

## 4 CONCLUSION

The present work described the synthesis and chemical properties of the three ruthenium(II) complexes with the new bidentate ligand, 2-(phenylazo)pyrazine or azine which prepared from 2-aminopyrazine and nitrosobenzene. All of compounds were characterized by using elemental analysis, FAB mass spectrometry, Infrared spectroscopy, UV-Visible absorption spectroscopy, 1D and 2D NMR spectroscopy and their electrochemical properties were studied by cyclic voltammetry. The solid state molecular structures of the two complexes, *ctc* and *tcc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] were determined by X-ray crystallography.

The ligand exhibited a sharp band at 1388 cm<sup>-1</sup>, corresponded to N=N stretching mode. In the three complexes,  $\nu(\text{N}=\text{N})$  was red shifted by 80-200 cm<sup>-1</sup>, which was a good indication of N-coordination. UV-Visible spectral studies of the complexes revealed that the blue complexes (*ctc* and *ccc*) exhibited highly intense MLCT transitions at higher energy than the green (*tcc*) complex. The energy of the MLCT transition is allowed transition. The <sup>1</sup>H, <sup>13</sup>C and DEPT NMR spectra between the ligand and complexes were compared in order to study the structures and the stereochemistry of the compounds. Results of 2D NMR experiments, <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>13</sup>C HMQC, corresponded with 1D NMR data. Cyclic voltammetric studies revealed that the free ligand displayed one quasireversible two-electron reduction at -1.28 mV. Nonetheless, the reduction potential of the ruthenium complexes showed a positive shift from the free ligand. In addition, the first ligand reduction potential of the *trans* isomer showed less negative values than the *cis* isomers. This indicated that the azine in the *trans* form could accept electron easier than that in the *cis* complexes. In the oxidation range, the *cis* complexes exhibited higher potentials than the *trans* complex. Therefore, the metal dπ levels in the *cis* isomers were more stabilized than the *trans* isomer. As a result Ru(II)→Ru(III) oxidation in *cis* became more difficult to

be oxidized and were observed at higher potential. The trend in the MLCT band positions of the three isomers also supported these experimental results.

The X-ray structural studies confirmed that the blue complex belonged to *ctc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] (C<sub>2</sub> symmetry) and the green complex belonged to *tcc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] (C<sub>2</sub> symmetry) configurations. The coordination geometry of the two complexes is distorted octahedral. The N-N distances of coordinated N=N in the *ctc* and *tcc* complexes were shorter than that in some free azo ligands family. This shortening may be due to the  $\pi$ -backbonding effect. Moreover, these results corresponded to the data from Infrared spectroscopy, the N=N stretching mode of the *ctc* and *tcc* isomers appeared at lower energy than the free azine ligand.