

Synthesis and characterization of a fluxional Re(I) carbonyl complex *fac*-[Re(CO)₃(dpop')Cl] with the nominally tri-dentate ligand dipyrido(2,3-*a*:3',2'-*j*)phenazine (dpop')

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Abstract

A new Re(I) carbonyl complex [Re(CO)₃(dpop')Cl] with nominally N-donor tri-dentate heterocyclic ligand dipyrido(2,3-*a*:3',2'-*j*)phenazine (dpop') was prepared and characterized. The ligand complexes in a bi-dentate mode undergoing fluxional behavior in room temperature solution. VT NMR results show ΔG^\ddagger of 61.1 kJ mol⁻¹ for [Re(CO)₃(dpop')Cl] is smaller than for comparable tpy related complexes. The electronic absorption spectrum shows solvent dependent MLCT energies at 483 and 368 nm in dichloromethane. A single irreversible Re centered oxidation at +1.29 V and a semi-reversible dpop' centered reduction at -0.71 V are observed by cyclic-voltammetry. Electrolysis of [Re(CO)₃(dpop')Cl] at -1.0 V produces complete loss of dpop' from the metal.

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1. Introduction

The aromatic N-donating ligand dpop' (dipyrido(2,3-*a*:3',2'-*j*)phenazine) has previously been shown to coordinate to metal centers including Ru(II) [1a,1b], Fe(II) [1c] and Os(II) [1d] in a tri-dentate manner, similar to that observed with tri-dentate N ligands such as tpy (tpy = 2,2':6',2''-terpyridine). The ligand dpop' is a structural isomer of dipyrido(2,3-*a*:3',2'-*h*)phenazine (dpop) which has previously been shown to bind to Re(I) and other metals in a bi-dentate manner (Fig. 1).

Studies of Re(I) carbonyl complexes established that tpy and similar ligands bind in a bi-dentate rather than tri-dentate mode with the formula *fac*-[Re(tpy)(CO)₃X]; X = Cl, Br [2–6]. Additionally, NMR studies of [Re(tpy)(CO)₃X]

and similar Re(I) complexes with tri-dentate N-donating ligands [2–6] demonstrated the fluxional nature of the tri-dentate ligand when coordinated in a bi-dentate mode. In those systems, the non-coordinated ring is attached to the central ring via a σ linkage, allowing rotation from coplanarity and makes bi-dentate coordination plausible. The crystal structure of [Re(tpy)(CO)₃Br] shows the non-coordinated pyridine ring to be rotated ~52.9° relative to the adjacent ring [2].

Dpop' is a planar tri-dentate ligand and non-coordinated ring planarity is defined. Within this constraint, our research group was interested in determining if dpop' would coordinate to Re(I) in a bi or tri-dentate fashion and, if it was bi-dentate, to establish the fluxionality, and elucidate NMR shifts and activation parameters. The results of this study lead to the conclusion that dpop' coordinates in a bi-dentate fluxional mode at room temperature with the formula *fac*-[Re(dpop')(CO)₃Cl]. At low temperature, the static structure may be isolated and is represented in Fig. 2.

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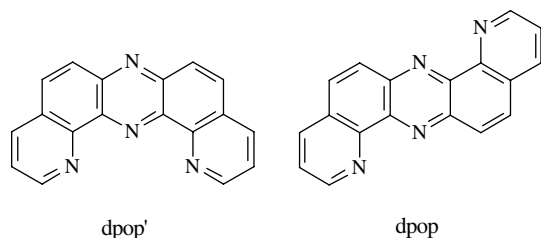


Fig. 1. Structural representations of the nominally tri-dentate dpop' and bi-dentate dpop ligands.

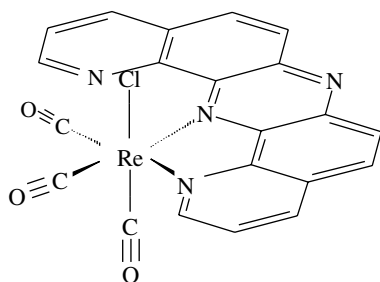


Fig. 2. Representation of the static structure of *fac*-[Re(dpdp')(CO)₃Cl].

2. Experimental

All chemicals and solvents used in the synthesis were reagent grade. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

2.1. Physical measurements

NMR spectra were obtained at the NMR lab, Department of Chemistry, University of Colorado-Boulder using a Varian Inova-400 NMR spectrometer operating at 400.16 MHz for ¹H observation. 2-Dimensional exchange experiments were performed on a Varian Inova-500 NMR spectrometer operating at 500.37 MHz for ¹H observation. The solvent was *d*₇-DMF (Aldrich). Sample temperatures were calibrated using methyl alcohol for temperatures below ambient, and ethylene glycol for temperatures above ambient. Dynamic NMR simulations were performed using the DNMR3 utilities in the SPINWORKS 2.4 software [7]. Complete assignment of the exchanging proton spin systems was accomplished using variable temperature 2D-Exchange Spectroscopy (EXCHSY), and 2D-gCOSY at −25 °C.

UV–Vis absorption spectra were recorded on a HP8453 Diode Array Spectrophotometer using 2–5 s collection and 1 nm resolution. Cyclic voltammograms were recorded in analytical grade CH₂Cl₂/0.010 M TBAH on a BAS CV-1B instrument at 100 mV/s at a Pt electrode and are reported versus Ag/AgCl (−0.045 V versus SCE). A BAS PRW-3 Electrolysis instrument and cell with a Pt gauze working electrode was used to generate oxidized and reduced complex metal ions. The bulk electrolysis cell was fused on top of a quartz spectrophotometer cell, and absorption spectra were recorded in situ following

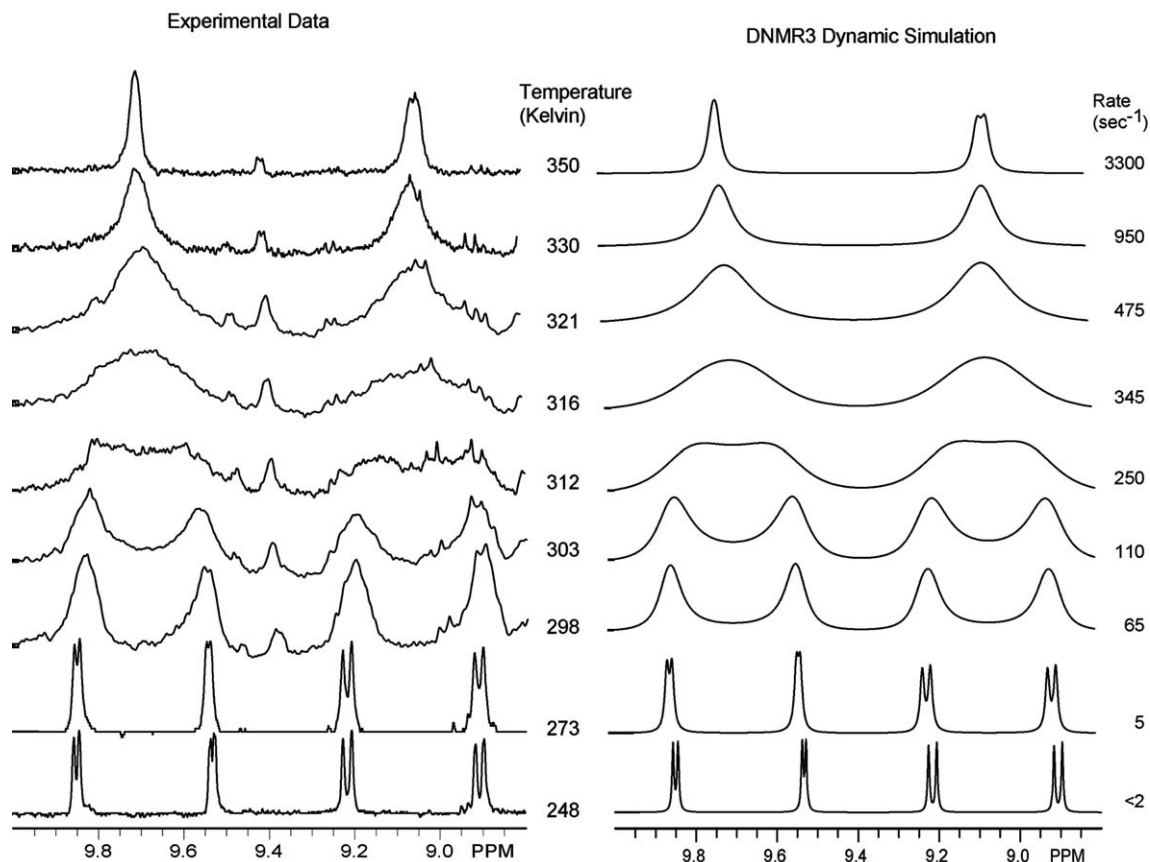


Fig. 3. Experimental and simulated variable temperature NMR results.

2D-gCOSY, Temperature = -20 Deg.C.

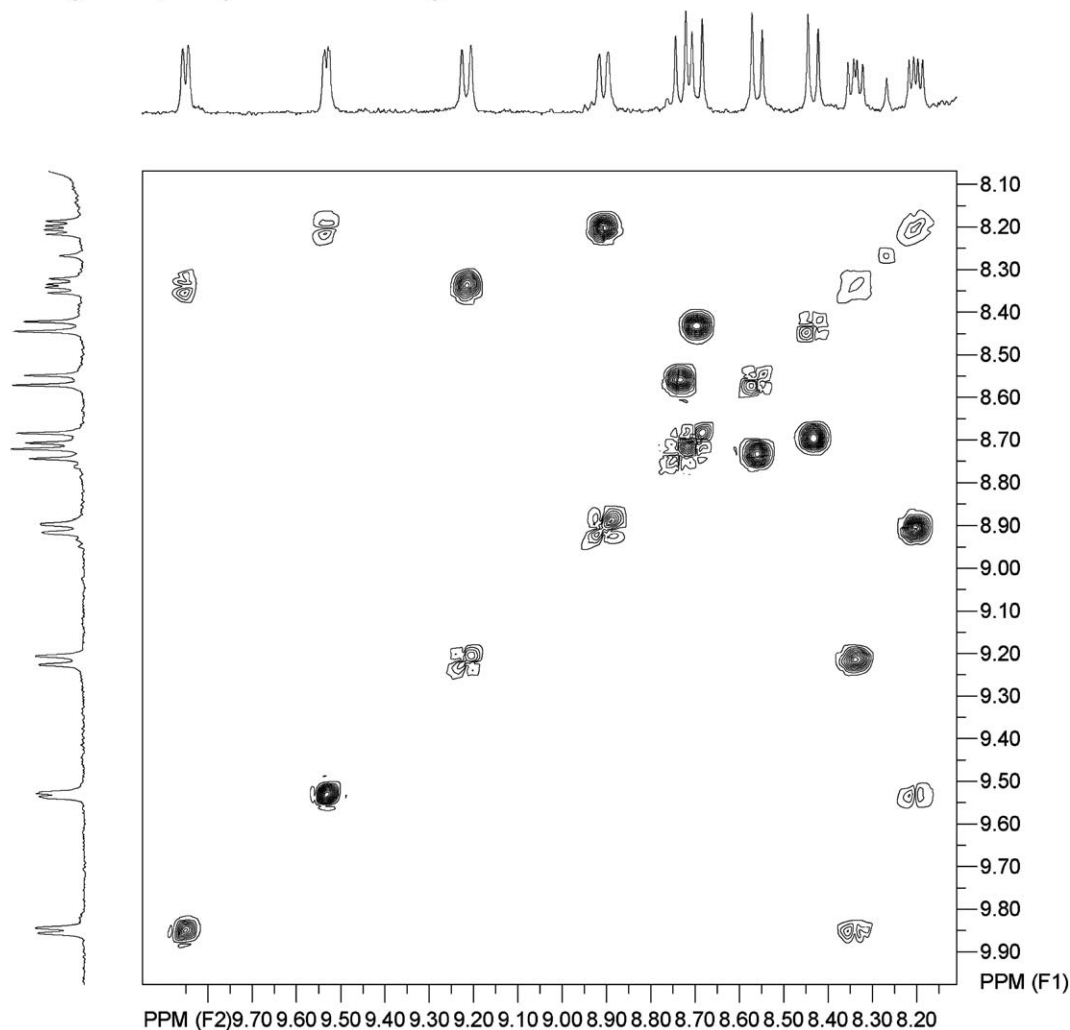


Fig. 4. 2D gCOSY spectrum demonstrating correlations within the separate spin-systems of the bound and unbound sides of dpdp'.

generation of the oxidized/reduced species. The solid reflectance infrared spectrum was recorded using a PE Spectrum One Spectrophotometer with a Universal ATR Sampling Accessory and 2 cm^{-1} resolution.

2.2. Synthesis

The ligand dpdp' was prepared according to the literature [8]. $[\text{Re}(\text{CO})_5\text{Cl}]$ was purchased from Aldrich.

$[\text{Re}(\text{CO})_3(\text{dpdp}')\text{Cl}]$. In a typical synthesis, a sample of 0.0648 g ($1.79 \times 10^{-4}\text{ mol}$) of $[\text{Re}(\text{CO})_5\text{Cl}]$ and 0.0532 g ($1.88 \times 10^{-4}\text{ mol}$) dpdp' were mixed in approximately 50 mL of MeOH in a ground glass round bottom flask and heated at reflux under Ar for 6 h. A brown flakey precipitate formed and the warm solution was filtered to collect the crude $[\text{Re}(\text{CO})_3(\text{dpdp}')\text{Cl}]$ product. The product was washed with excess hot CHCl_3 to remove excess or un-reacted dpdp',

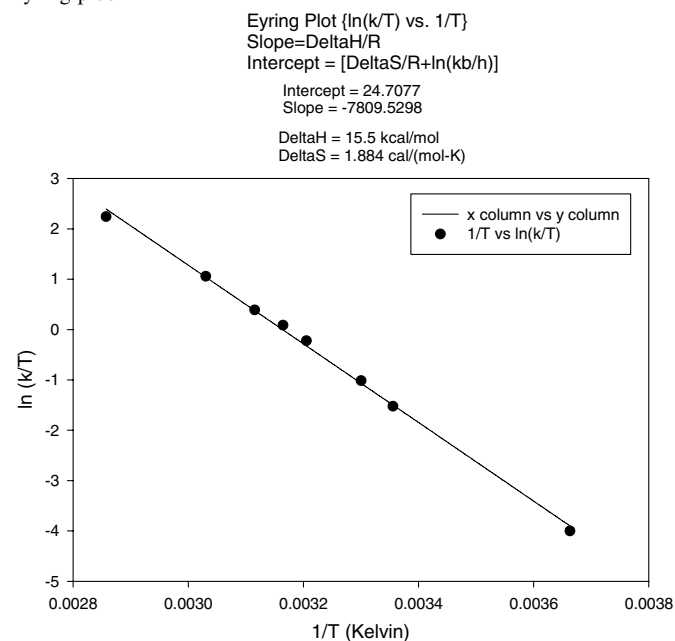
Table 1

^1H NMR data for $[\text{Re}(\text{CO})_3(\text{dpdp}')\text{Cl}]$, δ in ppm vs. TMS

Complexed ring				
H ₂	H ₃	H ₄	H ₅	H ₆
δ 9.84, d ($J = 5.2\text{ Hz}$)	δ 8.34, dd ($J = 4.3, 8.2\text{ Hz}$)	δ 9.22, d ($J = 8.2\text{ Hz}$)	δ 8.58, d ($J = 9.1\text{ Hz}$)	δ 8.73, d ($J = 9.1\text{ Hz}$)
Uncomplexed ring				
H _{2'}	H _{3'}	H _{4'}	H _{5'}	H _{6'}
δ 9.53, d ($J = 4.3\text{ Hz}$)	δ 8.20, dd ($J = 4.3, 8.0\text{ Hz}$)	δ 8.90, d ($J = 8.0\text{ Hz}$)	δ 8.44, d ($J = 9.2\text{ Hz}$)	δ 8.69, d ($J = 9.2\text{ Hz}$)

Table 2

VT NMR rate constant simulation results for $[\text{Re}(\text{dpop}')(\text{CO})_3\text{Cl}]$ and Eyring plot



T	$1/T$	K	$\ln(k)$
248	0.004032	<2	N/A
273	0.003663	5	1.609438
298	0.003356	65	4.174387
303	0.00333	110	4.70048
312	0.003205	250	5.521461
316	0.003165	345	5.843544
321	0.003115	475	6.163315
330	0.00303	950	6.856462
350	0.002857	3300	8.101678

rinsed with diethyl ether and dried in vacuum overnight at 40 °C. The $[\text{Re}(\text{CO})_3(\text{dpop}')]$ complex had insufficient solubility for re-precipitation or chromatography purification. Weight product: 0.0749 g (1.27×10^{-4} mol) 71.2% yield. *Anal.* Calc. for $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ (587.97 g/mol): C, 42.90; H, 1.72; N, 9.52. Found: C, 43.07; H, 1.73; N, 9.49%. IR: 2027 cm^{-1} (strong), 1916 cm^{-1} (strong); 1900 cm^{-1} (strong).

3. Results and discussion

3.1. Structure and NMR

The air stable flakey brown $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ complex was easily and directly prepared. The reflectance IR spectrum shows three intense stretches similar to those for $[\text{Re}(\text{CO})_3(\text{tpy})\text{Cl}]$ [2] and $[\text{Re}(\text{CO})_3(\text{ph-tpy})\text{Br}]$ [3] and other tricarbonyl complexes with bi-dentate ligands [9,10] which indicate the *fac* arrangement of carbonyls.

The ^1H and ^{13}C NMR spectra for dpop' complexed in a tri-dentate manner has been reported for $[\text{Ru}(\text{dpop}')_2]^{2+}$ showing five ^1H and nine ^{13}C resonances [1a]. Thus, when the initial room temperature NMR spectrum of $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ showed nine broad ^1H NMR reso-

nances (eight integrating 1:1, one with a 2:1 ratio), it suggested that a dynamic fluxional process was occurring (Supplementary). Fluxional behavior of several tri-dentate N coordinating ligands has been previously established with Re(I) and other metals [2–6]. The 2D-Exchange spectrum (EXCHSY/NOESY pulse-sequence) of $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ at RT showed that the related fluxion resonances occur between the closest broadened signals (Supplementary). In order to isolate the static structure and determine activation parameters, temperature dependent NMR spectra were collected and a stacked plot diagram is presented in Fig. 3.

At 253 K the 2D gCOSY spectrum clearly establishes through-bond correlations within the separate spin-systems of protons in the bound and unbound sides of dpop' (Fig. 4).

Previous studies show a downfield shift (larger ppm δ) of the coordinated versus un-coordinated ring fluxional systems such as tpy and 4'-phen-tpy [2–4,6]. Based on those results, and those comparing uncomplexed dpop' with $[\text{Ru}(\text{dpop}')_2]^{2+}$ [1a], we believe that in all related pairs of signals for $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$, the coordinated ring resonances are downfield from the un-coordinated signals. On this basis, ^1H NMR assignments are presented in Table 1 along with the proposed static structure in Fig. 2. NMR spectra were measured over the temperature range of 248–350 K, and the exchange rate constant at each temperature was determined using the DNMR3 simulation algorithm (Table 2). The activation energy ΔG^\ddagger for the fluxion over the temperature range of 248–350 K, was determined to be $62.3 \pm 0.4 \text{ kJ mol}^{-1}$ ($14.9 \pm 0.1 \text{ kcal mol}^{-1}$) based on a coalescence temperature of 314 K. An Eyring plot was used for calculation of $\Delta H^\ddagger = 64.9 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 7.87 \text{ J mol}^{-1} \text{ K}^{-1}$. Energies of activation for other tricarbonyl Re(I) complexes are reported 55–74 kJ mol^{-1} [2–6], with a value of 70.3 kJ mol^{-1} reported for $[\text{Re}(\text{CO})_3(\text{tpy})\text{Cl}]^2$. The lower range of activation energies was reported for bis-(R_n -pyrazole)pyridine fluxions and the range of values (54–71 kJ mol^{-1}) was attributed as related to the steric influence of the pendant rings of the ligand [5]. The ΔG^\ddagger of 61.1 kJ mol^{-1} for $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ is smaller than activation energies of 70–75 kJ mol^{-1} for comparable tpy related complexes [2,4], and may be due to minimal steric interactions of the planar dpop' ligand, without non-planar rotation of the non-coordinated ring.

3.2. Electronic absorption spectroscopy

$[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ is sparingly soluble in several organic solvents and displays a broad solvent dependent absorption 460–510 nm with several more intense absorptions in the near UV (Fig. 5(a)). Quantitative samples were prepared in DCM and placed in an ultrasonic vibrating bath to insure complete dissolution. All UV-Vis data are presented in Table 3. Based on the structural similarity with multiple previously reported complexes of the type $[\text{Re}(\text{CO})_3(N-N)\text{X}]$ with $N-N$ = bi-dentate ligands [9–15] and $[\text{Re}(\text{CO})_3(N-N)\text{X}]$ (where N = bound; N = unbound nitrogen in

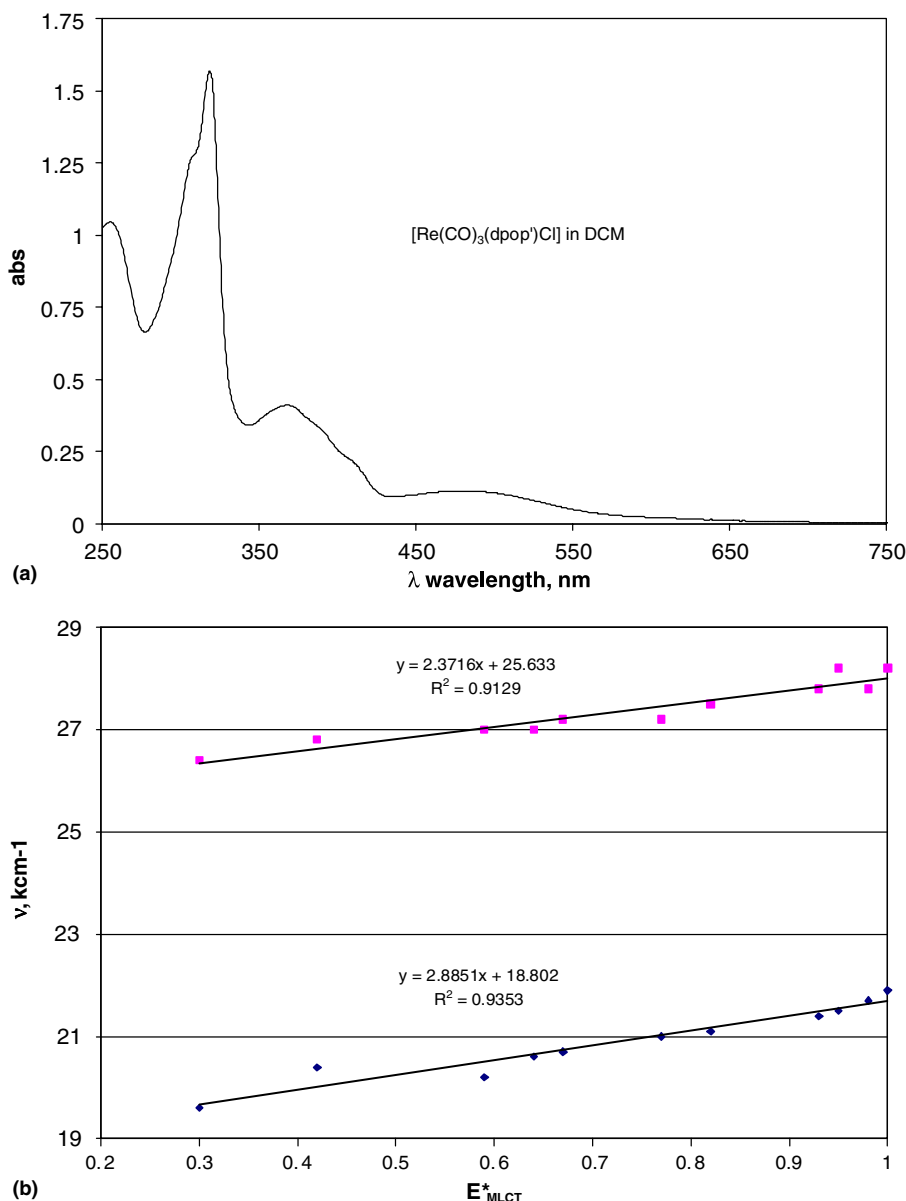


Fig. 5. (a) UV–Vis electronic absorption spectrum of $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ in dichloromethane. (b) Plot of MLCT transition energies vs. solvent polarity scale.

Table 3
Electronic absorption and electrochemical data for $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$

Species	Wavelength (nm)	$(\epsilon \times 10^{-3})$	Assignment	E_{ox}	E_{red}	E_{red}
$[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]^{\text{a}}$	483	2.83	$\text{Re } d\pi \rightarrow \text{dpop}' \pi^*$	1.29 ^b	−0.71	−1.44 ^c
	410(s)	5.43	$\text{Re } d\pi \rightarrow \text{dpop}' \pi^*$			
	368	10.7	$\text{Re } d\pi \rightarrow \text{dpop}' \pi^*$			
	318	41.4	$\text{dpop } \pi \rightarrow \pi^*$			
	310(s)	34.4	$\text{dpop } \pi \rightarrow \pi^*$			
	255	27.3	$\text{dpop } \pi \rightarrow \pi^*$			

^a This work.

^b Irreversible anodic peak.

^c Irreversible cathodic peak.

polydentate heterocyclic ligands) [2–6] the lowest energy absorption for $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ is assigned to a $\text{Re}(\text{I}) d\pi \rightarrow \text{dpop } \pi^*$ MLCT transition. The lowest energy $\text{Re}(\text{I}) d\pi \rightarrow \text{dpop}' \pi^*$ MLCT transition displays negative solvatochromic behavior (Table 4), red shifting in solvents of lower polarity, similar to observation for other $\text{Re}(\text{I})$ complexes with di-imine ligands [10,11]. A plot of $E_{\text{MLCT}} \text{ k cm}^{-1}$ versus solvent polarity [12], gives a straight line typical for $\text{Re}(\text{I}) d\pi \rightarrow \text{dpop } \pi^*$ MLCT transitions (Fig. 5(b)). While more quantitative models yield the transition dipole and dipole length [16], the observed transition energy versus single parameter dielectric functions were non-linear. In complexes including $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ with an expected ground state dipole, dual parameter fitting is required to produce good correlations, however due to the limited solubility of the complex, a complete data set was not obtained to give sufficient dual parameter fitting.

The negative solvatochromic behavior of the second intense absorption suggests that it is also a second Re(I) $d\pi \rightarrow dpop \pi^*$ MLCT transition. This assignment is consistent with a resonance Raman [14] study for bi-

dentate $[\text{Re}(N-N)(\text{CO})_3\text{Cl}]$ complexes which determined two Re(I) $d\pi \rightarrow L \pi^*$ MLCT transitions for near 440 and 370 nm. Higher energy absorptions for $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ at 318, 310(s) and 255 nm are attributed to $dpop'$ IL transitions. While many $[\text{Re}(N-N)(\text{CO})_3\text{Cl}]$ bi-dentate complexes including $[\text{Re}(\text{CO})_3(\text{dpop})\text{Cl}]$ (where $dpop$ the bi-dentate ligand = dipyrdo(2,3-*a*:3',2'-*h*)phenazine) luminescence [10,11,13], the fluxional $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ complex did not emit in de-oxygenated RT solution.

Table 4

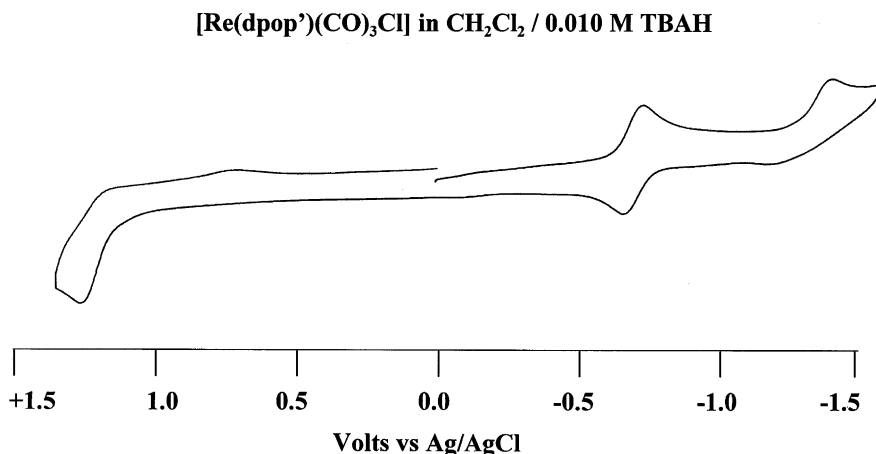
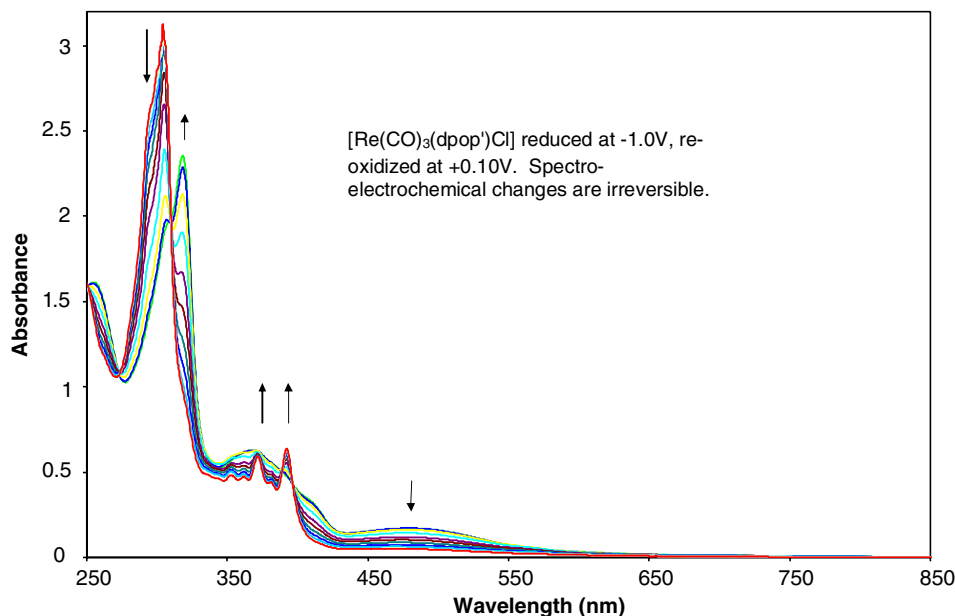
Electronic absorption data for MLCT transitions in different solvents

Solvent	E_{MLCT}^* [12]	ν (k cm^{-1}) MLCT I	ν (k cm^{-1}) MLCT II
DMSO	1.00	21.9	28.2
CH_3CN	0.98	21.7	27.8
DMF	0.95	21.5	28.2
DMA	0.93	21.4	27.8
Acetone	0.82	21.1	27.5
Pyridine	0.77	21.0	27.2
CH_2Cl_2	0.67	20.7	27.2
1,2-DCE	0.64	20.2	27.0
THF	0.57	20.2	27.0
CHCl_3	0.43	20.4	26.8
Toluene	0.30	19.6	26.4

3.3. Electro and spectro-electrochemistry

The cyclic voltammogram of the $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ complex is shown in Fig. 5 and the results are presented in Table 2.

When scanned towards positive potentials, an irreversible oxidation typical [10,11,13,14] for Re(I) complexes

Fig. 6. Cyclic voltammogram of $[\text{Re}(\text{dpop}')(\text{CO})_3\text{Cl}]$ in DCM at Pt electrode vs. Ag/AgCl.Fig. 7. Irreversible spectroelectrochemical changes upon one electron reduction and re-oxidation of $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$.

was observed with E_{anodic} at +1.29 V. A semi-reversible reduction wave was observed at -0.71 V, with a second irreversible reduction at E_{cathodic} at -1.44 V. Based on the CV data for previously reported complexes with dpop', the reductive waves are attributed to the $\text{dpop}'^{0/-1}$ and $\text{dpop}'^{-1/-2}$ reductions (see Fig. 6).

Reductive spectro-electrochemistry is shown in Fig. 7. After the $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ complex is reduced at -1.0 V, the spectrum shows the sharp characteristic peaks associated with the uncomplexed dpop' ligand leading to the conclusion that the $1e^-$ reduction causes irreversible dpop' loss.

This is somewhat surprising since the CV appears to show a mostly reversible wave. The two electron reduction at -1.5 V causes similar spectral changes. Oxidative spectro-electrochemistry produces irreversible loss of the 480 and 368 nm absorptions, as expected since the transitions are $\text{Re}(\text{I}) d\pi \rightarrow \text{dpop}' \pi^*$ MLCT transitions.

4. Conclusion

Although dpop' undergoes tri-dentate N coordination with other metals, it is established that the dpop' ligand undergoes bi-dentate fluxional coordination at room temperature when coordinated to $\text{Re}(\text{I})$ in the $[\text{Re}(\text{CO})_3(\text{dpop}')\text{Cl}]$ complex with $\Delta G^\ddagger = 61.1 \pm 0.4$ kJ mol^{-1} . The absorption spectrum shows solvent dependent $\text{Re}(\text{I}) d\pi \rightarrow \text{dpop}' \pi^*$ MLCT transitions in the Vis–Near UV and $\text{dpop}' \pi \rightarrow \text{dpop}' \pi^*$ transitions in the UV spectrum. Spectroelectrochemistry shows that even upon one electron reduction, the complex dissociates with loss of the dpop' ligand.

Acknowledgments

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Appendix A. Supplementary data

Supporting Information Available: RT ^1H NMR resonances, 2D-Exchange spectrum (EXCHSY/NOESY pulse-sequence). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.11.042.

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