Synthesis and Spectroscopic Analysis of Novel Polynuclear Rhenium(I) Complexes of the Form [Re(CO)$_3$Cl]$_n$(tppq) (n = 1, 2, 3, or 4; tppq = 2,3,7,8-tetra-2-pyridylpyrazino[2,3-g]quinoxaline)

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A number of transition metal complexes have been investigated as potential electrocatalysts for CO_2 reduction. Among these are rhenium monometallic complexes, which have shown unique activity towards CO_2 reduction. Further development of multimetallic systems, capable of storing multiple equivalents of electrons has shown some potential in increasing the selectivity of the CO_2 conversion processes toward highly reduced products. This study reports the synthesis and characterization of novel polynuclear rhenium(I) complexes where rhenium is incorporated to the bridging ligand tppq (2,3,7,8-tetra-2-pyridylpyrazino[2,3-g]quinoxaline), which is capable of attaching up to four metal centers. The resulting complexes were characterized using different spectroscopic techniques (infrared, UV-Vis, emission) and cyclic voltammetry. The results suggest that the synthetic procedure adopted was successful.

Keywords: polynuclear complexes, bridging ligand, electrocatalyst

INTRODUCTION

The reduction of CO_2 to substances like HCHO, HCOOH, and CH_3OH is a significant and intriguing problem in contemporary inorganic chemistry because CO_2 is a greenhouse gas as well as a potential raw material-source for carbon atom. Studies concerning the development of CO_2 as an efficient alternate carbon source for commercial fuels have dramatically increased. Several transition metal complexes have been investigated as electrocatalysts for such CO_2 conversion schemes.[1-6] Among these electrocatalysts are
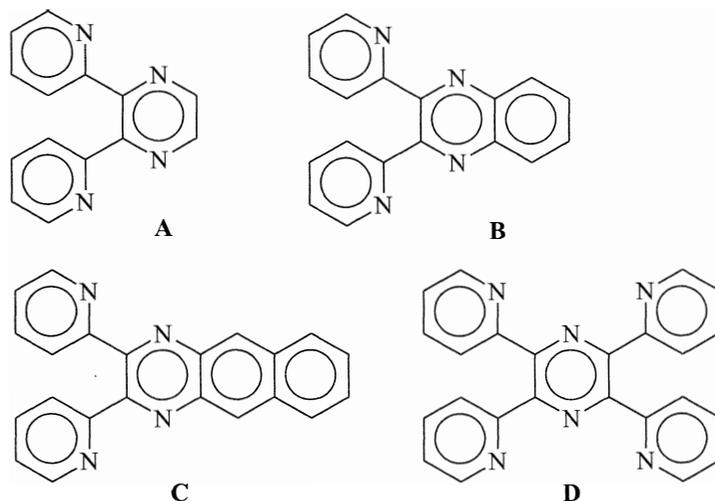
Fig 1. *Structures of the bridging ligands dpp (A), dpq (B), dpb (C), and tpp (D)*

metal polypyridyl complexes where the polypyridyl ligands act as "electron reservoirs" by utilizing vacant π orbitals and stabilize metals in a variety of oxidation states.[7-15] In addition, these complexes have been used as light absorbing moieties for photoinitiated catalytic processes.[13,16-21]

Rhenium polypyridyl complexes exhibit electrocatalytic activity towards the reduction of CO_2 whether in solution or as immobilized systems.[22-27] The complex *fac*-[Re(bpy)(CO)$_3$Cl] (where bpy = 2,2'=bipyridine) and related complexes have been found to be highly selective for the conversion of CO_2 to CO (98% current efficiency) in aprotic solvents both photochemically and electrochemically (approximately -1.25 V vs. NHE).[22, 23] Its reactivity is associated with the concerted reaction of the complex with CO_2 and the dissociation of the chloride ligand. The chloride ligand is labilized upon initial one-electron reduction of the complex. [27]

Similar reactivity was also observed with [Re(CO)$_3$(dmbpy)Cl] (where dmbpy = 4,4'-dimethyl-2,2'-bipyridine).[22] The catalytic activity of the complex was found to involve a *sesqui*-coordinated bipyridine intermediate which allowed coordination of CO_2 to the empty coordination site generated on the rhenium metal center. Immobilization of rhenium catalysts onto an electrode surface by either using a polymerizable analog, such as [Re(vbpy)(CO)$_3$Cl] (where vbpy = 4-vinylbipyridine) or by incorporating into a Nafion membrane did not alter the reactivity toward CO_2 reduction; in fact, the efficiency of the process was even increased.[22,24]

Both mononuclear and polynuclear polypyridyl complexes, particularly those incorporating polyazine bridging ligands, have been studied for both photochemical and electrochemical applications.[12,13,16-21] Bridging ligands such as 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq) and 2,3-bis(2-pyridyl)-benzoquinoxaline and the tridentate ligand, 2,3,5,7-tetrakis(2-pyridyl)pyrazine (tpp) (Fig. 1) have been used to couple various chromophores and redox active moieties in the development of multimetallic systems. Incorporation of metal centers such as rhodium and iridium has been accomplished to design multicomponent complexes. [16-21] .

The objective of this work is to investigate the catalytic activity of multimetallic polypyridyl-

based complexes, particularly for the electrochemical reduction of CO_2. Rhenium monometallic complexes, which have been shown to exhibit excellent activity towards CO_2 reduction, were used as model complexes for the preparation of rhenium-based polymetallic systems. The bridging ligand tppq (Fig. 2) which is capable of attaching one to four metal centers was utilized. This synthetic design allows us to further utilize known electrochemical and photochemical properties of rhenium in multimetallic systems that may result to unique catalytic activity for CO_2 reduction, as observed with the previously studied iridium and rhodium trimetallic systems.[16-18,20,22,28]
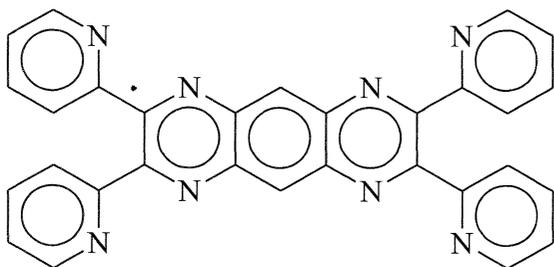

Fig 2. *Structure of the bridging ligand tppq*

EXPERIMENTAL

Reagents and Materials.

The transition metal salt precursor, $Re(CO)_5Cl$ and the ligand precursors 1,2,4,5-benzenetetraamine tetra-hydrochloride and 2,2'-pyridyl were all purchased from Aldrich Chemical Company and used without further purification. The reagents used in all procedures are analytical reagent grade, unless otherwise specified. Absolute ethanol, diethyl ether, *n*-pentane, and dichloromethane were all purchased from Merck. Acetonitrile (both AR and HPLC grades) were acquired from J.T. Baker. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAHP), which is used for the electrochemical characterization of the complexes was prepared from the metathesis

of tetrabutlyammonium bromide (Aldrich) with potassium hexafluorophosphate (Sigma), then recrystallized several times over hot ethanol and vacuum dried.

Synthesis

2,3,7,8-tetra-2-pyridylpyrazino[2,3-g]qui-noxaline, (tppq). The bridging ligand tppq was synthesized following the procedure developed by D.P. Rillema and K.B. Mack.[29] In a typical procedure, 1,2,4,5-benzenetetraamine tetrahydrochloride (0.5 g, 1.76 mmol) and 2,2'-pyridyl (0.75 g, 3.52 mmol) were dissolved in 25-mL of absolute ethanol. Triethylamine was added dropwise until the suspension cleared and the pH became nearly neutral. The undissolved materials remaining in the solution were separated via gravity filtration and discarded. The filtrate was then heated under reflux for 5 hours at ambient conditions, producing yellowish crystals. Purification of the mixture was accomplished by washing with small portions of cold absolute ethanol. The purified tppq was dried under vacuum then stored in a desiccator. Typical yield is ~40%; m/z 491.7.

[Re(CO)₃Cl]ₙ(tppq) where n = 1, 2, 3, or 4.

The polynuclear rhenium(I) complexes were synthesized according to the procedure by M. Wrighton and D.L. Morse [30], with some modifications. Stoichiometric amounts of $Re(CO)_5Cl$ and the bridging ligand (BL), tppq, were mixed in 50 mL benzene. The resulting mixtures were stirred and heated under reflux for 5 hours at 60°C. The products were filtered under vacuum then purified by dissolving in dicholoromethane and recrystallizing in *n*-pentane. The purified complexes were filtered again under vacuum and air-dried. Typical yield varies from ~50% for monometallic complexes to ~90% in tetrametallic complexes.

[Re(CO)₃Cl](tppq). Brownish precipitate with a typical yield of 57%; m/z 797.4; $ReClO_3C_{33}H_{18}N_8$: 59.04% C, 1.74% H, 16.12% N

[Re(CO)₃Cl]₂(tppq). Dark brown precipitate *with a typical yield of 78%; m/z 1099.8;*

$Re_2Cl_2O_6C_{36}H_{18}N_8$: 42.09% C, 1.36% H, 10.03% N

[Re(CO)₃Cl]₃(tppq).   Black precipitate with a typical yield of ~94%; m/z 1406.3; $Re_3Cl_3O_9C_{39}H_{18}N_8$:   50.44%C,   1.50%H, 12.75%N

[Re(CO)₃Cl]₄(tppq).   Black precipitate with a typical yield of ~92%; m/z 1714.1; $Re_4Cl_4O_{12}C_{42}H_{18}N_8$:   40.16%C,   1.02%H, 10.21%N

Characterization

The electronic absorption spectra of the complexes were obtained in acetonitrile at room temperature using a Shimadzu UV-3101PC UV-VIS-NIR Scanning Spectrophotometer. Fluorescence spectroscopy was conducted in acetonitrile using a Shimadzu RF-5301PC Spectrofluorophotometer with a 150 W Xenon arc excitation lamp as light source and a photomultiplier tube as detector. The infrared spectra of the bridging ligands and the complexes were obtained in peak view mode using a Bio-Rad FTS-40A FTIR Spectrophotometer using a tungsten halogen lamp as light source and a DTGS–Nd-YAG dual system as the detector. The mass spectra of the samples were obtained using an LCQ-Finnigan MAT Liquid Chromatography Mass Spectrometer employing a capillary temperature of 200^0C and capillary voltage of 42.0 V. The proton NMR spectra of the synthesized ligands and complexes were obtained using a JEOL Lambda 400 MHz High Resolution Nuclear Magnetic Spectrometer (NMR) using deuterated chloroform as solvent. Cyclic voltammetry was conducted using a Powerlab ADI Potentiostat interfaced to a computer. A typical three electrode system was used for the analysis: Ag/AgCl electrode as reference electrode; Pt disc (2.0 mm) as working electrode; and Pt rod (2.0 mm) as auxiliary electrode. The supporting electrolyte used was a TBAHP/acetonitrile electrolyte/solvent system. The instrument was preset using a Metrohm 693 VA Processor. Potential sweep rate was 200 mV/s using a scan range of –1800 mV to +1800 mV.

RESULTS AND DISCUSSION

The polynuclear rhenium(I) complexes were obtained at very reasonable yields. It was observed that as the synthesis proceeded from mono- to tetrametallic complexes, the yields became considerably higher. This may be attributed to the absence of any special purification processes except for simple recrystallization and washing. The metal salt $(Re(CO)_5Cl)$ attached to the bridging ligand was added in slight excess to ensure the complete attachment to the BL. The chelating nature of the bridging ligands, which have four bidentate sites allows them to form stable polymetallic complexes with rhenium(I). The two nitrogen (N) atoms in the pyridyl and pyrazyl groups of the BL's allow for the attachment of one rhenium(I) center. The number of coordinated metal centers formed actually depends on the molar ratio of the starting materials.

The basic features of the electronic absorption spectra of the synthesized rhenium(I) complexes, as shown in Table 1, which were also found in analogous complexes, such as $Re(CO)_3XCl$ [X = 5-Y-1,10-phenanthroline (Y = H, CH_3, Cl, Br, NO_2), 4,7-diphenyl-1,10-phenanthroline-5,6-dione, and 2,2'-biquinoline][31] include the appearance of lower energy absorption bands between 352–416 nm arising from metal-to-ligand charge transfer (MLCT) transitions from the dπ orbitals of Re(I) to the π* orbitals of the BL's, and that of a higher energy absorption band at around ~ 275 nm arising from a ligand-localized π → π* transition in the BL's. The relative molar absorptiviy (ε) of the complexes confirm the occurrence of MLCT transition, which have ε values 10^3–10^6, and ligand based transitions that have magnitudes greater than 10^3. From the results obtained, it can be inferred that upon the attachment of more metal centers, the absorption maxima of the complexes shift to shorter wavelengths. A probable explanation for such occurrence would be that by increasing the number of rhenium(I) metal centers, the BL's become harder to reduce.

Table 1. Electronic absorption spectro-scopy data for the ligand and the rhenium complexes in acetonitrile at $25^{0}C$

Complex	Absorbance (nm)
tppq	266.0, 287.5, 394.0
[Re(CO)$_3$Cl](tppq)	307.0, 414.5
[Re(CO)$_3$Cl]$_2$(tppq)	300.5, 398 (sh)
[Re(CO)$_3$Cl]$_3$(tppq)	328, 412
[Re(CO)$_3$Cl]$_4$(tppq)	324, 400.5

Although it is known that ligand field transitions can be observed at lower energies in the visible region, the results obtained from this work are consistent with data previously reported in the literature [31-33], where MLCT Re $\rightarrow$ π^* transitions occur somewhere in the 240–332 nm regions and, $\pi \rightarrow \pi^*$ at the ultraviolet regions somewhere between 486–650 nm.

Fluorescence spectroscopy was another technique used to characterize the synthesized Re(I) complexes (Table 2). The complexes were excited at wavelengths corresponding to their maximum absorbance wavelengths (λ_{max}), between 300 and 400 nm. Only the monometallic and bimetallic complexes exhibit emission. The trimetallic and tetrametallic complexes are non-luminescent at room temperature. One plausible explanation would be that luminescence at room temperature is hindered or quenched by the presence of a high number of metal centers. The presence of these metal centers may have led to the decrease in the delocalization of the electrons in the conjugated system of the BL's, leading to an almost permanent "localization" by the electrons. Furthermore, the results may indicate that the complexes are not planar, as previously believed. Preliminary theoretical studies through simulation via the programs ACD ChemDraw® and CS ChemOffice® showed that the pyridine moieties attached to the fused rings of the bridging ligands are skewed out of plane, and therefore gave results that are inconsistent to complexes whose rigidity is enhanced by the attachment of more metal centers.

Table 2. Fluorescence spectroscopy data for the rhenium complexes in acetonitrile at $25^{0}C$.

Complex	λ_{ex} (nm)	λ_{em} (nm)
[Re(CO)$_3$Cl](tppq)	307	512
	414.5	496
[Re(CO)$_3$Cl]$_2$(tppq)	300.5	564.0,
	398	472.0,
		377.0
		470
[Re(CO)$_3$Cl]$_3$(tppq)	328	-
	412	-
[Re(CO)$_3$Cl]$_4$(tppq)	324	-
	400.5	-

Infrared spectroscopy (Table 3) showed that the complexes exhibited characteristic group absorptions corresponding to C–H, C–N, and C–C stretching vibrations. The metal salt precursor, Re(CO)$_5$Cl (Fig. 3) exhibited characteristic group vibrations attributed to Re–Cl (500–600 cm^{-1}) and C–O (2060–1900 cm^{-1}) stretching vibrations. The synthesized complexes possess characteristic group absorptions similar, but not identical to those of their precursors, Re(CO)$_5$Cl and tppq, another confirmation of the success of the synthetic procedure. The peaks corres-ponding to the C–O stretch somehow confirm the attachment of Re(I) metal center. As observed for all spectra, the C–O stretching frequencies are a bit lower compared to that of their precursor metal complex, largely due to the presence of strongly π-accepting bridging ligands. Broad bands in the C–O region of the spectra indicate the overlap of numerous peaks, another clear indication of binding of the 1, 2, 3, and 4 Re(I) metal centers to the BL's. Although

the number of peaks in the spectra are not a clear indication or conclusive of the attachment of the metal centers, it is still helpful to monitor any changes in the spectra as the complexes progress from mono- to tetrametallic.
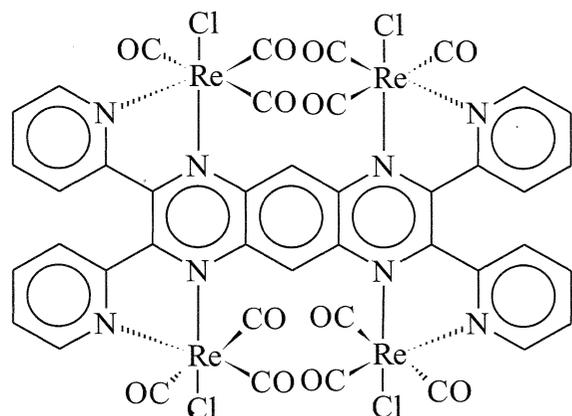

Figure 3. *Proposed structure of the tetra-metallic complex, [Re(CO)₃Cl]₄(tppq)*

Mass spectroscopy is another very useful technique in confirming the structure of the synthesized complexes. By examining and monitoring the molecular weights produced in the spectra, it can be concluded whether the desired number of metal centers have been successfully synthesized, exhibited by the presence of the molecular ion peak of each complex. Further fragmentation would lead to one of the most basic components of the complex, the BL as a result of fragmentation. The result of this technique alone may imply the success of the synthetic route employed. However, the technique does not determine the specific point of attachment of the metal centers on the ligands, especially for the bimetallic and trimetallic complexes. Only the molecular weights are the main concern for mass spectrometry. But further coupling the technique with other spectroscopic and electrochemical techniques would ensure the establishment of the photochemical and photophysical properties of the synthesized novel complexes.

Table 3. FT-IR data for the ligand and the rhenium complexes at 25⁰C

Complex	Transmittance (cm⁻¹)
tppq	3058.10, 3010.01, 2000–1650.65, 1586.87–1401.08, 1344.87–1270.85
[Re(CO)₃Cl](tppq)	3058.59, 2023.97, 1923.39, 1881.07, 1607.29, 1345.09, 531.51, 497.643
[Re(CO)₃Cl]₂(tppq)	3084.94, 2024.63, 1923.76, 1881.43, 1721.50, 1602.90–1349.49, 1349.49, 1271.32, 558.63, 535.61, 496.62, 434.71
[Re(CO)₃Cl]₃(tppq)	3060.59, 2022.38, 1922.04 (broad), 1601.70–1474.32, 1350.83, 1258.20, 1165.57–991.89, 891.55–714.09
[Re(CO)₃Cl]₄(tppq)	3056.73, 2026.24, 1937.47, 1914.32, 1597.84–1458.89, 1161.71–988.03, 899.27–729.45, 532.61, 528.75, 478.58

Proton (¹H) nuclear magnetic resonance (NMR) is still another technique very useful in characterizing inorganic complexes, such as the polymetallic rhenium(I) complexes. The ¹H NMR data are shown in Table 4. The bridging ligand tppq is symmetric with respect to both the x-axis and y-axis and only has 5 types of protons. Electron-withdrawing groups such as amino groups (–NR) cause a downfield shift of NMR signals, and therefore protons within their vicinity somewhat have higher chemical shifts. Rhenium(I) is paramagnetic, and should therefore produce a spectra beyond the δ = 0 to 8 ppm. But subjecting the complexes to the regions beyond 8 ppm did not show any peaks at all, therefore the study has been confined to the δ = 0 to 8 ppm region only.

Table 4. ^{1}H NMR data in CDCl$_3$

Complex	δ (ppm)
tppq	9.14 (s, 2H), 8.38 (dm, 4H), 8.20 (d, 4H), 7.93 (td, 4H), 7.31 (dd, 4H)
[Re(CO)$_3$Cl](tppq)	9.22 (s, 2H), 8.45 (dm, 4H), 8.09 (d, 4H), 7.60 (td, 4H), 7.26 (dd, 4H)
[Re(CO)$_3$Cl]$_2$(tppq)	9.23 (s, 2H), 8.03 (d, 4H), 7.62 (td, 4H), 7.26 (dd, 4H)
[Re(CO)$_3$Cl]$_3$(tppq)	9.85 (t, 4H), 9.59 (s, 1H), 9.54 (s, 1H), 9.21 (t, 4H), 8.60 (d, 4H), 8.20 (t, 4H)
[Re(CO)$_3$Cl]$_4$(tppq)	9.87 (d, 4H), 9.59 (s, 1H), 9.54 (s, 1H), 9.23 (t, 4H), 8.60 (d, 4H), 8.12 (t, 4H)

By close observation, it is striking to note that the ^{1}H-NMR spectra of the complexes have similar chemical shifts. This may lead to the conclusion that these complexes may have nearly the same symmetry, differing only in the presence of one Re(I) center. It is also possible that the addition of more Re(I) metal centers does not significantly affect the applied field strength experienced by the protons.

Establishment of the electrochemical property of the synthesized complexes is important especially if they were to be applied in electrocatalysis. Distinct peaks at the positive (+) and negative (–) regions of the voltammogram, similar to those seen in analogous complexes such as Re(CO)$_3$Cl(dpp), [Re(CO)$_3$Cl]$_2$(dpp), Re(CO)$_3$Cl(dpq), and [Re(CO)$_3$Cl]$_2$dpp are evident.[25,29,31,32,33] The cyclic voltammograms (see Table 5) of all complexes are dominated by metal-localized oxidation and ligand-localized reductions, as observed in analogous complexes. Reduction in the complexes is attributed to the tppq/tppq$^-$ reductive couple. While oxidation is attributed to Re^I/Re^{II}, a more positive value for oxidation and reduction generally implies greater ease of oxidation of the Re(I) metal centers and easier reduction of the BL's. It can be observed experimentally that as more metal centers are bound to the BL's, the more difficult it is to reduce the BL's, meaning the more Re(I) metal

is attached to the BL, the more "localized" the electrons become, thus hindering the oxidative ability of the BL.

Table 5. Electrochemical data

Complex	$E_{1/2}$ (V)
[Re(CO)$_3$Cl](tppq)	+1.501, –0.596, –1.093
[Re(CO)$_3$Cl]$_2$(tppq)	+1.576 (E_a), –0.612, –1.342
[Re(CO)$_3$Cl]$_3$(tppq)	–0.875, –1.239 (E_c)
[Re(CO)$_3$Cl]$_4$(tppq)	+1.019, +1.538 (E_a), –0.950, –1.400 (E_c)

CONCLUSION

By combining all known spectroscopic techniques, with the addition of cyclic voltammetry, it was deduced that the synthesis of the polymetallic rhenium(I) complexes was a success with all conditions optimized, although no single characterization technique for identification was conclusive. It was observed that by comparing the synthesized complexes with other rhenium(I) polypyridyl analogs, a similarity between their spectroscopic properties was disclosed and therefore was a very useful reference in the characterization and analysis of the novel complexes. The electrochemical properties were shown to consist mainly of metal-localized oxidation and ligand-localized reduction, a property shared by most common rhenium complexes. More detailed techniques however are recommended for a more efficient characterization of the synthesized complexes, which include spectroelectrochemical technique for the confirmation of the assignments of the electronic transitions observed, elemental analysis and Raman spectroscopy for a more precise determination of the number of attached rhenium centers in each complex.

Since the polymetallic rhenium(I) complexes have been successfully synthesized and characterized, the next phase for the project is the application of these complexes towards the electrochemical reduction of CO$_2$. This phase would then determine which among the complexes, if not all of them, are effective

electrocatalysts towards the conversion of CO_2 into various products ideally CO and methane.

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