Bis(*N,N*) Chelated Rhenium(III): The [ReL$_2$Cl$_2$]Cl Family [L = 2-(arylazo)pyridine]

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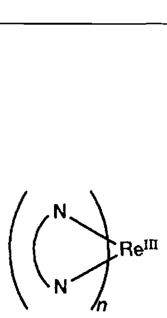
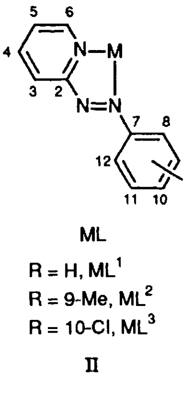
The reaction of *mer*-[Re(MeCN)(PPh$_3$)$_2$Cl$_3$] with 2-(arylazo)pyridines (L) affords dark green, diamagnetic, 1 : 1 electrolytes [ReL$_2$Cl$_2$]Cl (aryl of L = Ph, *m*-MeC$_6$H$_4$ or *p*-ClC$_6$H$_4$). The ReCl$_2$ moiety is *cis* (two Re–Cl stretches) and the cation has an overall two-fold symmetry axis (^{1}H NMR spectra). The co-ordinated pyridine-nitrogen atoms and azo-nitrogen atoms of each ligand are assigned relative *trans* and *cis* geometries respectively. The N=N stretching frequencies are low (1280–1290 cm^{-1}) implying significant Re(t$_2$)–azo(π*) back bonding. In MeCN solution three nearly reversible redox couples occur with $E_{\frac{1}{2}}$ values of ≈0.9 V [rhenium(IV)–rhenium(III)] and ≈ −0.4, ≈ −0.8 V (azo redox) *vs.* the saturated calomel electrode (SCE). A metal-to-ligand charge-transfer (m.l.c.t.) absorption is observed near 600 nm. The reduction potentials and m.l.c.t. frequencies are mutually consistent. The remarkable spectral and electrochemical similarities between [Re^{III}L$_2$Cl$_2$]Cl and [Os^{II}L$_2$Cl$_2$] are noted and rationalised.

Authentic rhenium(III) complexes of *N,N*-chelating bidentate ligands are uncommon and the known systems are limited to monochelates (**I**, *n* = 1) of only a few ligands.[1,2] Bis(chelates) incorporating the Re(N,N)$_2$ fragment (**I**, *n* = 2) are virtually unknown. In the present work we report such complexes based on 2-(arylazo)pyridines (L). We were prompted to utilise ligands L because of their proven strong affinity (*via* the chelating mode **II**) for osmium[3–5] as well as towards other metals.[6–14] Monochelate binding of rhenium(V) by L occurs in [Re(NR)(L)Cl$_3$][R = aryl].[15]

The synthesis of a family of complexes of type [ReL$_2$Cl$_2$]Cl is described. Spectroscopic and electrochemical examinations are made to probe isomer geometry, back bonding, charge-transfer spectra, metal oxidation and ligand reduction. The results are rationalised and unified in relation to other chelates of L, particularly those of osmium.



I



ML

R = H, ML^1
R = 9-Me, ML^2
R = 10-Cl, ML^3

II

Results and Discussion

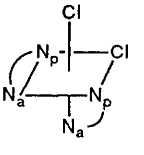
Synthesis.—In this work three ligands, 2-(phenylazo)pyridine (L^1), 2-(3′-methylphenylazo)pyridine (L^2) and 2-(4′-chlorophenylazo)pyridine (L^3), varying in the R substituent have been utilised. Dark green complexes, tc-[ReL$_2$Cl$_2$]Cl, are afforded in good yield by the reaction of equation (1) carried out in boiling

$$\textit{mer}\text{-[Re(MeCN)(PPh}_3)_2\text{Cl}_3] + 2\text{L} \longrightarrow \text{tc-[ReL}_2\text{Cl}_2]\text{Cl} + 2\text{PPh}_3 + \text{MeCN} \quad (1)$$

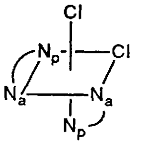
dry ethanol. The prefix tc refers to the assigned isomer geometry (see below). Selected characterisation data for the complexes are collected in Table 1. They behave as 1 : 1 electrolytes in MeCN and are diamagnetic.

The observed diamagnetism of the complexes is somewhat unusual for pseudo-octahedral mononuclear rhenium(III) complexes which usually display temperature-independent paramagnetism.[1,2,16]

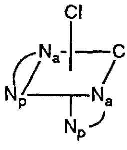
Isomeric Nature and Back Bonding.—Single crystals suitable for X-ray structure determination could not be grown for any of the complexes. Their isomer geometry has, however, been revealed by IR and ^{1}H NMR data. The complexes are always obtained in a single form characterised by two sharp and strong Re–Cl stretches in the region 300–350 cm^{-1} (Table 1). The ReCl$_2$ fragment is thus *cis* and three isomeric structures **A**–**C** are possible. These differ in the relative positions (*trans* or *cis*) of the co-ordinated pyridine nitrogen atoms (N$_p$,N$_p$) and/or azo nitrogen atoms (N$_a$,N$_a$).



trans-cis (tc)
A



cic-cis (cc)
B



cis-trans (ct)
C

The chelates show well resolved ^{1}H NMR spectra in CDCl$_3$ at 270 MHz. Chemical shift and coupling constant data are listed in Table 2 and a representive spectrum is shown in Fig. 1. Signal assignments are based on relative intensity, spin–spin structure, effect of the substituent R and comparison with the spectra of tc-[OsL$_2$Cl$_2$] and tc-[RuL$_2$Cl$_2$].[3,17] Since each kind of proton gives rise to only one signal (singlet or multiplet) it is clear that in each case only a single isomer is present and that the two L ligands are magnetically equivalent. A two-fold axis of symmetry is thus required and this excludes cc geometry, **B**. Dynamic averaging *via* fluxionality is not expected here; neither do the spectra display any new features at low temperatures (230 K). The ^{1}H NMR results demonstrate that the geometry is either tc, **A** or ct, **C**.

Complexes of type [OsL$_2$Cl$_2$] have been isolated[3,4] in both

Table 1 Analytical, electronic spectral,[a] selected IR[b] and conductivity data

Compound	Elemental analysis[c] (%) C	H	N	UV/VIS and NIR spectral data, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	IR cm^{-1} $\nu_{N=N}$	ν_{Re-Cl}	Λ_M/Ω^{-1} cm^2 mol^{-1}
tc-[ReL$^1{}_2$Cl$_2$]Cl	40.05 (40.10)	2.80 (2.75)	12.80 (12.75)	1 300 (105), 650 (sh) (6 150), 580 (8 350), 450 (11 650), 300 (14 950)	1 290	310, 328	150
tc-[ReL$^2{}_2$Cl$_2$]Cl	42.00 (41.95)	3.25 (3.20)	12.30 (12.25)	1 300 (100), 650 (sh) (6 300), 580 (8 560), 450 (12 000), 300 (14 200)	1 285	310, 325	140
tc-[ReL$^3{}_2$Cl$_2$]Cl	36.40 (36.30)	2.30 (2.20)	11.40 (11.55)	1 325 (90), 650 (sh) (5 400), 590 (7 220), 460 (10 200), 320 (16 840)	1 280	310, 325	140

[a] Spectral data and molar conductivity data in MeCN at 298 K. [b] KBr disk, 4 000–300 cm^{-1}. [c] Calculated values are in parentheses.

Table 2 ^{1}H NMR spectral data in CDCl$_3$

Compound	δ(*J*/Hz)[a] H^3	H^4	H^5	H^6	H^8	H^9	H^{10}	H^{11}	H^{12}
tc-[ReL$^1{}_2$Cl$_2$]Cl	7.77 (d) (7.8)	7.99 (t) (6.8)	7.53 (t) (6.8)	8.08 (d) (5.6)	5.82 (d) (6.8)	7.23 (t) (7.8)	7.33 (t) (7.8)	7.23 (t) (7.8)	5.82 (d) (6.8)
tc-[ReL$^2{}_2$Cl$_2$]Cl	8.03 (d) (7.3)	8.01 (t) (6.8)	7.60 (t) (6.8)	8.10 (d) (5.6)	5.35 (s)	*b*	7.14 (d) (9.0)	7.13 (t) (9.0)	5.53 (d) (6.8)
tc-[ReL$^3{}_2$Cl$_2$]Cl	7.78 (d) (7.3)	7.98 (t) (7.6)	7.56 (t) (7.3)	8.06 (d) (7.7)	6.01 (d) (9.0)	7.23 (d) (8.0)	—	7.23 (d) (8.0)	6.02 (d) (9.0)

[a] Tetramethylsilane is the internal standard; s = singlet, d = doublet and t = triplet. [b] Singlet 9-Me signal at δ 2.23.

Table 3 Cyclic voltammetric data[a]

Compound	M^{z+1}–M^z couple[b] $E_{\frac{1}{2}}$/V(ΔE_p/mV)	azo redox $E_{\frac{1}{2}}$/V(ΔE_p/mV)
tc-[ReL$^1{}_2$Cl$_2$]Cl	0.92 (60)	−0.40 (70), −0.80 (60)
tc-[ReL$^2{}_2$Cl$_2$]Cl	0.90 (70)	−0.45 (70), −0.86 (60)
tc-[ReL$^3{}_2$Cl$_2$]Cl	0.94 (70)	−0.30 (80), −0.68 (80)
tc-[OsL$^2{}_2$Cl$_2$]	0.96 (60)	−0.63 (60), −0.83 (70)

[a] Conditions: 298 K; solvent, acetonitrile; supporting electrolyte, NEt$_4$ClO$_4$ (0.1 mol dm^{-3}); working electrode, platinum; reference electrode, SCE; solute concentration, ≈ 10^{-3} mol dm^{-3}; $E_{\frac{1}{2}} = 0.5\,(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate, 50 mV s^{-1}. [b] M = Re, *z* = 3; M = Os, *z* = 2.

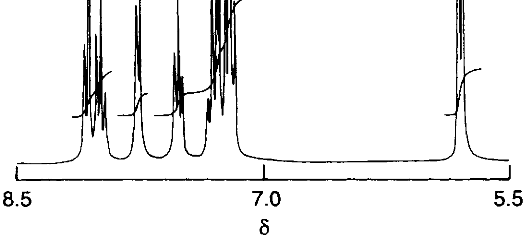


Fig. 1 Proton NMR spectrum of tc-[ReL$^1{}_2$Cl$_2$]Cl in CDCl$_3$

tc (major component) and cc forms while results on the ruthenium congeners suggest that the tc isomer is thermodynamically more stable.[10] The ligands L are good π acceptors and strong M(d$_\pi$)–azo(π*) back bonding is a persistent feature of chelates [ML] including the present species (see below). We note that in the ct isomer the *trans*-N$_a$,N$_a$ pair compete for the same metal d$_\pi$ orbital. This is expected to weaken back bonding in this isomer compared to tc and cc isomers in which the N$_a$,N$_a$ pairs are *cis*. Indeed the ct isomer has never been observed for [OsL$_2$Cl$_2$] and [RuL$_2$Cl$_2$]. On these grounds we assign tc geometry to [ReL$_2$Cl$_2$]Cl as isolated.

In the free ligand L^1, $\nu_{N=N}$ occurs[6] at 1425 cm^{-1} but in combination with d$_\pi$-donor metal ions the frequency is shifted to lower values due to back bonding.[6,11,14,15,18] The position of this band in tc-[OsL$_2$Cl$_2$] occurs at 1280 cm^{-1}.[3,4] Bond-distance data are fully consistent with the back-bonding hypothesis.[3,5,8,19,20] In tc-[ReL$_2$Cl$_2$]Cl the N=N stretch occurs as a sharp and strong band in the region 1280–1290 cm^{-1} (Table 1). Evidently a good degree of back bonding, qualitatively comparable to that in tc-[OsL$_2$Cl$_2$], is present in tc-[ReL$_2$Cl$_2$]$^+$.

Redox Activity and Charge Transfer Spectra.—The tc-[ReL$_2$Cl$_2$]Cl complexes were voltammetrically examined in acetonitrile solution at a platinum working electrode in the voltage range ±1.5 V *vs.* the saturated calomel electrode (SCE). Half-wave potentials are collected in Table 3 and representative voltammograms are displayed in Fig. 2. Three nearly reversible one-electron couples are systematically observed.

The couple near 0.9 V is assigned to metal oxidation, equation (2). The potential depends on the R substituent in the

$$\text{tc-[Re}^{IV}\text{L}_2\text{Cl}_2]^{2+} + e \longrightarrow \text{tc-[Re}^{III}\text{L}_2\text{Cl}_2]^{+} \qquad (2)$$

expected manner: 9-Me < H < 10-Cl. The net change is, however, relatively small (40 mV). The effects of R on the two couples at negative potentials are much larger (net change, 100–120 mV) suggesting that these couples may involve ligand redox, equation (3). Indeed this type of closely spaced successive

$$\text{tc-[ReL}_2\text{Cl}_2]^{+} + e \rightleftharpoons \text{tc-[Re(L}^{\cdot-}\text{)LCl}_2] \qquad (3a)$$

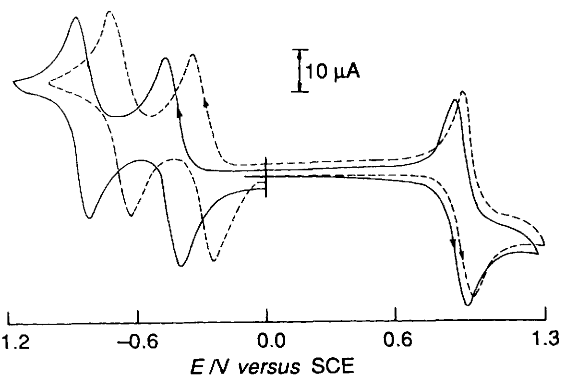


Fig. 2 Cyclic voltammograms (scan rate 50 mV s^{-1}) of ≈10^{-3} mol dm^{-3} solutions of tc-[ReL$^2{}_2$Cl$_2$]Cl (——) and tc-[ReL$^3{}_2$Cl$_2$]Cl (– – –) in acetonitrile (0.1 mol dm^{-3} NEt$_4$ClO$_4$) at a platinum electrode (298 K)

$$\text{tc-[Re(L}^{\bullet-}\text{)LCl}_2] + e \rightleftharpoons \text{tc-[Re(L}^{\bullet-})_2\text{Cl}_2]^- \quad (3b)$$

redox is a characteristic feature of bis- and tris-chelates of L.[3,4,21,22] Electron transfer involves the azo π* orbital and the two couples correspond to successive reduction of the two azo functions. The onset of ligand reduction has precluded possible observation of metal reduction, rhenium(III)–rhenium(II).[23] Bulk generation of the metal-oxidised [equation (2)] and ligand-reduced [equation (3)] species by constant potential coulometry has not been successful due to their inherent instability.

Voltammograms of tc-[ReL$_2$Cl$_2$]$^+$ and tc-[OsL$_2$Cl$_2$][4] are strikingly similar. Relevant results for one pair measured under identical conditions are given in Table 3. The rhenium(IV)–rhenium(III) and osmium(III)–osmium(II) $E_{\frac{1}{2}}$ values lie close to each other. The two successive azo reductions in tc-[OsL$^2{}_2$Cl$_2$] are reversible on platinum (Table 3) unlike those on glassy carbon.[4]

The above results reveal that there is only moderate energy separation between the highest-filled metal orbital (t$_2$) and the lowest-unoccupied ligand orbital (azo π*). The situation is thus conducive for observation of m.l.c.t. transitions, M(t$_2$) ⟶ azo(π*), at relatively low energies. Spectral data are collected in Table 1. The band near 600 nm is assigned to m.l.c.t. excitation as in the case of the ≈500 nm band of tc-[OsL$_2$Cl$_2$].[4] The energies of m.l.c.t. bands depend among other factors on the difference (ΔE) between the $E_{\frac{1}{2}}$ values of the first metal oxidation and the first ligand reduction.[21,22,24] Since ΔE values have similar magnitudes (Table 3) in tc-[ReL$_2$Cl$_2$]$^+$ and tc-[OsL$_2$Cl$_2$], the gross features of their m.l.c.t. spectra should indeed be similar as observed.

More specifically, ΔE values for tc-[ReL$^2{}_2$Cl$_2$]$^+$ and tc-[OsL$^2{}_2$Cl$_2$] are 1.35 V (10 900 cm^{-1}) and 1.59 V (12 800 cm^{-1}) respectively (Table 3). The M(t$_2$) ⟶ azo(π*) band of the rhenium(III) complexes therefore appears at a lower (by 2000–2500 cm^{-1}) energy than that of the osmium(II) complex. We note that the quantity (in cm^{-1}) $\Delta E + 6500$ reproduces well the energies of the m.l.c.t. bands of both the complexes. The assignment of the relatively weak band near 1300 nm in tc-[ReL$_2$Cl$_2$]$^+$ (Table 1) is less certain. It could be due to a ligand-field transition within split components of the t$_2$ shell as in the case of the d^5 complexes of type tc-[OsL$_2$Cl$_2$]$^+$ (≈1450 nm, ε ≈200 dm^3 mol^{-1} cm^{-1})[25] or due to spin-forbidden m.l.c.t. excitation as in the case of tc-[OsL$_2$Cl$_2$] (≈1000 nm, ε ≈1000 dm^3 mol^{-1} cm^{-1}).[4]

In summary we note that back bonding, redox activity and charge-transfer spectra of tc-[Re$^{\text{III}}$L$_2$Cl$_2$]Cl are strikingly similar to those of tc-[Os$^{\text{II}}$L$_2$Cl$_2$]. This is consistent with the closeness of the rhenium(IV)–rhenium(III) and osmium(III)–osmium(II) $E_{\frac{1}{2}}$ values as well as of the azo redox $E_{\frac{1}{2}}$ values for L ligated to rhenium(III) and osmium(II). We are presently searching Re$^{\text{III}}$L systems that can be structurally characterised by X-ray crystallography so that the π-donor ability of rhenium(III) can be quantified in terms of bond parameters *vis-a-vis* those of osmium(II).[3,5]

Experimental

Starting Materials.—The 2-(arylazo)pyridine ligands, L were prepared using reported procedures.[6] Potassium perrhenate received from Aldrich was used to prepare *trans*-[ReOCl$_3$(PPh$_3$)$_2$] which was then converted to *mer*-[Re(MeCN)(PPh$_3$)$_2$Cl$_3$] following literature methods.[26,27] Purification of solvents and preparation of tetraethylammonium perchlorate for electrochemical work was done as before.[28] Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulfuric acid. All other chemicals and solvents were reagent-grade commercial materials.

Physical Measurements.—UV/VIS–NIR spectra were recorded on a Hitachi 330 spectrophotometer. Infrared (4000–300 cm^{-1}) spectra were taken on a Perkin-Elmer 783 spectrophotometer. Magnetic properties were examined on a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Electrochemical measurements were done by using a PAR model 370–4 Electrochemistry System as described elsewhere.[28] Solution electrical conductivities were measured by using a Philips PR 9500 bridge. Microanalytical data (C, H, N) were obtained with a Perkin-Elmer model 240C elemental analyzer. Proton NMR data were collected in CDCl$_3$ solvent on a Bruker 270 MHz spectrometer using tetramethylsilane as internal standard.

Preparation of Complexes.—The complexes [ReL$_2$Cl$_2$]Cl were synthesised using a general procedure. Yields varied in the range 70–75%. Details for one complex are given below.

Dichlorobis[2-(*phenylazo*)*pyridine*]*rhenium*(III) *chloride*, [ReL$^1{}_2$Cl$_2$]Cl. The complex *mer*-[Re(MeCN)(PPh$_3$)$_2$Cl$_3$] (250 mg, 0.29 mmol) was suspended in dry ethanol (30 cm^3), and a stream of dry nitrogen was passed through the solution for 15 min. To this was added 2-(phenylazo)pyridine (125 mg, 0.68 mmol) and the mixture was heated to reflux for 8 h under a dinitrogen atmosphere. A deep green solution resulted which was evaporated to afford a green solid. This was dissolved in a minimum volume of dichloromethane, and was run through an alumina column (20 × 1 cm). An orange band (free ligand) was eluted with dichloromethane. A deep green band was then collected using a 1:1 benzene–acetonitrile mixture as eluent. Upon evaporation of the green solution, [ReL$^1{}_2$Cl$_2$]Cl deposited. It was dried *in vacuo* over P$_4$O$_{10}$ (yield 70%).

Acknowledgements

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