Notes

Geometric Effects on the Redox Properties of Complexes $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ and the Implications for Oxidation Catalysis

Dennis Riley * **and James Lyon, III**
The Monsanto Company, 800 North Lindbergh Blvd., St. Louis, MO 63167, USA

The electrochemistry of ruthenium(II) complexes of the type $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ (where n = 1–4) have been studied with examples for fourteen of the fifteen possible isomers for this system. Cyclic voltammograms in CH_2Cl_2 reveal that a plot of $E_{\frac{1}{2}}$ *versus* n is linear with a slope of +0.22 V, indicating that each replacement of a sulphoxide ligand with a thioether donor increases the energy of the highest occupied molecular orbital (d_π) by *ca.* 4.8 kcal (*ca.* 20.08 kJ). When n = 2 five different structural isomers are possible, all of which have been synthesized. Their $E_{\frac{1}{2}}$ values range from + 0.72 to 1.42 V. Ligand-additivity theory provides a consistent rationale for interpretation of the results. Catalytic studies are described which reveal that only one structure, all-*trans*-$[RuX_2(R_2SO)_2(R_2S)_2]$, is catalytically active for O_2 oxidations of alcohol. A discussion of the relationship between structure and redox catalysis is included.

In previous studies[1,2] we have shown that ruthenium(II) complexes of the type $[RuX_2L_4]$ where L = Me_2SO, R_2S, MeCN or pyridine can serve as precursor complexes for catalytic thioether oxidations in alcohol solvents using O_2 as oxidant. Studies of this reaction reveal that under the reaction conditions many different ruthenium(II) complexes of the type $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ (X = Cl or Br, n = 0–4), are formed. In studies designed to identify the actual catalyst structure a large number of complexes from the group $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ were prepared and characterized.[3–5] From this group of fifteen different complexes that are possible by varying both stoichiometry and geometry, we have prepared examples of all but one possibility (see Fig. 1).[3–5] and studied their electrochemistry by standard cyclic voltammetric techniques in which the ruthenium(II,III) couples ($E_{\frac{1}{2}}$) are measured (Table 1).

Our approach to understanding and explaining the oxidation potential trends, and ultimately the uniqueness of the all-*trans*-$[RuX_2(R_2SO)_2(R_2S)_2]$ isomer for oxygen oxidation catalysis, utilizes concepts from the ligand-additivity theory developed by Bursten[7] and utilized for other ruthenium(II) complexes.[8] Herein, we present a discussion of this theory as applied to this system of low-spin d^6 ruthenium(II) complexes and demonstrate its validity in a qualitative sense.

Results

Synthesis.—The synthesis of each of the complexes has been reported previously, except for complex **3** whose synthesis is described. This complex was characterized by standard methods and shown by ^1H NMR spectroscopy to possess the *cis*-dihalogeno-*trans*-dimethyl sulphoxide (equivalent Me_2SO ligands) (structure **D**, Fig. 1) arrangement.

Catalytic Studies.—Each of the complexes of the series $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ listed in Table 1 was tested for both alcohol and thioether oxidation catalysis as per the protocol of ref. 2 (the solvent is ethanol). Only four structural types gave any indication of thioether oxidation catalysis, structures **A**–**C** and the all-*trans* isomer **J**. The actual complexes exhibiting catalysis were **1**, **2** and **8**–**13**, while for alcohol (solvent) oxidation catalysis in the absence of added thioether only one isomer gave any catalytic alcohol oxidation [at 95 °C in neat absolute EtOH, 200 p.s.i.g. O_2 (1.38×10^6 Pa)]. This isomer was the all-*trans*-$[RuX_2(R_2SO)_2(R_2S)_2]$ **J** corresponding to complexes **12** and **13**. In these studies the catalyst activity decreased with time, so that by 1 h all oxidation activity had ceased, although several hundred turnovers were observed.

Electrochemical Studies.—In Table 1 are listed the Ru^{II}–Ru^{III} oxidation potentials for the $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ complexes. For two complexes, *trans*-$[RuBr_2(Me_2SO)_2(EtSCH_2CH_2SEt)]$ **11** and *cis*-$[RuCl_2(Me_2SO)\{MeC(CH_2SEt)_3\}]$ **17** controlled-potential electrolysis experiments were carried out until current had fallen to *ca.* 1% of the initial value. The number of electrons transferred per ruthenium was then calculated and found to be one, confirming that we are observing the 2+ to 3+ oxidation in this series of ruthenium(II) complexes.

The oxidation potentials follow a linear correlation (coefficent > 0.99) within this series of complexes $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$, for n = 0, 1, 3 or 4 (see Fig. 2). This correlation is virtually independent of the co-ordinated halide (either Cl or Br), and is also unaffected by the presence of polydentate ligands. This correlation also reveals that the S-bound sulphoxide ligand is more effective than thioether ligands in stabilizing the low-spin d^6 ruthenium(II) ion to oxidation. It is noteworthy that comparison of the oxidation potential of *trans*-$[RuBr_2(Me_2SO)_4]$, *ca.* 1.52 V, to that of *trans*-$[RuBr_2(Me_2SO)_3(PPh_3)]$, $E_{\frac{1}{2}}$ = 1.09 V,[9] shows that triphenylphosphine is also poorer than sulphoxide at stabilizing Ru^{II} to oxidation.

Another important feature associated with this linear correlation of oxidation potential with degree of substitution (n) is that structure does not appear to play an important role in determining the oxidation potential for n = 0, 1, 3 or 4. For example, the *cis*- or *trans*-$[RuBr_2(R_2S)_4]$ complexes have similar oxidation potentials and *cis*-$[RuCl_2(Me_2SO)\{MeC(CH_2SEt)_3\}]$ **17** or *trans*-$[RuCl_2(Me_2SO)(Me_2S)_3]$ **16** have virtually identical oxidation potentials. However,

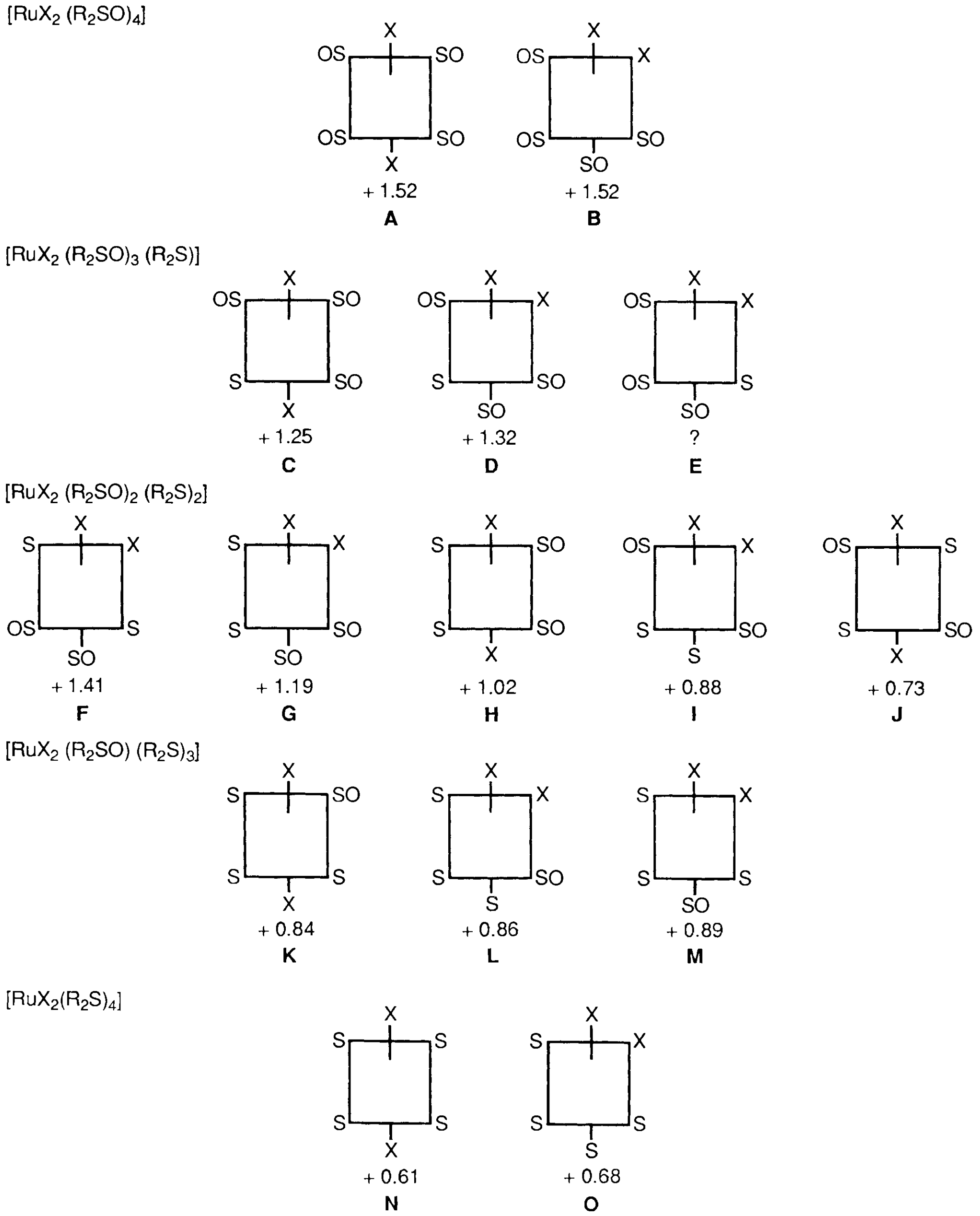

Fig. 1 The structure of every complex of possible stoichiometry $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ where X = Cl or Br, shown in general terms for each stoichiometry (where SO = sulphoxide) with $E_{\frac{1}{2}}$ values (in V)

geometry is significant for $n = 2$. In the series of complexes $[RuX_2(R_2SO)_2(R_2S)_2]$ five geometric isomers are possible (Fig. 3) and at least one example of each structure has been prepared. They range in oxidation potential from 0.72 V for all-*trans*- to 1.42 V for the *trans*-R_2S-*cis* isomer.

Discussion

Catalytic Activity.—The catalytic oxygen oxidation of thioethers using $[RuX_2(Me_2SO)_4]$ complexes as catalyst precursors generates a large variety of complexes of different stoichiometry and geometry $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ depending on the thioether used.[2–5] The rate-determining step is the oxidation of a ruthenium(II) complex by oxygen to yield hydrogen peroxide and oxidized ruthenium (Ru^{III} which disproportionates to Ru^{II} and Ru^{IV}).[2] Ruthenium(II) is regenerated by reduction with the solvent alcohol to give an aldehyde or ketone, while the thioether substrate is oxidized with hydrogen peroxide. Nevertheless, thioether must be present with the $[RuX_2L_4]$ type complexes in these systems for catalytic alcohol oxidations to occur; the thioether serves as a ligand for the ruthenium generating the actual catalyst species *in situ*. A likely structure leading to catalysis in these systems should be a complex which will reduce oxygen, since the rate-determining step is oxidation of a ruthenium(II) complex with O_2 at lower O_2 pressures (<200 p.s.i.g.). Based on oxidation potentials and the experimental results described here and in previous catalytic studies,[2–5] the all-*trans*-$[RuX_2(R_2SO)_2(R_2S)_2]$ complex, generated *in situ*, is the ruthenium(II) complex involved in the catalytic cycle. Such all-*trans* complexes are easily oxidized, in fact at potentials very nearly as low as the air-sensitive and catalytically inactive $[RuX_2(R_2S)_4]$ complexes.

In the oxidation studies reported here all of the complexes containing mixed stoichiometries of R_2SO and R_2S ligands were used. Since the mechanism for the ruthenium(II)-catalyzed O_2 oxidations of thioethers involves a catalytic alcohol oxidation, we should only observe catalytic O_2 oxidations of alcohol with those complexes that are indeed catalysts. Only the

Table 1 Oxidation potentials for the $\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$ redox couple for $[\mathrm{RuX_2(R_2SO)}_n\mathrm{(R_2S)}_{4-n}]$ (n = 0–4)

Complex	$E_{\frac{1}{2}}{}^a$/V	Isomer
1 *trans*-$[\mathrm{RuBr_2(Me_2SO)_4}]$	1.52^b	**A**
2 *trans*-dihalogeno-$[\mathrm{RuBr_2(Me_2SO)_3(Bu^t{}_2S)}]$	1.25	**C**
3 *cis*-dihalogeno-$[\mathrm{RuBr_2(Me_2SO)_2\{PhS(CH_2)_2SOPh\}}]$	1.32^b	**D**
4 *trans*-RS$_2$-*cis,cis*-$[\mathrm{RuBr_2(Me_2SO)\{[EtS(CH_2)_3]_2SO\}}]$	1.41^b	**F**
5 *trans*-RS$_2$-*cis,cis*-$[\mathrm{RuCl_2(Me_2SO)\{[EtS(CH_2)_3]_2SO\}}]$	1.42^b	**F**
6 all-*cis*-$[\mathrm{RuCl_2(Me_2SO)_2\{EtS(CH_2)_2SEt\}}]$	1.19	**G**
7 all-*cis*-$[\mathrm{RuBr_2\{\overline{S(CH_2)_3C}H_2\}\{[EtSO(CH_2)_3]_2S\}}]$	1.17	**G**
8 *trans*-dihalogeno-*cis,cis*-$[\mathrm{RuCl_2(Me_2SO)_2(Me_2S)_2}]$	1.01	**H**
9 *trans*-dihalogeno-*cis,cis*-$[\mathrm{RuBr_2(Me_2SO)_2(Et_2S)_2}]$	0.99	**H**
10 *trans*-dihalogeno-*cis,cis*-$[\mathrm{RuCl_2(Me_2SO)_2\{EtS(CH_2)_2SEt\}}]$	1.02	**H**
11 *trans*-dihalogeno-*cis,cis*-$[\mathrm{RuBr_2(Me_2SO)_2\{EtS(CH_2)_2SEt\}}]$	1.04	**H**
12 all-*trans*-$[\mathrm{RuCl_2(Me_2SO)_2(Me_2S)_2}]$	0.72	**J**
13 all-*trans*-$[\mathrm{RuCl_2(Me_2SO)_2(Et_2S)_2}]$	0.75	**J**
14 *trans*-SO-*cis,cis*-$[\mathrm{RuBr_2\{\overline{S(CH_2)_3C}H_2\}\{[EtSO(CH_2)_3]_2S\}}]$	0.88	**I**
15 *trans*-halogeno-$[\mathrm{RuBr_2(Me_2SO)(Et_2S)_3}]$	0.85	**K**
16 *trans*-halogeno-$[\mathrm{RuCl_2(Me_2SO)(Me_2S)_3}]$	0.82	**K**
17 *cis*-halogeno-*fac*-*S*$_3$-$[\mathrm{RuCl_2(Me_2SO)\{MeC(CH_2SEt)_3\}}]$	0.86	**L**
18 *cis*-halogeno-*mer*-S$_3$-$[\mathrm{RuBr_2(Me_2SO)\{[EtS(CH_2)_2]_2S\}}]$	0.89	**M**
19 *trans*-$[\mathrm{RuCl_2(Me_2S)_4}]$	0.58	**N**
20 *trans*-$[\mathrm{RuBr_2(Me_2S)_4}]$	0.62	**N**
21 *trans*-$[\mathrm{RuBr_2\{EtS(CH_2)_2SEt\}_2}]$	0.67	**N**
22 *trans*-$[\mathrm{RuBr_2\{\overline{S(CH_2)_3C}H_2\}_4}]$	0.56	**N**
23 *trans*-$[\mathrm{RuCl_2\{\overline{S(CH_2)_3C}H_2\}_4}]$	0.54	**N**
24 *cis*-$[\mathrm{RuBr_2([14]aneS_4)}]^c$	0.68	**O**

^{a} All potentials are reported as the reversible half-wave potential in $\mathrm{CH_2Cl_2}$ incorporating a ferrocene internal standard at 0.4 V *vs.* SHE ^{b} Irreversible. ^{c} Ref. 6; [14]aneS$_4$ = 1,4,8,11-tetrathiacyclotetradecane.

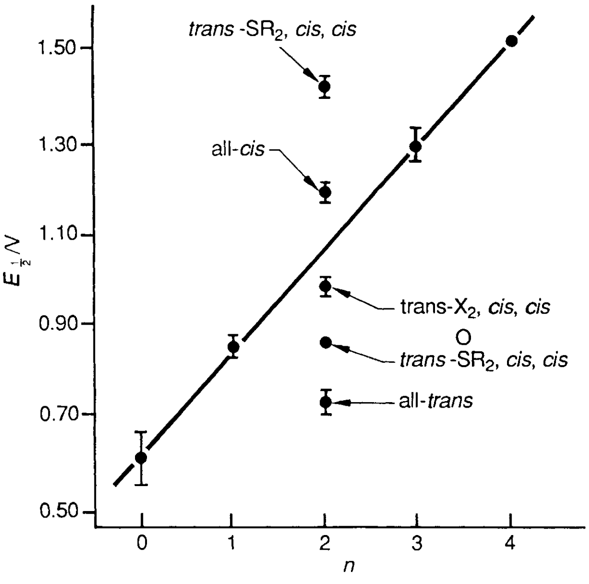

Fig. 2 Plot (slope 0.22 V) of oxidation potential *versus* n for complexes of the type $[\mathrm{RuX_2(R_2SO)}_n\mathrm{(R_2S)}_{4-n}]$

complexes **12** and **13**, possessing the all-*trans*-$[\mathrm{RuX_2(R_2SO)_2(R_2S)_2}]$, structure gave any indication of catalytic alcohol oxidation. They did lose activity, although not until over 200 turnovers had occurred. Clearly, all-*trans*-$[\mathrm{RuX_2(R_2SO)_2(R_2S)_2}]$ complexes are not only unique in a thermodynamic sense, but in their catalytic activity as well. Given the trend in oxidation potentials observed for these complexes $[\mathrm{RuX_2(R_2SO)}_n\mathrm{(R_2S)}_{4-n}]$, that thioether ligands seem to donate much greater electron density to the ruthenium(II) ion than do the S-bound sulphoxide ligands, it seems unusual that a bis(sulphoxide) bis(thioether) stoichiometry would in fact be so easy to oxidize and be the structure that leads to catalysis in these systems.

Thermodynamic Considerations and Ligand Additivity.—The electrochemical studies clearly show that $\mathrm{R_2S}$ ligands destabilize the $\mathrm{Ru^{II}}$ to oxidation more than a S-bound sulphoxide by about 0.22 V. Since a linear trend in $E_{\frac{1}{2}}$ values is observed for the stoichiometry n = 0, 1, 3 or 4 in $[\mathrm{RuX_2(R_2SO)}_n\mathrm{(R_2S)}_{4-n}]$ complexes, it is consistent with a single additive effect. In this case it appears that the thioether donor is simply a much better σ donor than are S-bound sulphoxide ligands.

If the oxidation potential for complexes $[\mathrm{RuX_2(R_2SO)}_n\mathrm{(R_2S)}_{4-n}]$ of the stoichiometry n = 0, 1, 3 or 4 follows a linear σ-bonding-based trend, why does the correlation break down when n = 2? For the complexes $[\mathrm{RuX_2(R_2SO)_2(R_2S)_2}]$ σ-bonding effects should have little or no role in determining oxidation potentials since the ligand set is constant. In the n = 2 case it appears that π-bonding effects must be invoked to rationalize the profound differences observed in $E_{\frac{1}{2}}$ values for isomers.

To rationalize the observed oxidation-potential dependence on structure for the n = 2 stoichiometry we have utilized concepts from the ligand additivity theory.[7,8] Two fundamental concepts need to be emphasized in using this approach: (1) the oxidation potential of these low-spin d^6 ruthenium(II) complexes is a measure of the energy required to remove an electron from the highest-occupied molecular orbital (HOMO) of the complex, one of the filled d_π orbitals, and (2) the energy of the HOMO can be depicted by a linear combination of terms relating to the charge on the metal, the σ-donating effect of each ligand, and the π-donating or -accepting effects of each ligand (interacting with the filled HOMO orbital). Rigorous adaptation of this theory requires that the ligands be axially symmetrical about the Ru–S bond axis, and this is not possible with either the thioether or the sulphoxide ligands, but this limitation should not detract from the use of ligand additivity to describe qualitatively the bonding in these complexes and to predict oxidation-potential ordering for the different complexes.

The ligand-additivity depiction of the bonding involved in generating the HOMO in this system of complexes $[\mathrm{RuX_2(R_2SO)}_n\mathrm{(R_2S)}_{4-n}]$ requires the relative ranking of the three ligand types as to their π-bonding ability. Clearly the halide ligands are

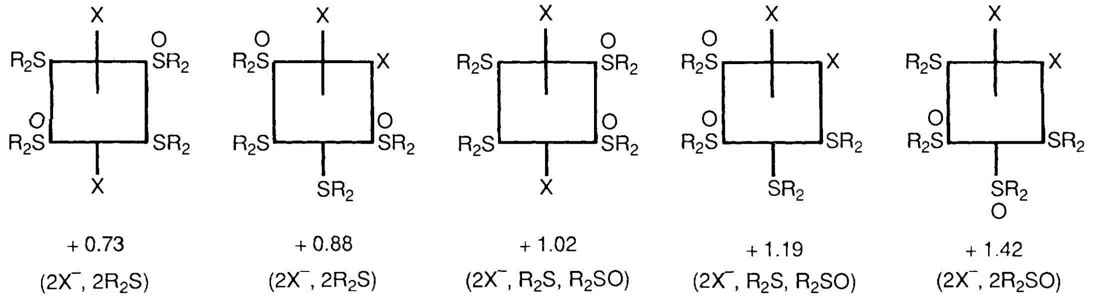

Fig. 3 Each isomer of $[RuX_2(R_2SO)_2(R_2S)_2]$ stoichiometry with representative $E_{\frac{1}{2}}$ value (in V) and the four coplanar ligands which interact with a filled t_2 (O_h) orbital to generate the HOMO

the best π-donor and poorest π-acceptor ligands; consequently they are the most destabilizing in their π interactions with the filled d_π orbitals. Thioether ligands (with a non-bonded electron pair) are potential π-donor ligands, and are possibly π-acceptor ligands into their vacant 3d orbitals. Sulphoxide ligands appear to be good π-acceptor ligands especially when mutually *cis*-, and also *trans*- to a non-π-acceptor ligand. This conclusion is based on observations that mutually *trans*-S-bound sulphoxide ligands on Ru^{II} have bond lengths (>2.35 Å) similar to the Ru^{II}–S bond lengths with thioether ligands, and both are much longer than mutually *cis*-S-bound sulphoxide Ru^{II}–S bond lengths (typically 2.25–2.27 Å).[4,5,10,11] These results and other spectral correlations reveal that π bonding is considerably more important in sulphoxide than in thioether bonding.[12] Consequently, the order for destabilizing a filled d_π (of t_2 origin in O_h symmetry) orbital is $R_2SO < R_2S < X^-$, and the HOMO in these systems for a given stoichiometry will be that d_π orbital which interacts with the maximum halide ligands, followed by thioether ligands, and the minimum number of sulphoxide ligands (recognizing that each of the d_{xy}, d_{yz} or d_{xz} orbitals will π-interact with the four ligands in the plane of that orbital[7]). It should be emphasized that for the complexes of stoichiometry $n = 2$, $[RuX_2(R_2SO)_2(R_2S)_2]$, only the π-bonding ligands have an effect on the energy of the HOMO and hence the oxidation potential of each complex. For example, the *trans*-thioether, *cis-cis* isomer of $[RuX_2(R_2SO)_2(R_2S)_2]$ has the two sulphoxide ligands coplanar with the halide ligands. This is, of course, the most stabilizing arrangement of π ligands for generating the HOMO. Not surprisingly, this is the hardest isomer for $n = 2$ to oxidize. For the all-*trans* $n = 2$ isomer two thioether ligands are now coplanar with the halide ligands. This is the most destabilizing arrangement of π ligands for generating a HOMO, and experimentally we observe that this geometry is indeed the easiest to oxidize. The other possible *trans*-sulphoxide complex with *cis*-halide and *cis*-thioether ligands should according to this approach (to the first approximation) have the same HOMO generating ligands and hence the same $E_{\frac{1}{2}}$ value. However, inspection of this structure reveals that the strong π-donor halide ligands are now *trans* to the potential π-acceptor thioether ligands. This is clearly a more effective geometric arrangement for relieving π-electron density than the all-*trans* arrangement in which the potential π-acceptor thioether ligands are now *trans*. Thus, the all-*trans* is expected to be at least somewhat easier to oxidize than the *trans*-SOR_2-*cis,cis* isomer (complex **14**). In the all-*cis* geometry there are two different ligands, one thioether and one sulphoxide, coplanar with the two halide ligands, and, as a consequence, a lower-energy HOMO is predicted. Since the all-*cis* isomers oxidize near 1.20 V, the magnitude of the stabilization relative to the all-*trans* geometry is over 0.3 V.

The *trans*-dihalogeno-*cis,cis* complexes have lower oxidation potentials and, consequently, a higher-energy HOMO than that of the all-*cis* isomers, even though they do possess the same HOMO ligand descriptor. This discrepancy could conceivably be due to two factors: (1) the *trans*-halogeno, *cis,cis* isomer possesses a doubly degenerate HOMO giving rise to a Jahn–Teller splitting of the ruthenium(III) ion, or more likely (2) the subtle differences in π-bonding effects arising from *cis*- and *trans*-halogeno ligands. For example, the all-*cis* isomer has a π-acceptor ligand(s) (sulphoxide and thioether potentially) *trans* to halide ligands in the plane of the HOMO, whereas the *trans*-halogeno-*cis* isomer has the halogeno ligands mutually *trans*. Thus, the all-*cis* isomer would appear to be a better configuration for removing electron density and hence stabilizing Ru^{II} to oxidation. The trends we observe in the $E_{\frac{1}{2}}$ values for these five $n = 2$ isomers are both consistent with π-bonding effects and the qualitative aspects of a ligand-additivity approach.

Based on this geometric analysis of the π-bonding effects we note that the all-*trans*-$[RuX_2(R_2SO)_2(R_2S)_2]$ geometry is predicted to be one of the most easily oxidized complexes in the series $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$. This is due to the high-energy HOMO generated by π interactions with the *trans*-SR_2 and *trans*-X ligands. It is significant that this is the identical set of ligands which generates the HOMO in the *trans*-$[RuX_2(SR_2)_4]$ complexes. Significantly, the all-*trans*-$[RuX_2(R_2SO)_2(R_2S)_2]$ complexes are nearly as easy to oxidize. Given the ease of oxidation of the all-*trans*-$[RuX_2(R_2SO)_2(R_2S)_2]$ complexes, it is reasonable to anticipate that they could be significant for oxidation catalysis. Since there are other members of this family of $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ complexes which are very easy to oxidize {*e.g.* $[RuX_2(R_2S)_4]$} why are they not catalysts? This, we propose, lies in another unique feature of the all-*trans* isomers; namely, that the Ru–S (sulphoxide) bond distances are much longer when those sulphoxides are *trans* rather than *cis*.[3–5,10,11] As a consequence, we believe that the all-*trans* isomer is poised kinetically to be a catalyst. In its oxidized form the ruthenium centre will be reduced *via* a co-ordinated alcohol. This requirement of a vacant co-ordination site on the oxidized Ru necessitates that a labilized ligand be poised to exchange. In fact, from the work of Taube and co-workers[13] it is recognized that upon oxidation ruthenium(II) S-bound Me_2SO complexes undergo isomerization to O-bonding. In this system we propose that an all-*trans* $n = 2$ complex possesses the proper combination of structural attributes which makes it possible not only to oxidize the ruthenium centre easily, but also to promote a more facile reduction process.

Experimental

Electrochemical Studies.—All cyclic voltammograms were measured in 0.20–0.40 mol dm^3 tetrabutylammonium tetrafluoroborate in methylene chloride. The methylene chloride was dried by passage through two columns of dry alumina and distillation from CaH_2 under N_2. The supporting electrolyte was recrystallized twice from ethyl acetate–hexane solution. A three-electrode cell was utilized with a glassy carbon working electrode with a platinum reference electrode utilizing ferrocene as an internal standard. The cyclic voltammograms were measured with both a Bioanalytical Systems CV-1B cyclic voltammograph and a PAR 173 potentiostat and a PAR universal programmer at different sweep rates of 100–1000 mV s^{-1} to insure that the potential measured was not a function of scan rate. Voltammograms were recorded on a Houston

Instruments 100 XY recorder. The reversible Fe^{II}–Fe^{III} couple of ferrocene was measured as an internal standard in methylene chloride and all reported potentials are referenced to SHE assuming +0.40 V for ferrocene *versus* SHE[14]

Syntheses.—The synthesis of complexes **1**, **2** and **4**–**24** have been reported elsewhere.[3–5]

1-*phenylsulphinyl-2-phenylthioethane.* This potentially bidentate mixed sulphide–sulphoxide ligand was prepared from the corresponding bis(thioether), 1,2-bis(phenylthio)ethane (Fairfield Chemical), by treating the thioether (1.0 g) in dry acetone (50 cm^3) at 0 °C with 30% H_2O_2 (0.7 cm^3). The reaction was carried out until all the starting thioether was consumed (several hours). This step requires an excess of H_2O_2 which was destroyed by adding a small amount of Pt/C. The solution was filtered through Celite to remove Pt/C and taken to dryness. The resultant white solid was extracted with hot hexane and filtered to yield 0.73 g of analytically pure product (Found: C, 63.90; H, 5.55; S, 24.1. Calc. for $C_{14}H_{14}OS_2$: C, 64.1; H, 5.40; S, 24.4%). The mass spectrum also agrees with this formulation (parent ion *m/z* 262, calc. 262).

Dibromobis(*dimethyl sulphoxide*)(1-*phenylsulphinyl-2-phenylthioethane*)*ruthenium*(II) **3**. To an ethanol slurry containing *trans*-$[RuBr_2(Me_2SO)_4]$ (0.5 g, 8.7 mmol) in degassed absolute EtOH (100 cm^3) was added the above ligand (0.25 g, 9.5 mmol) with vigorous stirring. The solution was stirred for 2 d at room temperature. A yellow solid was filtered off and washed with ethanol and diethyl ether. Yield 0.49 g (83%) (Found: C, 32.00; H, 3.75; Br, 23.85; S, 18.55. Calc. for $C_{18}H_{26}Br_2O_3RuS_4$: C, 31.85; H, 3.85; Br, 23.55; S, 18.85%). Infrared spectrum (Nujol mull, CsBr windows): ν_{SO} at 1092 and 1060 cm^{-1}, characteristic of S-bound sulphoxide moieties.[10] Proton NMR ($CDCl_3$): δ 7–7.5 (10 H, phenyl H), 3.65 (s, 12 H, CH_3SO), 3.3 (t, 2 H, J = 8, CH_2SO) and 2.6 (t, 2 H, J = 8 Hz, CH_2S).

Oxidation Reactions.—Oxidation studies were carried out using methods, equipment and analytical techniques described in ref. 2.

Acknowledgements

The authors would like to acknowledge the helpful suggestions of Professor Bruce Bursten of The Ohio State University.

References

1 D. P. Riley, *Inorg. Chem.*, 1983, **22**, 1965.
2 D. P. Riley and R. E. Shumate, *J. Am. Chem. Soc.*, 1984, **106**, 3179.
3 D. P. Riley and J. D. Oliver, *Inorg. Chem.*, 1986, **25**, 1814.
4 D. P. Riley and J. D. Oliver, *Inorg. Chem.*, 1986, **25**, 1821.
5 D. P. Riley and J. D. Oliver, *Inorg. Chem.*, 1986, **25**, 1825.
6 C.-K. Poon, S.-S. Kwong, C.-M. Che and Y.-P. Kan, *J. Chem. Soc., Dalton Trans.*, 1982, 1457.
7 B. E. Bursten, *J. Am. Chem. Soc.*, 1982, **104**, 1299.
8 M. Haga, T. M.-Inoue, K. Shimizu and G. P. Sato, *J. Chem. Soc., Dalton Trans.*, 1989, 371.
9 D. P. Riley, *Inorg. Chim. Acta*, 1985, **99**, 5.
10 D. P. Riley and J. D. Oliver, *Inorg. Chem.*, 1984, **23**, 156.
11 E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sava and S. Zorzet, *Inorg. Chem.*, 1988, **27**, 4099.
12 J. Chatt, G. J. Leigh and A. P. Storace, *J. Chem. Soc. A*, 1971, 1380.
13 A. Yeh, N. Scott and H. Taube, *Inorg. Chem.*, 1982, **21**, 2542.
14 R. R. Gagne, C. A. Koval and E. C. Lisensky, *Inorg. Chem.*, 1980, **19**, 2855.

Received 16*th May* 1990; *Paper* 0/02163F