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Synthesis, structure, and electrochemical characterization of a mixed-ligand diruthenium(III,II) complex with an unusual arrangement of the bridging ligands†

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A mixed-ligand metal-metal bonded diruthenium complex having the formula $Ru_2(2,4,6-(CH_3)_{3}ap)_{3-}$ (O₂CCH₃)Cl where ap is the anilinopyridinate anion was synthesized from the reaction of Ru₂(O₂CCH₃)₄Cl and H(2,4,6-(CH₃)₃ap), after which the isolated product was structurally, spectroscopically and electrochemically characterized. The crystal structure reveals an unusual arrangement of the bridging ligands around the dimetal unit where one ruthenium atom is coordinated to one anilino and two pyridyl nitrogen atoms while the other ruthenium atom is coordinated to one pyridyl and two anilino nitrogen atoms. To our knowledge, $Ru_2(2,4.6-(CH_3)_{3}ap)_3(O_2CCH_3)Cl$ is the only example of a mixed-ligand diruthenium complex of the type [Ru₂L₃(O₂CCH₃)]⁺, where L is an unsymmetrical anionic bridging ligand that has been structurally characterized with a "(2,1)" geometric conformation of the bridging ligands, all others being "(3,0)". The initial Ru_2^{5+} compound in CH_2CI_2 or CH_3CN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) undergoes up to four one-electron redox processes involving the dimetal unit. The $Ru_2^{5+/4+}$ and $Ru_2^{5+/6+}$ processes were characterized under N_2 using thin-layer UV-visible spectroelectrochemistry and this data is compared to UV-visible spectral changes obtained during similar electrode reactions for related diruthenium compounds having the formula Ru_2L_4Cl or $Ru_2L_3(O_2CCH_3)Cl$ where L is an anionic bridging ligand. Ru₂(2,4,6-(CH₃)₃ap)₃(O₂CCH₃)Cl was also examined by UV-visible and FTIR spectroelectrochemistry under a CO atmosphere and two singly reduced Ru₂⁴⁺ species, $[Ru_2(2,4,6-(CH_3)_3ap)_3(O_2CCH_3)(CO)CI]^-$ and $Ru_2(2,4,6-(CH_3)_3ap)_3(O_2CCH_3)(CO)$ were in situ generated for further characterization. The CO-bound complexes could be further reduced and exhibited additional reductions to their Ru₂³⁺ and Ru₂²⁺ oxidation states.

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Introduction

A large number of metal-metal bonded diruthenium complexes with anionic bridging ligands have been synthesized and characterized as to their structural, electrochemical and spectroscopic properties.^{1–18} The compounds which have been investigated in most detail are represented as $[Ru_2L_4]^{n+}$ and $[Ru_2(L)_x(L')_{4-x}]^{n+}$, where x = 1, 2 or 3, n = 0 or +1, L is a symmetrical or unsymmetrical anionic bridging ligand and L' is usually an acetate ligand.^{2,19–27}

The totally substituted diruthenium complexes with unsymmetrical bridging ligands can exist in up to four different

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isomeric forms that have been labeled as having (4,0), (3,1), (2,2)-*cis* and (2,2)-*trans* conformations^{9,13,28-30} but generally only one or two isomers have been isolated in a given synthesis. For example, in the case of substituted ap ligands (ap = 2-anilinopyridinate anion), $Ru_2(2,6-F_2ap)_4Cl$ and $Ru_2(2,4,6-F_3ap)_4Cl$ were isolated as a mixture of (3,1) and (4,0) isomers,¹³ while $Ru_2(2-Fap)_4Cl$ exists exclusively in its (3,1) isomeric form¹³ and $Ru_2(2-CH_3ap)_4Cl$ is obtained only as the (4,0) isomer.²⁸ The fact that two different geometric arrangements are formed for Ru_2L_4Cl complexes with 2-CH₃ap and 2-Fap anionic ligands is surprising since substitution occurs at the *ortho* position of the anilinopyridinate bridging ligands in both Ru_2^{5+} compounds.

In an attempt to better understand the factors that control the isomeric form in the final substitution product, *i.e.* Ru_2L_4Cl , we opted to use a sterically crowded bridging ligand with electron donating substituents, *i.e.* 2,4,6-(CH₃)₃ap (see Chart 1). This study reports that only three of the acetate

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(2,4,6-(CH₃)₃ap)⁻ Ligand Chart 1

groups on Ru₂(O₂CCH₃)₄Cl are substituted by the newly investigated bridging ligand. The final reaction product which is formulated as Ru₂(2,4,6-(CH₃)₃ap)₃(O₂CCH₃)Cl was obtained in good yield. Its crystal structure was determined and its electrochemistry and spectroelectrochemistry investigated in CH₂Cl₂ and CH₃CN under N₂ as well as CH₂Cl₂ under a CO atmosphere. The data are then discussed in light of what has been reported for other related metal-metal bonded diruthenium complexes of the type Ru₂L₄Cl and Ru₂(L)_{*x*}(OAc)_{4-*x*}Cl where L is a substituted ap ligand.² For simplicity, the notations Ru₂(OAc)₄Cl and Ru₂L₃(OAc)Cl will be used in the manuscript for Ru₂(O₂CCH₃)₄Cl and Ru₂(2,4,6-(CH₃)₃ap)₃-(O₂CCH₃)Cl, respectively.

Experimental

Chemicals and reagents

Ultra high purity nitrogen (N₂) and carbon monoxide (CO) were purchased from Matheson-Trigas. N₂ was passed through a glass column packed with anhydrous calcium sulfate and potassium hydroxide pellets to remove traces of moisture and oxygen before use while CO was used without further purification. Hexane (95% min, Aldrich), acetone (GC grade, EM Science), methanol (99.9% anhydrous, Aldrich), acetic acid (GR, EM Science), and dichloromethane (99.8%, EMD Chemicals) were used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemicals Co. and stored in a vacuum oven at 40 °C before use. 2-Bromopyridine (C₅H₄NBr), 2,4,6-trimethylaniline ((CH₃)₃-C₆H₄NH₂), ruthenium chloride trihydrate, lithium chloride and CD₂Cl₂ (99.8% atom in D, for NMR measurements) were purchased from Aldrich and used as received.

Physical measurements

Cyclic voltammetry was performed with a three-electrode system using an IBM Model EC225 voltammetric analyzer or an EG&G Princeton Applied Research (PAR) Model 173/175 potentiostat/signal generator, a PAR Model 174A/175 polarographic analyzer/universal programmer and a Houston Instrument Model 2000 or EG&G Princeton Applied Research (PAR) Model REO151 X-Y recorder. A glassy carbon electrode was used as a working electrode. A Pt wire was used as a counter electrode and a homemade saturated calomel electrode (SCE) was used as the reference electrode. This electrode was separated from the bulk of the solution by a fritted glass bridge containing the non-aqueous solvent with TBAP as the supporting electrolyte. The solvent was saturated with N₂ gas prior to taking measurements. Ferrocene (Fc) was used as an internal standard for all measurements. The half-wave potential of the Fc/Fc⁺ couple under our conditions was $E_{1/2} = 0.49$ V.

Thin-layer cyclic voltammograms and UV-visible spectra were obtained using a cell whose design has been reported in the literature.³¹ The cell consists of a platinum gauze sandwiched by two glass sides in order to reduce the diffusion of the species from the electrode. Measurements were carried out with a scan rate of 20 mV s⁻¹. All experiments were performed in degassed non-aqueous solvents containing TBAP as a supporting electrolyte. A stream of high purity nitrogen was maintained over the solution while making the measurements. The applied potential was controlled by an EG&G Model 173 potentiostat which was coupled with a Hewlett-Packard model 8453 diode array spectrophotometer. Thin-layer time-dependent infrared spectroelectrochemical measurements were performed using a FTIR Nicolet 550 Magna-IR spectrophotometer with a specially constructed light-transparent FTIR spectroelectrochemical cell.32

Mass spectra were obtained at the University of Houston with an Applied Biosystem Voyager DE-STR MALDI-TOF mass spectrometer equipped with a nitrogen laser (337 nm) or with a high-resolution hybrid tandem VG analytical model 70-SEQ (EEQQ geometry) mass spectrometer. A standard fast atom bombardment (FAB) source was used in the latter case with *m*-nitrobenzyl alcohol (NBA) as the liquid matrix. Elemental Analyses were carried out by Atlantic Microlab Inc., Norcros, Georgia.

Synthesis of starting compound

 $Ru_2(O_2CCH_3)_4Cl$ was synthesized according to a procedure reported in the literature.³³

Synthesis of H(2,4,6-(CH₃)₃ap)

2-Bromopyridine (5.53 g, 35.0 mmol) and 2,4,6-trimethylaniline (9.47 g, 70.0 mmol) were heated under N₂ for 6 hours at 175 °C. Upon cooling, a light brown solid was formed. A 10% NaOH solution (w/v) was added to the flask and the unreacted materials were steam distilled to remove excess aniline. The compound was extracted with CH2Cl2 and the resulting organic layer dried over MgSO4. The solvent was removed with a rotary evaporator and the compound was recrystallized several times in hexanes to give white rhombshaped crystals in 67% yield. Mass spectral data [m/z, (fragment)]: 212 $[H((CH_3)_3ap)]^+$; 197 $[H((CH_3)_2ap)]^+$; 182 [H- $(CH_3ap)]^+$. Anal. Calcd for $C_{14}H_{16}N_2$: C, 79.20; H, 7.60; N, 13.19. Found: C, 79.40; H, 7.64; N, 13.22. ¹H NMR (CD₂Cl₂): δ 8.08 (d, 1H), 7.37 (t, 1H), 6.96 (s, 2H), 6.60 (t, 1H), 6.14 (bs, 1H), 6.03 (d, 1H), 2.30 (s, 3H), 2.17 (s, 6H) ppm (key: d, doublet; t, triplet; bs, broad singlet).

Synthesis of Ru₂L₃(OAc)Cl

The reaction between $Ru_2(O_2CCH_3)_4Cl$ and $H(2,4,6-(CH_3)_3ap)$ followed procedures described in the literature.34,35 Ru2-(O₂CCH₃)₄Cl (0.43 g, 0.91 mmol) and H(2,4,6-(CH₃)₃ap) (3.86 g, 18.16 mmol) were placed in a round-bottom flask and heated for 10 hours at 140 °C under N2. The green compound obtained upon cooling was extracted with CH₂Cl₂. After removal of the solvent, the excess ligand was sublimed at 140 °C under N2. The crude product was subjected to column chromatography and eluted with CH₂Cl₂. A blue-green band was isolated and further purified on a second column with a mixture acetone-*n*-hexane 3:7 (v/v) as eluent. The title compound was obtained in 36% yield. Mass spectral data [m/z], 931 $[Ru_2(2,4,6-(CH_3)_3ap)_3(O_2CCH_3)Cl]^+;$ 896 (fragment)]: $[Ru_2(2,4,6-(CH_3)_3ap)_3(O_2CCH_3)]^+; 837 [Ru_2(2,4,6-(CH_3)_3ap)_3]^+$ 622 $[Ru_2(2,4,6-(CH_3)_3ap)_2]^+$. Anal. Calcd for $C_{44}H_{48}N_6ORu_2Cl$: C, 56.72; H, 5.19; N, 9.02. Found: C, 56.71; H, 5.13; N, 9.42. UV-vis spectrum in CH₂Cl₂ [λ_{max} nm (10⁻³ ε , mol⁻¹ L cm⁻¹)]: 425 (2.7), 468 (2.2), 656 (6.0), 1033 (0.8). μ_{eff} (298 K) = 3.90 μ_{B} .

X-ray crystallography

Dark blue-green flat single crystals of Ru₂L₃(OAc)Cl·EtOH were obtained by slow evaporation from an absolute ethanol solution. X-ray crystallographic measurements were carried out at the University of Houston's MRSEC/TcSUH shared experimental facilities. All measurements were made with a Siemens SMART platform diffractometer equipped with a 4K CCD APEX II detector. A hemisphere of data (1271 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30° in ω and an exposure time of 40 s per frame. The data were integrated using the Bruker-Nonius SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A ψ scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 8016 reflections having $I > 10\sigma(I)$. The Laue symmetry was determined to be mmm, and from the systematic absences noted the space group was shown to be either Pna2(1) or Pnma (orthorhombic). These along with other information pertinent to data collection and refinement, are listed in Table 1. The asymmetric unit of Ru₂L₃(OAc)Cl·EtOH consists of one-half Ru₂L₃(OAc)Cl molecule and one-half ethanol solvent molecule, both situated about a mirror plane. The solvent molecules are massively disordered, with at least six main orientations spread over each crystallographic site. The three most probable orientations comprising the asymmetric unit were refined using ideal rigid body models, with occupancies roughly based on comparison of isotropic displacement parameters. Two of the refined positions seem fairly accurate since they show reasonable hydrogen bonding to Cl. The third position does not seem to be accurate since it does not show hydrogen bonding and gives short H…H contacts with the main molecule; however all attempts to shift the location to a more reasonable position failed.

Table 1 Crystal data and structure refinement for $Ru_2(2,4,6-(CH_3)_3ap)_3(OAc)$ CI-EtOH

Empirical formula	$C_{46}H_{54}ClN_6O_3Ru_2$
$F_{\rm w} ({\rm g \ mol}^{-1})$	976.54
Temp (K)	223(2)
λ (Mo Ka) (Å)	0.71073
Space group	Pnma (orthorhombic)
Cell constant	,
a (Å)	15.1363(8)
$b(\dot{A})$	14.0416(7)
c (Å)	20.7216(10)
α (°)	90
$\beta(\circ)$	90
γ (°)	90
$V(A^3)$	4404.1(4)
Z	4
$\rho_{\rm calcd} ({\rm g}{\rm cm}^{-3})$	1.473
$\mu ({\rm mm^{-1}})$	0.793
F(000)	2004
Crystal color and shape	Dark blue-green flat column
Crystal size (mm ³)	$0.45 \times 0.10 \times 0.05$
Collection range (°)	$1.67 \le 2\theta \le 25.07$
Limiting indices	$0 \le h \le 18, 0 \le k \le 16, 0 \le l \le 24$
Reflections collected/unique	22652/4366[R(int)=0.0649]
Completeness to theta = 25.07	99.8%
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7444
Refinement method	Full-matrix least-squares of F^2
Number of parameters refined	301
Goodness-of-fit on F^2	1.08
Final <i>R</i> indices $[I > 4\sigma(I)]$	$R_1 = 0.0307, wR_2 = 0.0806$
R indices (all data)	$R_1 = 0.0494, wR_2 = 0.0948$
$R(F_{\rm o})^a$	0.0649
$R_{\rm w} \left(F_{\rm o}\right)^b$	0.025

 ${}^{a}R = \sum ||F_{\rm o}| - |F_{\rm c}|| / \sum |F_{\rm o}|. {}^{b}R_{\rm w} = [\sum_{\rm w}(|F_{\rm o}| - |F_{\rm c}|)^{2} / \sum_{\rm w}|F_{\rm o}|^{2}]^{1/2}.$

Results and discussion

Synthesis

The reaction between $\text{Ru}_2(\text{OAc})_4\text{Cl}$ and $\text{H}(2,4,6-(\text{CH}_3)_3\text{ap})$ was initially expected to produce a substitution product of the type $\text{Ru}_2\text{L}_4\text{Cl}$ where all four acetate groups had been replaced by the incoming bridging ligand, L.^{13,28,35} However, this was not the case under molten conditions, where only three of the four OAc^- ligands were replaced in the substitution reaction, giving $\text{Ru}_2(2,4,6-(\text{CH}_3)_3\text{ap})_3(\text{OAc})\text{Cl}$ as the final isolated diruthenium product. Generally, at temperatures above the melting point of the ligand, complete displacement of the four acetates is observed, $^{9,13,28-30}$ but this was not the case in synthesis of the compound reported in the present study.

Molecular structure

The ORTEP diagrams of $\text{Ru}_2\text{L}_3(\text{OAc})\text{Cl}$ are shown in Fig. 1. A projection view along the Ru(2)–Ru(1)–Cl unit is included to show the bulkiness of the 2,4,6-(CH₃)₃ap ligand (Fig. 1b) in addition to the side view structure (Fig. 1a). The coordination of Ru1 and Ru2 is essentially octahedral and square pyramidal, respectively with three "substituted ap ligands" arranged in a *trans* fashion and one acetate bridging ligand forming the equatorial plane. Ru1 is coordinated to the chloride axial ligand, two pyridyl nitrogens, one anilino nitrogen and one



Fig. 1 ORTEP diagram of $Ru_2L_3(OAc)Cl$ (a) side-view projection and (b) projection view along the Ru(2)-Ru(1)-Cl unit. Thermal ellipsoids are 40% equiprobability envelopes with hydrogen atoms omitted for clarity.

oxygen atom while Ru2 is coordinated to two anilino nitrogens, one pyridyl nitrogen and one oxygen atom. Assuming that the putative intermediate in the ligand replacement reaction is Ru₂L₂(OAc)₂Cl, where the bound 2,4,6-(CH₃)₃ap ligands (L) have the same trans geometric arrangement as that of an earlier characterized Ru₂(2-Fap)₂(OAc)₂Cl derivative,² the addition of a third 2,4,6-(CH₃)₃ap ligand on the dimetal unit would then require the bridging ligand to "flip" to give a "(2,1)" trans conformational framework reported in this work instead of a "(3,0)" isomer obtained for Ru₂(admp)₃(O₂CCH₃)Cl²³ and Ru₂(chp)₃(O₂CCH₃)Cl,²⁷ both of which were structurally characterized. Actually, two (2,1) isomers Ru₂L₃(OAc)Cl are theoretically possible, one with two pyridines *cis* to each other and the other trans, as observed in the current study. Neither isomer has previously been reported in the literature and, to our knowledge, the title compound is the only example of a mixed-ligand diruthenium complex of the type $[Ru_2(L)_3(O_2CCH_3)]^+$ that has been structurally characterized with a "(2,1)" geometric conformation framework.

Table 2 Selected average bond lengths and bond angles of Ru₂L₃(OAc)Cl

Ru(1)–Ru(2)	2.2917(6)
Ru(1)–Cl	2.4726(14)
$Ru(2) - N_a^a$	2.028
$Ru(1) - N_p^b$	2.113
Ru(1) - O(1)	2.075(3)
$\operatorname{Ru}(2) - O(2)$	2.061(3)
Bond angle (°)	
Ru(2)-Ru(1)-Cl	178.22(4)
$Ru(1)-Ru(2)-N_a$	92.55
$Ru(2)-Ru(1)-N_p$	87.99
Ru(2)-Ru(1)-O(1)	90.99(11)
$R_{1}(1) - R_{1}(2) - O(2)$	87.56(11)

^{*a*} N_a: anilino nitrogen. ^{*b*} N_p: pyridyl nitrogen.

Selected bond lengths and bond angles of Ru₂L₃(OAc)Cl are listed in Table 2. The Ru–Ru bond length falls within the Ru– Ru bond distances of other diruthenium compounds with similar mixed bridging ligands such as Ru₂(ap)₂(OAc)₂(Hap)Cl (2.308(1) Å)²⁷ and Ru₂(2-Fap)₂(OAc)₂(ac)Cl (2.2945(7) Å) (ac = acetone).² The Ru–Cl bond length is 2.4726(14) Å and this value can be compared to the Ru–Cl bond distances of Ru₂(ap)₄Cl (2.437(7) Å),³⁵ Ru₂(2-CH₃ap)₄Cl (2.487 Å)²⁸ and Ru₂(2-Fap)₄Cl (2.461(7) Å),² all of which have either four ap or four "ap-type" bridging ligands.

Some structural changes are observed as one of the two acetate groups in Ru₂L₂(OAc)₂Cl, where L = ap²⁷ or 2-Fap,² is substituted by one ap-type bridging ligand. For example, the two Ru–O bond distances of the title compound are longer than the average Ru–O bond lengths in Ru₂(ap)₂(OAc)₂(Hap)Cl²⁷ (2.045 Å) and Ru₂(2-Fap)₂(OAc)₂(ac)Cl² (2.041 Å). This can be attributed to the strong σ -donation properties of the 2,4,6-(CH₃)₃ap ligand. There is also a slight increase of the Ru(1)–Ru(2)–N_a bond angle, a slight decrease of the Ru(2)–Ru(1)–N_p bond angle and a slight increase of the Ru(2)–Ru(1)–O(1) bond angle in the title compound as compared to the other two mixed-ligand diruthenium complexes.

Electrochemistry in CH₂Cl₂ and CH₃CN under N₂

Cyclic voltammograms of Ru₂L₃(OAc)Cl in CH₂Cl₂ and CH₃CN containing 0.1 M TBAP under N2 are shown in Fig. 2. The compound undergoes two one-electron reductions and two oneelectron oxidations within the potential window of the solvent. All four reactions involve the dimetal unit, as has been reported for related Ru₂L₄Cl compounds.^{2,20,28} The first reduction $(Ru_2^{5+/4+})$ and two oxidations $(Ru_2^{5+/6+})$ and $(Ru_2^{6+/7+})$ are reversible in both solvents but the second reduction in CH₂Cl₂ is irreversible due to a following coupled chemical reaction. The change in solvent from CH₂Cl₂ to CH₃CN leads to a shift of all $E_{1/2}$ values and an increase in reversibility of the Ru₂^{4+/3+} process (the second reduction) as illustrated in Fig. 2. The reversible first reduction of Ru₂L₃(OAc)Cl occurs at -0.60 V in CH₃CN and is anodically shifted by 210 mV from the $E_{1/2}$ value for the same reaction in CH₂Cl₂ (-0.81 V) whereas the first and second reversible oxidations of the



Fig. 2 Cyclic voltammogram of Ru₂L₃(OAc)Cl in (a) CH₂Cl₂ and (b) CH₃CN, 0.1 M TBAP. Scan rate = 0.1 V s⁻¹. The process with an asterisk is assigned to a product of a reaction following the $Ru_2^{4+/3+}$ process of the compound.

diruthenium compound are cathodically shifted by 70 and 80 mV, respectively, upon going from CH_2Cl_2 to CH_3CN (see Fig. 2). The potential separation between the first reduction and first oxidation amounts to 1.29 V in CH_2Cl_2 and this difference in potentials can be compared to a separation of 1.32 V between the same two reactions of $Ru_2(2-Fap)_3(OAc)Cl^2$ under the same solution conditions. A slightly smaller potential separation of 1.26 V is observed in CH_3CN between the $Ru_2^{5+/4+}$ and $Ru_2^{5+/6+}$ processes of $Ru_2(2-Fap)_3(OAc)Cl^{16}$ but, as seen in Fig. 2, this separation decreases from 1.29 V in CH_2Cl_2 to 1.01 V in CH_3CN , thus suggesting a stabilization of the Ru_2^{6+} and Ru_2^{4+} oxidation states of $Ru_2L_3(OAc)Cl$ by solvent coordination to the dimetal center of the electrooxidized and electroreduced compounds.

When the negative potential sweep in CH₂Cl₂ is reversed after the second reduction (Fig. 2a), a new reoxidation peak appears on the reverse scan at $E_{pa} = -1.02$ V. This new peak is indicated by an asterisk in the figure and occurs at all temperatures when scanning past the second reduction process, but is not observed when the scan is reversed at about -1.40 V, i.e. after the first reduction (dashed line in Fig. 2a). This result suggests that the "new" oxidation peak at $E_{pa} = -1.02$ V can be attributed to a species formed in a chemical reaction after the second reduction of the compound. Although the nature of the chemical reaction involving doubly reduced Ru₂L₃(OAc)Cl in CH₂Cl₂ was not investigated in the present study, we suggest that it is due to the transient formation of a metalcarbon bonded diruthenium derivative, as was demonstrated for $Rh_2(dpf)_4(R)$ after reduction of $Rh_2(dpf)_4$, (dpf = N, N'diphenylformamidinate anion) in THF containing added of alkyl iodides (RI).36

Benzonitrile (PhCN) is also known to axially bind to the Ru_2^{4+} unit of Ru_2L_4 where L = a substituted ap ligand³⁷ and solvent binding should also occur in the case of CH₃CN. To verify this point, we added small aliquots of CH₃CN to Ru_2L_3 (OAc)Cl in CH₂Cl₂, 0.1 M TBAP and monitored changes in the cyclic voltammogram as a function of the added CH₃CN



Fig. 3 Plot of $E_{1/2}$ vs. log[CH_3CN] for the first oxidation of Ru_2L_3(OAc)Cl in CH_2Cl_2, 0.1 M TBAP.

concentration. The resulting correlation is shown in Fig. 3 where a plot of $E_{1/2}$ for the first oxidation vs. log[CH₃CN] consists of two linear portions; the first has a slope of -63 mV while the second has a zero slope, with the same $E_{1/2}$ value (0.41 V) being measured in CH₃CN, 0.1 M TBAP as in CH₂Cl₂-CH₃CN mixtures containing 1.0 M added CH₃CN. The data in Fig. 3 suggests that one CH₃CN ligand binds to the Ru₂⁶⁺ form of the compound at low concentrations of added acetonitrile while at higher concentrations of CH₃CN in the CH₂Cl₂-CH₃CN mixture, a single CH₃CN ligand also binds to the Ru₂⁵⁺ form of the compound. This is in agreement with formulation of the title compound as Ru₂L₃(OAc)Cl(CH₃CN) in CH₃CN, 0.1 M TBAP. The same formulation is suggested by the UV-visible data discussed in later sections of the manuscript.

A titration was also carried out for the first reduction of $Ru_2L_3(OAc)Cl$ in $CH_2Cl_2-CH_3CN$ mixtures but the cyclic voltammograms were ill-defined in the mixed solvent system, being reversible only in neat CH_2Cl_2 , or neat CH_3CN containing 0.1 M TBAP. Nonetheless, the fact that $E_{1/2}$ for reduction of $Ru_2L_3(OAc)Cl$ is easier by 210 mV in CH_3CN than in CH_2Cl_2 can only be accounted for by axial coordination of the Ru_2^{4+} electroreduction product with the solvent molecule.

The Ru₂^{5+/4+} reactions of Ru₂L₄Cl where L = 2-CH₃ap, 2-Fap and 2,4,6-F₃ap in CH₂Cl₂–PhCN mixtures were previously shown to shift anodically from $E_{1/2}$ values measured in CH₂Cl₂, and this was interpreted by a coordination of one solvent molecule (PhCN) to the Ru₂⁴⁺ form of each compound. The magnitude of the potential shift with solvent binding involving coordination of CH₃CN is smaller than in the present study, amounting to only 100–140 mV,³⁷ and the larger (210 mV) shift in the Ru₂^{5+/4+} process of Ru₂L₃(OAc)Cl upon changing the solvent from CH₂Cl₂ to CH₃CN can be attributed to a stronger coordination of CH₃CN than PhCN.

The binding of CH_3CN to the Ru_2^{6+} form of $Ru_2L_3(OAc)Cl$ can also be accounted for by a stronger binding ability of CH_3CN than PhCN to the Ru_2^{6+} form of the compound

(actually PhCN seems not to bind at all to the singly oxidized $[Ru_2L_4Cl]^+$).³⁷ The structure of the currently studied diruthenium complex may also play a role in the strong binding of CH₃CN, since Ru₂L₃(OAc) is not as sterically crowded around the dimetal core as other previously investigated Ru₂L₄Cl complexes. The dimetal unit of Ru₂L₃(OAc)Cl is also more electron rich than other related previously investigated diruthenium complexes.^{2,9,28,37}

UV-visible spectroscopy in CH₂Cl₂ and CH₃CN

Fig. 4 shows UV-visible spectra of Ru₂L₃(OAc)Cl in CH₂Cl₂ and CH₃CN. In both solvents the compound is characterized by one strong absorption band (at 656 nm in CH₂Cl₂ and 663 nm in CH₃CN) due to the charge transfer transition π (ligand, metal) $\rightarrow \pi^*$ (Ru₂) or σ^* (Ru₂) as previously assigned to related Ru₂⁵⁺ complexes,⁴ and three less intense bands as indicated in the figure. The overall shape of the spectrum is not significantly different in the two solvents, but variations are seen in the 400–500 and 900–1100 nm regions, thus suggesting two different forms of the compound in these solvents.

An earlier study of related diruthenium compounds with substituted ap ligands suggested that a solvent molecule does not displace the chloride axial ligand when Ru_2L_4Cl is dissolved in PhCN³⁷ and this is most likely also the case for $Ru_2L_3(OAc)Cl$ in CH₃CN. On the other hand, CH₃CN is able to bind to $Ru_2L_3(OAc)Cl$ *trans* to the axial chloride, and this could account for the differences in UV-vis spectra between the two solvents in Fig. 4. Solvent binding to the Ru_2^{5+} form of the compound is also implied by data from the electrochemically monitored titration in CH₂Cl₂ (Fig. 3).

The UV-visible spectral changes which occur during the $Ru_2^{5+/4+}$ and $Ru_2^{5+/6+}$ processes of $Ru_2L_3(OAc)Cl$ were monitored by thin-layer spectroelectrochemistry in CH_2Cl_2 and



Fig. 4 UV-visible spectra of Ru₂L₃(OAc)Cl in (a) CH₂Cl₂ and (b) CH₃CN.

CH₃CN containing 0.2 M TBAP. As illustrated in Fig. 5a, the major absorption band at 656 nm in CH₂Cl₂ decreases in intensity and shifts to 609 nm as the compound is converted to its Ru₂⁴⁺ form. This contrasts with what occurs during the Ru₂^{5+/4+} process in CH₃CN, 0.2 M TBAP where the 663 nm band of the reduced compound decreases in intensity as a new band grows in at 490 nm (Fig. 5b). The Ru₂⁴⁺ products are proposed to be Ru₂L₃(OAc) in CH₂Cl₂ and Ru₂L₃(OAc)(CH₃CN) in CH₃CN, 0.1 M TBAP is consistent with the electrochemical data in both CH₃CN, 0.1 M TBAP and CH₂Cl₂-CH₃CN mixtures (see earlier discussion). Differences in UV-visible spectra have also been reported in the literature between related Ru₂⁴⁺ complexes of the type Ru₂(L)₄ and Ru₂(L)₄(S), where S = solvent and L = 2-CH₃ap, 2-Fap and 2,4,6-F₃ap.³⁷

The UV-visible spectral changes measured during the $Ru_2^{5+/6+}$ oxidation process of Ru_2L_3 (OAc)Cl in CH_2Cl_2 and CH_3CN containing 0.2 M TBAP resemble each other. In both solvents, the major absorption band of the initial compound vanishes as a new red-shifted absorption band develops (Fig. 5c and 5d). There are multiple isosbestic points, indicating the lack of a spectrally detectable intermediate during the oxidation. The Ru_2^{6+} species generated in the two solvents exhibit similar UV-visible spectra and the 9 nm shift in λ_{max} upon going from CH_2Cl_2 to CH_3CN can be attributed to the presence of one bound CH_3CN molecule, thus providing additional evidence for the proposed electron transfer mechanism shown in Scheme 1.

Electrochemistry in CH₂Cl₂ under a CO atmosphere

In the present study, neither the IR nor the UV-visible spectrum of $\text{Ru}_2\text{L}_3(\text{OAc})\text{Cl}$ under CO indicates the binding of CO to Ru_2^{5+} in the absence of an applied potential. A similar lack of CO binding was seen in the case of $\text{Ru}_2(\text{dpf})_3(\text{O}_2\text{CCH}_3)\text{Cl}$ (dpf is the *N*,*N*'-diphenylformamidinate anion) and the presence of the chloride anion was proposed to inhibit the axial binding of CO to the Ru_2^{5+} complex.³⁸ In fact, the only example in the literature for CO being axially bound to a stable mixed-ligand Ru_2^{5+} occurs for $\text{Ru}_2(\text{dpf})_3(\text{OAc})\text{BF}_4$,³⁸ which has a weakly bound BF_4^- anion.

A cyclic voltammogram showing the reduction of Ru₂L₃(OAc)Cl in CH₂Cl₂, 0.1 M TBAP under a CO atmosphere is illustrated in Fig. 6 along with a cyclic voltammogram of Ru₂(ap)₄Cl under the same experimental conditions for comparison purposes. Ru₂L₃(OAc)Cl exhibits four electroreductions labeled, as I", I, II and III in Fig. 6a but only process II is reversible. The first and second reductions (Processes I" and I) are located at $E_{pc} = -0.50$ and -0.84 V while the third and fourth reductions (II and III) are seen at $E_{1/2} = -0.95$ and $E_{pc} = -2.02$ V for a scan rate of 0.1 V s⁻¹.

The cyclic voltammogram of $Ru_2L_3(OAc)Cl$ under CO (Fig. 6a) can be compared to the cyclic voltammogram of $Ru_2(ap)_4Cl$ (Fig. 6b) under the same solution conditions. As was previously reported in the literature,³⁰ the latter compound undergoes three reductions labeled as I, II, and III in Fig. 6b. A key difference between $Ru_2L_3(OAc)Cl$ and $Ru_2(ap)_4Cl$

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Fig. 5 Time-dependent UV-visible spectral changes of $Ru_2L_3(OAc)CI$ upon the first reduction in (a) CH_2CI_2 and (b) CH_3CN and the first oxidation in (c) CH_2CI_2 and (d) CH_3CN containing 0.2 M TBAP.



is that only one reduction process precedes the reversible reaction II in the case of Ru₂(ap)₄Cl, but two reduction processes are seen prior to the reversible reaction II in the case of Ru₂L₃(OAc)Cl. It was earlier reported³⁰ that the Ru₂^{5+/4+} reduction of Ru₂(ap)₄Cl under CO (process I) was coupled with the oxidation process I' and this is shown by the dotted line in Fig. 6b. In a similar manner, the reduction process I'' of Ru₂L₃(OAc)Cl at $E_p = -0.50$ V is coupled with the oxidation process I' at $E_p = 0.06$ V, as shown by the dotted line in Fig. 6a, thus suggesting that processes I'' and I both involve a Ru₂⁵⁺ to Ru₂⁴⁺ conversion in the case of Ru₂L₃(OAc)Cl. Further evidence for this assignment is given by the fact that processes I'' and I have similar peak currents, the sum of which is approximately equal to the peak current of process II (see Fig. 6a). In a previous study,³⁰ the $Ru_2^{5+/4+}$ processes of $Ru_2(L)_4Cl$ (L is ap or a substituted ap anion) in CH_2Cl_2 , 0.1 M TBAP under CO were shown to generally shift positively by 10–80 mV with respect to the same electrode processes under N_2 , the only exception being in the case of $Ru_2(F_5ap)_4Cl$ where the electrode reaction under CO was shifted negatively by 40–70 mV, *i.e.* the reduction under CO was more difficult than under N_2 . For all of the investigated diruthenium compounds, including $Ru_2(F_5ap)_4Cl$, the $Ru_2^{5+/4+}$ process was proposed to involve a dissociation of the chloride axial ligand after electron transfer and the final Ru_2^{4+} product was formulated as $Ru_2L_4(CO)$.³⁰ Process I in Fig. 6a is only 30 mV more negative than the $Ru_2^{5+/4+}$ process under N_2 (Fig. 2), suggesting that this electron transfer can be described by a reduction of



 $Ru_2L_3(OAc)(Cl to Ru_2L_3(OAc)(CO)$.^{9,30} Although process I" also involves a Ru_2^{5+}/Ru_2^{4+} reaction, it is 310 mV easier than the same electrode reaction under N_2 . This result might be accounted for by the occurrence of a chemical reaction prior to the electron transfer which would lower the electron density on the dimetal unit. A probable chemical reaction could be the binding of a CO molecule *trans* to the chloride axial ligand, thus generating the transient electroactive Ru_2^{5+} species in solution, $Ru_2L_3(OAc)(CO)Cl$.

The product of the reduction in process I" is formulated as $[Ru_2L_3(OAc)Cl(CO)]^-$, and would be expected to have a lower electron density on the Ru_2^{4+} dimetal unit than in the case of $[Ru_2L_3(OAc)Cl]^-$ because of the π -back donation by the CO axial group. If the Cl⁻ anion did not readily dissociate, one might then observe a CO vibration for both Ru_2^{4+} products, *i.e.* $[Ru_2L_3(OAc)Cl(CO)]^-$ and $Ru_2L_3(OAc)(CO)$. This seems to be the case as shown by the presence of two CO vibrations at 1918 and 1898 cm⁻¹ in the IR spectrum obtained after the first reduction of the title compound in CH₂Cl₂, 0.2 M TBAP under a CO atmosphere (see Fig. 7a).

The second reduction of Ru₂L₃(OAc)Cl in CH₂Cl₂, 0.1 M TBAP under a CO atmosphere (*i.e.* process II in Fig. 6a) is attributed to a Ru₂⁴⁺ to Ru₂³⁺ electrode reaction and, as was the case for the previously examined diruthenium compounds with similar bridging ligands,^{9,30} is proposed to involve the addition of a second axial CO molecule to give [Ru₂L₃(OAc)-(CO)₂]⁻. As shown by the IR spectrum in Fig. 7b, the bis-CO Ru₂³⁺ complex exhibits ν_{CO} stretches at 1874 and 1822 cm⁻¹, values which fall in the range of previously investigated diruthenium CO complexes.³⁰ Thus, the electron transfer mechanism in CH₂Cl₂ under CO is proposed to occur as shown in Scheme 2.



Fig. 7 In situ FTIR absorbance spectral changes of $Ru_2L_3(OAc)CI$ in CH_2CI_2 , 0.1 M TBAP under CO atmosphere upon (a) the first reduction (process I'', Fig. 6a) and (b) the second reduction (process II, Fig. 6a).

Summary

A mixed-ligand complex of the type Ru₂L₃(OAc)Cl was successfully synthesized and structurally characterized by X-ray crystallography, revealing a "(2,1)" geometric conformation in the solid state. $Ru_2L_3(OAc)Cl$ is a paramagnetic Ru_2^{5+} complex with three unpaired electrons, that can be reversibly converted to its Ru_2^{4+} , Ru_2^{6+} and Ru_2^{7+} oxidation states in CH_2Cl_2 containing 0.1 M TBAP under an N_2 atmosphere. A $Ru_2^{4+/3+}$ process is also observed to occur under the above experimental conditions. This reaction is irreversible in CH₂Cl₂ owing to a coupled chemical reaction that involves the Ru_2^{3+} species and the solvent itself but the process becomes reversible when $\rm CH_3CN$ axially coordinates to the $\rm Ru_2^{~4+}$ form of $\rm Ru_2L_3(OAc)Cl.$ Acetonitrile will also bind to the $\rm Ru_2^{~5+}$ and $\rm Ru_2^{~6+}$ forms of Ru₂L₃(OAc)Cl in neat CH₃CN and this axial ligand coordination most likely occurs trans to the bound chloride axial ligand. A similar type of axial coordination also occurs with CO under an applied potential and two diruthenium(π,π) species, [Ru₂L₃(OAc)(CO)Cl]⁻ and Ru₂L₃(OAc)(CO), are proposed to exist in CH₂Cl₂, 0.1 M TBAP under CO.

A binding of CO *trans* to the chloride axial ligand has not been reported for other metal–metal bonded diruthenium complexes with ap or ap-type bridging ligands and can be attributed, in the present study, to the fact that the $(2,4,6-(CH_3)_3ap)$ anion has a much richer electron density than other

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Scheme 2 Electrode reactions of Ru₂L₃(OAc)Cl in CH₂Cl₂ under CO (the anionic ligands have been omitted for clarity).

previously utilized anionic bridging ligands, thus allowing more π -back donation between the dimetal unit and the incoming group. It could also be due to the fact that Ru₂L₃(OAc)Cl has only three ap-type ligands at the dimetal periphery as compared to four in the case of the other investigated diruthenium complexes. This might also be a key factor because it would help minimize steric hindrance at the axial position *trans* to the chloride axial ligand. Further studies are now in progress in our laboratory to elucidate these points.

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