Structural and Mechanistic Studies of Co-ordination Compounds. Part 34.[1] Electrochemical Behaviour of Some Octahedral Ruthenium(III)/Ruthenium(II) Couples containing Tetra-amine or -thioether Ligands

By **Chung-Kwong Poon,* Si-San Kwong, Chi-Ming Che,** and **Yan-Ping Kan,** Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Several factors have been found to affect the half-wave potentials ($E_{\frac{1}{2}}$) of some *cis*- and *trans*-$[RuL(A)X]^{n+,(n-1)+}$ couples, where L represents either four unidentate, two bidentate, or one quadridentate amines or thioethers, and A and X are unidentate π-acid ligands. A variation in the π-accepting capability of these L, A, or X ligands appears to be the most dominating factor. Thus, for analogous *cis*-$[RuLCl_2]^{+,0}$ couples, a change from L = L^7 (1,4,8,11-tetra-azacyclotetradecane) to L = L^{16} (1,4,8,11-tetrathiacyclotetradecane) results in an anodic shift of *ca.* 1.0 V in both aqueous and CH_3CN solutions. For some common acid ligands, the $E_{\frac{1}{2}}$ values of *cis*- and *trans*-$[RuLX_2]^{+,0}$ couples increase in the following order of X: $N_3^- < Cl^- < Br^- < NCS^- < NO_2^-$ over a span of *ca.* 0.7 V. Other factors, such as the presence of α-di-imine functions in the chelate rings, steric, ligand-chelation, ring-size effects and geometrical configuration of the complexes, and solvents also affect the $E_{\frac{1}{2}}$ values of these Ru^{III}/Ru^{II} couples. It thus appears that a suitable combination of the above factors may ' tune ' a Ru^{III}/Ru^{II} couple to possess any desired $E_{\frac{1}{2}}$ value over the range −0.80 to +0.83 V *vs.* Ag/Ag^+ (0.1 mol dm^{-3}).

THE electrochemical study of Ru^{III}/Ru^{II} amine couples has been of interest for a number of years.[2-4] Most of the studies have been concentrated on either penta-ammine or tetra-ammine systems containing π-acid ligands. So far, no systematic study of the variations of half-wave potentials ($E_{\frac{1}{2}}$) of Ru^{III}/Ru^{II} couples with other structural parameters, such as steric factors, chelation, and degrees and types of ligand unsaturation, has been reported. Such a systematic study has been carried out on several occasions on other metal systems,[5,6] in particular, of macrocyclic amine complexes [7-11] of the type *trans*-$[ML(A)X]^{n+,(n-1)+}$ where L represents a quadridentate macrocyclic amine, and A and X are unidentate acid ligands. It has been found that the $E_{\frac{1}{2}}$ values for the Co^{III}/Co^{II} couples are very sensitive to the steric, strain, and ring size effects of L and also to the nature of A and X, but are much less sensitive to the degrees and types of ligand unsaturation.[7-9] For the Fe^{III}/Fe^{II} [10] and Ni^{III}/Ni^{II} [11] couples, a more elaborate study has demonstrated that the $E_{\frac{1}{2}}$ values are increased additively by the presence of a larger macrocyclic ring, the presence of axial methyl groups in the chelate rings, and the presence of ligand unsaturation.

As part of our programme to investigate the chemistries of amine and thioether complexes of ruthenium(III) and ruthenium(II),[1,12-15] we report here our investigation into the effects of various electronic and structural parameters on the $E_{\frac{1}{2}}$ values of some closely related *cis*- and *trans*-$[RuL(A)X]^{n+,(n-i)+}$ couples, where L represents either four unidentate, two bidentate, or one quadridentate amines or thioethers.

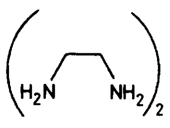
EXPERIMENTAL

All the amine and thioether complexes under the present investigation were prepared according to published methods [12,13,16-19] from this laboratory. Water was doubly redistilled and h.p.l.c. (high performance liquid chromatography) grade acetonitrile was used as purchased from Mallinckrodt, U.S.A., without further purification. All other reagents were recrystallized as necessary before use.

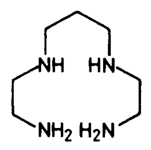
Cyclic voltammograms (c.v.) were obtained with Princeton Applied Research (PAR) instruments which have been described previously.[20] Measurements were made against either a PAR model 9311 saturated calomel electrode (s.c.e.) in aqueous solutions or a PAR model K103 Ag/Ag^+ (0.1 mol dm^{-3} $AgNO_3$) electrode in acetonitrile. The latter electrode was used in conjunction with a PAR model K65 reference electrode bridge tube with a Vycor tip. Ferrocene, purified by sublimation, was used as an internal standard (+0.054 V *vs.* Ag/Ag^+) for all c.v. scans in acetonitrile.

RESULTS AND DISCUSSION

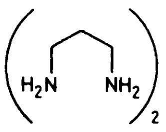
In general most of the Ru^{III} complexes under the present investigation undergo one-electron reversible electrochemical reactions. In slightly acidic aqueous solution [0.01 mol dm^{-3} toluene-*p*-sulphonic acid (Hpts)], with $I = 0.2$ mol dm^{-3} using K[pts], the electrochemical behaviour of *trans*-$[RuL^1Cl_2]^+$, which has been described in detail previously,[20] or of *trans*-$[RuL^7Cl_2]^+$ (Table 1), can be taken as representatives of that of most saturated amine complexes of Ru^{III} under the present investigation. At suitably fast scan rates to avoid hydrolysis of the reduced products, the cyclic voltammograms show only one forward cathodic (E_{cp}) and one reverse anodic peak (E_{ap}) with a peak current ratio (i_{ap}/i_{cp}) close to unity (>0.9). At slower scan rates, a second set of peaks and finally a third set of peaks at progressively more positive potentials appear, which correspond to the redox systems, *trans*-$[RuLCl(OH_2)]^{2+,+}$ and *trans*-$[RuL(OH_2)_2]^{3+,2+}$ respectively. A peak separation (ΔE_p) of 65 ± 6 mV, being independent of scan rates, remains a constant feature in these different sets of peaks. The half-wave potential for each set of couples has been taken to be the average value of the corresponding E_{cp} and E_{ap}. Some complexes, such as *trans*-$[RuLCl_2]^+$ [L = L^{11} (C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) or L^{13} (C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-



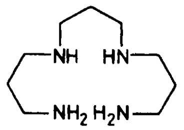
L^1



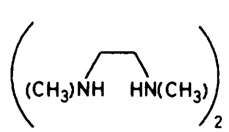
L^5



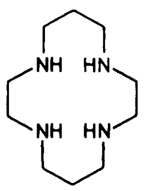
L^2



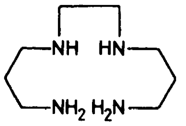
L^6



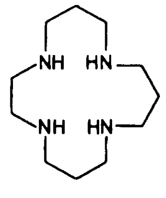
L^3



L^7

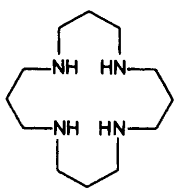


L^4

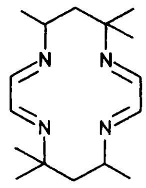


L^8

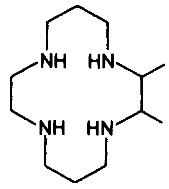
tetra-azacyclotetradeca-1,3,8,10-tetraene)] and *cis*-[Ru-LCl_2]$^+$ [L = L^7 (1,4,8,11-tetra-azacyclotetradecane), L^{15} (1,4,7,10-tetrathiacyclotridecane), or L^{16} (1,4,8,11-tetrathiacyclotetradecane)], are quite labile towards hydrolysis and they have to be studied in fairly concentrated HCl solutions (3.0 mol dm^{-3}). Even then for *trans*-[RuL^{11}-Cl_2]$^+$, reversible scans can only be achieved at relatively fast scan rates (>2 V s^{-1}) because the electrochemically reduced Ru^{II} species is very labile. In acetonitrile solutions, the behaviour of all the dichloro-complexes studied is typical of that for a one-electron reversible redox system. Here, the peak separations are slightly larger (65—80 mV) * than those in aqueous solutions, but the peak current ratios are all close to unity. The diazido-, dibromo-, di-isothiocyanato-, and dinitro-complexes of L^{13}, L^{15}, and L^{16} are available only in the Ru^{II} state and they are not soluble in water. Studies of these complexes were only carried out in acetonitrile solutions with the forward scans corresponding to the oxidation of Ru^{II} to Ru^{III} (anodic waves). For the series of L^{16} complexes, while the dichloro- and diazido-couples are truly reversible and the dibromo-couple is marginally reversible, the di-isothiocyanato- and dinitro-couples are almost totally irreversible. Thus *cis*-[RuL^{16}(NCS)$_2$]$^{+,0}$ gives a current ratio of 1.9 with a peak separation of 91 mV at a scan rate of 50 mV s^{-1} and *cis*-[RuL^{16}(NO$_2$)$_2$]$^{+,0}$ only gives an oxidation peak with the cathodic peak nearly completely disappearing, even on the first reverse scan over a range of scan rates. For these two couples, the $E_{\frac{1}{2}}$ values were deduced[21] from the first c.v. scan at the potentials of 0.8517 peak currents (cathodic peak if available). For the dinitro-couple,



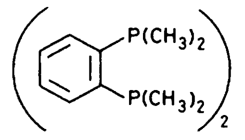
L^9



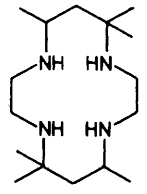
L^{13} (*C-meso*)



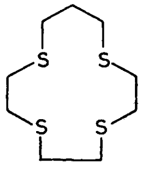
L^{10}



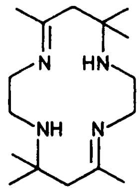
L^{14}



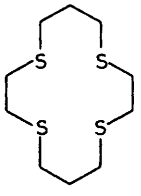
L^{11} (*C-meso*)



L^{15}



L^{12}



L^{16}

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* ΔE_p for ferrocene in MeCN containing tetra-n-butylammonium tetrafluoroborate (tbab) (0.1 mol dm^{-3}) was found to be 75 mV at 50 mV s^{-1} scan rate.

the $E_{\frac{1}{2}}$ value so deduced should be taken as an approximate measure only. The electrochemical characteristics of the c.v. scans of these couples for complexes of L^{16} (Figure 1) together with those of other typical couples are collected in Table 1. The electrochemical behaviour of the *cis*-$[RuL^{15}(NCS)_2]^{+,0}$ couple is very similar to that of *cis*-$[RuL^{16}(NO_2)_2]^{+,0}$ without showing the reverse cathodic peak, while all other couples in acetonitrile are either reversible or nearly reversible. All these $E_{\frac{1}{2}}$ values, after being corrected for the $E_{\frac{1}{2}}$ of s.c.e. (+0.241 V *vs.* standard hydrogen electrode,[22] s.h.e.) in aqueous solutions, are collected in Table 2. Abbreviations of other ligands employed in this work are L^1 [bis(ethane-1,2-diamine)], L^2 [bis(propane-1,3-diamine)], L^3 [bis(*NN'*-dimethylethane-1,2-diamine)], L^4 (4,7-diazadecane-1,10-diamine), L^5 (3,7-diazanonane-1,9-diamine), L^6 (4,8-diazaundecane-1,11-diamine), L^8 (1,4,8,12-tetra-azacyclopentadecane), L^9 (1,5,9,13-tetra-azacyclohexadecane), L^{10} (2,3-dimethyl-1,4,8,11-tetra-azacyclotetradecane), L^{12} (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene), and L^{14} {bis[*o*-phenylenebis(dimethylphosphine)]}.

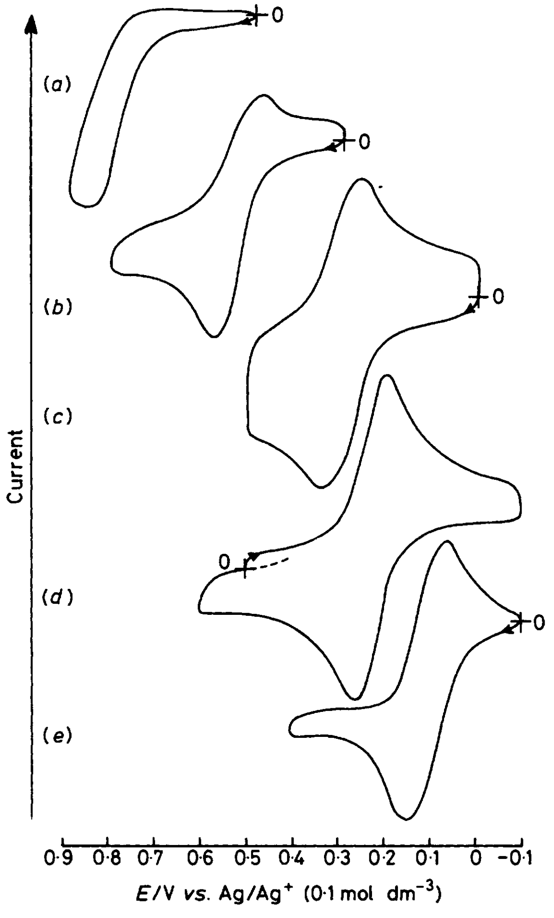

FIGURE 1 Cyclic voltammograms of *cis*-$[RuL^{16}X_2]^{+,0}$ couples in CH_3CN ([tbab] = 0.1 mol dm^{-3}). Current scales vary with each couple: (*a*) X = NO_2^- (scan rate 200 mV s^{-1}), (*b*) X = NCS^- (scan rate 50 mV s^{-1}), (*c*) X = Br^- (scan rate 500 mV s^{-1}), (*d*) X = Cl^- (scan rate 100 mV s^{-1}), and (*e*) X = N_3^- (scan rate 200 mV s^{-1})

Among various electronic and structural parameters which influence the $E_{\frac{1}{2}}$ values of these ruthenium couples, the π-accepting capability of the ligands appears to be most dominating. Although an increase in the $E_{\frac{1}{2}}$ value of a couple means either an increase in the relative stability of the complex in the Ru^{II} state or a decrease in that of the Ru^{III} state, or both, the present observation indicates that factors stabilizing complexes in the Ru^{II} state appear to be most important. For neutral ligands (L) a change in the ligating atoms can greatly alter the potentials of these complexes. A striking observation is the great anodic shift of 1.034 V when the four saturated nitrogen atoms in *cis*-$[RuL^7Cl_2]^{+,0}$ couple are replaced by four sulphur atoms in the structurally similar *cis*-$[RuL^{16}Cl_2]^{+,0}$ couple in acetonitrile. A comparison between the $E_{\frac{1}{2}}$ value of *trans*-$[RuL^{14}Cl_2]^{+,0}$ with that of *trans*-$[RuL^7Cl_2]^{+,0}$ in acetonitrile, though not ideal because of structural differences between L^{14} and L^7, is still useful in giving a rough estimate of an anodic shift of *ca.* 0.95 V when four saturated nitrogen atoms are replaced by four phosphorus atoms. These observations illustrate well the importance of metal-to-ligand π back-bonding in the chemistry of these Ru^{II} complexes. The great stability [13] of *cis*-$[RuL^{16}(N_3)_2]$ and *cis*-$[RuL^{16}(NO_2)_2]$ with respect to thermal decomposition of the $Ru-N_3$ and $Ru-NO_2$ moieties to the corresponding $Ru-N_2$ and Ru-NO units respectively further illustrates this property. Such decompositions are well known [23] in Ru^{II} saturated amine chemistry. In the saturated amine systems, the $t_{2g}{}^6$ electrons are extensively involved in stabilizing the $Ru-N_2$ and Ru-NO units by metal-to-ligand π back-bonding. In the thioether system, however, these $t_{2g}{}^6$ electrons have already been delocalized to the L^{16} macrocycle and hence the driving force to decompose the $Ru-N_3$ and $Ru-NO_2$ units into $Ru-N_2$ and Ru-NO respectively is greatly reduced.

The effect of introducing two α-di-imine functional groups into the cyclic ligand L^{11} to produce the structurally similar L^{13} results in an anodic shift of $E_{\frac{1}{2}}$ by 0.463 V in acetonitrile or 0.594 V in aqueous solutions. This effect is slightly less important than that on the Fe^{III}/Fe^{II} couple (0.62 V) [11] but is much greater than that on the Ni^{III}/Ni^{II} (0.32 V) [10] and Co^{III}/Co^{II} (0.21 V) [8] couples in acetonitrile. It should be noted, however, that the present estimate of the effect of the α-di-imines on the ruthenium couple is derived from the unipositive *trans*-$[RuLCl_2]^+$ species whereas those for iron, nickel, and cobalt were obtained from the tripositive *trans*-$[ML(CH_3CN)_2]^{3+}$ [M = Fe^{III}, Ni^{III}, or Co^{III}] systems. A change in the charge type of a system usually affects the relative contributions of various electronic and structural effects on $E_{\frac{1}{2}}$, being magnified with increasing charge of the couples.[20] The observed effect of the α-di-imines on $E_{\frac{1}{2}}$ is consistent with the concept of π back-bonding from Ru^{II} to these α-di-imine functions as demonstrated by the presence of intense low-energy metal-to-ligand charge-transfer transitions in all Ru^{II} complexes of L^{13}.[16]

Variation in the nature of uninegative acid ligands

TABLE 1

Electrochemical characteristics of some $[RuLX_2]^{+,0}$ couples

Compound	Medium [a]	Working electrode [b]	Scan rate/ mV s^{-1}	Forward scan	E_{ap} [c]/V		E_{cp} [c]/V		i_{ap}/i_{cp}
					vs. s.h.e.	*vs.* Ag/Ag$^+$	*vs.* s.h.e.	*vs.* Ag/Ag$^+$	
trans-$[RuL^7Cl_2]^+$	Hpts (0.01) + K[pts] (0.19) in H_2O	h.m.d.e.	200	reduction	−0.114		−0.174		0.99
	Hpts (0.01) + K[pts] (0.19) in H_2O	glassy carbon	100	reduction	−0.121		−0.190		0.95
	tbab (0.1) in CH_3CN	graphite	100	reduction		−0.722		−0.788	0.92
trans-$[RuL^7(NCS)_2]^+$	tbab (0.1) in CH_3CN	graphite	100	reduction		−0.293		−0.362	1.1
trans-$[RuL^{11}Cl_2]^+$	HCl (3.0)	glassy carbon	2 000	reduction	−0.087		−0.146		1.0
	tbab (0.1) in CH_3CN	graphite	100	reduction		−0.586		−0.668	0.92
trans-$[RuL^{13}Cl_2]^+$	HCl (3.0)	glassy carbon	500	reduction	+0.512		+0.441		1.0
	tbab (0.1) in CH_3CN	graphite	100	reduction		−0.128		−0.200	1.0
cis-$[RuL^{15}Cl_2]^+$	HCl (3.0)	glassy carbon	500	reduction	+0.949		+0.887		1.0
cis-$[RuL^{15}Cl_2]$	tbab (0.1) in CH_3CN	graphite	200	oxidation		+0.308		+0.240	1.2
cis-$[RuL^{16}Cl_2]$	HCl (3.0)	glassy carbon	500	oxidation	+0.884		+0.821		1.0
	HCl (3.0)	graphite	500	oxidation	+0.883		+0.825		1.2
cis-$[RuL^{16}Cl_2]^+$	tbab (0.1) in CH_3CN	graphite	100	reduction		+0.264		+0.196	1.0
cis-$[RuL^{16}(N_3)_2]$	tbab (0.1) in CH_3CN	graphite	200	oxidation		+0.135		+0.073	1.0
cis-$[RuL^{16}Br_2]$	tbab (0.1) in CH_3CN	graphite	500	oxidation		+0.340		+0.267	1.2
cis-$[RuL^{16}(NCS)_2]$	tbab (0.1) in CH_3CN	graphite	50	oxidation		+0.578		+0.487	1.9
cis-$[RuL^{16}(NO_2)_2]$	tbab (0.1) in CH_3CN	graphite	200	oxidation		+0.868		*d*	*d*

[a] Concentrations (mol dm^{-3}) are given in parentheses. [b] h.m.d.e. = Hanging mercury drop electrode. [c] In aqueous solutions, c.v. measurements were made against a saturated calomel electrode (s.c.e.), but data entered were against standard hydrogen electrode (s.h.e.) ($E_{\frac{1}{2}}$ of s.c.e. was taken to be +0.241 V *vs.* s.h.e.); in CH_3CN solutions, measurements were made against Ag/Ag$^+$ (0.1 mol dm^{-3}) with $E_{\frac{1}{2}}$ (+0.054 V) of ferrocene/ferrocenium couple as an internal reference. [d] The cathodic peak disappears even on the first reverse scan and the current ratio cannot be determined.

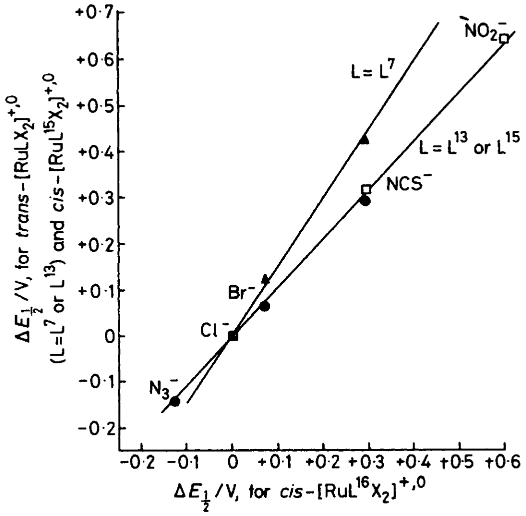

FIGURE 2 Linear plots of $\Delta E_{\frac{1}{2}}$ for *trans*-[RuL^{7}X$_2$]$^{+,0}$ (▲), *trans*-[RuL^{13}X$_2$]$^{+,0}$ (□), and *cis*-[RuL^{15}X$_2$]$^{+,0}$ (●) *versus* $\Delta E_{\frac{1}{2}}$ for *cis*-[RuL^{16}X$_2$]$^{+,0}$ in CH$_3$CN ([tbab] = 0.1 mol dm^{-3})

also affects the $E_{\frac{1}{2}}$ values rather significantly. Taking *cis*-[RuL^{16}Cl$_2$]$^{+,0}$ as a reference, the effects of other dianion ligands can be expressed in terms of $\Delta E_{\frac{1}{2}}$, the difference between the $E_{\frac{1}{2}}$ values of *cis*-[RuL^{16}X$_2$]$^{+,0}$ and those of the coresponding dichloro-couple. The $\Delta E_{\frac{1}{2}}$ values for other systems in acetonitrile solutions, *trans*-[RuL^{7}X$_2$]$^{+,0}$, *trans*-[RuL^{13}X$_2$]$^{+,0}$, and *cis*-[RuL^{15}X$_2$]$^{+,0}$ are similarly deduced. As shown in Figure 2, a plot of these $\Delta E_{\frac{1}{2}}$ values for the L^{13} and L^{15} systems against those of the corresponding L^{16} series is linear over a span of *ca.* 0.8 V with a slope of 1.08. However, the linear plot for the L^7 system, though only a straight line of three points, gives a greater slope of 1.5. This clearly indicates that the relative contributions to the $E_{\frac{1}{2}}$ values by these dianion ligands are dependent on the nature of the neutral macrocycles L and further illustrates the importance of metal-to-ligand π back-bonding in the stabilization of the Ru^{II} state. Since the Ru^{II} state is much more stabilized in the π-accepting L^{13}, L^{15}, and L^{16} systems than in the π-neutral L^7 system, it is expected that the additional contributions to the $E_{\frac{1}{2}}$ values by the acid ligands would be much more significant in the L^7 than in the other three systems. This explains the greater slope for the L^7 system *versus* L^{16} than for the other linear plot (Figure 2). The nearly unit slope in the other plot indicates that the relative contributions to $E_{\frac{1}{2}}$ by these acid ligands are very similar for the L^{13}, L^{15}, and L^{16} systems. It is further noted that these acid-ligand contributions to $E_{\frac{1}{2}}$ are not seriously affected by ring size and steric effects since the bromide contribution * is nearly constant for the L^7, L^8, and L^{11} systems in acetonitrile [$\frac{1}{2}\Delta E_{\frac{1}{2}} = +64$ (L^7), +59 (L^8), and +66 mV (L^{11})], but are quite dependent on the nature of solvents, as demonstrated by a much smaller bromide contribution for the L^1 system in aqueous solution ($\frac{1}{2}\Delta E_{\frac{1}{2}} = +13$ mV). It is, therefore, quite clear that the additive-potential concept [8,10] for ligand contributions should be exercised with care. Although the absolute contributions by these acid ligands may vary from one system to another, it seems reasonable, however, from the data available, to arrange them in an order of increasing contributions: $N_3^- < Cl^- < Br^- < I^- < NCS^- < NO_2^-$. This order represents combined σ and π effects in opposite directions. The order (halides < NCS$^-$ < NO$_2^-$) clearly indicates an increasing π-accepting capability of these acid ligands to stabilize the Ru^{II} state. On the other hand, the order ($N_3^- < Cl^- < Br^- < I^-$) represents the decreasing σ-donating power of the ligands which would destabilize the Ru^{III} state more than Ru^{II}. Endicott and co-workers [7] have obtained a different order † of contributions, over a span of *ca.* 0.65 V, by these acid ligands to the $E_{\frac{1}{2}}$ values of *trans*-[CoL^{12}X$_2$]$^{+,0}$ couples in acetonitrile solutions ($NO_2^- \leqslant NCS^- \leqslant N_3^- < Cl^- < Br^-$). This is the order of decreasing ligand field strength of X.[7] The difference in the order of X contributions in the ruthenium and cobalt systems is a clear reflection of the different responses of X towards the different electronic structures of the central metal ions. We have shown in the present investigation that the change from t_{2g}^5 to t_{2g}^6 when Ru^{III} is reduced to Ru^{II} is most sensitive to the π-accepting capability of the ligands. However, the reduction of Co^{III} to Co^{II} means that an electron is added to the σ* level, *i.e.* a change from t_{2g}^6 to $t_{2g}^6e_g^1$. Clearly, this change would be most sensitive to the σ strength, but not the π effects, of X.

The half-wave potentials of these Ru^{III}/Ru^{II} couples are also influenced by steric effects. The introduction of six methyl groups into L^7 makes the $E_{\frac{1}{2}}$ value for *trans*-[RuL^{11}Cl$_2$]$^{+,0}$ more anodic than for *trans*-[RuL^{7}Cl$_2$]$^{+,0}$ by +33 mV in aqueous solution or +128 mV in acetonitrile. This effect is comparable to those observed for some macrocyclic amine couples of Co^{III}/Co^{II} (+170 mV),[8] Fe^{III}/Fe^{II} (+110 mV),[11] and Ni^{III}/Ni^{II} (+183 mV) [10] in acetonitrile solutions. In these latter three systems comparison was made between the $E_{\frac{1}{2}}$ values of *trans*-[ML^{11}(NCMe)$_2$]$^{3+,2+}$ and *trans*-[ML^{10}(NCMe)$_2$]$^{3+,2+}$, where M represents Co^{III}, Fe^{III}, or Ni^{III}. Hence, the observed effects in these three systems may not truly represent those produced by the introduction of six methyl groups into the two six-membered chelate rings of the macrocyclic complexes. Although it may be true that axial methyl groups exert much greater effects relative to equatorial methyl groups,[8,10] the effects arising from the latter, probably due to differing de-solvation effects, may not be negligible.

Chelate ring strain and macrocyclic ring size have relatively small effects on the $E_{\frac{1}{2}}$ values of these Ru^{III}/Ru^{III} couples. For some common saturated amines (L)

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* The contribution by each acid ligand is roughly taken as half of the corresponding $\Delta E_{\frac{1}{2}}$ value.

† The entries of positive $E_{\frac{1}{2}}$ values for *trans*-[CoL^{12}(NCS)$_2$]$^{+,0}$ in Table 1 of ref. 7 were probably printing errors since Figure 3 and the Discussion section in the same paper clearly indicate that they should be negative.

TABLE 2

Half-wave potentials ($E_{\frac{1}{2}}$) for one-electron reductions of some ruthenium(III) complexes of the type *cis*- and *trans*-$[\mathrm{RuL(A)X}]^{n+}$

Redox couples	Medium [a]	Working electrode	$E_{\frac{1}{2}}$ [b]/V	
			vs. s.h.e.	*vs.* Ag/Ag$^+$
cis-$[\mathrm{Ru(NH_3)_4Cl_2}]^{+,0}$ [c]	$\mathrm{Na[O_2CCF_3]}$ (0.2) in H_2O	h.m.d.e.	−0.100	
cis-$[\mathrm{RuL^1Cl_2}]^{+,0}$ [d]	H_2O	h.m.d.e.	−0.090	
cis-$[\mathrm{RuL^7Cl_2}]^{+,0}$	HCl (3.0)	graphite	−0.082	
	CH_3CN	graphite		−0.804
cis-$[\mathrm{RuL^{15}(N_3)_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.130
cis-$[\mathrm{RuL^{15}Cl_2}]^{+,0}$	HCl (3.0)	glassy carbon	+0.918	
cis-$[\mathrm{RuL^{15}Cl_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.274
cis-$[\mathrm{RuL^{15}Br_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.334
cis-$[\mathrm{RuL^{15}(NCS)_2}]^{+,0}$ [e,f]	CH_3CN	graphite		~+0.560
cis-$[\mathrm{RuL^{16}(N_3)_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.104
cis-$[\mathrm{RuL^{16}Cl_2}]^{+,0}$	HCl (3.0)	glassy carbon	+0.853	
	CH_3CN	graphite		+0.230
cis-$[\mathrm{RuL^{16}Br_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.304
cis-$[\mathrm{RuL^{16}(NCS)_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.522
cis-$[\mathrm{RuL^{16}(NO_2)_2}]^{+,0}$ [e,f]	CH_3CN	graphite		~+0.830
cis-$[\mathrm{Ru(NH_3)_4Cl(OH_2)}]^{2+,+}$ [g]	Hpts (0.1) + K[pts] (0.1) in H_2O	h.m.d.e.	0.00	
cis-$[\mathrm{Ru(en)_2Cl(OH_2)}]^{2+,+}$ [d]	H_2O	h.m.d.e.	+0.151	
cis-$[\mathrm{Ru(NH_3)_4(OH_2)_2}]^{3+,2+}$ [c]	$\mathrm{Na[O_2CCF_3]}$ (0.2) in H_2O	h.m.d.e.	+0.100	
trans-$[\mathrm{Ru(NH_3)_4Cl_2}]^{+,0}$ [d]	H_2O	h.m.d.e.	−0.164	
trans-$[\mathrm{RuL^2Cl_2}]^{+,0}$	H_2O	h.m.d.e.	−0.190	
trans-$[\mathrm{RuL^1Cl_2}]^{+,0}$ [d]	H_2O	h.m.d.e.	−0.188	
trans-$[\mathrm{RuL^1Br_2}]^{+,0}$ [d]	H_2O	h.m.d.e.	−0.162	
trans-$[\mathrm{RuL^1ICl}]^{+,0}$	HCl (0.5)	graphite	−0.146	
trans-$[\mathrm{RuL^1IBr}]^{+,0}$	$\mathrm{Na[ClO_4]}$ (0.1) + $HClO_4$ (0.01) in H_2O	graphite	−0.090	
trans-$[\mathrm{RuL^1(NCS)_2}]^{+,0}$ [d]	H_2O	h.m.d.e.	+0.122	
trans-$[\mathrm{RuL^3Cl_2}]^{+,0}$	H_2O	h.m.d.e.	−0.118	
trans-$[\mathrm{RuL^4Cl_2}]^{+,0}$	H_2O	h.m.d.e.	−0.167	
trans-$[\mathrm{RuL^5Cl_2}]^{+,0}$ [d]	H_2O	h.m.d.e.	−0.168	
trans-$[\mathrm{RuL^6Cl_2}]^{+,0}$	H_2O	h.m.d.e.	−0.144	
trans-$[\mathrm{RuL^7Cl_2}]^{+,0}$ [d]	H_2O	h.m.d.e.	−0.144	
	H_2O	glassy carbon	−0.156	
	CH_3CN	graphite		−0.755
trans-$[\mathrm{RuL^7Br_2}]^{+,0}$	CH_3CN	graphite		−0.628
trans-$[\mathrm{RuL^7(NCS)_2}]^{+,0}$	CH_3CN	graphite		−0.328
trans-$[\mathrm{RuL^8Cl_2}]^{+,0}$	H_2O	h.m.d.e.	−0.130	
	CH_3CN	graphite		−0.736
trans-$[\mathrm{RuL^8Br_2}]^{+,0}$	CH_3CN	graphite		−0.618
trans-$[\mathrm{RuL^9Cl_2}]^{+,0}$	HCl (0.2)	graphite	−0.100	
trans-$[\mathrm{RuL^{11}Cl_2}]^{+,0}$	HCl (3.0)	glassy carbon	−0.117	
	CH_3CN	graphite		−0.627
trans-$[\mathrm{RuL^{11}Br_2}]^{+,0}$	CH_3CN	graphite		−0.496
trans-$[\mathrm{RuL^{13}Cl_2}]^{+,0}$	HCl (3.0)	glassy carbon	+0.477	
	CH_3CN	graphite		−0.164
trans-$[\mathrm{RuL^{13}(NCS)_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.150
trans-$[\mathrm{RuL^{13}(NO_2)_2}]^{+,0}$ [e]	CH_3CN	graphite		+0.482
trans-$[\mathrm{RuL^{14}Cl_2}]^{+,0}$ [h]	teap (0.1) in CH_3CN	platinum		+0.20
trans-$[\mathrm{Ru(NH_3)_4Cl(OH_2)}]^{2+,+}$ [d]	H_2O	h.m.d.e.	−0.070	
trans-$[\mathrm{RuL^2Cl(OH_2)}]^{2+,+}$	H_2O	h.m.d.e.	−0.071	
trans-$[\mathrm{RuL^1Cl(OH_2)}]^{2+,+}$ [d]	H_2O	h.m.d.e.	−0.066	
trans-$[\mathrm{RuL^4Cl(OH_2)}]^{2+,+}$	H_2O	h.m.d.e.	−0.029	
trans-$[\mathrm{RuL^5Cl(OH_2)}]^{2+,+}$ [d]	H_2O	h.m.d.e.	−0.027	
trans-$[\mathrm{RuL^6Cl(OH_2)}]^{2+,+}$	H_2O	h.m.d.e.	−0.013	
trans-$[\mathrm{RuL^7Cl(OH_2)}]^{2+,+}$ [d]	H_2O	h.m.d.e.	−0.019	
trans-$[\mathrm{RuL^8Cl(OH_2)}]^{2+,+}$	H_2O	graphite	+0.035	
trans-$[\mathrm{RuL^9Cl(OH_2)}]^{2+,+}$	H_2O	graphite	+0.065	
trans-$[\mathrm{Ru(NH_3)_4(OH_2)_2}]^{3+,2+}$ [d]	H_2O	h.m.d.e.	+0.046	
trans-$[\mathrm{RuL^2(OH_2)_2}]^{3+,2+}$	H_2O	h.m.d.e.	+0.074	
trans-$[\mathrm{RuL^1(OH_2)_2}]^{3+,2+}$ [d]	H_2O	h.m.d.e.	+0.092	
trans-$[\mathrm{RuL^4(OH_2)_2}]^{3+,2+}$	H_2O	h.m.d.e.	+0.103	
trans-$[\mathrm{RuL^5(OH_2)_2}]^{3+,2+}$ [d]	H_2O	h.m.d.e.	+0.117	
trans-$[\mathrm{RuL^6(OH_2)_2}]^{3+,2+}$	H_2O	h.m.d.e.	+0.131	
trans-$[\mathrm{RuL^7(OH_2)_2}]^{3+,2+}$ [d]	H_2O	h.m.d.e.	+0.145	
trans-$[\mathrm{RuL^8(OH_2)_2}]^{3+,2+}$	H_2O	h.m.d.e.	+0.190	
trans-$[\mathrm{RuL^9(OH_2)_2}]^{3+,2+}$	H_2O	graphite	+0.225	

Concentrations (mol dm^{-3}) are given in parentheses.

[a] Supporting electrolytes are either Hpts (0.01 mol dm^{-3}) + K[pts] (0.19 mol dm^{-3}) in aqueous solution or tbab (0.1 mol dm^{-3}) in CH_3CN, except as indicated. teap = Tetraethylammonium perchlorate. [b] In aqueous solutions, c.v. measurements were made against s.c.e., but data entered were against s.h.e. ($E_{\frac{1}{2}}$ of s.c.e. is taken to be +0.241 V *vs.* s.h.e.); in CH_3CN solution, measurements were made against Ag/Ag$^+$ (0.1 mol dm^{-3}) with $E_{\frac{1}{2}}$ (+0.054 V) of ferrocene/ferrocenium couple as an internal reference. [c] H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460. [d] Ref. 20. [e] Complexes were available in the Ru$^{\mathrm{II}}$ state; the forward c.v. scans represent the oxidation processes $\mathrm{Ru^{II}} \longrightarrow \mathrm{Ru^{III}}$. [f] The reverse cathodic waves were not well defined and the $E_{\frac{1}{2}}$ values were deduced from the forward anodic waves. [g] J. A. Marchant, T. Matsubara, and P. C. Ford, *Inorg. Chem.*, 1977, **16**, 2160. [h] L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126; using stationary platinum working electrode.

they can be arranged in the following order of influence: $(NH_3)_4 < L^2 < L^1 < L^4 < L^5 < L^6 < L^7 < L^8 < L^9$. These effects become more prominent with increasing charge of the complexes, with an overall span of 90 mV for *trans*-$[RuLCl_2]^{+,0}$, 136 mV for *trans*-$[RuLCl(OH_2)]^{2+,+}$ and 179 mV for *trans*-$[RuL(OH_2)_2]^{3+,2+}$ couples in aqueous solutions. This order may be partially explained in terms of solvation effects. As a complex gets larger with an increased chelation, it becomes less solvated, the effect being more pronounced in the higher charged Ru^{III} than the Ru^{II} state. In other words, a large complex is less destabilized on reduction by this desolvation effect and hence it has a greater $E_{\frac{1}{2}}$ value. However, for Co^{III}/Co^{II} and Ni^{III}/Ni^{II} amine couples, very prominent ring-size effects have been observed. A change from L^7 to L^9 for *trans*-$[CoLCl_2]^{+,0}$ shifts $E_{\frac{1}{2}}$ by 580 mV [9] and for *trans*-$[NiL]^{3+,2+}$ by 375 mV [10] in acetonitrile solutions. These effects are satisfactorily correlated [9,10] with the strain energy for the complexes. It would be expected that the larger ruthenium ions are more susceptible to these strain energy effects and it is not clear why they behave otherwise.

TABLE 3

The effects of ligating atoms and functional groups on the $E_{\frac{1}{2}}$ values of some *cis*- and *trans*-$[RuLX_2]^{+,0}$ couples in aqueous or CH_3CN solutions

	$\Delta E_{\frac{1}{2}}$/V	
Ligating atoms or functional groups	H_2O (*vs.* s.h.e.)	CH_3CN (*vs.* Ag/Ag^+)
Replacement in *cis* L of 4 N by 4 S atoms	0.935 [a]	+1.034 [a]
Replacement in *trans* L of 4 N by 4 P atoms		*ca.* +0.955 [b]
Addition of 6 methyl groups in 2 six-membered chelate rings	0.033 [c]	+0.128 [c]
Addition of 2 α-di-imines in 2 five-membered chelate rings	+0.594 [d]	+0.463 [d]

[a] $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}$(*cis*-$[RuL^{16}Cl_2]^{+,0}$) − $E_{\frac{1}{2}}$(*cis*-$[RuL^7Cl_2]^{+,0}$). [b] $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}$(*trans*-$[RuL^{14}Cl_2]^{+,0}$) − $E_{\frac{1}{2}}$(*trans*-$[RuL^7Cl_2]^{+,0}$); this value only gives an approximate estimate of the effect since L^{14} and L^7 are structurally different. [c] $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}$(*trans*-$[RuL^{11}Cl_2]^{+,0}$) − $E_{\frac{1}{2}}$(*trans*-$[RuL^7Cl_2]^{+,0}$). [d] $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}$(*trans*-$[RuL^{13}Cl_2]^{+,0}$) − $E_{\frac{1}{2}}$(*trans*-$[RuL^{11}Cl_2]^{+,0}$).

From the limited number of data in Table 2, it is clear that $E_{\frac{1}{2}}$ values of *cis* complexes are slightly greater than those of the *trans* analogues. It has been pointed out previously [20] that this *cis–trans* effect could be explained in terms of a nephelauxetic effect where the *d*-electron cloud could diffuse away from the metal ion much more effectively in the *cis* complexes than in the more symmetrical *trans* complexes.

Finally, it is expected that the charge of a complex will affect the $E_{\frac{1}{2}}$ values. However, it is not possible to study this effect in isolation because changing the net charge of a complex invariably involves a change of the nature of one or more ligands. The gradual increase in $E_{\frac{1}{2}}$ with the gradual replacement of a co-ordinated chloride by an aqua-ligand, for any set of complexes with the ligand L, would probably arise partly from the charge effect.

CONCLUSION

With reference to Table 3 and Figure 2, it seems possible at least in principle, to ' tune ' a Ru^{III} or Ru^{II} complex to possess any desired $E_{\frac{1}{2}}$ potential over the range −0.80 to +0.83 V *versus* Ag/Ag^+ (0.1 mol dm^{-3}). First, a suitable amine or thioether macrocyclic ligand with a certain degree of π-accepting capability is chosen which would approximately fix $E_{\frac{1}{2}}$ at a certain potential. This potential is then altered by a suitable choice of the unidentate ligands. Finer adjustments of $E_{\frac{1}{2}}$ to the desired value may be obtained either by a further modification of these ligands by incorporating additional steric or ring-size effects or by altering the geometrical configuration of the complex. Work is now in progress to investigate the correlation between electron-transfer kinetics and $E_{\frac{1}{2}}$ values of these ruthenium complexes.

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