Synthesis, structures and properties of a new series of platinum-diimine-dithiolate complexes[†]

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The new square-planar platinum-diimine-dithiolate compounds [Pt(mesBIAN)SS] have been synthesised {mesBIAN = bis(mesityl)biazanaphthenequinone; SS = 1,2-dithiooxalate (dto) **1**, maleonitriledithiolate (mnt) **2**, 1,2-benzenedithiolate (bdt) **3**, 3,4-toluenedithiolate (tdt) **4** and 1,3-dithia-2-thione-4,5-dithiolate (dmit) **5**}, and the X-ray crystal structures of **3** and **5** determined. Cyclic voltammetry reveals that all the compounds form stable anions, and ESR spectroscopy of these anions shows that the SOMO is based upon the mesBIAN ligand; compounds **2–5** also show a reversible oxidation wave in their CV. Computational studies reveal that charge-transfer processes from orbitals that are combinations of metal and dithiolate ligand to a mesBIAN π^* -based LUMO are responsible for the low energy absorptions seen in the UV/visible spectra of these compounds, and that the reverse process is responsible for the observed room-temperature solution luminescence of [Pt(mesBIAN)Cl₂] and **1**, **2** and **5**. Compounds **3** and **4**, containing aromatic thiolates, were not found to luminesce under the same conditions. Resonance Raman experiments have shown the origin of band-broadening of the lowest-energy absorption band in the absorption spectra of **2–5** to be due to vibronic structure within one electronic transition.

Introduction

The past twenty years have seen a great deal of interest in the photophysical properties of compounds of the general form [Pt(NN)(SS)], where NN is a bidentate N-heterocyclic ligand such as bipyridine or phenanthroline (or a derivative thereof), and SS is a bidentate dithiolate ligand. The reason for such interest is the observation that these compounds photoluminesce, not only in glassy media at low-temperature, but also in fluid solution at room temperature.¹ This indicates a long-lived excited state, the energy of which might be utilised in applications that require photo-induced charge separation; studies of the dithiolates as dyes for solar cells,² for the sensitisation of the excited states of oxygen,³ as cation sensors⁴ and as non-linear optical materials⁵ have been reported. By peripheral modification of the dithiolate ligand, the precise details of the photophysical properties can be fine tuned.⁶

A crucial feature in preparing luminescent compounds of this type is to minimise the effect of radiationless deactivation pathways. In practice, such pathways often occur *via* non-emissive d-d (*i.e.* ligand field) excited states, so to avoid such radiationless deactivation it is important to ensure that the energy of such excited states is much higher than that of the excited state responsible for the emission. Conversely, if the energy of the charge-transfer excited state is too low, then it can fall victim to the 'energy gap law' and be quenched by efficient internal conversion to the ground state.

Within this context we have recently reported our preliminary studies on platinum compounds of the bis(mesityl)biazanaphthenequinone ligand (mesBIAN).7 In this ligand the ligating nitrogen atoms are exocyclic rather than incorporated into the carbocyclic system, but otherwise it functions much as an analogue of bipyridine and phenanthroline, forming air stable platinum compounds [Pt(NN)(LL)] with a variety of coligands L. An important feature of such compounds is that the mesBIAN ligand has a very low-energy π^* orbital that forms the LUMO. This means that whilst [Pt(bipy)Cl₂] is reduced at -1.14 V vs. SCE,⁸ [Pt(mesBIAN)Cl₂] is reduced at -0.60 V on the same scale,7 and that the longest wavelength absorption maximum in the UV/visible spectrum of [Pt(mesBIAN)Cl₂] is at 518 nm, compared to 393 nm for [Pt(bipy)Cl₂].⁹ Such a low energy LUMO significantly affects the photophysical properties of the compounds; we have shown that whereas [Pt(bipy)Cl₂] does not luminesce from fluid solution because of the metalcentered nature of its lowest excited state,10 [Pt(mesBIAN)Cl₂] emits at 777 nm from a mixed platinum/chlorine-to-diimine charge-transfer excited state.7 This is, to the best of our knowledge, the first platinum-diimine-dichloride compound to exhibit this behaviour.

Unlike bipyridine and its derivatives, the presence of the methyl groups in the 2 and 6 positions of the mesityl ring allows the mesBIAN ligand to shield the axial positions of the platinum atom, which might potentially hinder solvent interaction at these sites and thus prevent solvent mediated non-radiative relaxation of any excited states. Furthermore, the rigidity of the ligand might lead to improved luminescence behaviour. We report herein on a new series of [Pt(mesBIAN)(SS)] complexes (Fig. 1), where SS represents a dithiolate ligand {SS = 1,2-dithiooxalate (dto) 1, maleonitriledithiolate (mnt) 2, 1,2-benzenedithiolate (bdt) 3,

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Fig. 1 Structures of the dithiolate compounds reported herein.

3,4-toluenedithiolate (tdt) 4 and 1,3-dithia-2-thione-4,5-dithiolate (dmit) 5}. The use of strong σ-donor ligands such as dithiolates is a recognised strategy for creating luminescent platinum– diimine compounds,¹¹ and we show that in complexes which also contain the mesBIAN diimine ligand (which gives them a low lying LUMO), small HOMO–LUMO gaps and low-energy charge transfer excited states are produced. These have been fully characterised by experimental and computational methods.

Results and discussion

Synthesis and characterisation

The dithiolate compounds [Pt(mesBIAN)(SS)] **1–4** (Fig. 1) were synthesised by a metathesis reaction between [Pt(mesBIAN)Cl₂] and the appropriate dimethyltin dithiolate [Me₂Sn(SS)], with SS = 1,2-dithiooxalate (dto) **1**, maleonitriledithiolate (mnt) **2**, 1,2-benzenedithiolate (bdt) **3** and 3,4-toluenedithiolate (tdt) **4**. Compound **5** contains the 1,3-dithia-2-thione-4,5-dithiolate (dmit) ligand, and was obtained from reaction of the same platinum-containing starting material with the salt [Bu₄N][Zn(dmit)₂] because of the instability of the dimethyltin compound of dmit. Complexes **1–4** were simply crystallised from the appropriate reaction mixture, and **5** required only a simple workup prior to isolation. All new compounds are air stable as solids and as solutions, and were fully characterised by elemental analysis and NMR spectroscopy.

The X-ray crystal structures of **3** and **5** were determined (Fig. 2 and 3). Important bond lengths and angles are given in Tables 1 and 2, and crystallographic data in Table 3. The compounds are, as expected, approximately square planar about the platinum atom, with deviation due to the small bite angle of the mesBIAN ligand (about 80°). The molecules are essentially planar apart from the mesityl rings of the mesBIAN ligand, which lie approximately perpendicular to the rest of the molecule, and which effectively prevent π -interactions between neighbouring molecules. This may prove useful in preventing the excimer emission and self-quenching



Fig. 2 The molecular structure of **3**. Hydrogen atoms have been removed for clarity.



Fig. 3 The molecular structure of **5**. Hydrogen atoms have been removed for clarity.

behaviour that many platinum–diimine compounds display in solution.¹¹ The Cambridge Structural Database (CSD)¹² contains six structures that contain the platinum–diimine–bdt unit, in all of which the diimine is 2,2'-bipyridine or a derivative thereof.^{3,13} The metrical parameters of the platinum–bdt unit in the structure of **3** are similar to those in these six structures; thus, for example, the platinum–sulfur distances of **3** {2.232(2) to 2.244(2) Å} may be compared with those of [Pt(bipy)(bdt)]³ {2.244(2) and 2.250(2) Å}, and the platinum–nitrogen distances of 2.027(5) to 2.054(5) Å in **3** with 2.050(4) and 2.049(5) Å in [Pt(bipy)(bdt)]. The CSD

Pt(1)–N(1)	2.027(5)	Pt(101)–N(101)	2.053(5)
Pt(1) - N(2)	2.044(5)	Pt(101)–N(102)	2.054(5)
Pt(1)-S(1)	2.2321(18)	Pt(101)–S(101)	2.2409(18)
Pt(1)-S(2)	2.2439(17)	Pt(101)–S(102)	2.2439(17)
N(1)-C(1)	1.297(7)	N(101)–C(101)	1.289(8)
N(1)-C(13)	1.462(7)	N(101)–C(113)	1.462(7)
N(2)-C(11)	1.298(8)	N(102)–C(111)	1.288(7)
N(2)-C(22)	1.462(7)	N(102)–C(122)	1.457(7)
S(1) - C(32)	1.751(7)	S(101)-C(132)	1.744(6)
S(2)-C(31)	1.746(7)	S(102)–C(131)	1.747(7)
N(1)-Pt(1)-N(2)	79.9(2)	N(101) - Pt(101) - N(102)	79.2(2)
N(1)-Pt(1)-S(1)	93.86(15)	N(101)–Pt(101)–S(101)	95.90(15)
N(2)-Pt(1)-S(1)	172.12(15)	N(102)-Pt(101)-S(101)	174.69(15)
N(1)-Pt(1)-S(2)	175.43(15)	N(101)-Pt(101)-S(102)	173.95(15)
N(2)-Pt(1)-S(2)	96.04(15)	N(102)-Pt(101)-S(102)	94.99(15)
S(1) - Pt(1) - S(2)	90.37(6)	S(101)-Pt(101)-S(102)	89.98(6)

Table 2Selected bond lengths (Å) and angles (°) for 5

Pt(1) - N(2)	2.042(4)	S(1)-C(32)	1.743(5)
Pt(1) - N(1)	2.042(3)	S(2) - C(31)	1.738(5)
Pt(1)-S(2)	2.2523(12)	C(31) - C(32)	1.357(6)
Pt(1)-S(1)	2.2580(13)	C(31) - S(4)	1.743(5)
N(1) - C(1)	1.302(6)	C(32) - S(3)	1.749(5)
N(1)-C(13)	1.448(5)	S(3) - C(33)	1.724(5)
N(2)-C(11)	1.291(6)	S(4) - C(33)	1.734(5)
N(2)-C(22)	1.455(5)	C(33) - S(5)	1.662(5)
N(2)-Pt(1)-N(1)	80.37(14)	C(31)-C(32)-S(1)	122.2(4)
N(2)-Pt(1)-S(2)	93.38(11)	C(31)-C(32)-S(3)	115.7(4)
N(1)-Pt(1)-S(2)	173.65(10)	S(1)-C(32)-S(3)	122.1(2)
N(2)-Pt(1)-S(1)	174.33(10)	C(33)–S(3)–C(32)	97.7(2)
N(1)-Pt(1)-S(1)	94.45(10)	C(33)-S(4)-C(31)	97.6(2)
S(2)-Pt(1)-S(1)	91.75(4)	S(5)-C(33)-S(3)	125.6(3)
C(32)-C(31)-S(2)	123.2(4)	S(5)-C(33)-S(4)	121.4(3)
C(32)-C(31)-S(4)	116.1(4)	S(3)-C(33)-S(4)	112.9(3)
S(2)-C(31)-S(4)	120.7(3)		

contains no platinum–diimine–dmit structures comparable to **5**. Comparison of the bond lengths and angles in the structure of **5** to those of **3** reveal no significant differences in the coordination environment about the platinum atom and in the geometry of the mesBIAN ligand.

Table 3 Summary crystallographic data for 3.0.75CH₂Cl₂ and 5.2CHCl₃

Electronic absorption spectroscopy

The compounds are all bold colours. Solutions of 1 are red, 2 is blue, and 3, 4 and 5 are green. These colours are due to strong absorption bands between 500 and 850 nm ($\varepsilon \approx 2 \times$ $10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (Table 4 and Fig. 4), which are the singlet electronic transitions from a mixed dithiolate-metal HOMO to a mesBIAN π^* LUMO (see below), and which are therefore mixed metalligand to ligand charge transfer (MMLL/CT) transitions. This assignment is supported by the nature of their solvatochromism; the lowest energy absorption band for all compounds moves to lower energy as the polarity of the solvent is decreased.^{14,15} This is illustrated graphically in Fig. 5, which plots the lowest energy absorption maximum for each compound in a variety of solvents against the solvent polarity parameter (as empirically determined by Eisenberg and Cummings for [Pt(NN)(SS)] compounds).¹⁵ It is apparent from Fig. 5 that compounds 1, 2 and 5 give less good linear correlations to the scale than 3 and 4, particularly for the data points pertaining to dichloromethane (polarity 0.765). 1, 2 and 5 have dithiolate ligands that have lone pairs of electrons and protuberant π -bonds, and CH_2Cl_2 is the only solvent used that does not possess either of these features.



Fig. 4 UV/visible spectra of 1-5 in CH_2Cl_2 .

The lowest energy absorption in **2–5** is apparently composed of at least two separate bands of similar energy (Fig. 4); a deconvolution of the spectrum of **4** into three separate components is shown in Fig. 6. These components appear to have slightly different

Compound	3.0.75CH ₂ Cl ₂	5·2CHCl ₃
Empirical formula	$C_{36.75}H_{33.50}Cl_{1.50}N_2PtS_2$	$C_{35}H_{30}Cl_6N_2PtS_5$
Formula weight	815.54	1046.70
Temperature/K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a/Å	14.971(3)	15.048(4)
b/Å	18.145(4)	11.847(4)
c/Å	24.787(5)	21.948(7)
β/°	90.83(3)	94.33(2)
Volume/Å ³	6732(2)	3902(2)
Ζ	8	4
μ/mm^{-1}	4.440	4.305
Reflections collected	76 537	26 993
Independent reflections	15442[R(int)=0.1076]	8951 [R(int) = 0.0494]
Final <i>R</i> indices $[I > 2 \sigma(I)]$	R1 = 0.0442, wR2 = 0.0750	R1 = 0.0377, wR2 = 0.0812
R indices (all data)	R1 = 0.0820, wR2 = 0.0819	R1 = 0.0486, wR2 = 0.0850

MeCN DMSO DMF Acetone DCM thf λ λ λ λ λ λ З З З \mathcal{E} Е 11 564

Table 4 Lowest absorption maxima (nm) and extinction coefficients $(M^{-1} \text{ cm}^{-1})$ in various solvents for 1–5



Fig. 5 The energy of the lowest energy transition in compounds 1–5 plotted against the solvent polarity, showing lines of best fit with R^2 values. The values for the polarity are taken from Eisenberg and Cummings,¹⁵ and are as follows: MeCN, 1; DMSO, 0.973; DMF, 0.901; acetone, 0.797; CH₂Cl₂, 0.765; thf, 0.494.



Fig. 6 Deconvolution of the low-energy absorption envelope of 4 (bold line) into three separate Gaussian components (at 12706, 13750 and 15135 cm^{-1}).

solvatochromism, as their resolution increases with decreasing solvent polarity. This effect is also apparent in the spectra of analogous 4,4'-bis(*tert*-butyl)-2,2'-bipyridine compounds.¹⁵

Electrochemistry and ESR spectroscopy

All compounds 1–5 display a fully reversible one-electron reduction at a potential between -0.5 and -1 V, and 2–4 also show a reversible oxidation wave between 0.75 and 1.4 V (Table 5). As the reduction potential is related to the energy of the LUMO of the complex, and the oxidation potential to the energy of the HOMO, then the difference between them should relate to the HOMO–

Table 5 Electrochemical data for 1–5

Compound	$E^{\circ}(\text{red})/\text{V}$	$E^{\circ}(\mathrm{ox})/\mathrm{V}$
1 2 3 4 5	-0.57 -0.63 -0.86 -0.85 -0.71	 1.34 0.82 0.77 0.77

LUMO gap. As this gap is also related to the lowest energy transition in the UV/visible spectrum, a correlation between the two may be observed (Fig. 7).



Fig.7 Correlation of ΔE , the difference in oxidation and reduction potentials for **2–5** (×), with ν , the energy of the corresponding HOMO–LUMO transition.

ESR spectra of the anions 1^- , 2^- , 4^- and 5^- were recorded on 2:1 thf-CH₂Cl₂ solutions of the compounds chemically reduced in-situ in an ESR tube. As fluid samples they all show a single broad peak which overlaps with the satellites caused by coupling to ¹⁹⁵Pt. As frozen glasses a well defined rhombic spectrum is observed, with ¹⁹⁵Pt satellites on all three g components, and coupling to the two nitrogen atoms of the mesBIAN ligand on the high field component. Fig. 8 shows the spectrum of 4^- as a representative example, and g and A values for all complexes are presented in Table 6. Assignment of these values follows the methodology of McInnes and co-workers8 which also allows calculation of the values of a^2 and b^2 , the coefficients of the 5d_{yz} and 6p_z orbitals in the SOMO. ESR spectroscopy on samples of compound 3 reduced under identical circumstances did not provide a spectrum showing a single paramagnetic species, possibly due to molecular aggregation within the sample.[‡]



Fig. 8 The experimental (top) and simulated (bottom) ESR spectrum of 4^- , recorded in frozen 2 : 1 thf–CH₂Cl₂ solution at 110 K.

The hyperfine coupling constants of the anions 1^- , 2^- , 4^- and 5⁻, and of $[Pt(mesBIAN)Cl_2]^-$, indicate a contribution of between 7% and 14% from metal orbitals to the SOMO (Table 6). For 2^{-} , 4^{-} , 5^{-} and [Pt(mesBIAN)Cl₂]⁻ the majority of this (between 4 and 8%) is from the $5d_{yz}$ orbital and the remainder from the $6p_z$. The hyperfine coupling constants A for 1⁻ contrast with those for the remaining compounds. At 50×10^{-4} cm⁻¹, the magnitude of the isotropic coupling constant $\langle A \rangle$ is much smaller than for the other species, for which it is around 75 \times 10⁻⁴ cm⁻¹. Also, uniquely for 1^- the anisotropic hyperfine coupling constants indicate a value of a^2 which is lower than b^2 , indicating a larger contribution to the SOMO from the $6p_z$ orbital than from the $5d_{vz}$. Taken together, these facts would seem to indicate that whilst the metal contribution to the SOMO of 1^- is of the same magnitude as in the other compounds, the precise composition is different. For all compounds, the total contribution of metal orbitals to the SOMO calculated in this way agrees to within 5% of the value from computational modelling of the anions (Table 6).

Table 6 ESR spectros	scopic para	ameters for	1-, 2 ⁻ , 3 ⁻ a	nd 5 ⁻ , and 1	for [Pt (me	sBIAN)	Cl ₂] ⁻ for con	nparison. A	values are gi	ven in 10 ⁴ cı	n ⁻¹				
Compound	$g_{\rm iso}$	$g_1 = g_y$	$g_2 = g_x$	$g_3 = g_z$	< g >	$A_{ m iso}$	$A_1 = A_y$	$A_2 = A_x$	$A_3 = A_z$	< 4>	<i>A</i> ₃ (2 N)	a^2	b^2	$a^{2} + b^{2}$	Computed metal contribution (%)
1-	2.014	2.043	2.017	1.978	2.013	50	-55	-73	-22	-50.00	13.5	0.038	0.068	0.107	10.2
2-	2.012	2.060	2.022	1.946	2.009	75	-71	-90	-55	-72.00	13	0.040	0.033	0.074	11.2
-4	2.020	2.078	2.025	1.949	2.017	75	-68	-92	-55	-71.67	14	0.051	0.027	0.078	12.8
5-	2.015	2.065	2.023	1.948	2.012	73	-70	-95	-50	-71.67	14	0.053	0.041	0.095	11.8
[Pt(mesBIAN)Cl ₂] ⁻	2.011	2.074	2.003	1.952	2.010	75	-73	-112	-48	-77.67	13.6	0.083	0.052	0.135	11.5

[‡] Throughout this paper, we use a coordinate system with the *y*-axis bisecting the diimine and dithiolate ligands (*i.e.* the C_2 rotational axis), the *z*-axis perpendicular to the plane of the molecule, and the *x* axis perpendicular to *y* and *z*.

Computational studies

In an attempt to more thoroughly understand the electronic properties of 1–5, and of [Pt(mesBIAN)Cl₂], we have used a standard DFT approach to optimise their ground state geometries and hence visualise their frontier orbitals (Table 7 and Fig. 9), as well as TD-DFT to aid in the interpretation of allowed UV/visible transitions (Table 8).¹⁶ All calculations used a dielectric continuum to approximate dichloromethane solvation (see the Experimental for details of calculations).

The compounds all have a LUMO of b_1 symmetry (in the C_{2v} point group) and common origin, being based mainly (between 80 and 90%) upon the π^* system of the mesBIAN ligand with contributions from the metal d_{yz} orbitals (between 4 and 10%), in accord with the interpretation of the ESR spectra of their anions. One noticeable anomaly is that the dithiooxalate complex 1 has a smaller contribution to this MO from the donor sulfur atoms of the dithiolate ligand (0.5% from each sulfur atom) than any other compound (which have contributions of 3 to 4% from each sulfur

atom). This may account for the different LUMO constitution of this compound apparent from the ESR spectrum. The LUMO + 1 in all cases is also essentially a mesBIAN π^* orbital, of a₂ symmetry.

The nature of the HOMO varies between compounds. In [Pt(mesBIAN)Cl₂] and **1**, it is a π^* orbital of a₂ symmetry, with major contributions from the metal d_{xz} orbital and the chlorine or sulfur atoms respectively. It is metal–ligand antibonding. In **2–5** it is of b₁ symmetry, comprised mainly of a dithiolate π^* orbital (70–80%), which again is out of phase with a small metal contribution. The equivalent b₁(π^*) orbital is the HOMO-2 of **1** and HOMO-5 of [Pt(mesBIAN)Cl₂].

The computed electronic transitions (Table 8) shed light upon the UV/vis spectra of the compounds. We have correlated the computed and observed transitions by neglecting computed transitions with oscillator strengths f lower than 0.1; calculations of transitions often give many transitions with very low oscillator strengths, and matching computed and observed transitions can be problematic. In all cases, the lowest energy transition visible

 Table 7
 Calculated compositions of orbitals involved in visible transitions

			Contribution to orbital (%)		(%)	
			Pt	mesBIAN	Ligand	
Compound	Orbital	Symmetry	Total	Total	Total	From each S atom
[Pt(mesBIAN)Cl ₂]	132 (HOMO – 5)	b ₁	50.2	15.8	16.9, 17.0	
	137 (HOMO)	a ₂	41.2	31.3	13.8, 13.6	
	138 (LUMO)	b_1	9.7	88.2	1.0, 1.0	
	139 (LUMO + 1)	a_2	1.2	98.7	0, 0	_
1	148 (HOMO – 2)	b_1	39.5	11.7	48.8	18.8
	150 (HOMO)	a ₂	33.3	8.6	58.1	24.9
	151 (LUMO)	b_1	8.5	87.6	3.9	0.5
	152 (LUMO + 1)	a_2	1.01	98.9	0	0
2	155 (HOMO)	b ₁	13.5	10.5	76.0	26.6
	156 (LUMO)	\mathbf{b}_1	9.6	83.9	6.5	2.9
3	156 (HOMO)	b_1	11.2	13.5	75.4	24.0
	157 (LUMO)	\mathbf{b}_1	10.8	80.7	8.4	3.5
4	159 (HOMO - 1)	b ₁	22.9	3.7	73.4	28.8, 20.1
	160 (HOMO)	b ₁	10.2	13.3	76.5	19.3, 26.6
	161 (LUMO)	b_1	10.8	80.6	8.6	3.5, 3.6
5	166 (HOMO – 3)	b ₁	18.4	6.0	75.6	7.2
	169 (HOMO)	b_1	6.0	9.7	84.3	18.9
	170 (LUMO)	b	10.1	81.2	8.6	3.5
	172 (LUMO + 2)	b	0.2	0.1	99.8	0



Fig. 9 Frontier orbitals of [Pt(mesBIAN)Cl₂], illustrating the general form of these orbitals in 1–5. From left to right: orbital 132 (b_1 symmetry), 137 (HOMO, a_2), 138 (LUMO, b_1), 139 (a_2).

-5

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	Observed	Calculated			
Compound	Energy/eV	Energy/eV	State no.	f	Constitution
[Pt(mesBIAN)Cl ₂]	2.40	2.82	8	0.17	132–138 (79%), 137–139 (5%)
	2.56	3.36	13	0.26	137–139 (83%),
1	2.34	2.57	5	0.25	148–151 (83%)
	2.55	3.03	10	0.19	150-152 (90%)
2	1.82	1.92	1	0.26	155–156 (84%)
3	1.66	1.73	1	0.30	156–157 (79%)
4	1.61	1.68	1	0.26	160–161 (71%), 159–161 (11%)
5	1.50	1.57	1	0.28	169–170 (82%)
		2.77	8	0.21	169–172 (75%), 166–170 (16%)

in the UV/visible spectrum is predicted to be between two orbitals of b_1 symmetry; that is from HOMO to LUMO in 2– 5, from HOMO-2 to LUMO in 1, and from HOMO-5 to LUMO in [Pt(mesBIAN)Cl₂]. This is from the occupied mixed metaldithiolate π^* orbital to the empty mesBIAN π^* orbital, and is thus mixed metal-ligand to ligand charge transfer (MMLL/CT) in nature. Transitions from the dithiolate (or chloride) ligand to mesBIAN move charge along the molecular y-axis, creating a substantial transition dipole moment in this direction and a very small transition dipole moment in the perpendicular x and z directions. Given this, the properties of the C_{2v} point group mean that the overlap integral $\langle \psi_e | \mu_y | \psi_g \rangle$ is only appreciable when ψ_g and ψ_e are both orbitals of the same symmetry. This explains why transitions from the HOMO to other orbitals in the mesBIAN manifold which do not have b₁ symmetry have very small computed oscillator strengths and are hence not likely to be observed experimentally. Compared with the experimentally observed transitions, the calculated values are generally between 0.05 to 0.1 eV too large, while for compound 1 there is a much larger difference (0.2 eV). For 2-5, the calculated transition energy is within the broad envelope of the observed transition, generally at a point midway between the two discernable peaks that contribute to the envelope.

The calculations also predict that for [Pt(mesBIAN)Cl₂] and for **1** there is a second strong transition within 80 nm of that of lowest energy. In both cases this is from HOMO to LUMO + 1, again mixed metal-dithiolate to mesBIAN π^* MMLL/CT in character and strongly symmetry allowed (both orbitals having a₂ symmetry). This would explain the characteristic double peak seen at around 515 nm in the spectra of these compounds. In contrast, for the remaining compounds the calculations do not predict any other strong absorptions within 250 nm of that at the lowest energy. We therefore surmised that the observed broadness of this lowest energy absorption band in **2–5** is probably due to poorly resolved vibrational structure, as described for [M(baba)(mnt)] (M = Ni or Pd, baba = bisacetylbisaniline)¹⁷ and [Pt(bipy)(pz)₂] (pz = pyrazolate)¹⁸ complexes, which is not captured by our TD-DFT studies, rather than the presence of more than one transition.

This hypothesis was confirmed by resonance Raman spectroscopy on [Pt(mesBIAN)Cl₂] and **4**. The Raman spectrum of [Pt(mesBIAN)Cl₂], obtained using 514.5 nm excitation in resonance with the lowest allowed electronic transition of this compound, is shown in Fig. 10. It is dominated by a band at 1570 cm⁻¹, which we assign to CN stretching vibrations of the coordinated mesBIAN ligand by comparison with data on related metal–diazabutadiene complexes.^{17,19} An enhancement of



Fig. 10 Resonance Raman spectrum of polycrystalline [Pt(mesBIAN)-Cl₂] under 514.5 nm excitation.

the v(CN) mode would also be consistent with our assignment of the electronic transition at 514 nm, and the fact that the LUMO involved has a large component on the CN fragment of the mesBIAN ligand (Fig. 9 and Table 7, transition between orbitals 132 and 138). The lack of Raman bands characteristic of the phenyl ring in the region 1080–1100 cm⁻¹ indicates that the mesityl substituents on the mesBIAN ligand are not involved in the electronic transition of interest, and is also consistent with the calculated composition of the frontier orbitals.

The other vibrational bands observed at 533, 656, 1149, 1161, 1200, 1311, 1416, 1438, 1604 and 1787 cm⁻¹ are also assigned to the coordinated mesBIAN ligand. The low-frequency bands at 365 and 440 cm⁻¹ are tentatively attributed to ν (Pt-Cl)²⁰ and ν (Pt–N)²¹ respectively, while the band at 226 cm⁻¹ is likely to be due to an intra-mesBIAN vibration, since vibration in this region has been reported for coordinated 2,2'-bipyridine.²²

The resonance Raman spectrum of polycrystalline [Pt-(mesBIAN)(tdt)] **4** was obscured by the emission background, and the only prominent bands detected were those at 456, 531 and 1095 cm⁻¹. Both the 456 cm⁻¹ band and that at 531 cm⁻¹ have counterparts in the Raman spectrum of [Pt(mesBIAN)Cl₂], and can therefore be attributed to the Pt–mesBIAN framework. The spectrum is dominated by the vibration at 1095 cm⁻¹, which is not present in the rR spectrum of [Pt(mesBIAN)Cl₂], is characteristic of intra-phenyl ring vibrations, and is therefore attributed to the tdt ligand. This interpretation is consistent with the proposed MMLL/CT nature of the lowest allowed electronic transition in **4**.

The multi-Gaussian deconvolution of the lowest absorption envelope of 4 in CH₂Cl₂ shown in Fig. 6 reveals contributions

 Table 9
 Calculated energy difference between the ground state and the lowest triplet excited state for all compounds, and the corresponding predicted and observed emission maxima

		Emission maximum/nm			
Compound	$\Delta E/\mathrm{eV}$	Predicted	Observed		
[Pt(mesBIAN)Cl ₂]	1.57	791	777		
1	1.50	829	820		
2	1.29	964	1010		
3	1.03	1199			
4	0.99	1254			
5	0.94	1325			

from three transitions, at 15 093, 13 786 and 12 702 cm⁻¹. Although care should be taken while interpreting the results of such deconvolutions, the pattern obtained would account for 1307 and 1084 cm⁻¹ vibrational progressions, which matches (within experimental error) the intra-mesBIAN vibration at 1311 cm⁻¹, and the intra-tdt vibration at 1095 cm⁻¹, seen in the resonance Raman spectra of [Pt(mesBIAN)Cl₂] and **4** respectively. Thus, we conclude that the broadness of the low-energy absorption band is due to an unresolved vibrational progression originating from vibrational modes of both ligands.

Luminescence studies

Our preliminary studies reported upon the emission of [Pt(mesBIAN)Cl₂] and of 1 from fluid solution at room temperature (at 777 and 820 nm respectively).⁷ The purpose of the work reported herein was to try and extend the class of dithiolate compounds exhibiting this property. Assuming that emission occurs from the lowest-lying excited state, we have used the calculated energy difference between the singlet ground state and the lowest triplet state to estimate the wavelength of emission in each case.§ These values are shown in Table 9, and they suggest that compounds 2-5 would emit at much longer wavelengths than [Pt(mesBIAN)Cl₂] and 1. Indeed, we were able to obtain emission from 2 in degassed CH₂Cl₂ (Fig. 11) and MeCN solutions at room temperature, from a broad band centred at 1010 nm in the near-IR region, following excitation at a range of energies between 350 and 450 nm. The lifetime ($\lambda_{ex} = 355$ nm, $\lambda_{em} = 1000$ nm) of the emission was relatively long-lived, single exponential in character, and mildly solvent dependent, with $\tau = 287$ and 259 ns in dichloromethane and acetonitrile respectively. Unfortunately, we were unable to confidently observe luminescence at room temperature from degassed solutions of complexes 3-5, although 5 looked the most promising with a very weak broad band, again around 970-1100 nm, which possessed a lifetime <10 ns. The emission was extremely weak, which precluded any further investigations. No emission was detected for the derivatives of aromatic thiolates 3 and 4.



Fig. 11 Emission spectrum of 2 in degassed CH_2Cl_2 solution at room temperature.

One of the applications of the long-lived triplet excited states of transition metal complexes is in the production of singlet oxygen, ¹O₂, by triplet-triplet energy transfer²³ to the ground state of molecular oxygen. We observed that the phosphorescence of [Pt(mesBIAN)(mnt)] 2 was quenched in the presence of oxygen. Emission quenching was accompanied by the generation of singlet oxygen, as indicated by the appearance of a characteristic $O_2(^{1}\Delta_g) \rightarrow {}^{3}O_2$ phosphorescence at $\lambda > 1200$ nm. The yield of formation of ${}^{1}O_{2}$, $\phi({}^{1}O_{2})$, was determined by measuring its phosphorescence intensity using an optically matched solution of phenalenone as a reference sensitizer.24 Consistent with its relatively long excited state lifetime, **3** produces ${}^{1}O_{2}$ in aerated CH₂Cl₂ with a yield of 45%. The emission decay in the region >1200 nm was monoexponential, with a rate constant of 1.24×10^4 s⁻¹ (*i.e.* a lifetime of *ca*. 80 μ s), very similar to that tabulated for ¹O₂ in CH_2Cl_2 ²⁵ and to that detected for 1O_2 produced by irradiation of a solution of the phenolenone reference $(1.4 \times 10^4 \text{ s}^{-1})$, confirming that the emission signal detected was indeed originating from ${}^{1}O_{2}$.

Conclusions

We have shown that platinum–dithiolate compounds containing the mesBIAN ligand are readily synthesised and are stable. The dark colours of the compounds are caused by MMLL'CT transitions which have a common charge transfer basis in all compounds, irrespective of the energy of the orbitals involved. This means that, whilst the appropriate transition is HOMO to LUMO in 2–5, the originating b_1 symmetry orbital lies deeper in the occupied manifold for 1 and for [Pt(mesBIAN)Cl₂].

Generally it is found that platinum-diimine compounds that luminesce in solution have a charge-transfer state as the lowest excited state, and two strategies are commonly employed to generate emissive platinum(II) complexes. The first is to use strong σ -donor ligands (often alkynyls²⁶) opposite the diimine, which has the effect of raising the energy of the empty metal d_{xy} orbital so that excited states involving it are high energy. The second strategy is to lower the energy of the diimine LUMO below that of the d_{xy} orbital, normally *via* substitution with electron withdrawing groups. In the compounds herein, both of these strategies have been combined-strong-donor dithiolate ligands, and a diimine with a low-energy LUMO. Calculations predict low energy differences between the lowest energy triplet excited state and the ground state, with a very good match for the emission energies obtained for the parent [Pt(mesBIAN)Cl₂] and the thiolate complexes 1 and 2. Thus, the present work extends

[§] TD-DFT calculations could also be used to predict emission wavelengths and orbital compositions, but the reliable assignment of transitions is again problematic, especially where experimental reference data is limited. The spin-forbidden triplet–singlet transitions associated with emissions only acquire intensity due to spin–orbit coupling effects, which are not captured by the current implementations of TD-DFT.

the range of Pt(II)-based NIR emitters. The 'energy-gap law' predicts that the rate of vibrational non-radiative decay of an excited state increases as its energy relative to the ground state decreases,²⁷ meaning that the excited states of compounds **3**–**5**, which possess small HOMO–LUMO gaps, are apparently deactivated too efficiently to allow emission.

Experimental

[Pt(mesBIAN)Cl₂] and [Pt(mesBIAN)(dto)] 1 were prepared as reported.7 The dimethyltin dithiolate compounds $[Me_2Sn(bdt)]$, $[Me_2Sn(tdt)]^{28}$ and $[Me_2Sn(mnt)]^{29}$ and the reagent [Bu₄N]₂[Zn(dmit)₂]³⁰ were prepared by literature methods. Preparations of new compounds were carried out under nitrogen using dried solvents. NMR spectra were obtained in CDCl₃ on a JEOL ECP300 spectrometer and referenced to SiMe₄. ESR spectra were recorded on a Bruker ESP300E spectrometer calibrated with dpph, and simulated using Bruker Simfonia. Radicals were generated for ESR study by adding the reductant ($[Co(\eta-C_5Me_5)_2]$) to a frozen 2:1 thf-CH₂Cl₂ solution of the appropriate compound and allowing the system to warm in the ESR cavity until a signal was observed. Microanalysis was carried out by the microanalytical laboratory of the University of Bristol School of Chemistry. Electrochemical studies were carried out using an EG&G model 273A potentiostat linked to a computer using EG&G Model 270 Research Electrochemistry software in conjunction with a threeelectrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum disc (1.6 mm diameter). The reference electrode was an aqueous saturated calomel electrode separated from the test solution by a fine porosity frit and an agar bridge saturated with KCl. Solutions in CH_2Cl_2 were 1.0 × 10^{-3} mol dm⁻³ in the compound and 0.1 mol dm⁻³ in [NBuⁿ₄][PF₆] as the supporting electrolyte. Under these conditions, $E^{\circ'}$ for the one-electron oxidation of $[Fe(\eta-C_5H_5)_2]$, added to the test solutions as an internal calibrant, is 0.47 V.

Syntheses

[Pt(mesBIAN)(mnt)] 2. 0.046 g (0.067 mmol) of [Pt-(mesBIAN)Cl₂] and 0.020 g (0.068 mmol) of [Me₂Sn(mnt)] were stirred overnight in 50 ml of dichloromethane. The solution was then filtered, and reduced in volume on the rotary evaporator to approximately 20 ml. An equal volume of hexane was added, and overnight refrigeration yielded metallic-purple needles, which were isolated by filtration, washed with hexane, and dried to give 0.036 g (0.048 mmol, 72%) of product. Elemental analysis (as a dichloromethane solvate): Calc. C, 50.24; H, 3.61; N, 6.70%. Found: C, 49.84; H, 3.65; N, 6.55%. ¹H NMR (δ , ppm.): 2.36 (12H, s, Me); 2.51 (6H, s, Me); 6.84 (2H, d, ³*J* = 7 Hz); 7.16 (4H, s); 7.49 (2H, t, ³*J* = 8 Hz); 8.22 (2H, d, ³*J* = 8 Hz).

[Pt(mesBIAN)(bdt)] 3. 0.105 g (0.154 mmol) of [Pt-(mesBIAN)Cl₂] and 0.049 g (0.169 mmol) of [Me₂Sn(bdt)] were stirred overnight in 10 ml of dichloromethane. The solution was then filtered through a small pad of Celite, and hexane slowly added until solid material became apparent. Storage at -5 °C yielded the product as black–green needles, which were isolated by filtration, washed with hexane, and dried to give 0.077 g (0.102 mmol, 66%) of product. Elemental analysis: Calc. C, 57.51; H, 4.29; N, 3.73%. Found: C, 57.20; H, 4.51; N, 3.76%. ¹H NMR

(δ , ppm.): 2.42 (12H, s, Me); 2.52 (6H, s, Me); 6.71 (2H, dd, ${}^{3}J = 6$ Hz, ${}^{4}J = 2$ Hz); 7.16 (4H, s); 7.21 (1H, s); 7.36–7.42 (4H, m); 8.14 (2H, d, ${}^{3}J = 8$ Hz).

[Pt(mesBIAN)(tdt)] 4. 0.049 g (0.072 mmol) of [Pt-(mesBIAN)Cl₂] and 0.025 g (0.083 mmol) of [Me₂Sn(tdt)] were stirred overnight in 10 ml of dichloromethane. The solution was then filtered through a small pad of Celite, and hexane slowly added until solid material became apparent. Storage at -5 °C yielded the product as black–green needles, which were isolated by filtration, washed with hexane, and dried to give 0.036 g (0.047 mmol, 65%) of product. Elemental analysis: Calc. C, 58.02; H, 4.47; N, 3.66%. Found: C, 58.48; H, 4.66; N, 3.78%. ¹H NMR (δ , ppm.): 2.19 (3H, s, Me); 2.41 (12H, s, Me); 2.51 (6H, s, Me); 6.54 (1H, dd, ³*J* = 8 Hz, ⁴*J* = 2 Hz); 6.84 (2H, dd, ³*J* = 7, 5 Hz); 7.16 (4H, s); 7.21 (1H, s); 7.27 (1H, d, ³*J* = 8 Hz); 7.38 (2H, t, ³*J* = 7 Hz); 8.13 (2H, d, ³*J* = 8 Hz).

[Pt(mesBIAN)(dmit)] 5. 0.113 g (0.166 mmol) of [Pt- $(mesBIAN)Cl_2$ and 0.065 g (0.090 mmol) of $[{}^{n}Bu_4N]_2[Zn(dmit)_2]$ were stirred overnight in 10 ml of dichloromethane. The resulting solution was then washed three times with saturated NaCl solution, then once with water, and then dried with magnesium sulfate. It was then filtered to remove the drying agent, and the volume of the solution reduced to approximately 20 ml on the rotary evaporator. Hexane was slowly added until solid material became apparent, and subsequent storage at -5 °C yielded the product as a microcrystalline black-green solid, which was isolated by filtration, washed with hexane, and dried to give 0.058 g (0.064 mmol, 38%) of product. Elemental analysis (as a CH₂Cl₂ solvate): Calc: C, 45.74; H, 3.39; N, 3.14%. Found: C, 45.71; H, 3.24; N, 2.94%. ¹H NMR (δ, ppm.): 2.41 (12H, s, Me); 2.51 (6H, s, Me); 6.76 (2H, d, ${}^{3}J = 7$ Hz); 7.15 (4H, s); 7.43 (2H, t, ${}^{3}J = 8$ Hz); 8.18 (2H, d, ${}^{3}J = 8$ Hz).

Crystallography[†]

Many of the details of the crystallographic structure determinations of **3** and **5** are given in Table 3. The structure of **3** contains two independent molecules of **3** in the asymmetric unit; these have been given the same numbering scheme but 100 apart (*e.g.* Pt(1) in one molecule corresponds to Pt(101) in the other, *etc.*). There are also two molecules of CH_2Cl_2 , one of which is disordered equally over two sites related by a crystallographic inversion centre. The largest residual electron density peaks remaining are near this disordered solvent molecule. The structure of **5** contains two molecules of $CHCl_3$, one of which shows twofold orientational disorder. This structure has the largest residual electron density peaks near the atom Pt(1).

Computational studies

All calculations were performed with Gaussian 03 (Revision C.02)³¹ and used the popular B3LYP density functional.³² The Stuttgart–Dresden (SDD) basis set³³ was used with a relativistic effective core potential for Pt and all ligand atoms (C, H, N, O, S, Cl) were described by the all-electron 6-31G* basis set. In agreement with results reported by other groups, we found that changing the basis set or the density functional had little effect on the calculated transitions and orbital compositions.³⁴ All calculations were performed in a dichloromethane ($\varepsilon = 8.93$)

continuum solvation field, using the default polarisable continuum model PCM³⁵ as implemented in G03 with radii from the UFF force field (explicit hydrogens). To avoid problems with cavity generation and slow convergence, solvated calculations were run without symmetry, and some scrf solvation parameters were changed from their default settings (of ac = 0.8, rmin = 0.5). Orbital symmetry labels were confirmed by optimisation and TD-DFT in vacuo with C_{2v} symmetry; despite optimisations without symmetry, we observed no significant departure from these geometries. Typically, TD-DFT calculations³⁶ were used to calculate the 10-15 lowest singlet transitions. Only singlet transitions with calculated oscillator strengths >0.1 have been considered in this work. Due to the size of the complexes (up to 76 atoms, no symmetry), loose geometry optimisation criteria were used. Molecular orbital compositions were calculated as described by Liu et al.37

Emission spectroscopy

Emission experiments were performed at room temperature, in CH₂Cl₂ solutions degassed by freeze-pump-thaw methods. Emission spectra were recorded on a home built system (Sheffield) comprising a cw Ar ion laser (2 mW) or He-Ne laser (1 mW), Bentham TMC600 spectrograph, and Andor iDUS CCD camera. The spectrograph and CCD detection system was calibrated with a Bentham CL2 tungsten calibration lamp. The emission spectra were corrected for the overall system sensitivity. Emission kinetic decay were registered on an Edinburgh Instruments MiniTau machine with R928 PMT, a cut-off filter >750 nm, and a picosecond 410 nm diode laser with a 75 ps pulse duration as an excitation source. Steady-state and time-resolved emission experiments were also performed in Cardiff, on a JobinYvon-Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module and a Hamamatsu R5509-73 detector (cooled to -80 °C using a C9940 housing). The pulsed laser source was a Continuum Minilite Nd: YAG configured for 355 nm output. Lifetimes were obtained using the JY-Horiba FluorHub single photon counting module.

Raman spectroscopy

For [Pt(mesBIAN)Cl₂], spectra were recorded with a Renishaw Raman microscope system with a 514.5 nm Ar ion laser, using a $\times 50$ objective (~0.25 mW at the sample), in the 100–2000 cm⁻¹ range. The microscope was set up in a standard configuration using a holographic notch filter. The system was calibrated to the 520.0 cm⁻¹ line of a single crystal silicon wafer. For [Pt(mesBIAN)(tdt)] **4**, spectra were recorded with 785 nm excitation (~10 mW at the sample), within the 100–1800 cm⁻¹ available range.

Singlet oxygen measurements

The 1270 nm luminescence of singlet oxygen $({}^{1}\Delta_{g} O_{2})$ was produced by photo excitation of [Pt(mesBIAN)(mnt)] **2** at RT in air saturated CH₂Cl₂ solution using the third harmonic of a Nd:YAG laser (355 nm, 7 ns). The luminescence was detected by a liquid nitrogen cooled Germanium Detector/Amplifier (Applied Detector Corporation 403HS) close-coupled to the laser photolysis cell in a right-angled geometry. A 1 mm thick, 20 mm diameter piece of AR-coated silicon (II-IV Inc) was placed between the diode and the cell to act as a cut-off filter for light below 1100 nm. The 403HS power supply bias voltage was operated at 450 V. The amplifier output was AC coupled to the digitizer. The output was displayed on a Tektronix TDS 380 digitizing oscilloscope. Data processing was performed on an IBM PC using in-house developed software.

The quantum yield of ${}^{1}O_{2}$ production was determined by comparing the slopes of the linear plots of initial emission intensity *vs.* laser energy for optically matched solutions (λ_{exc} 355 nm) of the compound under study and that of the standard (phenolenone, $\phi({}^{1}O_{2}) = 95\%$).

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