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Synthesis and reactions of dimethyltin dithiooxalate: a convenient dithiooxalate transfer reagent

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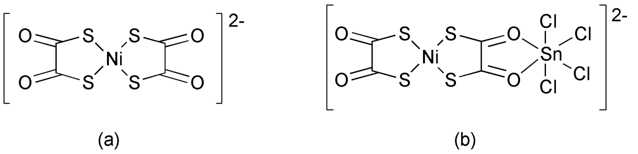
Dimethyltin dithiooxalate has been synthesised by the reaction of dimethyltin dichloride with potassium dithiooxalate. It may be used as a dithiooxalate (dto) transfer reagent, reacting with $[\mathrm{PtL_2Cl_2}]$ ($\mathrm{L_2}$ = 1,4-cyclooctadiene or 4,4′-bis(*tert*-butyl)-2,2′-bipyridine) to eliminate $\mathrm{SnMe_2Cl_2}$ and form the corresponding platinum dithiooxalate compounds [Pt(COD)(dto)] **1** and $[\mathrm{Pt}({}^t\mathrm{Bu_2bipy})(\mathrm{dto})]$ **2**. Reaction with the ruthenium compound $[\mathrm{Ru(Me_2bipy)(PPh_3)_2Cl_2}]$ **3** ($\mathrm{Me_2bipy}$ = 4,4′-dimethyl-2,2′-bipyridine) does not proceed analogously however, eliminating from the ruthenium one chloride and one triphenylphosphine ligand, and thus producing not $\mathrm{SnMe_2Cl_2}$ but "$[\mathrm{SnMe_2Cl}]^+$". This moiety becomes chelated within the dithiooxalate to produce the new 'Coucouvanis' type compound [*cis*-$\mathrm{Ru(Me_2bipy)(PPh_3)Cl(\mu\text{-}dto)(SnMe_2Cl)}$] **4**. Reaction of **4** with DMSO causes the elimination of $\mathrm{SnMe_2Cl_2}$ by abstracting the tin centre and the second chloride ligand, producing *cis*-$[\mathrm{Ru(Me_2bipy)(PPh_3)(DMSO)(dto)}]$ **5**. Upon treating **3** with $[p\text{-}\mathrm{N{\equiv}NC_6H_4F}][\mathrm{BF_4}]$ the oxidation product $[\mathrm{Ru(Me_2bipy)(PPh_3)_2Cl_2}][\mathrm{BF_4}]$ **6** is formed. **6** reacts with $\mathrm{SnMe_2(dto)}$ to produce a second bimetallic complex, $[\mathrm{Ru(Me_2bipy)(PPh_3)_2(\mu\text{-}dto)(SnMe_2Cl)}][\mathrm{BF_4}]$ **7a**. The nature of the reduction products of **4** and **7** is explored, and the X-ray crystal structures of **2** and **5** are presented.

Introduction

It is now over 90 years since the first synthesis of the dithiooxalate (dto) ligand was reported.[1] Jones and Tasker used the dipotassium salt to synthesise several metal bis-dithiooxalate complexes, such as $\mathrm{K_2[Ni(dto)_2]}$ (Fig. 1a), and to this day the great majority of inorganic dithiooxalate chemistry has focused on the use of such $[\mathrm{M(dto)_2}]^{2-}$ anions as chelating agents for other metal species, which can be co-ordinated between the oxygen atoms of the dithiooxalate group.[2] A large number of these, the so-called 'Coucouvanis' compounds, involve the chelation of tin tetrahalides (Fig. 1b),[3–5] but it is also possible to trap transition metal ions.[5–8] The only monometallic mixed-ligand complexes reported are of the form $[\mathrm{M(dto)P_2}]$, where P is a tertiary phosphine ligand or $\mathrm{P_2}$ is a bidentate phosphine, and M is nickel, palladium or platinum (Fig. 2).[9]



(a) (b)

Fig. 1 The nickel bis-dithiooxalate anion (a), and a typical 'Coucouvanis' compound (b).

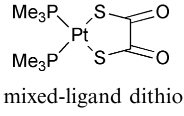


Fig. 2 A square planar mixed-ligand dithiooxalate compound (from ref. 9).

One of the problems encountered in dithiooxalate chemistry is the unstable nature of the starting material: potassium dithiooxalate ($\mathrm{K_2dto}$) decomposes rapidly and must be prepared shortly before use. The current report concerns the synthesis and reactions of an alternative source of the dithiooxalate anion, namely dimethyltin dithiooxalate ($\mathrm{SnMe_2(dto)}$). Tin complexes are commonly used as transmetallating agents for a wide variety of anions, having the advantages of being soluble in organic solvents, and of producing as by-products tin(IV) halide compounds which are easily removed by washing.

$\mathrm{SnMe_2(dto)}$ is readily prepared by reaction between $\mathrm{SnMe_2Cl_2}$ and (freshly prepared) $\mathrm{K_2dto}$ in aqueous solution, precipitating as an analytically pure microcrystalline solid from the reaction mixture. Though soluble in acetone $\mathrm{SnMe_2(dto)}$ is insoluble in most common organic solvents, possibly due to a polymeric structure. However, it reacts readily as a suspension in organic solvents, and unlike $\mathrm{K_2dto}$ it appears to be indefinitely stable in air.

Results and discussion

Platinum complexes

A large number of platinum dithiolate compounds have been synthesised in recent years, particularly by the group of Eisenberg.[10] These complexes, containing a mutually *trans* arrangement of diimine ligand and dithiolene, have been shown to possess excellent photophysical and non-linear optical properties. These properties are due largely to the totally conjugated nature of the molecule, which facilitates ready movement of electrons between HOMO and LUMO, and gives the molecules a large dipole moment. This dipole moment means, in turn, that crystals of such materials often contain head-to-tail stacks of molecules, whose centrosymmetric nature means that any molecular optoelectronic properties are cancelled out in the bulk material. The aim of the study reported herein was to try and prepare similar molecules possessing hydrogen-bonding capability—hence the choice of the dithiooxalate unit—and to try to use this interaction to influence crystal packing.

$\mathrm{SnMe_2(dto)}$ reacts as anticipated with $[\mathrm{Pt(COD)Cl_2}]$ and $[\mathrm{Pt}({}^t\mathrm{Bu_2bipy})\mathrm{Cl_2}]$; that is, in each case the two chloride atoms are exchanged for one S,S′-bound dithiooxalate ligand, giving square planar [Pt(COD)(dto)] **1** and $[\mathrm{Pt}({}^t\mathrm{Bu_2bipy})(\mathrm{dto})]$ **2** respectively. The mode of dithiooxalate bonding is readily

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

Pt(1)–N(1)	2.029(5)	C(19)–O(1)	1.207(8)
Pt(1)–N(2)	2.045(6)	C(19)–C(20)	1.555(10)
Pt(1)–S(1)	2.2556(19)	S(2)–C(20)	1.728(8)
Pt(1)–S(2)	2.260(2)	C(20)–O(2)	1.201(9)
S(1)–C(19)	1.733(8)		
N(1)–Pt(1)–N(2)	79.0(2)	O(1)–C(19)–C(20)	119.4(7)
N(1)–Pt(1)–S(1)	95.63(16)	O(1)–C(19)–S(1)	123.1(6)
N(2)–Pt(1)–S(1)	174.64(18)	C(20)–C(19)–S(1)	117.5(5)
N(1)–Pt(1)–S(2)	175.75(15)	C(20)–S(2)–Pt(1)	108.2(3)
N(2)–Pt(1)–S(2)	96.74(18)	O(2)–C(20)–C(19)	119.0(7)
S(1)–Pt(1)–S(2)	88.63(7)	O(2)–C(20)–S(2)	123.5(7)
C(19)–S(1)–Pt(1)	108.1(3)	C(19)–C(20)–S(2)	117.5(6)

established from the IR spectra, the free (C=O) stretches appearing at 1655 and 1641 cm^{-1}. In common with many other platinum(II) diimine dithiolate compounds[10] **2** is luminescent in fluid solution, having an absorption maximum at 399 nm ($\varepsilon = 1 \times 10^4$ mol^{-1} dm^3 cm^{-1}), and a broad emission at 595 nm.

Orange needle-shaped crystals were obtained by allowing a dichloromethane solution of **2** to stand in an NMR tube for 3 days, and the resulting X-ray crystal structure is shown in Fig. 3. The molecule crystallises in the space group *Pnma*, with the molecule (apart from the *tert*-butyl groups) lying on a crystallographic mirror plane, and thus being completely planar with approximately C_{2v} symmetry. The platinum–sulfur bond lengths are each 2.26 Å; selected bond lengths and angles are given in Table 1.

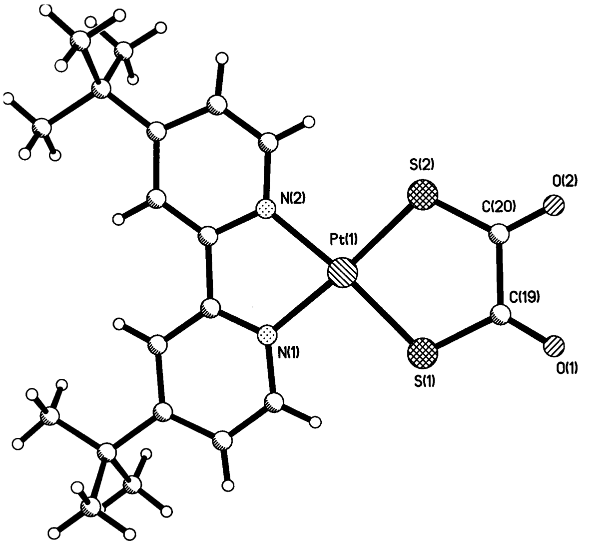


Fig. 3 The X-ray structure of **2**.

Ruthenium complexes

Unsubstituted square planar diimine–dithiolate complexes of platinum are generally soluble only in extremely polar solvents such as DMSO and DMF, and require alkyl-substituted ligands, such as the 4,4′-bis(*tert*-butyl)-2,2-bipyridine employed in **2**, to bestow solubility in a wider range of organic solvents. In order to try and create a more soluble analogue of **2** without the extensively substituted bipyridyl ligand, it was decided to attempt the reaction of similar ruthenium starting materials with SnMe$_2$(dto). In contrast to the large number of bipyridyl-1,2-dithiolate complexes of platinum that are known, few such ruthenium compounds have been reported. Those that do all contain two bidentate bipyridyl ligands, and so cannot have the desired *trans* geometry.[11]

To this end, [Ru(Me$_2$bipy)(PPh$_3$)$_2$Cl$_2$] **3** was prepared from [Ru(PPh$_3$)$_3$Cl$_2$] and 4,4′-dimethyl-2,2′-bipyridine.[12] This compound has *trans*-phosphine ligands and *cis*-chlorine atoms, so is geometrically similar to [Pt(^{t}Bu$_2$bipy)Cl$_2$]; however, with phosphines occupying the axial positions, the π stacking that often renders square planar compounds intractable is prevented. Unfortunately, the reactivity of **3** with SnMe$_2$(dto) does not mirror that of the platinum examples given above, in that instead of replacing the two chloride ligands on the ruthenium with retention of geometry, the dithiooxalate replaces one chloride and one triphenylphosphine ligand. Therefore, elimination of SnMe$_2$Cl$_2$ is not possible, and instead a "[SnMe$_2$Cl]$^+$" moiety is produced and remains chelated within the oxygen atoms of the dithiooxalate, producing the Coucouvanis-type compound [Ru(Me$_2$bipy)(PPh$_3$)Cl(μ-dto)(SnMe$_2$Cl)] **4** (Scheme 1). Although shown as S,S-bonded to the ruthenium, with the available evidence it is not possible to distinguish this mode of dithiooxalate co-ordination from S,O or O,O.

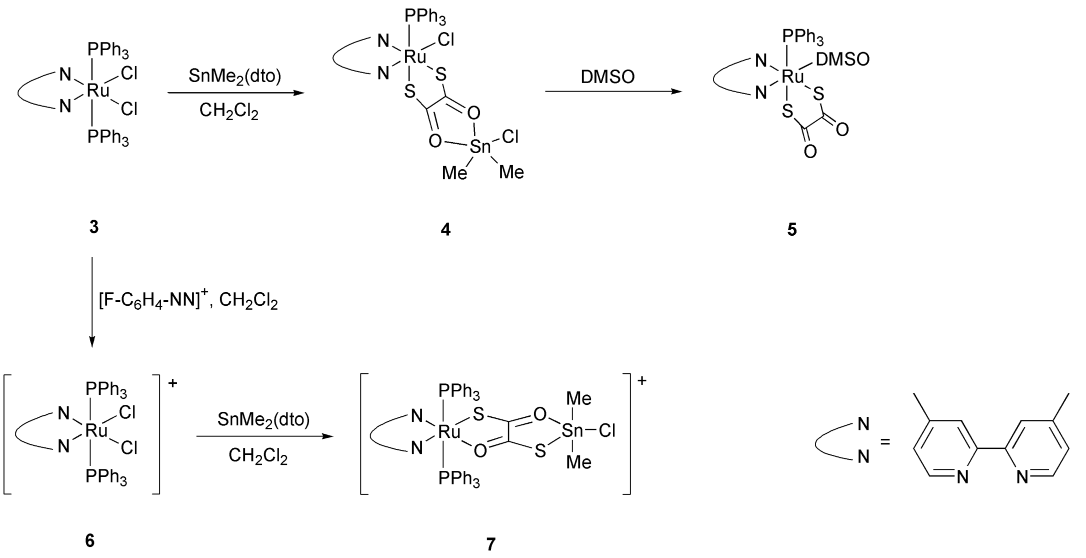
Coucouvanis compounds are often strongly coloured.[3] Co-ordination of the electron-withdrawing tin fragment lowers the energy of the π* LUMO of the dithiooxalate ligand, producing an intense low energy transition-metal to ligand π* charge transfer band that can appear in the visible region of the spectrum. In the UV-visible spectrum of **4** there are absorption maxima at 630 and 446 nm (in dichloromethane solution), making the compound dark green in solution; the solid is blue–black to the naked eye.

Another consequence of the low energy LUMO is that one-electron reduction of Coucouvanis compounds causes population of this orbital. The ESR spectrum of the resulting radical typically shows a *g* value close to that of the free electron (2.0023), with satellites due to hyperfine coupling to the I = 1/2 ^{117}Sn and ^{119}Sn isotopes; the isotropic hyperfine coupling constant a^{Sn} is typically in the 0–10 G range.[13] Cyclic voltammetry on **4** shows a reversible reduction at −0.86 V *vs.* SCE, and *in situ* reduction of a dichloromethane solution of **4** using CoCp$_2$[14] generates a radical showing an ESR signal consistent with the formulation of **4** as a Coucouvanis compound. g_{iso} is 2.0039, and although no tin coupling is observed, the linewidth of 6.75 G is much larger than those reported previously for similar compounds and is sufficiently great to obscure any hyperfine satellites. Reduction of **4** will also be expected to have the effect of destabilising the LUMO, raising it in energy and thus increasing the energy of the HOMO–LUMO transition. This is indeed the case, the two lowest energy bands in the UV-visible spectrum moving to 484 and 339 nm respectively upon reduction.

It is possible to remove the tin moiety from Coucouvanis compounds by using a strongly co-ordinating solvent such as DMSO.[3] Thus, allowing a DMSO solution of **4** to stand overnight causes a greenish–brown to orange colour change to occur, and if this is done in d$_6$-DMSO in an NMR tube a peak at δ = 1.00 is formed, in the same position as that seen for SnMe$_2$Cl$_2$. The remaining ruthenium species is therefore **5**, [Ru(Me$_2$bipy)(PPh$_3$)(DMSO)(dto)], in which the remaining chloride ligand has been lost from the ruthenium and replaced by a molecule of DMSO, and the tin has been removed from the dithiooxalate (Scheme 1). The IR spectrum shows a (C=O) stretch at 1598 cm^{-1}.

Crystals suitable for X-ray diffraction were grown by vapour diffusion of diethyl ether into a dichloromethane–DMSO solution of **5**. The molecule crystallises in the space group $P2_1/c$ with two molecules of **5**, one molecule of diethyl ether and one molecule of dichloromethane in the asymmetric unit. The two molecules of **5** are essentially identical, and one of them is shown in Fig. 4. The S-bound DMSO is *trans* to one of the nitrogen atoms of the bipyridine, and the *S,S′*-dithiooxalate is *trans* to the other bipyridine nitrogen atom and the triphenylphosphine ligand. Because the space group $P2_1/c$ is centrosymmetric and **5** is chiral, the unit cell necessarily contains pairs of molecules of opposite handedness.

The ruthenium atom is pseudo-octahedral, the small bite angles of the bipyridine and dithiooxalate ligands preventing



Scheme 1

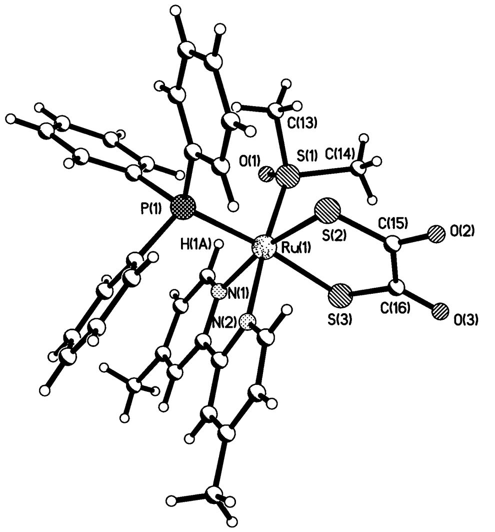


Fig. 4 The X-ray structure of one of the two crystallographically independent molecules of **5**. There is a hydrogen-bond of 2.30 Å between H(1A) and O(1), with an angle at H(1A) of 148°.

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

Ru(1)–N(2)	2.110(4)	S(1)–C(13)	1.794(5)
Ru(1)–N(1)	2.115(4)	S(1)–C(14)	1.794(5)
Ru(1)–S(1)	2.2757(14)	S(2)–C(15)	1.740(5)
Ru(1)–P(1)	2.3629(14)	S(3)–C(16)	1.739(5)
Ru(1)–S(2)	2.3707(14)	C(15)–O(2)	1.221(5)
Ru(1)–S(3)	2.3875(14)	C(15)–C(16)	1.543(7)
S(1)–O(1)	1.486(3)	C(16)–O(3)	1.220(6)
N(2)–Ru(1)–N(1)	77.10(14)	C(15)–S(2)–Ru(1)	107.04(16)
N(2)–Ru(1)–S(1)	173.94(10)	C(16)–S(3)–Ru(1)	107.07(17)
N(1)–Ru(1)–S(1)	101.10(11)	O(1)–S(1)–C(14)	104.2(2)
N(2)–Ru(1)–P(1)	89.13(10)	O(1)–S(1)–C(13)	106.4(2)
N(1)–Ru(1)–P(1)	92.03(11)	C(14)–S(1)–C(13)	96.5(2)
S(1)–Ru(1)–P(1)	96.74(5)	O(1)–S(1)–Ru(1)	119.15(14)
N(2)–Ru(1)–S(2)	94.45(10)	C(14)–S(1)–Ru(1)	114.23(18)
N(1)–Ru(1)–S(2)	169.14(11)	C(13)–S(1)–Ru(1)	113.61(18)
S(1)–Ru(1)–S(2)	86.58(4)	O(2)–C(15)–C(16)	118.1(4)
P(1)–Ru(1)–S(2)	94.69(5)	O(2)–C(15)–S(2)	121.7(4)
N(2)–Ru(1)–S(3)	84.21(10)	C(16)–C(15)–S(2)	120.1(4)
N(1)–Ru(1)–S(3)	86.01(11)	O(3)–C(16)–C(15)	118.4(5)
S(1)–Ru(1)–S(3)	89.90(5)	O(3)–C(16)–S(3)	122.8(4)
P(1)–Ru(1)–S(3)	173.32(5)	C(15)–C(16)–S(3)	118.7(4)
S(2)–Ru(1)–S(3)	86.35(5)		

all the *cis* angles from being 90°. At 2.27 Å the bond between Ru(1) and S(1) of the DMSO is considerably shorter than the sum of the van der Waals radii of these atoms (2.37 Å), but is within the normal range of ruthenium–DMSO bonds in mono-DMSO compounds of this type, which are often considered to have some multiple-bond character.[15] The bond lengths between Ru(1) and the sulfur atoms S(2) and S(3) of the dithiooxalate are much longer (2.37, 2.39 Å), there being less back-bonding to the negatively charged dithiooxalate ligand than to the neutral DMSO. The bipyridine ligand, the ruthenium atom and the sulfur and oxygen atoms of the DMSO are all coplanar, allowing an intramolecular hydrogen bond of 2.30 Å between this oxygen atom (O(1)) and H(1A) of the bipyridine. The dithiooxalate ligand is planar, with bond distances similar to those seen in the crystal structure of **2**. Selected bond lengths and angles are given in Table 2.

Complex **3** shows a fully reversible one-electron oxidation at 0.40 V *vs.* SCE, and reaction in air with the mild one-electron oxidant [p-$FC_6H_4N{\equiv}N$][BF_4][14] generates the corresponding ruthenium(III) species [Ru(Me_2bipy)(PPh_3)$_2$$Cl_2$][$BF_4$] **6**. Although no ESR signal could be detected from a 2 : 1 THF–DCM solution of **6**, upon freezing at 125 K a rhombic spectrum with $g_1 = 2.531$, $g_2 = 2.293$ and $g_3 = 1.752$ was obtained, similar to that reported for [Ru(bipy)(PPh_3)$_2$$Cl_2$]$^+$.[12] **6** appears to be completely air stable both as a solid and in solution.

The ruthenium(III) compound **6** reacts with $SnMe_2$(dto) to produce a ruthenium(II) Coucouvanis compound, which is in this case a deep purple colour (λ_{max} = 508, 274 nm) in solution and red–brown as a solid. Elemental analysis and mass spectrometric data suggest that the compound is [Ru(Me_2bipy)(PPh_3)$_2$(μ-$C_2S_2O_2$($SnMe_2Cl$))][BF_4] **7a**, constituting the loss of a chlorine atom from the two starting materials. The ^{31}P and ^{1}H NMR spectra show that the *trans* arrangement of phosphines at the ruthenium atom is maintained—there is only one set of signals for the two PPh_3 ligands—with the ^{1}H spectrum also containing only one signal for the $SnMe_2$ moiety. These facts suggest that the bipyridine–ruthenium–dithiooxalate moiety is planar, with the triphenylphosphine and methyl groups above and below the plane. However, the methyl groups of the bipyridine are not equivalent, and for that to be the case the two nitrogen atoms of the bipyridine ligand must be *trans* to different atoms on the ruthenium. In order to achieve this, the dithiooxalate has to be S,O bonded to both the ruthenium and tin atoms (Scheme 1), a mode of dithiooxalate co-ordination that has been observed before.[16–18] It is also possible to produce **7** by a more logical route; reaction of **3** with one equivalent of $TlPF_6$ removes the labile chloride, and then subsequent reaction with $SnMe_2$(dto) produces the PF_6 salt of the cation **7**, **7b**.

Reduction of a dichloromethane solution of **7a** with $CoCp_2$ generates a radical showing a 1 : 2 : 1 triplet due to coupling to

Table 3 ^{1}H and ^{31}P NMR data for new complexes[a]

Complex	Solvent	^{1}H	^{31}P
1 [Pt(COD)(dto)]	CD_2Cl_2	δ 2.3–2.7 (8 H, m, $-CH_2-$), 5.23 (m, 4H, $J_{H\text{-}Pt}$ = 56.1 Hz, –CH–)	
2 [Pt(^{t}Bu$_2$bipy)(dto)]	CD_2Cl_2	δ 1.45 (18 H, s, ^{t}Bu), 7.60 (2 H, dd, $^3J_{HH}$ = 6.1 Hz, $^5J_{HH}$ = 2.0 Hz, bipy), 8.05 (2 H, d, $^5J_{HH}$ = 1.8 Hz, bipy), 8.50 (2 H, d, $^3J_{HH}$ = 6.1 Hz, $^3J_{H\text{-}Pt}$ = 34 Hz, bipy)	
3 [Ru(Me$_2$bipy)(PPh$_3$)$_2$Cl$_2$]	CD_2Cl_2	δ 2.22 (6 H, s, Me), 6.24 (2 H, d, $^3J_{HH}$ = 6 Hz, bipy), 7.00–7.18 (18 H, m, Ph), 7.35 (2 H, d, $^5J_{HH}$ = 1.3 Hz, bipy), 7.42–7.51 (12 H, m, Ph), 8.43 (2 H, d, $^3J_{HH}$ = 6 Hz, bipy)	δ 24.79 (br)
4 [Ru(Me$_2$bipy)(PPh$_3$)Cl(μ-dto)-(SnMe$_2$Cl)]	$CDCl_3$	δ 1.01 (3 H, s, $^3J_{H\text{-}Sn}$ = 77.2, 73.9 Hz, MeSn), 1.17 (3 H, s, $^3J_{H\text{-}Sn}$ = 78.0, 74.7 Hz, MeSn), 2.34 (3 H, s, Me), 2.48 (3 H, s, Me), 6.49 (1 H, dd, $^3J_{HH}$ = 6.0 Hz, $^5J_{HH}$ = 1.4 Hz, bipy), 7.06–7.23 (16 H, m, Ph and bipy), 7.63 (1 H, s, bipy), 7.72 (1 H, d, $^3J_{HH}$ = 6.0 Hz, bipy), 7.77 (1 H, s, bipy), 9.33 (1 H, d, $^3J_{HH}$ = 5.8 Hz, bipy)	δ 59.54
5 [Ru(Me$_2$bipy)(PPh$_3$)(DMSO)(dto)]	$CDCl_3$	δ 2.27 (3 H, s, Me), 2.38 (3 H, s, Me), 2.69 (3 H, s, DMSO), 3.31 (3 H, s, DMSO), 6.63 (1 H, d, $^3J_{HH}$ = 5.8 Hz, bipy), 7.10–7.30 (16 H, m, Ph and bipy), 7.63 (1 H, s, bipy), 7.71 (1 H, s, bipy), 8.77 (1 H, d, $^3J_{HH}$ = 6.0 Hz, bipy), 9.86 (1 H, d, $^3J_{HH}$ = 6.1 Hz, bipy)	δ 33.31
7 [Ru(Me$_2$bipy)(PPh$_3$)$_2$(μ-dto)-(SnMe$_2$Cl)][BF$_4$]	$CDCl_3$	δ 0.70 (6 H, s, $^3J_{H\text{-}Sn}$ = 76 Hz, Me$_2$Sn), 2.43 (3 H, s, Me), 2.50 (3 H, s, Me), 6.80 (1 H, d, $^3J_{HH}$ = 4.4 Hz, bipy), 6.87–6.95 (12 H, m, Ph), 7.01 (1 H, d, $^3J_{HH}$ = 5.7 Hz, bipy), 7.16–7.4 (18 H, m, Ph), 7.83 (1 H, s, bipy), 8.15 (1 H, s, bipy), 8.66 (1 H, d, $^3J_{HH}$ = 6.1 Hz, bipy), 8.91 (1 H, d, $^3J_{HH}$ = 5.7 Hz, bipy)	δ 33.09

[a] Recorded on a JEOL ECP300 spectrometer at 300 MHz (^{1}H) and 121.4 MHz (^{31}P). ^{1}H shifts relative to internal TMS, and ^{31}P to external 85% H_3PO_4.

the two phosphorus atoms (a^P = 11.75 G). The value of g_{iso}, 2.0030, again indicates a ligand-based radical.

Conclusions

Dimethyltin dithiooxalate is readily synthesised, is much more stable than potassium dithiooxalate, and may be used as a dithiooxalate transfer reagent in exchange reactions with metal-bound chloride ions. In cases where $SnMe_2Cl_2$ is generated this is easily separated, but if $[SnMe_2Cl]^+$ is produced this is trapped by the dithiooxalate to produce dithiooxalate bridged bimetallic 'Coucouvanis' compounds.

Using SnMe$_2$(dto) as a dithiooxalate transfer reagent, [Pt(^{t}Bu$_2$bipy)(dto)] has been synthesised, and in common with many other platinum–diimine–dithiolate compounds is luminescent in fluid solution. It has not yet proved possible to make a geometrically related ruthenium compound, but the first mixed-ligand ruthenium dithiooxalate complexes have been synthesised.

Experimental

All new compounds are air stable in the solid state, and all apart from **4** and **5** are air stable in solutions of organic solvents such as CH_2Cl_2. **5** is stable in solution in the presence of added DMSO. The starting materials K$_2$dto,[1] [Pt(COD)Cl$_2$],[19] [Pt(^{t}Bu$_2$-bipy)Cl$_2$],[20] [RuCl$_2$(PPh$_3$)$_3$][21] and [p-FC$_6$H$_4$N≡N][BF$_4$][14] were prepared by literature methods. IR spectra were recorded in dichloromethane solution on a Perkin-Elmer 1600 series FTIR spectrometer, and UV-visible spectra with a Perkin-Elmer lambda-19 spectrophotometer. Cyclic voltammetry was carried out under an atmosphere of nitrogen using the standard three electrode configuration, with platinum working and counter electrodes, an SCE reference electrode, dichloromethane as solvent, 0.1 M [Bu$_4$N][PF$_6$] as electrolyte and FeCp$_2$ or FeCp*$_2$ as internal calibrant, and a substrate concentration of approximately 1 mM. ESR spectra were recorded on a Bruker ESP300E X-band spectrometer. UV/VIS-NIR spectroelectrochemical measurements were performed in CH_2Cl_2 at 243 K using a locally constructed OTTLE (optically transparent thin-layer electrode) cell in a Perkin-Elmer Lambda-19 spectrophotometer, as described previously.[22] Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry at the University of Bristol. NMR data are presented in Table 3.

Syntheses

SnMe$_2$(dto). 0.407 g (2.05 mmol) of freshly prepared K$_2$dto was dissolved in 10 ml of distilled water, and filtered through Celite if any cloudiness was present. Likewise, an aqueous solution of 0.450 g (1 equivalent) of $SnMe_2Cl_2$ was prepared. The two were mixed with vigorous stirring, and the resulting slightly off-white microcrystalline solid filtered out, washed with distilled water and dried in air and *in vacuo* to give 0.420 g (76%) of product. (Found: C, 18.0; H, 2.0%. $C_4H_6S_2O_2Sn$ requires C, 17.9; H, 2.2%).

[Pt(COD)(dto)] 1. 0.105 g of Pt(COD)Cl$_2$ (0.28 mmol) and 0.075 g of SnMe$_2$(dto) (1 equivalent) were refluxed for one hour in 20 ml of dichloromethane to give a yellow solution. The solution was then allowed to cool, and addition of diethyl ether gave the product **1** as a yellow crystalline solid (0.065 g, 55%). (Found: C, 28.6; H, 2.8%. $C_{10}H_{12}S_2O_2Pt$ requires C, 28.4; H, 2.9%); ν_{max}/cm^{-1} (CO) 1655 (s).

[Pt(^{t}Bu$_2$bipy)(dto)] 2. 0.156 g of Pt(^{t}Bu$_2$bipy)Cl$_2$ (0.31 mmol) and 0.083 g (1 equivalent) of SnMe$_2$(dto) were stirred overnight in 20 ml of dichloromethane to give a cloudy orange solution. This was filtered through Celite and then precipitated and washed with ethanol. Recrystallisation was performed by redissolving the compound in CH_2Cl_2 and allowing the solution to evaporate, giving 0.077 g (42%)of bright yellow–orange product. (Found: C, 41.3; H, 4.0; N, 4.7%. $C_{20}H_{24}N_2S_2O_2Pt$ requires C, 41.1; H, 4.1; N, 4.8%); ν_{max}/cm^{-1} (CO) 1641 (s) and 1622 (sh); UV-vis: λ_{max} = 399 ($\varepsilon = 1.0 \times 10^4$), 294 nm ($2.1 \times 10^4$ mol^{-1} dm^3 cm^{-1}).

[Ru(Me$_2$bipy)(PPh$_3$)$_2$Cl$_2$] 3. Under a nitrogen atmosphere, 2.10 g (0.22 mmol) of RuCl$_2$(PPh$_3$)$_3$ and 0.40 g of Me$_2$bipy (1 equivalent) were dissolved in 50 ml of dichloromethane and stirred for 30 minutes. 50 ml of hexane was then added to the stirred solution, causing the precipitation of **3** as a brown solid. This was filtered out, washed with hexane and dried *in vacuo* to give 1.24 g (64%) of product. Addition of a little more hexane to the filtrate and allowing it to stand affords another 0.55 g (to 93%) of product. The compound is sufficiently pure for further

Table 4 Crystal and refinement data for **2** and **5**

	2	**5**·$\frac{1}{2}CH_2Cl_2$·$\frac{1}{2}C_4H_{10}O$
Formula	$C_{20}H_{24}N_2O_2PtS_2$	$C_{36.5}H_{39}ClN_2O_{3.5}PRuS_3$
M	583.62	825.37
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/c$
a/Å	14.210(3)	17.182(5)
b/Å	7.121(2)	11.229(2)
c/Å	20.478(5)	38.208(10)
β/°		101.87(2)
U/Å^3	2072.1(10)	7214(3)
Z	4	8
μ/mm^{-1}	6.990	0.767
Reflections collected	8183	45958
Independent reflections (R_{int})	2566 (0.0518)	16462 (0.0879)
Goodness of fit on F^2	0.944	0.956
Final $R1$ [$I > 2\sigma(I)$]	0.0303	0.0530

work, but can be recrystallised from a 1: 1 dichloromethane–hexane solution. (Found: C, 65.4; H, 5.0; N, 3.1%. $C_{48}H_{42}N_2P_2Cl_2Ru$ requires C, 65.5; H, 4.8; N, 3.2%).

[Ru(Me$_2$bipy)(PPh$_3$)Cl(μ-dto)(SnMe$_2$Cl)] 4. 0.299 g (0.34 mmol) of **3** and 0.091 g (1 equivalent) of SnMe$_2$(dto) were stirred for 90 minutes in 10 ml of dichloromethane to give a blue–black solution. Slow addition of 20 ml of diethyl ether caused the product to precipitate as a microcrystalline black solid which was separated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 0.220 g (73%). (Found: C, 46.1; H, 3.8; N, 3.1%. $C_{34}H_{33}N_2O_2S_2Cl_2PRuSn$ requires C, 46.0; H, 3.7; N, 3.2%); UV-vis: $\lambda_{max} = 630$ ($\varepsilon = 3556$), 446 nm (4446 mol^{-1} dm^3 cm^{-1}).

[Ru(Me$_2$bipy)(PPh$_3$)(DMSO)(dto)] 5. A solution of 0.129 g (0.15 mmol) of **3** and 0.039 g of SnMe$_2$(dto) was stirred for 90 minutes to give a blue–black solution. 2 ml of DMSO was then added, and the solution refluxed for one hour. After cooling, the dichloromethane was removed on a rotary evaporator to give an orange–brown solution, which was crystallised by addition of 5 ml of diethyl ether and just enough dichloromethane to make the ether and DMSO miscible. Recrystallisation from 1 : 1 dichloromethane–diethyl ether containing a trace of DMSO gave 0.065 g (54%) of bright orange crystals of **5**·$\frac{1}{2}CH_2Cl_2$·$\frac{1}{2}C_4H_{10}O$ which were isolated by filtration, washed with ethanol and diethyl ether and dried *in vacuo*. It is difficult to remove all traces of free DMSO from this compound. (Found: C, 52.9; H, 5.1; N, 3.4%. $C_{36.5}H_{39}N_2O_{3.5}S_3ClPRu$ requires C, 53.1; H, 4.8; N, 3.4%); ν_{max}/cm^{-1} (CO) 1598 (s).

[Ru(Me$_2$bipy)(PPh$_3$)$_2$Cl$_2$][BF$_4$] 6. 0.115 g of **3** (0.13 mmol) and 0.028 g of [p-FC$_6$H$_4$N≡N][BF$_4$] (1 equivalent) were stirred (under air) in 10 ml of dichloromethane for 30 minutes to give a yellow–brown solution. This was filtered through Celite to remove any solid matter, and then slow addition of diethyl ether (10 ml) caused **6** to crystallise as a dark-yellow solid (0.105 g, 83%), which may be used for synthetic purposes. An analytical sample of **6**·$C_4H_{10}O$ was obtained by allowing diethyl ether to diffuse into a dichloromethane solution (Found: C, 58.3; H, 5.0; N, 2.7%. $C_{52}H_{52}N_2Cl_2RuBF_4O$ requires C, 60.0; H, 5.0; N, 2.7%).

[Ru(Me$_2$bipy)(PPh$_3$)$_2$(μ-dto)(SnMe$_2$Cl)][BF$_4$]·H$_2$O 7a·H$_2$O. 0.081 g (0.08 mmol) of **6** and 0.023 g of SnMe$_2$(dto) (1 equivalent) were refluxed for 90 minutes in 10 ml of dichloromethane to give a deep purple solution. The solution was cooled and filtered to remove any residual solid, and 10 ml of diethyl ether was added. Overnight refrigeration caused the product to crystallise as a red–brown solid which was separated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 0.027 g (26%). (Found: C, 50.7; H, 4.1; N, 2.1%. $C_{52}H_{50}N_2O_3S_2ClP_2RuBF_4$ requires C, 51.2; H, 4.1; N, 2.3%); UV-vis: $\lambda_{max} = 508$ ($\varepsilon = 804$), 274 nm (4794 mol^{-1} dm^3 cm^{-1}).

[Ru(Me$_2$bipy)(PPh$_3$)$_2$(μ-dto)(SnMe$_2$Cl)][PF$_6$]·H$_2$O 7b·H$_2$O. 0.107 g (0.12 mmol) of **6**, 0.043 g of TlPF$_6$ (1 equivalent) and 0.033 g of SnMe$_2$(dto) (1 equivalent) were stirred for 30 minutes in 10 ml of dichloromethane to give a deep purple solution. Filtration through Celite and addition of diethyl ether caused precipitation of the product, which was isolated by filtration and recrystallised from 1 : 1 dichloromethane–diethyl ether to give a microcrystalline red–brown solid. Yield 0.090 g (58%). (Found: C, 49.2; H, 3.8; N, 2.2%. $C_{52}H_{50}N_2O_3S_2ClP_3RuSnF_6$ requires C, 48.9; H, 4.0; N, 2.2%).

Structures of 2 and 5

Many of the details of the crystal structure analyses of **2** and **5** are presented in Table 4. The crystal structure determinations were carried out on a Bruker SMART diffractometer in a nitrogen stream at −100 °C. In all cases graphite-monochromated Mo-Kα radiation was used. Data correction was performed with the program SADABS.[23] The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 using the programs SHELXS-97 and SHELXL-97.[24]

CCDC reference numbers 172689 and 172700.

See http://www.rsc.org/suppdata/dt/b1/b109520j/ for crystallographic data in CIF or other electronic format.

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