.8(2)	S(1)–Bi–S(1A)	180.0
		S(1)–Bi–S(3)	88.1(2)
		S(3)–Bi–S(3A)	180.0
		S(1)–Bi–S(3A)	91.9(2)
		I(1)–Bi–I(1A)	180.0
		S(3)–Bi–I(1)	95.8(2)
		S(1)–Bi–I(1)	93.5(2)

Table 2. Selected bond lengths [Å] and angles [deg] of complex **5**

Bi–S(1)	2.693(2)
Bi–S(3)	2.771(2)
Bi–S(5)	2.803(2)
Bi–S(7)	2.801(2)
Bi–S(11)	2.866(2)
Bi–O(1)	2.708(3)
Bi–O(2)	2.747(2)
S–Bi–S (*cis*)	72.7(1) – 94.3(2)
S–Bi–S (*trans*)	161.5(2) – 163.3(2)
O–Bi–S (*cis*)	72.4(2) – 121.4(2)
O–Bi–S(1) (*trans*)	153.0(2) – 154.9(2)
O(1)–Bi–O(2)	46.9(2)

Complex **5** crystallises in the monoclinic space group $P2_1/n$. Its molecular structure is shown in Figure 3. This complex is of polymeric nature and is different in constitution compared to the related reported structures of $[Bi(Tr^{Et,Me})]NO_3$,[21] $[Bi(Tr^{Ph,Me})]NO_3$[22] and $[Bi(Tr^{Ph,Ph})]NO_3$.[23] In contrast to complex **5**, these three bismuth complexes are monomeric in nature and show regular octahedral coordination geometry. The nitrate ions in these three complexes[21-23] are present outside the coordination sphere. The Bi–S bond lengths in complex **5** (Table 2) (except Bi–S(11) 2.86 Å, slightly longer) lie within the range found in the CCSD data base for bismuth complexes with soft scorpionate ligands.[24] The coordination number around each bismuth ion is 7 with three $[HB(mtda^{Me})_3]^-$ ligands surroundingit. One of them exhibits a tridentate mode of coordination (κ^3-*S,S',S''*), while the other two coordinate in (κ^2-*S,S*') mode and use their remaining third sulphur atom to bind to the next bismuth atom resulting in a polymeric chain. Additionally, a nitrate ion also coordinates to the bismuth atom in a bidentate manner with distances Bi–O(1) 2.708(3) and Bi–O(2) 2.747(2) Å. Selected bond angles are listed in Table 3; they reveal a distorted geometry for this complex.

The molecular structure of complex **6** is shown in Figure 4. This complex crystallises with disordered molecules of chloroform in the unit cell. Complex **6** is monomeric and the bismuth atom is chelated by a tridentate Janus scorpionate ligand (κ^3-*H,S,S'*) ligand, and a bidentate co-ligand (phenanthroline). Two chloro ligands complete the coordination sphere resulting in coordination number 7. Some notable examples of mixed complexes with scorpionate ligands includes *cis*-$L_2Ru(Z)^{n+}$ [(L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen), Z= bis-coordinated scorpionate)[14] $[YCl_2(Tp^{Me2})(phen)]$ (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate).[25] To best of our knowledge, complex **6** is the first mixed complex of bismuth based on soft scorpionate ligands. The bond lengths of Bi–S (range 2.943(2) – 2.966(2) Å) and Bi–Cl (range 2.558(2) – 2.613(2) Å) compares well with those of complex **3**. A (B)H···Bi interaction at 2.76(3) Å is also present; it can be compared with literature values 2.58, 2.65 and 2.69 Å reported for $[BiBb_2Cl]$[26], $[Tm^{Ph}]_2Pb$[27] and $[Tl(Bm^{Me})]_x$[28] complexes, respectively. The structural parameters can also be compared with a mixed complex $[Bi(S_2CNC_5H_{10})_2(NO_3)(phen)(S_2CNC_5H_{10})$ = pyrrolinedithio-carbamate)] having a sulphur donor ligand and phenanthroline ligand.[29]

Table 3. Selected bond lengths [Å] and angles [deg] of complexes **6** and **7**

6		**7**	
Bi–S(1)	2.966(2)	Bi–S(1)	3.003(2)
Bi–S(3)	2.943(2)	Bi–S(3)	2.965(2)
Bi–N(7)	2.445(3)	Bi–N(7)	2.435(2)
Bi–N(8)	2.490(3)	Bi–N(8)	2.512(2)
Bi–Cl(1)	2.613(2)	Bi–Cl(1)	2.566(2)
Bi–Cl(2)	2.558(2)	Bi–Cl(2)	2.549(2)
(B)H···Bi	2.76(3)	(B)H···Bi	2.71(2)
S(1)–Bi–S(3)	117.1(2)	S(1)–Bi–S(3)	118.7(2)
S(1)–Bi–N(7)	78.1(2)	S(1)–Bi–N(7)	170.3(2)
S(1)–Bi–N(8)	92.5(2)	S(1)–Bi–N(8)	113.3(2)
S(3)–Bi–N(7)	162.3(2)	S(3)–Bi–N(7)	71.0(2)
S(3)–Bi–N(8)	101.5(2)	S(3)–Bi–N(8)	84.8(2)
Cl–Bi–S (*cis*)	80.5(2) – 100.0(2)	Cl–Bi–S (*cis*)	87.8(2) – 90.9(2)
Cl–Bi–S (*trans*)	162.4(2)	Cl–Bi–S (*trans*)	152.0(2)
Cl(1)–Bi–Cl (2)	90.3(2)	Cl(1)–Bi–Cl (2)	93.9(2)

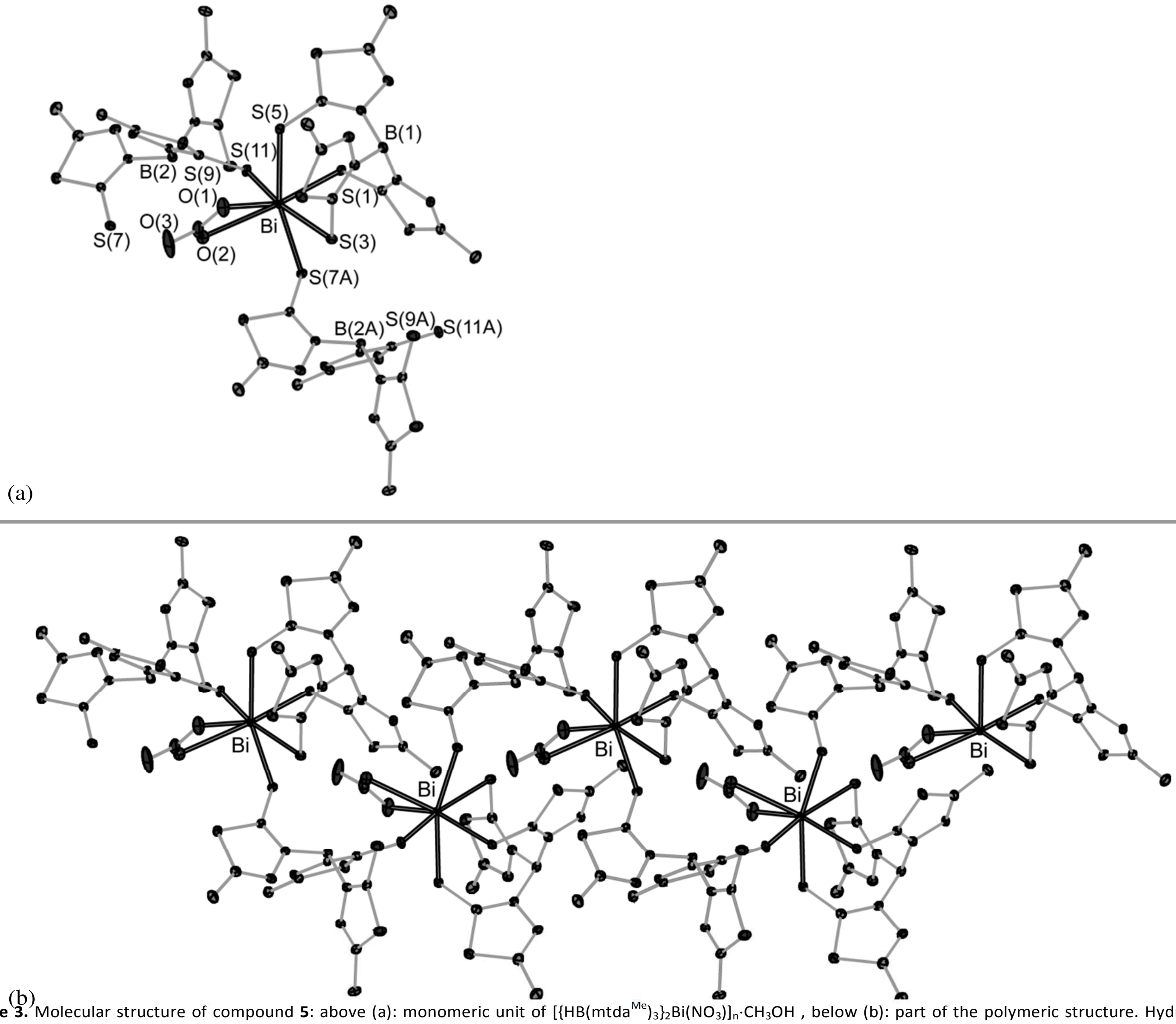


Figure 3. Molecular structure of compound **5**: above (a): monomeric unit of $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n \cdot CH_3OH$, below (b): part of the polymeric structure. Hydrogen atoms and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

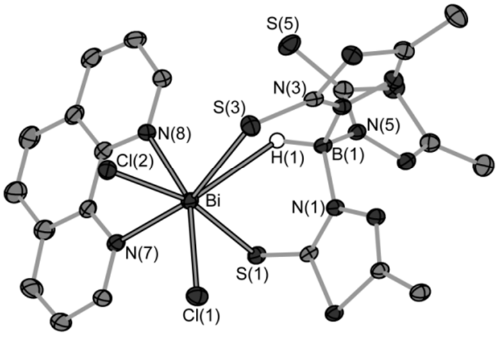


Figure 4. Molecular structure of $HB(mtda^{Me})_3\}Bi(phen)Cl_2$ (**6**). Hydrogen atomsexcept B–H and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

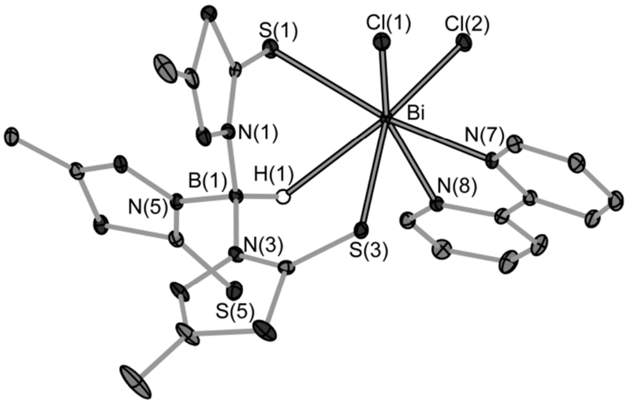


Figure 5. Molecular structure of $\{HB(mtda^{Me})_3\}Bi(Bipy)Cl_2$ (**7**). Hydrogen atoms except B–H and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

Solution NMR studies

The ^{1}H NMR spectra of complexes **3** – **5** were recorded. The resonances of the methyl protons show a significant chemical shift relative to that of the free ligand $[HB(mtda^{Me})_3]^-$. The three complexes **3**, **4** and **5** exhibit a broad singlet for the methyl protons at 2.52, 2.57 and 2.52 ppm, respectively, compared to $\delta = 2.37$ ppm for the free ligand $[HB(mtda^{Me})_3]^-$ indicating fluxional coordination behaviour. The dynamics have been studied exemplarily on compound **3** by variable temperature NMR experiments (VT-NMR) in the range between 188 and 383 K using CD_2Cl_2 and $C_2D_2Cl_4$ as solvents (Figures 6 and 7). Two methyl resonances were observable (Figure 6) at lower temperature with shifts at about 2.47 and 2.73 ppm. At 203 K two signals at $\delta = 2.46$ and 2.67 ppm are obtained for the methyl groups. This would be explicable if one of the ligands is coordinated to bismuth with all three heterocyclic units (κ^3-*S,S',S''* mode) and one in (κ^2-*S,S'*) mode, with rapid exchange of the coordinating functions. Upon cooling to 188 K the methyl resonances belonging to this (κ^2-*S,S'*)-bound ligand starts to split, which indicates a slower exchange process leading to distinguishable states on the NMR timescale. Above 293 K the two resonances merge into a single one which point to a situation in which both ligands in the complex are equally involved into dynamically changing their binding modes between (κ^3-*S,S',S''*) and (κ^2-*S,S'*).

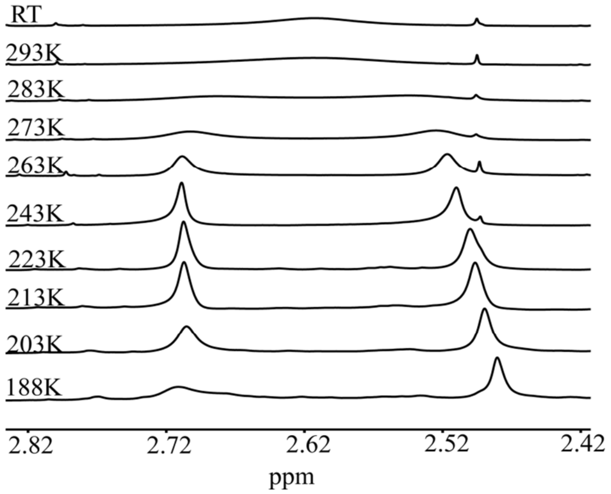


Figure 6. Variable temperature ^{1}H NMR spectra of complex **3** in CD_2Cl_2 solution

Surprisingly the broad singlet splits into two signals again when raising the temperature above 333 K (a change of the solvent is needed to $C_2D_2Cl_4$). A possible interpretation for this is that at higher temperature one of the ligands dissociates completely from the complex. Note, that this process is reversible upon cooling. The hypothesis of dissociation is supported by molar conductance measurements. With increasing temperature an acetonitrile solution of complex **3** was found to increase its molar conductance from 34 $\Omega^{-1}cm^2mol^{-1}$ (at RT) to 75 $\Omega^{-1}cm^2mol^{-1}$ at 70 °C. The non-equivalence of the ligands is obvious for a ligand split off. Spicer et al. have also observed dynamics at low temperature for an antimony complex based on a soft scorpionate ligand $[Sb(\kappa^3\text{-}Tm^{Me})(\kappa^1\text{-}Tm^{Me})Br]$ (Tm^{Me} = hydrotris(methimazolyl)borate).[11]

The most important feature of the ^{13}C NMR spectra of complexes **3** – **5** is an up-field shift for the resonance of the C═S unit compared to that of the free ligand (see experimental section). This can be attributed to the coordination of the thione unit to the bismuth atom. The resulting spectrum exhibited a broad peak for the methyl carbon atoms supporting the possibility of different environments of methyl groups in this complex. ^{1}H NMR spectra of complexes **3**, **6** and **7** were also recorded in dmf-*d7* and then compared to those of $[HB(mtda^{Me})_3]^-$ and the co-ligands. This comparison reveals that these complexes are significantly dissociated in dmf (see experimental section).

The dissociation was further proven by ^{1}H diffusion NMR experiments. Note that the diffusion coefficients are reciprocally proportional to the hydrodynamic radius of the particle under observation and that this allows only a coarse assignment of species. The discussion here can thus be only a tentative, although likely, assignment to molecular species and processes. Diffusion coefficients were determined using the proton resonance of the methyl groups of $[HB(mtda^{Me})_3]^-$ and complex **3**, respectively. As shown in Table 4, the diffusion co-efficient of complex **3** is of the same magnitude ($4.8\cdot10^{-10}$ m^2 s^{-1}) than that of the sodium salt $Na[HB(mtda^{Me})_3]$ of the same ligand ($4.6\cdot10^{-10}$ m^2 s^{-1}, note that the Janus ligand can bind the Na^+ ion with its nitrogen sites). This indicates that both solutions contain species of similar hydrodynamic radius and makes it likely that complex **3** is dissociated in dmf (Equation 1) because a complete molecule of **3** with two Janus ligands would be much bigger and thus have a markedly lower diffusion co-efficient.

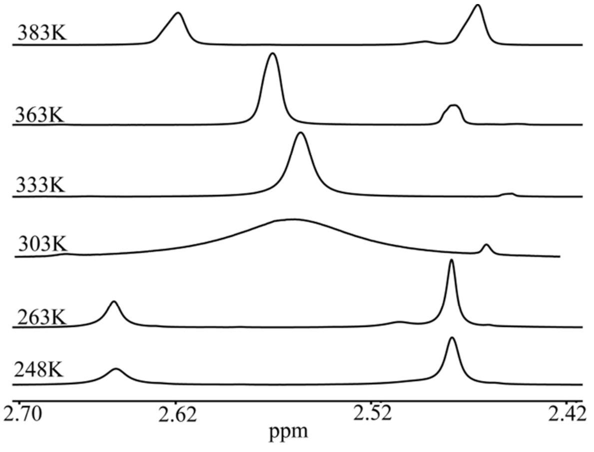


Figure 7. Variable temperature ^{1}H NMR spectra of complex **3** in $C_2D_2Cl_4$ solution

Similarly the diffusion coefficients of complexes **6** and **7** were determined using the proton resonance of the methyl group of $[HB(mtda^{Me})_3]^-$ and that of the aromatic amine i.e. the co-ligands. Table 4 shows that the diffusion coefficients of complexes **6** and **7** (determined for the methyl group signal of $[HB(mtda^{Me})_3]^-$) differ from the diffusion coefficients of their free co-ligands (phen and bipy), but are close to that of

Na[HB(mtda^{Me})$_3$]. This indicates that in dmf complexes **6** and **7** are also dissociated (Equation 2). The larger diffusion coefficient for the bipy part of compound **7** compared to the [HB(mtda^{Me})$_3$]$^-$ part might be due to a rapid dissociation equilibrium on the NMR timescale between complexed and free bipy and thereby averaging of the weighted contributions. This has been shown to be the case in other dynamically bound systems.[30]

Attempts to determine a reliable value for diffusion co-efficient for complex **4** were hampered by the width of the singlet of the methyl protons.

$$[\{HB(mtda^{Me})_3\}_2BiCl] \underset{-dmf}{\overset{+dmf}{\rightleftharpoons}} [\{HB(mtda^{Me})_3\}BiCl]^+ + [HB(mtda^{Me})_3]^-$$

Equation 1. Dissociation of complex **3** in dmf

$$[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2] \underset{-dmf}{\overset{+dmf}{\rightleftharpoons}} [(phen)BiCl_2]^+ + [HB(mtda^{Me})_3]^-$$

$$[\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2] \underset{-dmf}{\overset{+dmf}{\rightleftharpoons}} [(bipy)BiCl_2]^+ + [HB(mtda^{Me})_3]^-$$

Equation 2. Dissociation of complexes **6** and **7** in dmf

Table 4. Diffusion coefficients measured for solutions of complexes **3**, **6** and **7** (and the free ligand compounds of the corresponding respective complexes).

Compound	Diffusion coefficient (m^2 s^{-1})
3	$4.8 \cdot 10^{-10}$
Na[HB(mtda^{Me})$_3$]	$4.6 \cdot 10^{-10}$
6	$5.0 \cdot 10^{-10}$ (phen part), $4.9 \cdot 10^{-10}$ ([HB(mtda^{Me})$_3$]$^-$ part)
phen	$8.7 \cdot 10^{-10}$ (CH)
7	$8.6 \cdot 10^{-10}$ (bipy part), $4.5 \cdot 10^{-10}$ ([HB(mtda^{Me})$_3$]$^-$ part)
bipy	$1.0 \cdot 10^{-9}$

Photophysical Characterisation

Metal complexes bearing 2,2'-bipyridine and 1,10-phenanthroline frequently feature intense luminescence.[31,32] Thus, complex **6** and **7** were characterised by electronic absorption and emission spectroscopy (Table 5). The absorption spectrum of **2** features two peaks at 246 and 308 nm. Due to their high extinction coefficients, the signals can be assigned to π- π* transitions, possibly masking additional n- π* transitions. The phen complex **6** exhibits intensive absorption bands at 230, 264, and 309 nm. The latter is attributable to a transition located on the Tm ligand, whereas the two high-energy bands are very similar to reported phen related transitions.[31-33] In the bipy com plex, the spectrum is dominated by two intensive bands which originate from π- π * transitions of the bipy ligand.[34,35]

Both bismuth complexes are luminescent at 77 K but not under ambient conditions. At 77 K also the ligand **2** is luminescent and shows a broad low-energy emission band at 593 nm (Figure S2). The phen complex **6** features a structured band with less intensive maxima below 500 nm and a very dominate signal at 553 nm (Figure 8). The emission decay time is 0.37 ms and indicative for phosphorescence (Figure S3). The pattern of the emission bands is reminiscent of emission spectra of [(phen)Zn(SR)$_2$] (R = aryl), where the emission bands were assigned to a mix of a ligand-centred π- π* transition (LC, high-energy signals) and an overlapping ligand-to-ligand charge transfer state (LLCT, low-energy signal).[36,37] Thus, we tentatively assign the low-energy band of **6** to a S→ π* (phen) LLCT. The emission band of the bipy complex is somewhat bathochromic shifted compared to **6** (Figure 9).The structured band and its wavelength is typical for LC phosphorescence.[32,38] This assignment is further supported by the relatively long emission decay time of 3.35 ms and a Stokes-shift of ~14800 cm^{-1}. Hence, despite the high atomic number of bismuth the spin-orbit coupling promoted by the bismuth atom is comparably low and leads to relatively long phosphorescence lifetimes at 77 K. For all compounds investigated the excitation spectra match nicely the absorption spectra. It is interesting to note the difference to our previously reported Bi-complexes bearing similar scorpionate ligands;[13,26] in the absence of ligands with an extended π-system, the compounds are luminescent due to sp- or LMCT excited states. In the presence of chromophores with energetically low lying π*-orbitals like phen and bipy, a LC or LLCT is favoured.

Table 5. Electronic spectroscopic data of **2**, **6** and **7** in ethanol. Emission and excitation spectra recorded at 77 K.

	Absorption [nm] (lg ε)	Excitation [nm]	Emission [nm]	Emission decay τ [ms]
2	246 (4.04), 308 (4.50)	266, 309, 341, 374	406, 434, 593, 624	-
phen, **6**	230 (4.82), 264 (4.68), 309 (4.31)	270, 292, 313, 343, 368, 385	408, 449, 458, 487, 553	0.37
bipy, **7**	236 (4.37), 243 sh (4.35), 282 (4.44), 293 sh (4.37)	305	435, 452, 466, 485, 518	3.35

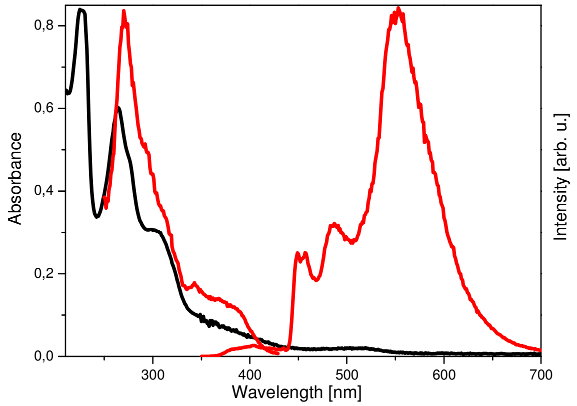


Figure 8. Absorption spectrum of **6** in ethanol (black, *c* = $1.3 \cdot 10^{-5}$ mol/l). Emission and excitation spectra of **6** in ethanol glass at 77 K (red, λ_{exc} = 310 nm, λ_{det} = 530 nm).

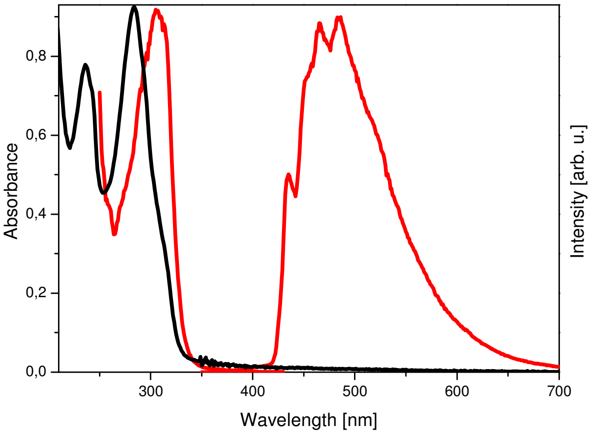


Figure 9. Absorption spectrum of **7** in ethanol (black, *c* = 3.3×10^{-5} mol/l). Emission and excitation spectra of **7** in ethanol glass at 77 K (red, λ_{exc} = 285 nm, λ_{det} = 450 nm).

Conclusions

We have successfully prepared and characterised bismuth complexes with the known second generation Janus ligand [HB(mtda^{Me})$_3$]$^-$. We have observed that in the presence of different counter anions such as chloride, iodide and nitrate, [HB(mtda^{Me})$_3$]$^-$ exhibits different coordination modes towards bismuth ions. Furthermore, two mixed metal complexes were also prepared and characterised. In both these mixed complexes, the interesting feature of a (B)H···Bi interaction (at 2.76(3) Å for **6** and 2.71(2) Å for **7**) was observed. This is in contrast to compounds **3**, **4** and **5** where such interactions are absent. All the resulting complexes are monomeric, except **5** which is polymeric in nature. Previously it has been established in the literature that the general preference of coordination mode of the scorpionate ligand is κ^3, resulting in the dominant structural motif of cationic sandwich complexes.[19] However, in this present investigation, none of the complexes possesses a sandwich structure with κ^3 coordination mode from both sides of the Janus scorpionate ligands. This demonstrates greater flexibility in binding than anticipated from previous results. The phen and bipy complexes (**6** and **7**) show phosphorescence at 77 K. For the phen complex **6**, the emission is assignable to a mix of ligand-centred and ligand-to-ligand charge transfer, whereas the bipy complex **7** features a ligand-centred emission.

Acknowledgements

We are thankful to Klaus-Peter Mester for recording NMR spectra and to Brigitte Michel for elemental analyses. M. I. acknowledges with special thanks the Deutscher Akademischer Austausch Dienst (DAAD) for providing a PhD stipend.

Experimental work

All the solvents used during this work were dried and distilled before use. $BiCl_3$, BiI_3, $BiNO_3\cdot5H_2O$, 2,2′-bipyridyine and10-phenanthroline were procured from Alfa Aesar and Acros Organics and used without further purification. NMR spectra were recorded on Bruker Advance 300, Bruker DRX 500 or Bruker-Advance 600 spectrometers and the chemical shifts were referenced to the residual proton (^{1}H) or the carbon signals of the deuterated solvents and are reported in ppm. Diffusion NMR measurements have been performed by using the LED sequence with bipolar gradients (ledbpgp2s) delivered by the manufacturer. The probe was disconnected from the gas supply and the sample has been allowed to equilibrate for four hours within the probe/magnet prior to data recording. The duration of the gradients was incremented linearly in 16 steps. The diffusion coefficients have been calculated by using the relaxation module of the Bruker software TOPSPIN®. Elemental analyses were performed using a Euro EA Elemental Analyser. ESI-MS and MALDI-TOF spectra were measured using Esquire 3000 (Bruker Daltonik 2000) and Voyager DE PE Bio-system 2000 spectrometers. Melting points were determined using a Büchi B 545 melting point apparatus and are uncorrected. Values of molar conductance (Ω^{-1}cm^{2}mol^{-1}) were determined at room temperature in acetonitrile solution (1 mmol L^{-1}) using a CG 853 conductometer (Schott GmbH, Germany). However for complex **3**, molar conductance was also measured at 70 °C.

Na[HB(mtda^{Me})$_3$](1)

Compound **1** was synthesised according to literature procedure.[9] ^{1}H NMR (dmso-*d6*) δ = 2.30 (s, 9H, CH_3); ^{13}C NMR (dmso-*d6*) δ = 190.1 (C═S), 154.3 (C═N), 16.3 (H_3C); ^{11}B NMR (dmso-*d6*) δ = –4.12 (br); ^{1}H NMR (dmf-*d7*) δ = 2.30 (s, 9H, CH_3); ^{13}C NMR (dmf-*d7*) δ = 191.1 (C═S), 154.3 (C═N), 15.9 (H_3C).

NBu$_4$[HB(mtda^{Me})$_3$] (2)

A sample was prepared according to a literature protocol.[9] Crystals suitable for diffraction were grown by slowly allowing a dichloromethane solution of **2** to evaporate in a refrigerator. ^{1}H NMR (CD_2Cl_2) 3.24 (m, 8H, NCH_2), 2.37 (s, 9H, mtda-CH_3), 1.64 (m, 8H, CH_2), 1.41 (m, 8H, CH_2), 0.98 (m, 12H, CH_3); ^{13}C NMR (CD_2Cl_2) 190.9 (C═S), 155.2 (HC═N), 58.9 (CH_3), 23.9 (CH_2), 19.7 (CH_2), 16.1 (CH_2), 13.3 (CH_3).

{HB(mtda^{Me})$_3$}$_2$BiCl (3)

A solution of Na[(mtda^{Me})$_3$] (**1**) (0.493 g, 1.15 mmol) in 50 mL of acetonitrile was slowly added to one of $BiCl_3$ (0.180 g, 0.574 mmol) in 50 mL of acetonitrile under N_2 atmosphere. The resulting orange yellow solution was stirred at room temperature for 4 h and then filtered. The volume of the sample was removed under vacuum and then dried. An orange solid was obtained, which was washed with small amount of methanol and then *n*-pentane. The product was recrystallised from acetonitrile. Single crystals with composition [{HB(mtda^{Me})$_3$}$_2$BiCl]·2CH_3CN (**3**) were obtained by slow diffusion of *n*-pentane into an acetonitrile solution of the complex. These crystals were dried under vacuum and analysed as follows. Yield 68%; m.p. 191 – 193 °C (with decomposition); Molar conductance 34 Ω^{-1}cm^{2}mol^{-1} at RT; 75 Ω^{-1}cm^2 at 70 °C; After drying the following elemental composition was found: Anal. calcd.

$C_{18}H_{20}B_2N_{12}S_{12}ClBi{\cdot}CH_3CN$ (found): C 21.91 (22.59), H 2.11 (2.18), N 16.61 (16.45); ^{1}H NMR ($C_2D_2Cl_4$), $\delta = 2.52$ (s, 18H, H_3C); ^{13}C NMR ($C_2D_2Cl_4$) $\delta = 187.5$ (C═S), 156.6 (C═N), 16.03 (H_3C); ^{1}H NMR (dmf-*d7*), $\delta = 2.32$ (s, 18H, H_3C); ^{13}C NMR (dmf-*d7*) $\delta = 190.91$ (C═S), 154.0 (C═N), 15.03 (H_3C); ESI-MS *m*/*z* [assignment] = 1018.8 $[Bi(L)_2]^+$ (L = $HB(mtda^{Me})_3{}^-$).

[{HB(mtda^{Me})$_3$}$_2$BiI](4)

This complex was prepared according to the same procedure as described above by reacting an acetonitrile solution of $Na[HB(mtda^{Me})_3]$ (0.493 g, 1.15 mmol) and a methanol solution of BiI_3 (0.338 g, 0.574 mmol) respectively. The following analytical data were obtained for the bulk solid of **4**. Yield, 63 %; m.p. 111 °C; Molar conductance at RT:42 $\Omega^{-1}cm^2mol^{-1}$; Anal. calcd. for $C_{18}H_{20}N_{12}S_{12}B_2BiI$ (found): C 18.85 (18.21), H 1.75 (1.98), N 14.53 (14.66); ^{1}H NMR (dmf-*d7*), $\delta = 2.46$ (s, br, 18H, H_3C); ^{1}H NMR (dmso-*d6*), $\delta = 2.76$ (s br, 18H, H_3C); ^{13}C NMR (dmso-*d6*) $\delta = 170.1$ (C═S), 154.7 (C═N), 16.4 (H_3C); ^{1}H NMR ($CDCl_3$), $\delta = 2.57$ (s, br, 18H, H_3C); ^{13}C NMR ($CDCl_3$) $\delta = 187.5$ (C═S), 163.4 (C═N), 16.5 (H_3C); ESI-MS *m*/*z* [assignment] = 1018.9 $[Bi(L)_2]^+$, 915.5 $[Na_2Bi(L)_2(I)_2]^+$, 871.7 $[Bi(LH)_2(I)_2]^+$.

Crystals were obtained by slow evaporation of an acetonitrile solution of complex **4**; this resulted only in two single crystals after several weeks. Their composition $Na[\{HB(mtda^{Me})_3\}_2BiI_2]{\cdot}CH_3CN.H_2O$ (**4a**) was determined by crystallography.

[{HB(mtda^{Me})$_3$}$_2$BiNO$_3$]$_n$ (5)

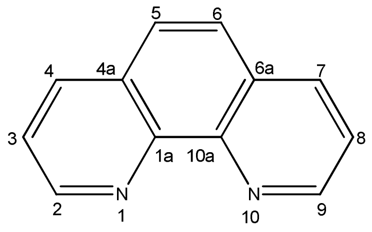
This complex was prepared according to same procedure as described above by reacting an acetonitrile solution of $Na[HB(mtda^{Me})_3]$ (0.493 g, 1.15 mmol) with a methanol solution of $Bi(NO_3)_3{\cdot}5H_2O$ (0.278 g, 0.574 mmol). It was recrystallised similar to **3**. The following analysis was carried out on bulk solid obtained after recrystallization from acetonitrile. Yield 73%; colour red; m.p. 125°C (decompose); Molar conductance at RT: 38 $\Omega^{-1}cm^2mol^{-1}$; ^{1}H NMR (dmso-*d6*), $\delta = 2.76$ (s, 18H, H_3C), 1.99 (s, H_3C-acetonitrile); ^{13}C NMR (dmso-*d6*) $\delta = 188.8$ (C═S), 154.3 (C═N), 16.4 (H_3C); ^{1}H NMR ($CDCl_3$), $\delta = 2.52$ (s, br,18H, H_3C), 2.08 (s, 3H, H_3C-acetonitrile); ^{13}C NMR ($CDCl_3$) $\delta = 169.0$ (C═S), 158.8 (C═N), 16.0 (H_3C); ESI-MS *m*/*z* [assignment] = 1018.8 $[Bi(L)_2]^+$, 612.8 $[Bi(LH)]^{2+}$. HRMS: calculated for $C_{18}H_{20}N_{12}S_{12}B_2Bi^+$ (found): 1018.85971, (1018.85668) (dev. 2.97 ppm).

Single crystals with composition $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n{\cdot}CH_3OH$ were obtained by cooling the methanol solution of complex **5** in a refrigerator for several weeks.

{HB(mtda^{Me})$_3$}$_2$Bi(phen)(Cl)$_2$ (6)

Equimolar solutions of $Na[HB(mtda^{Me})_3]$ (0.493 g, 1.15 mmol) and $BiCl_3$(0.362 g, 1.15 mmol) in 30 mL of anhydrous acetonitrile were prepared and mixed. The reaction mixture was stirred for 1 h at room temperature, and then the solution of 1,10-phenanthroline (0.207 g, 1.15 mmol) in 10 mL acetonitrile was added dropwise over a period of 45 minutes. The mixture was stirred for 6 h and the resulting precipitate were filtered, washed with small amounts of acetonitrile and methanol and dried in vacuum. The orange yellow solid was extracted three times with anhydrous chloroform (30 mL each). Removal of the solvent afforded compound **6** as a residue which was further washed with *n*-pentane and diethyl ether and again dried in vacuum. Single crystals of the composition $\{HB(mtda^{Me})_3\}_2Bi(phen)Cl_2{\cdot}2.1CHCl_3$ were obtained by slow evaporation of a chloroform solution of complex **6**. Below analysis was carried out on bulk solid. Yield 61 %; m.p. 206 – 208 °C (with decomposition); Molar conductance at RT: 16Ω^{-1} cm^2mol^{-1}; Anal. calcd. for $C_{21}H_{20}N_8S_6BBiCl_2$ (found): C 29.07 (29.52), H 2.32 (2.07), N 12.92 (10.83); ^{1}H NMR (dmf-*d7*) $\delta = 9.77$ (4H, dd, H(2,9), 8.97 (4H, dd, H(4,7)), 8.30 (4H, s, H(5,6)); 8.18 (4H, dd, H(3,8)), 2.32 (s, 9H, H_3C); ^{13}C NMR (dmf-*d7*) $\delta = 190.6$ (C═S), 153.8 (C═N), 150.6 (C2, C9), 143.6 (C1a, C10a), 139.6 (C4, C7), 130.4 (C4a, C6a), 127.4 (C5, C6), 125.1 (C3, C8), 15.0 (H_3C-mtda); ^{1}H NMR (dmso-*d6*) $\delta = 9.19$ (6H, dd, H(2,9)), 8.58 (6H, d, H(4,7)), 8.05 (6H, s, H(5,6)); 7.84 (6H, dd, H(3,8)), 2.30 (s, 9H, H_3C), ^{13}C NMR (dmso-*d6*) $\delta = 190.1$ (C═S), 154.3 (C═N), 150.6 (C2, C9), 145.4 (C1a, C10a), 137.5 (C4, C7), 129.0 (C4a, C6a), 127.2(C5, C6), 124.2 (C3, C8), 16.3 (H_3C-mtda); ESI-MS *m*/*z* [assignment] = 1018.8 $[Bi(L)_2]^+$, 828.9 $[Bi(L)(phen)(Cl)]^+$, 612.9 $[Bi(LH)]^+$

Free co-ligand (1,10-phenanthroline): ^{1}H NMR (dmf-*d7*) $\delta = 9.77$ (2H, dd, H(2,9), 8.97 (2H, dd, H(4,7)), 8.30 (2H, s, H(5,6)); 8.18 (2H, dd, H(3,8)), 2.32 (s, 9H, H_3C); ^{13}C NMR (dmf-*d7*) $\delta = 150.1$ (C2, C9), 146.2 (C1a, C10a), 136.2 (C4, C7), 129.0 (C4a, C6a), 126.7 (C5, C6), 123.5 (C3, C8).

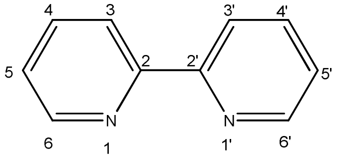


Scheme 4. Labelling scheme of 1,10-phenanthroline

{HB(mtda^{Me})$_3$}$_2$Bi(bipy)Cl$_2$ (7)

This complex was prepared using $Na[HB(mtda^{Me})_3$ (0.493 g, 1.15 mmol) and $BiCl_3$ (0.362 g, 1.15 mmol) and 2,2′-bipyrdyl (0.180 g, 1.15 mmol) in a similar way to that described for **7**. Crystals were grown by slow evaporation of acetonitrile solution of the complex **7** at room temperature with composition $\{HB(mtda^{Me})_3\}Bi(bipy)Cl{\cdot}CH_3CN$ (**7**).Below analysis was carried out on bulk solid. Yield 55 %; m.p. 161 – 164 °C (with decomposition); Molar conductance ($\Omega^{-1}cm^2mol^{-1}$) 23 at RT; Anal. calcd. for $C_{19}H_{18}N_8S_6BBiCl_2$ (found): C 27.12 (27.10), H 2.16 (1.95), N 13.32 (13.04); ^{1}H NMR (dmf-*d7*) $\delta = 8.80$ (3H, d, (6, 6´)), 8.49 (3H, d, H9) 8.05 (6H, m, (3, 3´)), 7.49 (3H, dd, (5, 5´)),2.32 (s, 9H, H_3C-mtda), ^{13}C NMR (dmf-*d7*) $\delta = 190.6$ (C═S), 155.6 (C═N), 153.8 (C2, C2´), 149.6 (C3, C3´), 137.4 (C5, C5´), 124.3 (C4, C4´), 120.6 (C6, C6´), 15.03 (H_3C-mtda); ^{1}H NMR (dmso-*d6*) $\delta = 8.69$ (2H, dd, H(6, 6´), 8.38 (2H, d, H(3, 3´), 7.96 (2H, dt, H(4, 4´), 7.47 (2H, dd, H(5, 5´), 2.30 (s, 9H, H_3C-mtda), ^{13}C NMR (dmso-*d6*) δ = 190.1 (C═S), 155.6 (C═N), 154.3 (C2,C2´), 149.8 (C3, C3´), 137.7 (C5, C5´), 124.6 (C4, C4´), 121.3 (C6, C6´), 16.4 (H_3C-mtda); ESI-MS *m*/*z* [assignment] = 767.3 $[BiL(bipy)]^+$, 685.5 $[BiLCl_2]^+$, 711.5 $[Bi(bipy)_3Cl]^+$.

Free co-ligand (2,2´-bipyridine): ^1H NMR (dmf-*d7*) δ = 8.90 (2H, dd, (6, 6´)), 8.66 (2H, d, H9) 8.15 (2H, m, (3, 3´)), 7.69 (2H, dd, (5, 5´).



Scheme 5. Labelling scheme of 2,2´-bipyridine

Photophysical characterisation

Spectroscopic-grade solvents were used for all photophysical characterizations. Absorption spectra were recorded with a Varian Cary300 double-beam spectrometer. Emission spectra at 300 and 77 K were recorded with a Jobin-Yvon Fluorolog 3 steady-state fluorescence spectrometer. For the emission measurements at room temperature the solutions were degassed by purging with argon for 20 min. Luminescence life-times were measured by using a Fluorolog FL-1040 phosphorimeter accessory. The estimated experimental errors are 5% in the molar absorption coefficients and phosphorescence life-times.

X-Ray diffraction experiments

X-ray diffraction data were collected from **2**, **3**, **4a**, **5**, **6** and **7**. Single-crystals suitable for X-ray diffraction were picked under inert paratone oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. Data sets for **5** and **6** were collected on a Bruker Nonius Kappa CCD diffractometer using Mo-K_α radiation, while data sets for compounds **2** and **3** were collected using a Bruker AXS Kappa (APEX II) with Cu-K_α radiation. Data sets for **4** and **7** were collected on a Super Nova using Mo-K_α radiation. A summary of data collection and structure refinement is reported in Table 6. The structures were solved by Direct Methods and refined by full-matrix least squares cycles (programs SHELXS-97 or SHELXL-97).[39] CCDC 970797–970802 contain 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.

Table 6. X-ray crystallographic data for compounds **2**, **3**, **4a**,**5**, **6** and **7**

Compound	**2**	**3**	**4a**	**5**	**6**	**7**
Empirical formula	$C_{16}H_{36}N$, $C_9H_{10}BN_6S_6 \cdot 0.25H_2O$	$C_{18}H_{20}B_2BiClN_{12}S_{12} \cdot 2CH_3CN$	$C_{25}H_{35}B_2BiI_2N_{15}NaO_2S_{12}$	$C_{18}H_{20}B_2BiN_{12}O_3S_{12} \cdot CH_3OH$	$C_{21}H_{18}BBiCl_2N_8S_6 \cdot 2.31(CHCl_3)$	$C_{21}H_{21}BBiCl_2N_9S_6$
M_r	652.36	1137.34	1469.79	1113.83	1140.63	882.52
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.2030(4)	9.5033(2)	14.92021(15)	14.0818(11)	9.3244(2)	8.98994(20)
b (Å)	12.2363(4)	15.4993(4)	17.08670(14)	12.7834(11)	15.4392(4)	11.7912(3)
c (Å)	13.4489(5)	28.4071(7)	20.8514(2)	22.436(3)	16.1384(4)	15.1964(4)
α (°)	69.855(1)	90	90	90	116.5277(11)	93.4539(19)
β (°)	65.230(1)	90	107.7276(11)	97.836(9)	92.9132(15)	99.5573(19)
γ (°)	69.921(1)	90	90	90	91.2053(14)	99.4185(18)
Z	2	4	4	4	2	2
V (Å^3)	1664.57(10)	4184.21(17)	5063.37(9)	4001.1(7)	2073.53(9)	1560.74(6)
F(000)	697	2232	2832	2184	1103	856
Crystal size (mm)	0.35 × 0.23 × 0.09	0.17 × 0.07 × 0.02	0.17 × 0.11 × 0.09	0.19 × 0.16 × 0.04	0.21 × 0.06 × 0.04	0.15 × 0.13 × 0.06
Reflections measured	39938	126049	136600	56524	47674	36667
Unique reflections (R_{int})	5956 (0.028)	7791 (0.039)	7384 (0.034)	9179 (0.054)	9473 (0.066)	9107 (0.035)
No. of parameters	547	477	373	468	490	369
R (I>2σ(I))	0.0254	0.0145	0.0210	0.0307	0.0314	0.0197
R_w(all reflections)	0.0681	0.0361	0.0494	0.0557	0.0693	0.0414
Goodness-of-fit	1.031	1.004	1.211	1.058	1.027	1.024
$\rho_{max/min}$(e Å^{-3})	0.37/–0.28	0.65/–0.83	0.98/–0.55	0.88/–0.79	1.16/–1.52	0.76/–0.85
Theta range for data collection (°)	3.72 – 69.90	3.11 – 69.39	2.60 – 30.03	3.51 – 25.50	2.95 – 27.49	2.66 – 30.00
Completeness to theta (%)	94.5	99.8	99.8	99.8	99.7	99.8
CCDC no.	970797	970798	970799	970800	970801	970802

Notes and references

[a] Universität Bielefeld, Lehrstuhl für Anorganische Chemie und Strukturchemie, Universitätsstraße 25, 33615 Bielefeld, Germany, Tel. +44 521 106 6182, Fax +44 521 106 6026, mitzel@uni-bielefeld.de

[b] Johannes-Keppler-Universität Linz, Institut für Anorganische Chemie, Altenbergerstraße 69, 4040 Linz, Austria, Tel. +43 732 2468 8801, Uwe.Monkowius@jku.at

† Electronic Supplementary Information (ESI) available: Graphs of the absorption spectrum of **2** and emission decay of **6** and **7**. See DOI: 10.1039/b000000x/

1 M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.* 1996, **16**, 1975.

2 G. Nuss, G. Saischek, B. N. Harum, M. Volpe, K. Gatterer, F. Belajand, N. C. Mösch-Zanetti, *Inorg. Chem.* 2011, **50**, 1991.

3 M. D. Spicer and J. Reglinski, *Eur. J. Inorg. Chem.* 2009, 1553.

4 M. Garner, K. Lewinski, A. Pattek-Janczyk, J. Reglinski, B. Sieklucka, M. D. Spicer and M. Szaleniec, *Dalton Trans.* 2003, 1181.

5 J. P. Jesson, S. Trofimenko and D. R. Eaton, *J. Am. Chem. Soc.* 1967, **89**, 3158.

6 C. A. Dodds, M. Garner, J. Reglinski and M. D. Spicer, *Inorg. Chem.* 2006, **45**, 2733.

7 G. Nuss, A. Ozwirk, B. N. Harum,G. Saischek, F. Belajand N. C. Mösch-Zanetti, *Eur. J. Inorg. Chem.* 2012, 4701.

8 R. M. Silva, C. Gwengo, S. V. Lindeman, M. D. Smith and J. R. Gardinier, *Inorg. Chem.* 2006, **45**, 10998.

9 R. M. Silva, C. Gwengo, S. V. Lindeman, M. D. Smith, G. J. Long, F. Grandjean and J. R. Gardinier, *Inorg. Chem.* 2008, **47**, 7233.

10 a) S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999; b) S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.* 1987, **28**, 1507.

11 P. J. Bailey, M. Lanfranchi, L. Marchiò and S. Parsons, *Inorg. Chem.* 2001, **40**, 5030.

12 R. Cammi, M. Gennari, M. Giannetto, M. Lanfranchi, L. Marchiò, G. Mori, C. Paiola and M. A. Pellinghelli, *Inorg. Chem.* 2005, **44**, 4333.

13 M. Imran, B. Neumann, H.-G. Stammler, U. Monkowius, M. Ertl and N. W. Mitzel, *Dalton Trans.* 2013, **42**, 15785.

14 L. Huang, K. J. Seward B. P. Sullivan, W. E. Jones, J. J. Mecholsky and W. J. Dressick, *Inorg. Chim. Acta* 2000, **310**, 227 and references therein.

15 a) P. J. Han, A. L. Rheingold, and W. C. Trogler, Inorg. Chem., 2013, **52**, 12033; b) R. J. F. Berger, D. Rettenwander, S. Spirk, C. Wolf, M. Patzschke, M. Ertl, U. Monkowius and N. W. Mitzel, Phys. Chem. Chem. Phys. 2012, **14**, 15520; c) A. C. Wibowo, M. D. Smith and H-C. zur Loye, Chem. Commun. 2011, **47**, 7371.

16 R. Diemer, U. Dittes, B. Nuber, V. Seifried, W. Opferkuchand B. K. Keppler, *Metal-Based Drugs* 1995, **2**, 271.

17 J. Reglinski, M. D Spicer, M. Garner and A. R. Kennedy, *J. Am. Chem. Soc.* 1999, **121**, 2317.

18 M. Bao, T. Hayashi and S. Shimada, *Dalton Trans.* 2004, 2055.

19 C. A. Dodds, J. Reglinski and M. D. Spicer, *Chem. Eur. J.* 2006, **12**, 931.

20 a) P. Pyykkö, *Chem. Rev.* 1988, **88**, 563; b) N. K. Yannis, *J. Chem. Soc. Dalton Trans.* 1997, 1.

21 M. Careri, L. Elviri, M. Lanfranchi, L. Marchiò, C. Mora and M. A. Pellinghelli, *Inorg. Chem.* 2003, **42**, 2109.

22 M. Lanfranchi, L. Marchiò, C. Mora and M. A. Pellinghelli, *Inorg. Chim. Acta* 2004, **357**, 367.

23 M. Shu, J. Cui and J. Sun, *Appl. Organomet. Chem.* 2005, **19**, 184.

24 We attempted to screen trivalent bismuth complexes with soft scorpionate ligands through a Cambridge Structural Data base search (version 5.33, updated May, 2012). Total 9 hits (FILZIK, HEBZOE, HEBZUK, HEBZUK01, HIXNAD, HIXNEH, IRARIC, QUOKOC, WUYHIH) for such compounds were found. In these hit listed compounds Bi–S bond length was found in the range 2.63 – 2.83 Å.

25 D. Roitershtein, A. Domingos, L. C. J. Pereira, J. R. Ascenso and N. Marques, *Inorg. Chem.* 2003, **42**, 7666

26 M. Imran, B. Neumann, H.-G. Stammler, U. Monkowius, M. Ertl and N. W. Mitzel, *Dalton Trans.* 2014, **43**, 1267

27 B. M. Bridgewater and G. Parkin, *Inorg. Chem. Comm.* 2000, **3**, 534.

28 C. Kimblin, B. M. Bridgewater, T. Hascall and G. Parkin, *J. Chem. Soc., Dalton Trans.* 2000, **6**, 891.

29 H. Yin and C. Wang, *Appl. Organomet. Chem.* 2004, **18**, 195.

30 J.-H. Lamm, P. Niermeier, A. Mix, J. Chmiel, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Angew. Chem. Int. Ed.* 2014, **53**, in press, DOI: 10.1002/anie.201402145R1; *Angew. Chem. Int. Ed.* 2014, **126**, 10.1002/ange.201402145R1.

31 G. Accorsi, A. Listorti, K. Yoosaf, N. Armaroli, *Chem. Soc. Rev.* 2009, **38**, 1690.

32 K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrine Complexes, Academic Press, London, 1992, pp. 92.

33 B. N. Bandyopadhyay, A. Harriman, *J. Chem. Soc., Faraday Trans. 1* 1977, **73**, 663.

34 J. Kotlicka, Z. R. Grabowski, *J. Photochem.* 1979, **11**, 413.

35 A. Harriman, *J. Photochem.* 1978, **8**, 205.

36 K. A. Truesdell, G. A. Crosby, *J. Am. Chem. Soc.* 1985, **107**, 1787.

37 G. A. Crosby, R. G. Highland, K. A. Truesdell, *Coord. Chem. Rev.* 1985, **64**, 41.

38 V. W.-W. Yam, Y.-L. Pui, K.-K. Cheung, *New J. Chem.* 1999, **23**, 1163.

39 SHELXL97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112.

TOC entry

Synthesis, structural and photo-physical studies of bismuth(III) complexes with Janus scorpionate and co-ligands

M. Imran,[a] A. Mix,[a] B. Neumann,[a] H.-G. Stammler,[a] U. Monkowius,[b] P. Bleckenwegner[b] and N. W. Mitzel[a,*]

Mixed bismuth complexes exhibiting unprecedented (B)H···Bi interactions and interesting photophysical behaviour are reported.