Ruthenium(II) Compounds containing a Novel Strong π-Accepting Ligand, 5,5'-Dimethyl-2,2'-bi-1,3,4-thiadiazole (dbtd). Crystal Structure of $[Ru(bipy)_2(dbtd)][PF_6]_2{\cdot}Me_2CO$ (bipy = 2,2'-bipyridine)†

Benne D. J. R. Fennema,[a] Rudolf A. G. de Graaff,[a] Ronald Hage,[a] Jaap G. Haasnoot,*[,a] Jan Reedijk[a] and Johannes G. Vos[b]

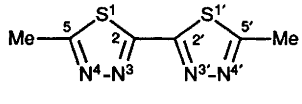
[a] *Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

[b] *School of Chemical Sciences, Dublin City University, Dublin 9, Ireland*

A series of ruthenium(II) complexes with a novel strong π-accepting ligand, 5,5'-dimethyl-2,2'-bi-1,3,4-thiadiazole (dbtd), has been synthesised and characterised. The complex $[Ru(bipy)_2(dbtd)][PF_6]_2{\cdot}Me_2CO$ (bipy = 2,2'-bipyridine) crystallises in the orthorhombic space group *Pbca* with unit-cell parameters $a = 13.513(3)$, $b = 16.763(4)$, $c = 33.057(5)$ Å and $Z = 8$. The two bipy ligands are orientated in a *cis* geometry and the bisthiadiazole ligand, co-ordinated *via* the N^3 atoms, occupies the fifth and sixth positions. All bidentate ligands have bite angles of 77–79° and ruthenium–nitrogen distances of 1.99–2.06 Å. Electrochemical and resonance Raman measurements on the thiadiazole-containing compounds show that this ligand has a low-lying π* level and is, therefore, expected actively to participate in the emission process. The mixed-chelate compound $[Ru(bipy)_2(dbtd)]^{2+}$ shows an unusual low-energy emission (760 nm at 300 K). The decreased emission intensity for the thiadiazole-containing complexes has been explained by the energy-gap law.

Since the paper of Paris and Brandt[1] in 1959, reporting the observed luminescence of the $[Ru(bipy)_3]^{2+}$ cation (bipy = 2,2'-bipyridine), much attention has been paid to studies on ruthenium co-ordination compounds. These ruthenium compounds are being studied as possible electrocatalysts and photocatalysts for the conversion of solar energy into chemical energy. The electrochemical and photochemical properties of the compounds are related to the electronic structure of the ligands used and in particular to their π-accepting and σ-donating capacities. In general five-membered heterocycles containing nitrogen atoms have better σ-donating properties and weaker π-accepting abilities than bipy.[2,3] Typical ligands of this type are (substituted) pyridyl-1,2,4-triazoles,[2–6] bisimidazoles[7–10] and pyridylpyrazoles.[11,12] Ligands with strong π-accepting properties are 2,2'-bipyrimidine, 2,2'-bipyrazine or biquinoline and many ruthenium complexes with these ligands have been reported.[13–35] Recently, also some ruthenium complexes with thiazole and thiadiazole have been reported.[36–38] A significant lowering of the energies of the lowest unoccupied molecular orbitals of these ligands has been observed, which has a profound influence on the electronic and electrochemical properties.

The present paper reports the synthesis, characterisation and photophysical and electrochemical properties of a series of ruthenium compounds based on the ligand 5,5'-dimethyl-2,2'-bi-1,3,4-thiadiazole (dbtd). As the photophysical properties of ruthenium complexes are governed by the (electronic) structure of the ligands, the X-ray structure of $[Ru(bipy)_2(dbtd)][PF_6]_2{\cdot}Me_2CO$ has been determined. As no X-ray structures of ruthenium complexes containing ligands consisting of two five-membered rings have been reported, it seemed of interest to study whether a different 'bite angle' would be present, as was suggested by Orellana *et al.*[36]



dbtd

Results and Discussion

General.—The following four compounds have been synthesised and characterised: $[Ru(dbtd)_2Cl_2]{\cdot}3H_2O$, $[Ru(bipy)_2(dbtd)][PF_6]_2{\cdot}Me_2CO$, $[Ru(bipy)(dbtd)_2][PF_6]_2{\cdot}Me_2CO$ and $[Ru(dbtd)_3][PF_6]_2$. The initial yield of the complexes was in general high (70–90%), but after purification the yield was much lower (see Experimental section). Due to the necessity of repeated purification of $[Ru(bipy)(dbtd)_2][PF_6]_2{\cdot}Me_2CO$ with Sephadex SP-25 and Al_2O_3 material, this compound was only isolated in very small amounts. Even after repeated purification, the isolated compound was not completely pure, which was detected by differential pulse measurements. Therefore, no photophysical experiments have been carried out on this compound.

The high yield obtained for the synthesis of $[Ru(dbtd)_2Cl_2]{\cdot}3H_2O$ and the infrared analysis of the isolated product show that very little $[Ru(dbtd)_2(CO)Cl]^+$ is formed as a by-product. This is of interest as the amount of monocarbonyl compounds formed in these reactions can be taken as a measure for the π-acceptor properties of the ligand dbtd.[39,40] During the synthesis of the analogous compound $[Ru(bipy)_2Cl_2]$ about 40% of the ruthenium is recovered as $[Ru(bipy)_2(CO)Cl]PF_6$,[39] while for pyridyltriazole ligands only the carbonyl compounds have been obtained.[40]

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† Bis(2,2'-bipyridine-κ^2N,N')(5,5'-dimethyl-2,2'-bi-1,3,4-thiadiazole-$\kappa^2N^3,N^{3'}$)ruthenium(II) bis(hexafluorophosphate)–acetonitrile (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 1 Fractional atomic coordinates (× 10^5 for Ru; × 10^4 for C, N, O and S) of $[Ru(bipy)_2(dbdt)][PF_6]_2 \cdot Me_2CO$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	12 140(7)	1 460(6)	12 894(3)
N(1)	34(8)	−558(6)	1 248(4)
N(2)	−73(9)	−1 347(7)	1 131(3)
C(3)	−1 003(11)	−1 582(8)	1 108(4)
S(4)	−1 839(3)	−856(2)	1 205(1)
C(5)	−867(9)	−238(8)	1 286(4)
N(6)	53(8)	927(6)	1 373(3)
N(7)	73(9)	1 739(7)	1 465(3)
C(8)	−791(10)	1 986(8)	1 532(4)
S(9)	−1 724(3)	1 293(2)	1 490(1)
C(10)	−852(10)	609(8)	1 359(4)
C(11)	−1 279(13)	−2 429(9)	979(5)
C(12)	−994(13)	2 845(10)	1 650(5)
N(20)	1 264(9)	193(7)	666(3)
C(21)	1 838(10)	−360(8)	506(4)
C(22)	2 023(13)	−396(9)	73(5)
C(23)	1 515(14)	209(13)	−165(5)
C(24)	906(12)	789(9)	34(5)
C(25)	826(11)	760(8)	445(5)
N(26)	2 191(8)	−757(6)	1 170(3)
C(27)	2 400(10)	−891(8)	768(4)
C(28)	3 068(10)	−1 507(8)	646(5)
C(29)	3 407(12)	−1 985(9)	940(5)
C(30)	3 320(10)	−1 824(7)	1 366(4)
C(31)	2 661(10)	−1 227(8)	1 477(5)
N(40)	1 394(8)	120(7)	1 909(3)
C(41)	2 110(10)	587(8)	2 061(4)
C(42)	2 284(13)	602(9)	2 479(5)
C(43)	1 671(14)	169(11)	2 718(6)
C(44)	929(13)	−339(10)	2 597(6)
C(45)	775(12)	−372(10)	2 163(5)
N(46)	2 357(7)	928(6)	1 380(3)
C(47)	2 651(10)	1 049(8)	1 763(4)
C(48)	3 430(11)	1 559(9)	1 855(5)
C(49)	3 882(13)	1 957(9)	1 549(5)
C(50)	3 587(12)	1 892(8)	1 169(5)
C(51)	2 819(12)	1 349(8)	1 083(5)
C(60)	585(19)	372(16)	4 463(8)
C(61)	810(18)	295(13)	4 080(8)
C(62)	15(16)	−136(12)	3 786(7)
O(63)	1 542(13)	396(11)	3 902(5)

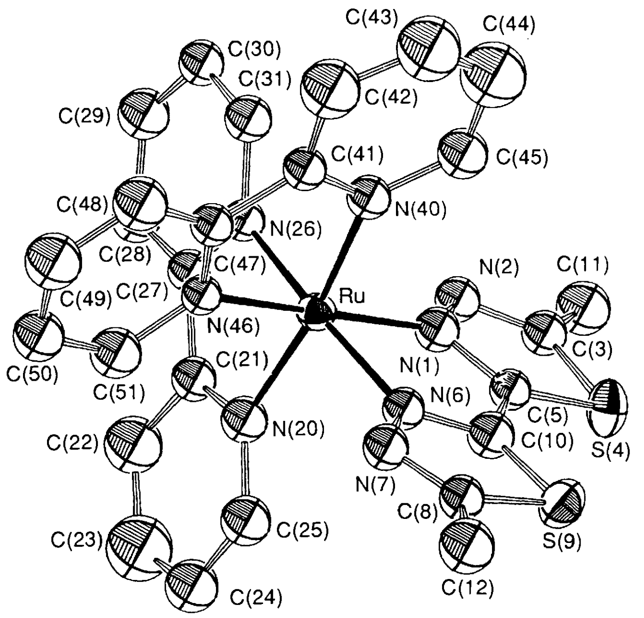

Fig. 1 ORTEP drawing of the $[Ru(bipy)_2(dbtd)]^{2+}$ cation. Atoms have been represented by ellipsoids showing a 50% probability of their thermal replacement. Hydrogen atoms, solvent molecules and the disordered PF_6 groups have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) of $[Ru(bipy)_2(dbtd)][PF_6]_2 \cdot Me_2CO$ with estimated standard deviations (e.s.d.s) in parentheses

Ru–N(1)	1.99(1)	Ru–N(6)	2.06(1)
Ru–N(20)	2.06(1)	Ru–N(26)	2.05(1)
Ru–N(40)	2.06(1)	Ru–N(46)	2.04(1)
N(1)–N(2)	1.38(2)	N(1)–C(5)	1.34(2)
N(2)–C(3)	1.32(2)	C(3)–C(11)	1.53(2)
C(3)–S(4)	1.69(1)	S(4)–C(5)	1.69(1)
C(5)–C(10)	1.44(2)	N(6)–C(10)	1.33(2)
N(6)–N(7)	1.39(2)	N(7)–C(8)	1.26(2)
C(10)–S(9)	1.70(1)	S(9)–C(8)	1.72(1)
C(8)–C(12)	1.52(2)		
N(1)–Ru–N(6)	77.1(4)	N(1)–Ru–N(20)	88.8(5)
N(1)–Ru–N(26)	93.7(4)	N(1)–Ru–N(40)	98.7(5)
N(1)–Ru–N(46)	174.1(5)	N(6)–Ru–N(20)	97.8(5)
N(6)–Ru–N(26)	170.4(4)	N(6)–Ru–N(40)	88.3(4)
N(6)–Ru–N(46)	98.4(4)	N(20)–Ru–N(26)	79.3(5)
N(20)–Ru–N(40)	171.3(5)	N(20)–Ru–N(46)	95.6(4)
N(26)–Ru–N(40)	95.7(4)	N(26)–Ru–N(46)	91.0(4)
N(40)–Ru–N(46)	77.3(4)	N(1)–N(2)–C(3)	114(1)
N(1)–C(5)–S(4)	116(1)	N(1)–C(5)–C(10)	114(1)
N(2)–C(3)–C(11)	122(1)	N(2)–C(3)–S(4)	114(1)
N(1)–N(2)–C(5)	108(1)	C(3)–S(4)–C(5)	87.3(7)
S(4)–C(3)–C(11)	124(1)	S(4)–C(5)–C(10)	130(1)
C(5)–C(10)–S(9)	134(1)	C(5)–C(10)–N(6)	114(1)
N(6)–N(7)–C(10)	115(1)	N(6)–C(10)–S(9)	111(1)
N(7)–C(8)–C(12)	122(1)	N(7)–C(8)–S(9)	116(1)
N(7)–N(6)–C(8)	110(1)	C(10)–S(9)–C(8)	88.1(7)
S(9)–C(8)–C(12)	122(1)		

Crystal Structure of $[Ru(bipy)_2(dbtd)][PF_6]_2 \cdot Me_2CO$.—An ORTEP drawing of the cation is presented in Fig. 1 (see also Tables 1 and 2). The structure is approximately octahedral with two bipy ligands oriented in a *cis* geometry and a bisthiadiazole ligand occupying the fifth and sixth positions of the ruthenium ion with co-ordination *via* the N^3 and $N^{3'}$ atoms. This geometry has been observed before.[39–46] The Ru–N distances and N–Ru–N angles in this structure are presented in Table 2 and are all in the range expected for this type of compound.[39–46] One molecule of acetone for every $[Ru(bipy)_2(dbtd)][PF_6]_2$ moiety is present in the lattice at a non-co-ordinating distance.

The structures of 5-acetamido-1,3,4-thiadiazole-2-sulphonamide (L)[47] and of $[Cu_2L_2(NH_3)_2(H_2O)_4]$[48] show similar distances and angles of the thiadiazole ring. Apparently, upon co-ordination to the $Ru(bipy)_2$ moiety the bisthiadiazole ligand is not distorted to a large degree. The binding N–N angle ('bite angle') of bisthiadiazole is very similar to that of the bipy ligands, suggesting that a favourable co-ordination geometry is also obtained for the ligand with the two five-membered rings. This is an interesting observation showing that an optimal orbital overlap is still present for the five-membered chelates, which is contrary to the suggestions made by Orellana *et al.*,[36] who stated that the five-membered ligands should have a larger binding angle and thus that a diminishing of the quantum yield of the emission processes would be expected.

NMR Spectroscopy.—The proton NMR spectrum of $[Ru(bipy)_2(dbtd)][PF_6]_2$ reveals the presence of four aromatic proton resonances originating from the bipy ligands and one singlet from the methyl groups. On co-ordination of dbtd a small change in the chemical shift of the methyl group is observed. It is surprising that only four different bipy proton

Table 3 Proton chemical shifts (δ)

	CH_3	bipy
$[Ru(dbtd)_3]^{2+}$	2.89	
$[Ru(dbtd)_2Cl_2]$	2.96, 2.88	
$[Ru(bipy)_2(dbtd)]^{2+}$	2.86	7.60 (H^5), 8.05 (H^6), 8.23 (H^4), 8.77 (H^3)

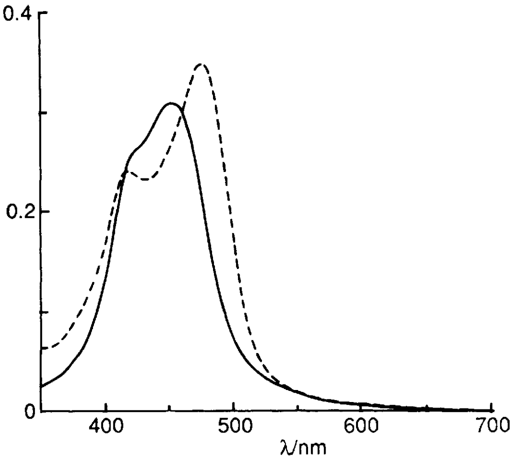

Fig. 2 Absorption spectra of $[Ru(dbtd)_3]^{2+}$ (———) and $[Ru(bipy)_2(dbtd)]^{2+}$ (– – – –) in acetonitrile at room temperature

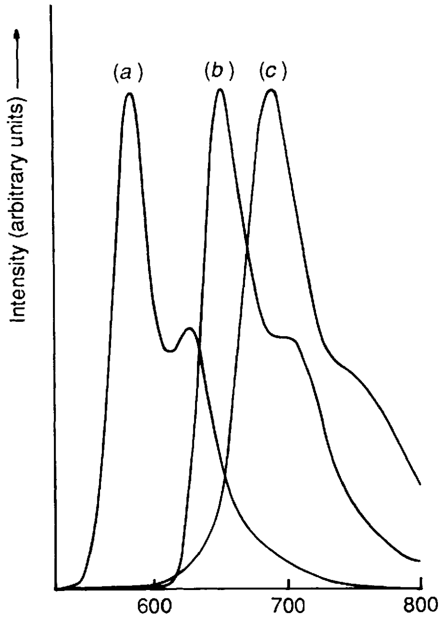

Fig. 3 Emission spectra of $[Ru(bipy)_3]^{2+}$ (*a*), $[Ru(dbtd)_3]^{2+}$ (*b*) and $[Ru(bipy)_2(dbtd)]^{2+}$ (*c*) in propionitrile–butyronitrile (4:5 v/v) at 77 K

signals are observed in the bipy region (Table 3). One would expect two separate sets containing four pyridine protons each, because of the differences in chemical environment. However, a similar observation has been made by Ernst and Kaim[24] for other compounds and apparently the differences in chemical environment between the bipy groups are too small to be resolved. The chemical shifts of the bipy resonances are in the normal range for ruthenium(II) bipy compounds.[2,3,11,12]

The NMR data indicate that no other geometrical isomers or impurities are present in the compound isolated, which is in agreement with the electrochemical measurements (see next section). In the spectrum of the complex $[Ru(dbtd)_3][PF_6]_2$ only one signal is present for the six methyl groups and again no significant change in the position of the methyl resonance upon co-ordination is observed. This spectrum is expected for a $[Ru(dbtd)_3]^{2+}$ compound when dbtd co-ordinates in a symmetrical manner. Again there were no indications for the presence of other species.

For $[Ru(dbtd)_2Cl_2]$ two clearly separated methyl signals are observed because two of the methyl groups are located above a thiazole ring and the two other ones are directed towards the chloride ligands.

Electronic Properties.—The absorption spectra of the compounds $[Ru(dbtd)_3]^{2+}$ and $[Ru(bipy)_2(dbtd)]^{2+}$ are presented in Fig. 2. Both compounds exhibit intense absorption bands in the visible region which have been assigned as m.l.c.t. (metal-to-ligand charge-transfer) bands.[49,50] An interesting feature in the spectrum of the mixed-chelate complex is the presence of two well resolved bands in the 350–600 nm region. As the electrochemical measurements have shown that the first reduction process is thiadiazole based (see below), the band located at low energy may be assigned to a $\text{Ru} \longrightarrow \pi^*(\text{dbtd})$ transition and the band at 418 nm to a $d_\pi \longrightarrow \pi^*(\text{bipy})$ transition. Similar observations have been made recently for complexes with 2,3-bis(pyridin-2-yl)quinoxaline, 2,2′-bipyrimidine, and 2,2′-bipyrazine.[13,14] The tris(bisthiadiazole) complex shows an intense $d_\pi \longrightarrow \pi^*(\text{dbtd})$ transition, with a shoulder located at higher energy. A similar effect has been observed for $[Ru(bipy)_3]^{2+}$.[50] The nature of the shoulder in the absorption band can most likely be explained by splitting of the filled d_π orbitals of the complex.

Electrochemistry.—The electrochemical data for the bisthiadiazole complexes are presented in Table 4. The cyclic voltammetry experiments have revealed that the separations in peak potentials are 60–100 mV and that the ratios of the oxidation to reduction peak heights are approximately 1:1, which indicates that the redox processes are (quasi-) reversible. For $[Ru(dbtd)_3]^{2+}$ all reduction waves are expected to be bisthiadiazole based. For this compound, compared to $[Ru(bipy)_3]^{2+}$, the reduction waves are located at less negative potentials, while the oxidation wave is at a higher potential (Table 4). Strong π-accepting ligands stabilise the filled d orbitals of the complexes and therefore the oxidation wave is observed at higher potentials. The low-lying π* orbital of dbdt is responsible for the low reduction potential, as has been observed earlier for chelating ligands such as 2,2′-bipyrazine or 2,2′-bipyrimidine.[13–19] Based on the fact that the first two reduction waves of $[Ru(bipy)(dbtd)_2]^{2+}$ are very similar to those of $[Ru(dbtd)_3]^{2+}$, it has been concluded that those reduction processes are also dbdt localised. The compound $[Ru(bipy)_2(dbtd)][PF_6]_2$ shows a similar behaviour, but in this case only the first reduction wave is dbdt based and the second and third reductions are bipy based. Comparison with literature data reveals that the oxidation and reduction potentials of $[Ru(dbtd)_3]^{2+}$ are very similar to those observed for ruthenium(II) complexes with 2-(2′-pyrazin-2-yl)thiazole and 5-(pyridin-2-yl)-1,2,4-thiadiazole.[36] This shows that the extent of σ-donation and π-back donation for these different thiadiazole systems is very similar.

Emission Spectra.—The compounds $[Ru(bipy)_2(dbtd)][PF_6]_2$ and $[Ru(dbtd)_3][PF_6]_2$ are luminescent at room temperature. Some representative spectra are depicted in Fig. 3, further data are given in Table 5. An important question to be asked is whether the dbdt ligand actively participates in the emission for the mixed-ligand complex. The electrochemical measurements have shown that the first reduction wave of $[Ru(bipy)_2(dbtd)]^{2+}$ is dbdt based. As shown in Fig. 4, a linear relationship holds between the emission energy (obtained at 300 K) and the difference in oxidation and reduction potential ($\Delta E_{\frac{1}{2}}$), indicating that the orbitals taking part in the electrochemical and emission processes are closely related. This feature

Table 4 Electrochemical potentials[a] and absorption maxima

Compound	E_{ox}/V	E_{red}/V			$\Delta E_{\frac{1}{2}}$/V	$\lambda_{max}(10^4\varepsilon)$[b]
$[Ru(dbtd)_3]^{2+}$	1.58	−0.89	−1.10	−1.40	2.47	451 (1.6)
$[Ru(bipy)(dbtd)_2]^{2+}$	1.51	−0.93	−1.19	−1.75	2.44	473 (1.5), 422 (sh)
$[Ru(bipy)_2(dbtd)]^{2+}$	1.32	−1.01	−1.52	−1.74	2.33	476 (1.3), 418 (sh)
$[Ru(bipy)_3]^{2+}$	1.27	−1.31	−1.50	−1.77	2.58	451 (1.4)[c]

[a] Measured in MeCN containing 0.1 mol dm^{-3} NBu_4ClO_4; potentials are *versus* saturated calomel electrode. [b] Measured in MeCN; ε is given in 10^4 dm^3 mol^{-1} cm^{-1} and the accuracy in λ is 2 nm. [c] The values for $[Ru(bipy)_3]^{2+}$ are taken from ref. 13.

Table 5 Luminescence properties of the dbtd complexes

	$\lambda^{em\,a}$/nm		Lifetime (μs)							
Compound	77 K	300 K	77 K	300 K		φ^a	$k^{r\,b}$/s^{-1}	$k^{nr\,b}$/s^{-1}	E_{red}^{*c}/V	E_{ox}^{*c}/V
$[Ru(dbtd)_3]^{2+}$	640	682	3.0	0.18[d]	0.20[a]	1.0×10^{-3}	5.6×10^3	3.3×10^5	1.05	−0.36
$[Ru(bipy)_2(dbtd)]^{2+}$	688	760	2.9	0.10[d]	0.12[a]	2.5×10^{-4}	2.5×10^3	3.4×10^5	0.79	−0.48
$[Ru(bipy)_3]^{2+}$	582	608	4.8	0.17[d]	0.80[a]	0.014	8.0×10^4	1.3×10^5	0.86	−0.90

[a] Aerated MeCN solution. [b] Calculated by using equations (1) and (2). [c] Calculated by using equations (3) and (4). [d] Deaerated propionitrile–butyronitrile (4:5 v/v).

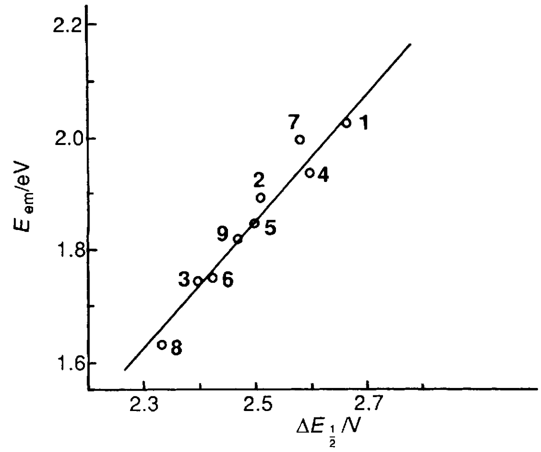

Fig. 4 Relationship between the emission energy obtained at room temperature and $\Delta E_{\frac{1}{2}}$. Complexes: **1**, $[Ru(bipyz)_3]^{2+}$; **2**, $[Ru(bipy)(bipyz)_2]^{2+}$; **3**, $[Ru(bipy)_2(bipyz)]^{2+}$; **4**, $[Ru(bipym)_3]^{2+}$; **5**, $[Ru(bipy)(bipym)_2]^{2+}$; **6**, $[Ru(bipy)_2(bipym)]^{2+}$; **7**, $[Ru(bipy)_3]^{2+}$; **8**, $[Ru(bipy)_2(dbtd)]^{2+}$; **9**, $[Ru(dbtd)_3]^{2+}$ where bipym = 2,2′-bipyrimidine[13] and bipyz = 2,2′-bipyrazine.[13] Slope = 1.15 eV V^{-1}, intercept = −1.01 eV, R = 0.972

has been observed earlier for several other ruthenium(II) systems.[43] Therefore, the presence of low-lying π* orbitals of dbtd, as deduced from the reduction potentials, shows that also these orbitals participate in the emission process.

The emission band at room temperature of $[Ru(bipy)_2(dbtd)]^{2+}$ is located at very low energy and it seemed of interest to elucidate the photophysical properties in some more detail. Using the measured quantum yields (φ) of the emission processes and luminescence lifetimes (τ) obtained for the complexes (Table 5), the radiative rate constants (k^r) can be calculated[6] [equation (1)]. The values for the non-radiative

$$k^r = \varphi/\tau \qquad (1)$$

decay constant (k^{nr}) can be obtained by using equation (2), if it is

$$k^{nr} = (1/\tau_{77K}) - k^r \qquad (2)$$

assumed that the radiative rate constant is temperature independent.[6] The values obtained for $[Ru(dbtd)_3]^{2+}$ and $[Ru(bipy)_2(dbtd)]^{2+}$ show that the k^{nr} values are much larger than those found for $[Ru(bipy)_3]^{2+}$. This fact has been observed for other ruthenium and osmium systems, where a linear relation between ln(k^{nr}) and E_{em} is present.[51,52] The higher non-radiative rate constants can be accounted for by the energy-gap law, which states that radiationless deactivation processes become more efficient when the energy difference between the ^{3}m.l.c.t. and ground states diminishes.[53]

The excited-state oxidation and reduction potentials can be calculated by using equations (3) and (4) where E_{red}* and E_{ox}*

$$E_{red}^* = E_{red} + E_{em} \qquad (3)$$

$$E_{ox}^* = E_{ox} - E_{em} \qquad (4)$$

are the excited-state reduction and oxidation potentials, E_{red} is the first ligand-based reduction potential, E_{ox} is the metal-based oxidation potential, and E_{em} is the emission energy obtained at 77 K (in eV). The results obtained (Table 5) show that in the excited state $[Ru(dbdt)_3]^{2+}$ and $[Ru(bipy)_2(dbtd)]^{2+}$ are stronger oxidants but weaker reductants than $[Ru(bipy)_3]^{2+}$. A similar behaviour has been observed for analogous systems like 2,3-bis(pyridin-2-yl)quinoxaline and 2,2′-bipyrimidine and 2,2′-bipyrazine[13,14] and they can be explained by the strong π-accepting properties, causing a lowering of the π* orbital and, therefore, an enhanced d_π–π* interaction.

Resonance Raman Spectroscopy.—Often resonance Raman (RR) spectroscopy has been used to assign electronic transitions.[54] Excitation into an allowed Ru ⟶ π*(dbdt) transition results in enhanced Raman scattering for the symmetrical stretching modes of this ligand. Resonance Raman spectroscopy can also be used to investigate whether different electronic transitions are present within one absorption band. In this case the effect of using different excitation wavelengths on the spectra is investigated.[55]

For the mixed-ligand $[Ru(bipy)_2(dbtd)]^{2+}$ complex, RR spectroscopy has been used in order to establish whether the lowest m.l.c.t. band is a transition from the ruthenium(II) centre towards a bipy or the bisthiadiazole ligand. The RR spectrum of $[Ru(dbtd)_3]^{2+}$ obtained by excitation at 458 nm is presented in Fig. 5. Strong RR peaks are observed at 1479, 1443, 1301, 927 and 663 cm^{-1}, which can be attributed to dbtd vibrations. Excitation at energies lower than 458 nm (488 and 514.5 nm) leads to the same pattern except that the intensity of the resonances is somewhat lowered. Comparison with the RR spectrum of $[Ru(bipy)_3]^{2+}$ (ref. 56) shows that the observed pattern of $[Ru(dbtd)_3]^{2+}$ differs significantly. Therefore, it is

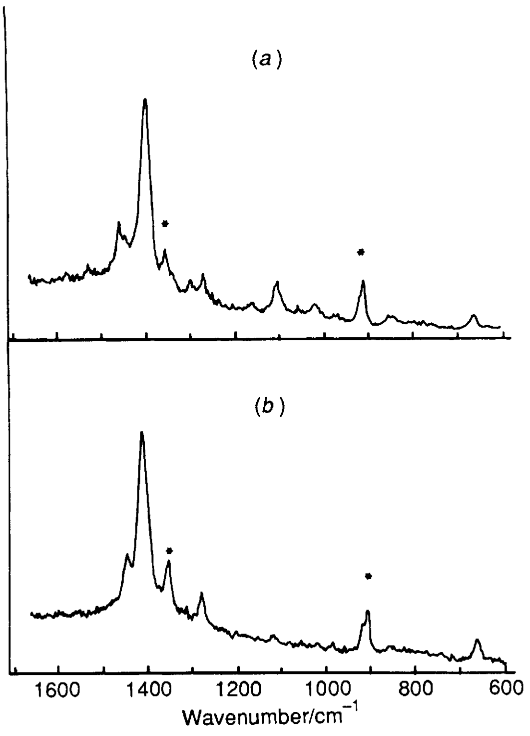

Fig. 5 Resonance Raman spectra of (*a*) [Ru(bipy)$_2$(dbtd)]$^{2+}$ and (*b*) [Ru(dbtd)$_3$]$^{2+}$ in acetonitrile at room temperature (excitation wavelength 458 nm). Bands marked * are solvent bands

possible to use RR spectroscopy to determine the nature of the ligand orbitals involved in the m.l.c.t. bands of [Ru(bipy)$_2$(dbtd)]$^{2+}$.

In Fig. 5 the RR spectrum of [Ru(bipy)$_2$(dbtd)]$^{2+}$ excited at 458 nm is shown. Extra peaks are observed at 1610, 1560, 1475, 1320, 1120, 860 and 664 cm^{-1} with respect to the RR spectrum of [Ru(dbtd)$_3$]$^{2+}$. The first three of these are rather small, however comparison with the spectrum obtained for [Ru(bipy)$_3$]$^{2+}$ indicates that most likely they are due to a m.l.c.t. transition involving bipy orbitals. Excitation at 488 nm yielded a RR spectrum very similar to that observed for [Ru(dbtd)$_3$]$^{2+}$; the bipy vibrations were not visible anymore. Excitation at 514.5 nm yielded the same RR spectrum as obtained for [Ru(dbtd)$_3$]$^{2+}$. Therefore, it can be concluded that the lowest m.l.c.t. band of [Ru(bipy)$_2$(dbtd)]$^{2+}$ is a Ru $\longrightarrow$ dbtd transition, while the band located at higher energy is most probably a transition involving a bipy ligand.

Conclusion

The X-ray structure of [Ru(bipy)$_2$(dbtd)][PF$_6$]$_2$·Me$_2$CO shows interesting and unexpected features. The two five-membered thiadiazole rings are co-ordinated *via* the nitrogen atoms, forming a bite angle of 77.1(4)° only. Apparently, even though five-membered rings are present instead of six-membered rings (like bipy), the most favourable co-ordination geometry is obtained. It can, therefore, be concluded that the decreased emission intensity observed in this and related systems[36] is not caused by an unfavourable co-ordination environment as was suggested by Orellana *et al.*[36] The explanation for the diminished emission intensities observed for the thiadiazole complexes is likely to be the decreased emission energy (energy-gap law) and possibly low-lying deactivating ^{3}m.c. (metal centred) states. The electrochemical measurements on the complexes clearly show that the thiadiazole ligand is reduced much more easily than is bipy. This shows that the π^* level of the bisthiadiazole ligand is much lower than that of bipy. This enhanced π-back donation also causes a decreased electron density on the metal centre and therefore a lower oxidation potential of the complex. The RR experiments have revealed that the lowest-energy m.l.c.t. band of [Ru(bipy)$_2$(dbtd)]$^{2+}$ is a Ru $\longrightarrow$ dbtd transition, while the Ru $\longrightarrow$ bipy transition is most likely present at higher energy. From these measurements it has also been concluded that the [Ru(bipy)$_2$(dbtd)]$^{2+}$ complex exhibits a dbtd-based emission.

All experiments have shown that the presence of the two sulphur atoms in the thiadiazole ligand causes a strong enhancement of the π-back bonding upon co-ordination to ruthenium. The properties of ruthenium complexes cannot only be altered by using six-membered rings containing more nitrogen atoms, as for pyrazine, pyrimidine, triazine, or tetrazine, but also by replacement of nitrogen atoms in triazoles or imidazoles with sulphur.

Experimental

X-Ray Crystallography.—A hexagonal-shaped single crystal of [Ru(bipy)$_2$(dbtd)][PF$_6$]$_2$·Me$_2$CO with dimensions 0.06 × 0.28 × 0.14 mm was selected for crystal structure determination. The density was determined by flotation, using dibromoethane and hexane.

Crystal data. $C_{29}H_{28}F_{12}N_8OP_2RuS_2$, $M = 959.71$, orthorhombic, space group *Pbca*, $a = 13.513(3)$, $b = 16.763(4)$, $c = 33.057(5)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 7488.0$ Å^3, $D_m = 1.70$ Mg m^{-3}, $Z = 8$, $D_c = 1.70$ Mg m^{-3}, $\mu = 6.96$ cm^{-1}, λ(Mo-Kα) = 0.710 73 Å, $F(000) = 3609$.

Data collection and processing. A unique data set was measured within $2 < \theta < 22°$ (using the ω–θ scan method) at 293 K using an Enraf-Nonius CAD4 diffractometer and monochromated Mo-Kα radiation. The intensities were corrected for Lorentz and polarisation effects. Cell parameters were obtained from 24 reflections with $10 < \theta < 12°$. The range for *h* was 0–14, for *k* 0–17 and for *l* 0–34. The intensity variation of the standard reflections was 6.06% from the mean value. The principal computer programs used in the crystallographic calculations were written or modified by Mrs. E. Rutten-Keulemans and Dr. R. A. G. de Graaff. Of the 5126 reflections measured, 1499 contributed to the refinement [$I > 2\sigma(I)$]. The function minimized was $[w(|F_o| - |F_c|)^2]$ with $w = 1/\sigma^2(F)$.

Solution and refinement of the structure. The position of the ruthenium atom was located by using standard Patterson techniques, those of the other heavy atoms (S, N, C and P) by using AUTOFOUR.[57] Due to the limited number of significant reflections (1499) only the Ru and S atoms were refined with anisotropic thermal parameters. All other non-hydrogen atoms were refined with isotropic thermal parameters. One degree of occupancy for the disordered atoms of the two PF$_6$ moieties was used (1.10 and 0.90 for the first and 1.66 and 0.34 for the second PF$_6$ groups). A P–F distance of 1.540 Å and an F–P–F angle of 90° with relative standard deviations of 0.01 Å and 0.1° respectively were applied using Waser constraints. Hydrogen atoms were placed in calculated positions at 1.00 Å from their parent atoms and not refined. The final Fourier difference synthesis had a minimum value of -0.653 e Å^{-3} and a maximum value of 0.303 e Å^{-3} at a noise level of 0.341 e Å^{-3}. Scattering factors were taken from ref. 58. The shift-to-error ratio in final cycle was <0.1. Final $R(R') = 0.066$ (0.075) for 1499 reflections with $I > 2\sigma(I)$ and $R'(R) = 0.097$ (0.246) based on the 4579 contributing reflections. The estimated standard deviations in the bond lengths and angles were calculated with the coordinates obtained from the refinement with all independent reflections.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Physical Measurements.—Ultraviolet/visible spectra were recorded on a Perkin-Elmer 330 or a Shimadzu UV–240 spectrophotometer using matched 1 cm quartz cells in acetonitrile. Emission spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrophotometer equipped with a Hamamatsu R928 phototube by using emission slit widths of 2.5 (77 K) and 10 nm (300 K). They were corrected for photomultiplier response. The room-temperature lifetimes (aerated) were obtained in an aerated MeCN solution, those at 300 and 77 K in freshly distilled deaerated propionitrile–butyronitrile (4:5 v/v). The emission lifetimes were obtained by using modified Applied Photophysics single-photon equipment. The proton NMR spectra of the complexes were obtained on a Bruker 300 MHz spectrometer in $(CD_3)_2CO$, that of the ligand on a JEOL FX-200 200 MHz spectrometer in $(CD_3)_2SO$. All peak positions are relative to $SiMe_4$.

Differential pulse polarographic measurements between -2.0 and $+2.0$ V were carried out in a 0.1 mol dm^{-3} solution of NBu_4ClO_4 in MeCN, by using an EG & G Par C 303 combined with an EG & G 384 B polarographic analyser. The scan rate was 4 mV s^{-1} with a pulse height of 20 mV; for the cyclic voltammograms a scan rate of 100 mV s^{-1} was used. The reference electrode was a saturated potassium chloride calomel electrode in combination with a glassy carbon working electrode and a platinum wire as counter electrode. Before each measurement the MeCN solutions were purged with argon for 30 s.

The resonance Raman spectra were obtained with a Dilors XY laser Raman spectrophotometer, equipped with a SP model 171 argon ion laser (laser power 60 mW, spectral slit width 100 μm). Excitation took place at 458, 488 and 514.5 nm.

Mass spectroscopy (LC-MS) was performed on a HP 5985 quadrupole mass spectrometer equipped with a direct insertion probe, operating in the electron ionisation mode (70 eV). A temperature gradient of 30 °C min^{-1} in the 50–300 °C range was used.

Elemental analyses were carried out at University College Dublin.

Materials.—The compound $RuCl_3 \cdot H_2O$ was obtained as a gift from Johnson Matthey and like the rest of the reagents used without further purification. The compound $[Ru(bipy)_2Cl_2] \cdot 2H_2O$ was synthesised as described earlier.[59]

Synthesis of 5,5′-*Dimethyl*-2,2′-*bi*-1,3,4-*thiadiazole*.—The ligand was prepared as described earlier by Stollé[60] and recrystallised from $CHCl_3$. Yield: 25%. Characterisation was carried out by means of mass and proton NMR spectroscopy. M.p. 237 °C (lit.,[60] 238 °C). Proton NMR $[(CD_3)_2SO]$: δ 2.92 (s, CH_3). MS: *m*/*z* 198 (molecular ion peak).

Synthesis of the Co-ordination Compounds.—$[Ru(dbtd)_2Cl_2] \cdot 3H_2O$. A mixture of $RuCl_3$ (1044 mg, 4 mmol), dbtd (784 mg, 8 mmol) and LiCl (120 mg, 2.8 mmol) was refluxed for 15 min in dimethylformamide (10 cm^3). After cooling to room temperature, acetone (50–100 cm^3) was added to the reaction mixture. After 2 h of storage at -20 °C the deep purple suspension was filtered, yielding a deep purple microcrystalline solid. The IR spectrum indicated the presence of a very small amount of $[Ru(dbtd)_2Cl(CO)]Cl$ (broad weak band around 2000 cm^{-1}), but this impurity seems to have a low reactivity in further syntheses and so is not troublesome. Yield 2.1 g (85%) (Found: C, 23.1; H, 2.5; N, 17.4; S, 19.9. $C_{12}H_{18}Cl_2N_8O_3RuS_4$ requires C, 23.2; H, 2.9; N, 18.0; S, 20.6%).

$[Ru(bipy)_2(dbtd)][PF_6]_2 \cdot Me_2CO$. This complex was prepared by refluxing $[Ru(bipy)_2Cl_2]$ (1 mmol, 0.52 g) with dbtd (1.5 mmol, 0.3 g) in ethanol–water (5:1 v/v, 120 cm^3) for 2 d. After filtration the volume of this reaction mixture was reduced under lowered pressure to 10–20 cm^3 and the complex was precipitated by adding a filtered saturated solution of 2 equivalents of NH_4PF_6. The suspension was filtered and the brown solid was dissolved in the minimal amount of acetone. Purification was performed by column chromatography (stationary phase alumina, eluent acetone). The volume of the fraction containing the desired product was reduced under lowered pressure to 50–60 cm^3 and some ethanol was added. Upon standing the dark brown compound crystallised. Yield 360 mg (40%) (Found: C, 36.0; H, 2.9; N, 11.6. $C_{29}H_{28}F_{12}N_8OP_2RuS_2$ requires C, 36.3; H, 2.9; N, 11.7%).

$[Ru(bipy)(dbtd)_2][PF_6]_2 \cdot Me_2CO$. A mixture of $[Ru(dbtd)_2Cl_2] \cdot 3H_2O$ (0.5 mmol, 0.3 g) and bipy (1 mmol, 0.16 g) was refluxed in ethanol–water (120 cm^3, 5:1 v/v). The brown-red solution was evaporated to dryness and the brown solid was dissolved in the minimal amount of water. Purification was performed by column chromatography (stationary phase Sephadex SP 25, eluent 0.2 mol dm^{-3} NaCl solution for the fraction yielding the product). The volume of this fraction was reduced under lowered pressure to 10–20 cm^3 and $[Ru(bipy)_2(dbtd)][PF_6]_2$ was precipitated by adding a filtered saturated solution of 2 equivalents of NH_4PF_6. Further purification was carried out by using alumina as stationary phase with acetone as eluent. Recrystallisation from acetone–ethanol yielded a brown compound. Yield 25 mg (8%) (Found: C, 29.7; H, 2.2; N, 14.4. $C_{25}H_{26}F_{12}N_{10}OP_2RuS_4$ requires C, 30.0; H, 2.6; N, 14.0%).

$[Ru(dbtd)_3][PF_6]_2$. A mixture of $RuCl_3$ (200 mg, 0.8 mmol) and dbtd (600 mg, 3 mmol) in ethanol–water (5:1 v/v, 120 cm^3) was refluxed for 2 d. An alternative route is refluxing 1 equivalent of $[Ru(dbtd)_2Cl_2] \cdot 3H_2O$ with 1.5 equivalents of dbtd in the same amount of solvent. Isolation and purification was carried out as described for the synthesis of $[Ru(bipy)_2(dbtd)][PF_6]_2$, obtaining a microcrystalline red solid, yield 291 mg (37%) (Found: C, 21.55; H, 1.80; N, 16.55; P, 6.35. $C_{18}H_{18}F_{12}N_{12}P_2RuS_6$ requires C, 21.95; H, 1.85; N, 17.05; P, 6.30%).

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