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Synthesis, Electrochemistry and Spectroscopy of Novel Ruthenium and Rhodium Complexes Bound to 2,2′-Bi-1,3-dithiol (TTF)

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Abstract

The $(TTF)_2MCl_3$ (M = Ru(II) and Rh(I), TTF (tetrathiafulvalene) = 2,2′-bi-1,3-dithiol) complexes have been prepared by direct reaction of TTF and the MCl_3 salt. Ultraviolet–visible spectra of the complexes are reported and indicate formation of a TTF^+ cation with a reduced metal center. The presence of the oxidized TTF^+ is further confirmed by resonance raman peaks near 1416 cm^{-1}. Electrochemistry indicates oxidation/reduction of the complexes is localized on the TTF ligand rather than from the metal.

Introduction

The use of 2,2′-bi-1,3-dithiol (tetrathiafulvalene) = TTF) in electron transport studies of crystals with a wide variety of organic acceptor molecules such as TCNQ, have been previously reported [1–8]. Preparation of metal–dithiolene complexes has focused on the production of complexes which show highly anisotropic electrical conductivity by stacking of these complexes [9–11]. Recently there have been several reports of the preparation and study of TTF bound to transition metals to form inorganic and organometallic complexes [12–21].

Our group is interested in the synthesis and study of molecules which may ultimately be used in intramolecular electron transport reactions, and our work has focused primarily on nitrogen aromatic ligands [22–25]. The sulfur containing analog molecule (TTF) appears ideal for preparation of polymetallic systems because of its ability to coordinate in a bidentate mode through the sulfur atoms to a metal center which may make it less susceptible to thermal instability. Additionally, the TTF molecule is easily oxidized to the TTF^+ cation or TTF^{2+} dication which may be expected to possess a large degree of delocalized π bonding through the aromatic rings.

We report here the preparation, electrochemisty, electronic absorption reflectance, infrared and resonance raman spectra of $Rh(TTF)_2Cl_3$ and $Ru(TTF)_2Cl_3$ complexes.

Experimental

Material

Analytical reagent grade compounds and solvents were used for preparations described in this work. $RuCl_3\cdot 3H_2O$ and $RhCl_3\cdot 3H_2O$ were obtained from Alfa Inorganics and used without purification. 2,2′-bi-1,3-dithiol (TTF) was purchased from Aldrich and used without purification. Argon used in solvent deoxygenation was obtained from Linde, passed through a chromous solution, then dried by passing through $CaSO_4$ before use. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA, with satisfactory results obtained for both complexes.

Instrumentation

Electronic absorption spectra were recorded on a Beckman Model 5240 Scanning Spectrophotometer in matching quartz cells. Solid reflectance spectra were recorded on the same instrument by suspending finely ground samples of the complex in nujol. Solid infrared spectra were obtained in KBr pellets on a Nicolet 20 DX FTIR from 4000 cm^{-1}–400 cm^{-1} with 2 cm^{-1} resolution.

Cyclic voltammograms were recorded on a Bio Analytical Systems CV-1B Cyclic Voltammograph with a Hewlett Packard 7044A XY recorder. The glassy carbon working electrode (3.0 mm diameter) was polished with alumina prior to each scan. An Ag|AgCl (3 M KCl, nominally −0.044 V *versus* SCE) reference electrode was used. All potentials are reported *versus* the AgCl electrode and are uncorrected for junction potentials. The potentials reported for oxidation couples $E_{1/2}$, are estimates obtained by averaging the anodic and cathodic peak potentials. Cyclic voltammograms were recorded in CH_3NO_2 using 0.10 M tetrabutylammonium perchlorate as an electrolyte. Scan rates were varied from 50–300 mV/s.

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Resonance-enhanced Raman spectra were recorded at Clemson University, using a Spectra Physics Model 165 argon ion laser, a Spex 1403 double monochromater, a Spex Scamp computer and Spex Compudrive. Spectra were detected by a cooled (−30 °C) RCA C31034 photomultiplier tube and a Spex DPC-2 photon counting system.

A low-cost prism dispersion device was designed at Clemson Univerisity and constructed to remove interfering plasma lines from the laser beam [31]. All spectra were obtained with rapidly spinning powder samples. Samples consisted of a mixture totaling approximately 250 mg, containing 5–50 mg of the metal complex, 45–100 mg Na_2SO_4 (internal standard), and 150–200 mg of KCl pressed onto a pre-pressed bed of 0.5 g of KCl.

Synthesis

Ru(TTF)$_2$Cl$_3$

Bis-(TTF) ruthenium(III) trichloride was prepared by dissolving 0.02401 g (9.1×10^{-5} mol) of $RuCl_3 \cdot 3H_2O$ in 20 ml of deoxygenated anhydrous ethanol heated at reflux with stirring. To the warm solution, 0.08032 g (3.9×10^{-4} mol) TTF was added as a solid, and the solution continued stirring under argon in the dark. After five minutes a brown precipitate formed. The flask was removed from the argon flow after 1 h, capped and cooled to 0 °C for 6 h. The precipitate was collected on a fine porosity filter funnel, washed with ethanol to remove excess TTF, then ether. The product was vacuum dried. Yield 0.05107 g (8.3×10^{-5} mol) 91%. *Anal.* Calc. for $C_{12}H_8S_8RuCl_3$: C, 23.40; H, 1.30; S, 41.64. Found: C, 23.43; H, 1.36; S, 41.66%.

Rh(TTF)$_2$Cl$_3$·1.5H$_2$O

Bis-(TTF) rhodium(III) trichloride was prepared by dissolving 0.04071 g (1.5×10^{-4} mol) $RhCl_3 \cdot 3H_2O$ in 15 ml of warm 40–50 °C deoxygenated anhydrous ethanol with stirring. To the orange–brown solution was added 0.12971 g (6.3×10^{-4} mol) TTF as a solid, and the solution immediately turned dark blue. After stirring in the dark for 1 h, the solution was allowed to cool to room temperature under argon. When cool, the precipitate was collected by filtration on a fine porosity filter funnel, washed with ethanol to remove excess TTF, then ether. The product was dried in vacuum. Yield 0.04470 g (6.5×10^{-5} mol) 46%. *Anal.* Calc. for $C_{12}H_8S_8RhCl_3 \cdot 1.5H_2O$: C, 22.33; H, 1.71; S, 39.76. Found: C, 22.40; H, 1.71; S, 39.53%.

Results and Discussion

(TTF)$_2$RuCl$_3$

The preparation of $(TTF)_2RuCl_3$ from $RuCl_3$ in deoxygenated ethanol heated at reflux with four equivalents of TTF demonstrates the conditional synthetic dependence in the synthesis of metal–TTF complexes*. Since $(TTF)_2RuCl_5$ has been previously reported as the product of the reaction of TTF and $RuCl_3$ in ethanol, an independent sample of $(TTF)_2RuCl_3$ was submitted for sulfur/chloride ratio determination [21]. The found analysis value of 2.68/1 confirmed $(TTF)_2RuCl_3$ product formation.

The $(TTF)_2RuCl_3$ complex was found to be slightly soluble (0.5 mg/ml) in a variety of solvents including nitromethane, propylene carbonate and dimethylformamide. Extensive stirring of finely ground samples was required to achieve complete dissolution. The dark red–brown $(TTF)_2RuCl_3$ solid produced markedly different electronic absorption spectra in different solvents (Fig. 1, Table I). In propylene carbonate or dimethylformamide, λ_{max} occurred at 310 nm with absoprtion shoulders at 430 nm and 380 nm. These wavelengths coincide with the absorption shoulders observed for TTF in solution, and indicate the probable dissociation of the $(TTF)_2RuCl_3$ complex producing free TTF [26]. The absorption spectrum of $(TTF)_2RuCl_3$ in nitromethane has $\lambda_{max} = 573$ nm ($\epsilon = 3.0 \times 10^3$ M^{-1} cm^{-1}) and $\lambda_{max} = 434$ nm ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}) with shoulders at 510 nm ($\epsilon = 3.3 \times 10^3$ M^{-1} cm^{-1}) and 402 nm ($\epsilon = 7.7 \times 10^3$ M^{-1} cm^{-1}) (Fig. 1b, Table I).

It has been previously shown for the free TTF^+ cation, and for solid $(TTF^+)_nMX_m$ (M = Cu, Au; n, m = 1–4; X = halide or nitrate) complexes, where TTF has been shown to be TTF^+, characteristic intraligand absorptions occur for the TTF^+ cation at 405 nm (shoulder), 435 nm and 500–600 nm (Table I) [20, 26]. The dication TTF^{2+} in $(TTF)_nMX_m$ complexes also has characteristic electronic absorption maxima only at 445–460 nm. Additionally,

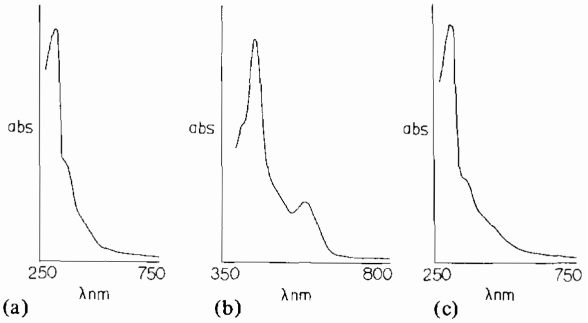

Fig. 1. Visible absorption spectra for $(TTF)_2RuCl_3$ in (a) *N,N*-dimethylformamide, (b) nitromethane, (c) propylene carbonate.

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*We have also prepared $(TTF)_3FeCl_3$ and $(TTF)FeCl_2$ by reacting various ratios of $FeCl_3$ and TTF in ethanol (manuscript in preparation). The same reactants have also been reported to produce $(TTF)_2FeCl_4$ (ref. 21).

TABLE I. Electronic Absorption Values of some TTF Metal Complexes

Complex	Solvent	(nm)	ϵ (M^{-1} cm^{-1})	Reference
TTF	CH_2Cl_2	310 365(sh)	4×10^4	26
TTF^+	H_2O	340 405(sh) 435 575	4.4×10^4 3.6×10^4 5.6×10^4 1.6×10^4	26
$(TTF^{2+})(BF_4)_2$	solid	380 540	–	20
$(TTF^+)_2CuCl_4$	solid	380 500 800		20
$(TTF^+)AuCl_2$	solid	410 550 850		20
$(TTF^{2+})CuCl_4$	solid	445	–	20
$(TTF^+)(TTF^{2+})_2(CuCl_2)_5$	solid	415 445 650(sh) 780		20
$(TTF)_2RuCl_3$	CH_3NO_2	402(sh) 434 510(sh) 573	7.7×10^3 1.2×10^4 3.3×10^3 3.0×10^3	
$(TTF)_2RuCl_3$	propylene carbonate	310 430 380		
$(TTF)_2RuCl_3$	solid/nujol	1000		
$(TTF)_2RhCl_3$	CH_3NO_2	435 510(sh) 660	2×10^3 1.7×10^3 1.6×10^3	
$(TTF)_2RhCl_3$	propylene carbonate	435 530(sh) 605	5×10^3 6×10^3 8×10^3	
$(TTF)_2RhCl_3$	DMSO	440 565	3.1×10^3 2×10^3	
$(TTF)_2RhCl_3$	solid/nujol	700		

in $(TTF^+)(TTF^{2+})MX_m$ complexes known to possess both discreet TTF^+ and TTF^{2+} ligands, the electronic absorption spectrum contains absorption maxima which are consistent with the combination of TTF^+ and TTF^{2+} absorption components [20].

The absorption spectrum of $(TTF)_2RuCl_3$ in CH_3NO_2 is thus consistent with à complex containing a bound TTF^+ cation, and the overall color of the complex is probably due to a localized intraligand TTF^+ transition. A one electron transfer from a single bound TTF ligand would be expected to produce the $(TTF)(TTF^+)RuCl_3$ complex, with the Ru center in a stable d^6 configuration. The coordination of a neutral TTF ligand cannot be verified spectrally since its characteristic absorption at 310 nm lies outside the CH_3NO_2 solvent window.

The reflectance spectrum of $(TTF)_2RuCl_3$ (Fig. 2) shows a single absorption although somewhat distorted by an abrupt wavelength scale change in the near infrared centered at 850–900 nm. The absorption energy is typical for cationic salts such as (TTF)Br or metal complexes such as $(TTF^+)_2CuCl_4$ and $(TTF^+)AuCl_2$ which exhibit absorptions between 880–725 nm assigned to solid state isovalence transitions of the type $2TTF^+ \rightarrow TTF^0, TTF^{2+}$ [20, 21, 26].

Cyclic voltammograms of TTF and the $(TTF)_2RuCl_3$ complex were recorded in CH_3NO_2/0.10 M tetrabutylammonium perchlorate (TBAP) from 0.00

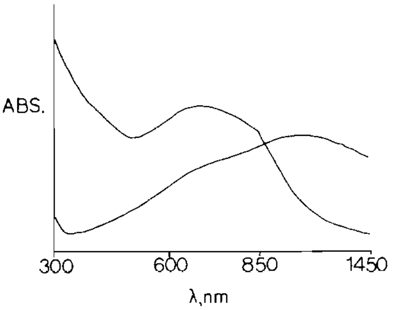


Fig. 2. Near-infrared–visible reflectance spectra of $(TTF)_2RhCl_3$ (upper curve) and $(TTF)_2RuCl_3$ (lower curve) suspended in nujol. Wavelength scale change at 850 nm.

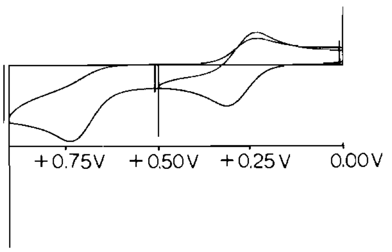


Fig. 3. Cyclic voltammogram of $(TTF)_2RuCl_3$ in CH_3NO_2/0.10 M TBAP at 50 mV/s *vs.* Ag|AgCl electrode. Peak pulse currents are recorded at 0.00 v, +0.50 V and +0.90 V. Background electrolytes are recorded at the same voltages but offset for viewing.

to +1.0 V *vs.* an Ag/AgCl electrode (Fig. 3). The cyclic voltammogram of TTF showed $E_{1/2}$ potentials at +0.29 V for the TTF/TTF^+ couple and at +0.69 V for the TTF^+/TTF^{2+} couple. The cyclic voltammogram of the $(TTF)_2RuCl_3$ complex also produces two waves at +0.29 V and +0.69 V and suggests oxidation/reduction of the complex is localized to the ligands rather than from the metal center. Additionally for the $(TTF)_2RuCl_3$ complex, a relative measure of the current as a function of applied potential was obtained at +0.90 V (positive of both waves), +0.50 V (between waves) and at 0.00 V (negative of both waves) by subtracting pulse current (pulse height) for the background electrolyte from the pulse current (pulse height) of the complex. The ratio of currents obtained was −2.8:−1.0:+1.1 (where − represents anodic and + represents cathodic current) at +0.90, +0.50 and 0.00 V respectively. These results are interpreted as a one electron transfer occurring from the $(TTF^+)(TTF^0)(Ru(II)$ complex to give either the oxidized $(TTF^+)(TTF^+)Ru(II)$ species at +0.50 V or the reduced $(TTF^0)(TTF^0)$-Ru(II) species at 0.00 V. Continued electrolysis at 0.00 V produced a decrease in the visible absorption maxima at 573 nm and 434 nm, consistent with a loss of the TTF^+ chromophore. The current ratio data is additionally consistent with a 3 electron oxidation of $(TTF^+)(TTF^0)Ru(II)$ at +0.90 V to produce $(TTF^{2+})(TTF^{2+})Ru(II)$. These results add additional support to the visible spectral assignments presented that the 573 nm absorption is due to an intraligand TTF^+ transition.

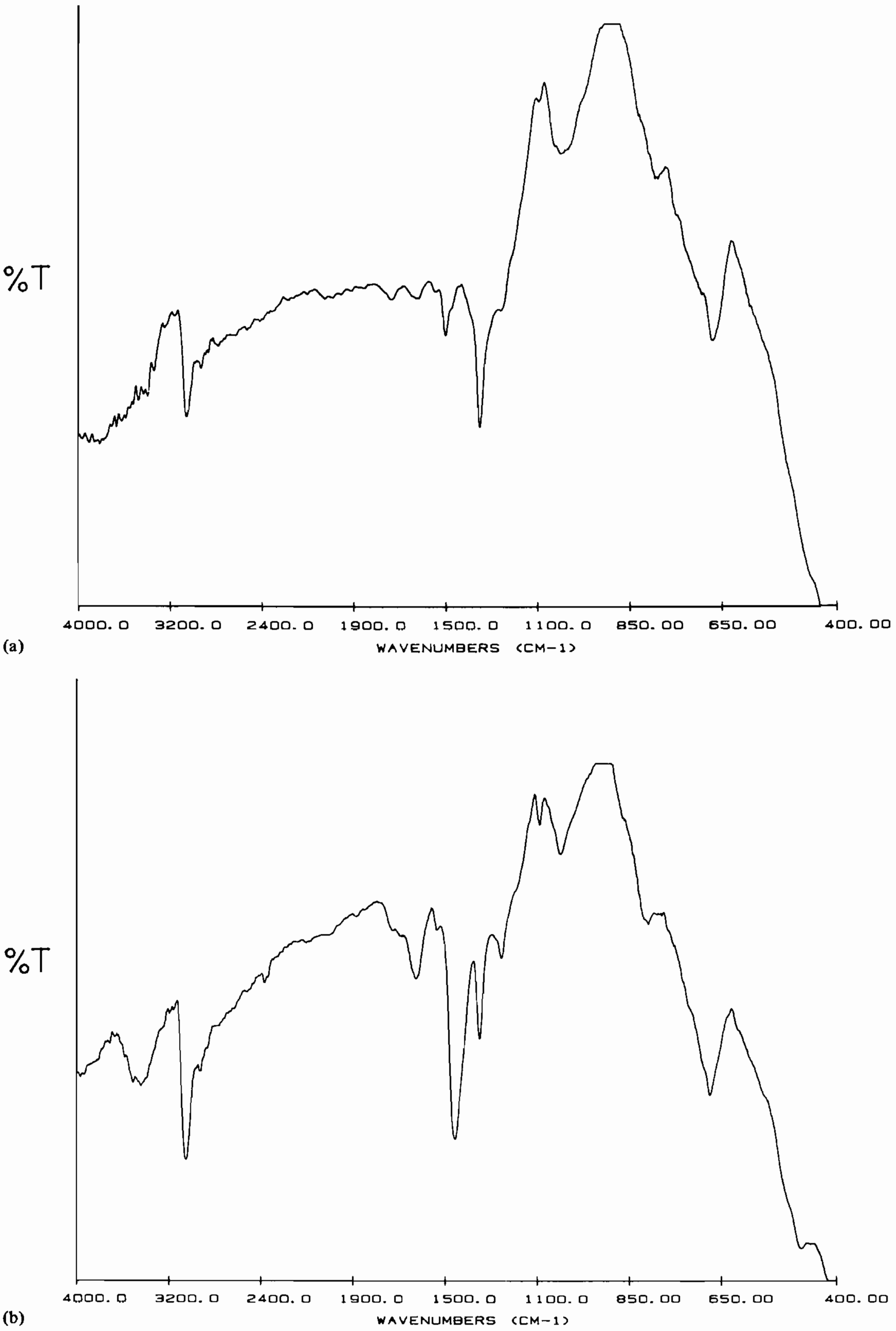
The infrared spectrum of $(TTF)_2RuCl_3$ shows medium–strong intensity bands at 3051 cm^{-1}, 1497 cm^{-1}, 1349 cm^{-1}, 793 cm^{-1} and 674 cm^{-1} (Fig. 4a). The 3051 cm^{-1} band lies in an area which has previously been attributed to C–H stretching while the 1600–1300 cm^{-1} region has been associated with ring and bridging C=C vibrations [20, 27]. While the predominant $(TTF)_2RuCl_3$ band at 1349 cm^{-1} is similar to previously reported values for $(TTF^+)_2CuCl_4$ at 1380 cm^{-1} and $(TTF^+)AuCl_2$ at 1355 cm^{-1}, exact assignment is not available [20].

A far more precise probe of the electronic environment of the TTF moiety in transition metal complexes has been demonstrated by the use of resonance raman spectroscopy [19–21]. The bridging C=C stretch in TTF undergoes vibrational shift upon oxidation from 1512 cm^{-1} for TTF^0, to 1416 cm^{-1} for TTF^+ and 1308 cm^{-1} for TTF^{2+}, as well as intermediate frequencies for non-integral oxidation states [20, 21, 28]. The resonance raman spectrum for $(TTF)_2RuCl_3$ (Fig. 5a) excited at 514.5 nm clearly shows strong vibration at 1418 cm^{-1}, confirming the presence of at least one TTF^+ ligand. Noticeably absent, however, is an equally intense TTF^0 band at 1512 cm^{-1} which would be expected for the $(TTF^+)(TTF^0)RuCl_2$ complex. The lack of this intense band may be understood in terms of the relative absorbance of the excitation radiation at 514.5 nm. While the TTF^+ species, which undergoes an intense ($\epsilon \cong 3 \times 10^3$) intraligand absorption and has $\lambda_{max} = 573$ nm, the TTF^0 ligand has little absorbance at wavelength longer than 400 nm. Thus in terms of localized resonance, the TTF^0 species which has little relative absorbance does not exhibit a strong vibration.

An alternative explanation for the lack of a strong vibration near 1512 cm^{-1} for TTF^0 would be the formation of the $(TTF^+)_2Ru(I)Cl_3$ complex in the solid state. While formation of the $Ru(I)d^7$ complex seems most unlikely, some Ru(I) complexes such as $Ru(NO)I_2bpy$ have been reported [29, 30], and therefore cannot be excluded.

$(TTF)_2RhCl_3$

The $(TTF)_2RhCl_3$ complex was found to dissolve slowly in nitromethane, propylene carbonate and dimethylsulfoxide. Addition of deoxygenated solvent to solid sample initially produced a deep blue solution, which changed (3–5 min) to green–yellow before dissolution of the solid was complete. Because of the slow rate of dissolution *versus* apparent $(TTF)_2RhCl_3$ decomposition, kinetic measurements were not possible. The approximate absorption spectrum of $(TTF)_2RhCl_3$, and its decomposition decay



(a)

(b)

Fig. 4. Infrared spectra of (a) $(TTF)_2RuCl_3$ and (b) $(TTF)_2RhCl_3$ in KBr.

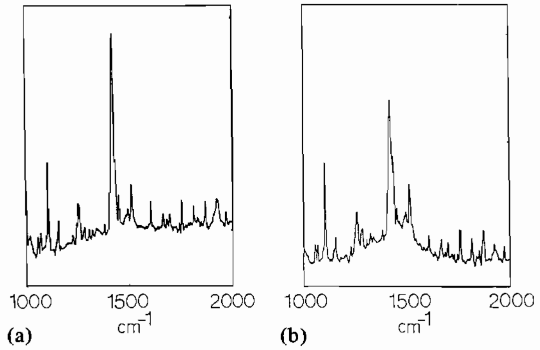


Fig. 5. Resonance raman spectra for (a) $(TTF)_2RuCl_3$ (b) $(TTF)_2RhCl_3$ in $KBr|Na_2SO_4$ powder using 514.5 nm excitation. Also observable in the spectra near 1100 cm^{-1} are A_{1g} vibrations nonsensitive to the TTF oxidation state.

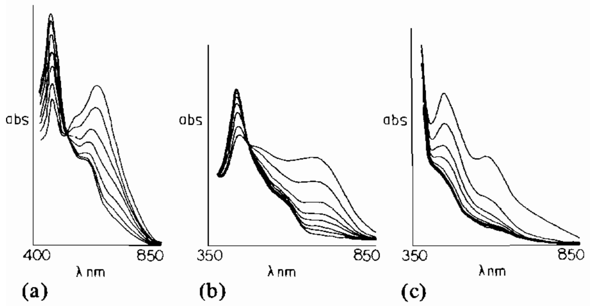


Fig. 6. Visible–ultraviolet spectra for $(TTF)_2RhCl_3$ in (a) nitromethane, (b) propylene carbonate, (c) dimethylsulfoxide.

spectra were obtained by addition of solvent to finely powdered sample, followed by stirring for 1 min, and vacuum filtration to remove the remaining undissolved metal complex (Fig. 6).

The initial absorption spectrum of the blue complex in CH_3NO_2 had absorption maxima at $\lambda = 660$ nm and $\lambda = 435$ nm with a shoulder at $\lambda = 510$ nm. As a function of time the absorbance at 660 nm decreased while the absorbance at 435 nm increased. An isosbestic point at 470 nm indicates a single decay process occurred during the decomposition. The extinction coefficients reported for the $(TTF)_2RhCl_3$ complex are therefore the lower limit for $\lambda = 660$ nm and upper limit for the $(TTF)_2RhCl_3$ complex for $\lambda = 435$ nm. A similar process is also observed for complex in propylene carbonate, although the low energy wavelength maxima is shifted 605 nm (Fig. 6b). Based on the wavelengths of the initial spectrum of the complex, and spectra for other complexes containing bound TTF^+, it is probable that the $(TTF)_2RhCl_3$ complex contains two bound TTF^+ cations resulting in the formation of a stable $Rh(I)d^8$ center. The loss of absorbance at 600 nm to 660 nm indicates either oxidation or reduction of TTF^+. While TTF has no absorption maxima at wavelengths greater than 310 nm, TTF^{+2} has been shown to have absorption maxima at $\lambda = 445$–460 nm. Based on the increase in absorbance at 435 nm as a function of time, the final form of the TTF after complex decomposition is most likely TTF^{2+}. The $(TTF)_2RhCl_3$ complex is also soluble in dimethylsulfoxide, although the rapid decomposition produces a spectrum which has no isosbestic point, and loses all absorption maxima at wavelengths greater than 400 nm (Fig. 6c).

The reflectance spectrum of $(TTF)_2RhCl_3$ (Fig. 2b) recorded from 1450 nm to 300 nm shows a single broad absorption centered at 700 nm, with a minimum at 500 nm and the onset of another intense absorption in the near ultraviolet. As previously mentioned, the position of the low energy absorption is typical of solid state $2(TTF^+) \rightarrow TTF^0$, TTF^{2+} isovalence transitions.

The infrared spectrum of $(TTF)_2RhCl_3$ shows medium–strong absorptions at 3051 cm^{-1}, 1628 cm^{-1}, 1455 cm^{-1}, 1350 cm^{-1}, 1251 cm^{-1}, 807 cm^{-1} and 674 cm^{-1} (Fig. 4b). Again the resonance raman spectrum provides more precise information on the oxidation state of TTF in the solid state complex. The resonance enhanced raman spectrum for the $(TTF)_2RhCL_3$ solid shows a strong vibrational band at 1416 cm^{-1} (Fig. 5b). As previously discussed, this frequency not only confirms the presence of the TTF^+ cation but due to the absence of any 1308 cm^{-1} band excluded the TTF^{2+} dication possibility. Thus, the $(TTF)_2RhCl_3$ complex is in the $(TTF^+)(TTF^+)Rh(I)Cl_3$ rather than $(TTF^{2+})(TTF^0)RhCl_3$ form.

Conclusions

Results indicate that the ease of oxidation of the TTF ligand, which make it ideal for electron transport complexes, may contribute to the overall solution instability of some TTF–metal complexes such as $(TTF)_2RhCl_3$. Syntheses of polymetallic TTF bridged complexes will be focused on the more stable $(TTF)_2RuCl_3$ complex. Work in our laboratories is currently in progress.

Acknowledgements

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