

Synthesis, Characterization with Photophysical and Ion Binding Properties of Ruthenium Complex

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Host-guest chemistry has attracted much attention in the past several decades and the design of highly selective and sensitive receptors for metal ions is of great importance in the area of ion transport, chemosensing, biomedical as well as environmental applications. Herein we report the synthesis, photophysics and ion-binding studies of new ruthenium(II) 2,2'-bipyridine complex containing crown pendants. The binding constants of the complex for different metal ions were determined by UV-visible absorption.

Keywords: Ion-binding, Ruthenium, Complex, Photophysics.

INTRODUCTION

Since the cation-binding ability of macrocycles was recognized by Pedersen¹. The design of highly selective and sensitive receptors for metal ions is of great importance in the area of ion transport, chemosensing, biomedical as well as environmental applications. Sodium, potassium, magnesium and calcium are involved in biological processes such as transmission of nerve impulses, muscle contraction, regulation of cell activity, etc.². Moreover, various metal ions are important components of metalloenzymes. In chemical oceanography, it has been demonstrated that some nutrients required for the survival of microorganisms in sea water contain zinc, iron and manganese as enzyme cofactors. Finally, it is well known that mercury, lead and cadmium are toxic for organisms and early detection in the environment is desirable. Thus there is a strong need to design selective and specific molecular chemoreceptors for ion recognition.

The design and synthesis of inorganic sensors have received considerable attention in the past decades³ and most of the works have been focused on the design of selective receptors for either alkali or alkaline earth cations. The first example of a phthalocyanine analogue of copper(II) with four crown ether voids was reported by Nishiyama and Kobayashi⁴ in which the complex showed a high tendency towards aggregation, especially K⁺-induced aggregation that gave rise to large spectrochemical changes, which enabled the phthalocyanine to be used as a colorimetric reagent. After that, there have been quite a number of reports on the utilization of transition metal complexes containing a macrocyclic binding site for the sensing of alkali and alkaline earth metal ions with the increasing

awareness of the interesting photochemical and photophysical properties associated with the metal-to-ligand charge-transfer (MLCT) excited state⁵⁻⁷.

Herein we report the synthesis of a new macrocyclic ligand as well as its corresponding ruthenium complex. The synthesis, photophysics and ion-binding studies are described. The binding constants of the complex for different metal ions were determined by UV-visible absorption.

EXPERIMENTAL

cis-[Ru(bpy)₂Cl₂].2H₂O,⁸ was prepared according to literature procedures. Lithium perchlorate was recrystallized from absolute ethanol prior to use. All other reagents and solvents were purchased of analytical grade from Acros or Fluka and used as received. ¹H NMR spectra were recorded on a Bruker DPX 400 (400 MHz) Fourier-transform NMR spectrometers with chemical shifts reported relative to tetramethyl silane, Me₄Si. Positive and negative ion fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Finnigan MAT95 mass spectrometer.

The ligand (L) was prepared by modification of a literature method¹⁰. To a mixture of 4,4'-diamino-2,2'-bipyridine (0.5 g, 2.69 mmol) and anhydrous Na₂CO₃ (0.7 g, 6.6 mmol) in dry CH₃CN (200 mL) under N₂ was added 1,11-diiodo-3,6,9-trioxaundecane (1.22 g, 2.9 mmol) in dry CH₃CN (50 mL) in a dropwise manner over 0.5 h, which was then heated to reflux for 5 days. The solvent was then removed in vacuo and water (100 mL) was added and the mixture was extracted three times with CH₂Cl₂. The combined extracts were dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure to

dryness. The residue was column chromatographed on silica gel using CHCl_3 -methanol (50:1, v/v) as eluent to afford the product. Subsequent trituration and recrystallization from CHCl_3 -hexane gave **L** as pale yellow crystals. Yield: 53 mg, 6%. $^1\text{H NMR}$ (CDCl_3): δ 9.05 (dd, $J_1 = 4.2$ Hz, $J_2 = 1.6$ Hz; 2H, bpy), 8.58 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.6$ Hz; 2H, bpy), 7.59 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.2$ Hz; 2H, bpy), 3.82 (m, 4H, NCH_2), 3.74 (m, 4H, CH_2O), 3.51 (m, 4H, CH_2O), 3.37 (m, 4H, CH_3).

The ruthenium complex $[\text{Ru}(\text{bpy})_2(\text{L})](\text{ClO}_4)_2$ was synthesized according to modification of a literature procedure for related compounds⁸ (Fig. 1). To a solution of *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (200 mg, 0.38 mmol) in absolute ethanol (80 mL) was added the ligand, **L**, (78 mg, 0.42 mmol) and the mixture was heated to reflux under N_2 for 5 h, during which the purple black solution turned red orange. After removal of the solvent under reduced pressure, the residue in the form of chloride salt was dissolved in a minimum amount of water and metathesis reaction upon addition of a saturated aqueous solution of LiClO_4 afforded the desired complex as a red orange solid, which was then obtained by filtration and subsequent recrystallization by vapor diffusion of diethyl ether into acetonitrile solutions of the complexes gave the complexes as red crystals. Yield: 40 mg, 31%. $^1\text{H NMR}$ (CD_3CN): δ 8.69 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz; 2H, L-bpy), 8.50 (m, 4H, bpy), 8.08 (m, 2H, bpy), 7.99 (m, 2H, bpy), 7.89 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.2$ Hz; 2H, L-bpy), 7.83 (d, $J = 5.6$ Hz; 2H, bpy), 7.62 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.1$ Hz; 2H, L-bpy), 7.55 (d, $J = 5.6$ Hz; 2H, bpy), 7.43 (m, 2H, bpy), 7.24 (m, 2H, bpy), 5.04 (b, 2H, NH), 3.74 (m, 8H, CH_2O), 3.41 (m, 4H, CH_2N). Positive FAB-MS: m/z 857 ($[\text{M}-\text{ClO}_4]^+$), 757 ($[\text{M}-2\text{ClO}_4]^+$).

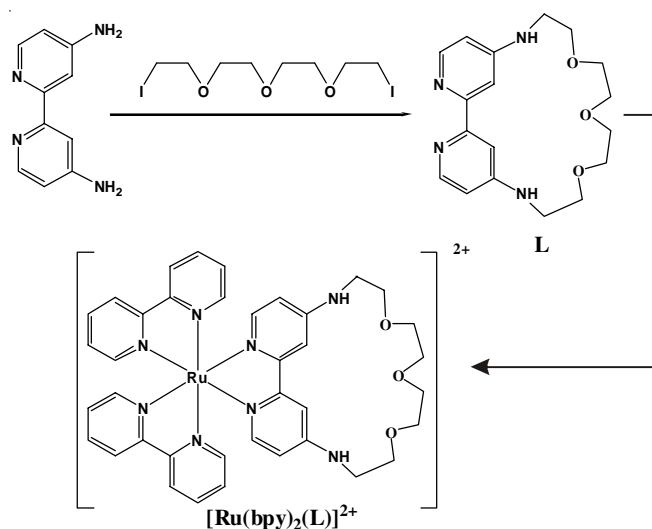


Fig. 1. Synthetic routes for the target ligand and complex

Ion-binding studies: The electronic absorption and emission spectral titration experiments for binding constant determination were performed on a Hewlett-Packard 8452A diode array spectrophotometer and on a Spex Fluorolog-2 Model F111 fluorescence spectrofluorometer, respectively, at a controlled temperature of 25 °C. Supporting electrolyte (0.1 M $n\text{Bu}_4\text{NClO}_4$) was added to maintain a constant ionic strength of the sample solution in order to avoid any changes arising from a change in the ionic strength of the medium.

The binding constants, K_s for the 1:1 complexation that control the equilibrium between a cation, M and complex, C and their adduct, C(M),



where K_s can be written as

$$K_s = \frac{[\text{C}(\text{M})]}{[\text{C}][\text{M}]}$$

was obtained by a nonlinear least-squares fit of the absorbance (X) vs. the concentration of the metal ion added (c_M) according⁹ to eqn. 1:

$$X = X_o + \frac{X_{\text{lim}} - X_o}{2c_o} \left[c_o + c_M + \frac{1}{K_s} - \left[\left(c_o + c_M + \frac{1}{K_s} \right)^2 - 4c_o c_M \right]^{1/2} \right]$$

where c_o is the initial concentration of complex, X_o , X and X_{lim} are the initial absorbance of complex, absorbance after the addition of a given amount of salt at concentration c_M and the limiting absorbance of complex in fully complexed state, respectively, at a selected wavelength. Eqn. 1 can also be used for the emission method, except that absorbance was replaced by emission intensity.

RESULTS AND DISCUSSION

The ruthenium(II) complex showed an intense band at 287 nm and low-energy absorption bands at 424 nm in acetonitrile. With reference to previous studies on the related ruthenium(II) polypyridine systems¹¹, the higher energy absorption was assigned as intraligand (IL) transition, while the low-energy bands were assigned to the metal-to-ligand charge transfer [MLCT, $d\pi(\text{Ru}) \rightarrow \pi^*(\text{bpy})$] transitions, which were absent in the electronic absorption spectra of the free ligands. The electronic absorption spectrum of the ruthenium(II) complex was shown in Fig. 2.

As shown in Fig. 3, the ruthenium(II) complex $[\text{Ru}(\text{bpy})_2(\text{L})](\text{ClO}_4)_2$ was found to emit strongly with emission maxima at 610 nm at room temperature upon excitation with UV in degassed CH_3CN solution, assigned as derived from a triplet MLCT state, similar to that observed in other related

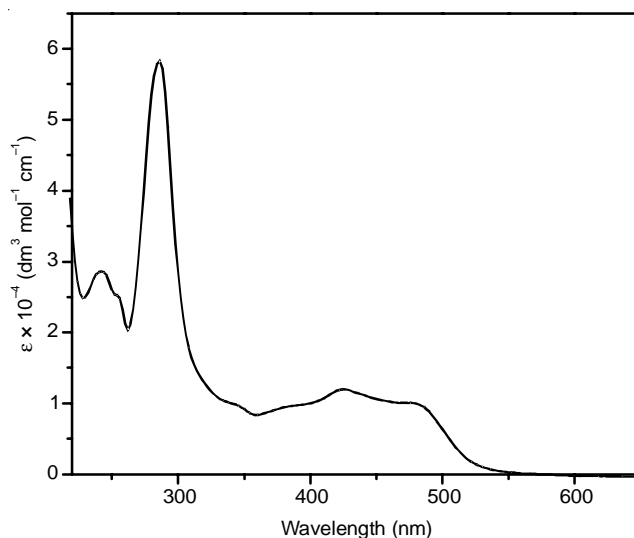


Fig. 2. Electronic absorption spectrum of $[\text{Ru}(\text{bpy})_2(\text{L})](\text{ClO}_4)_2$ in CH_3CN at 298 K

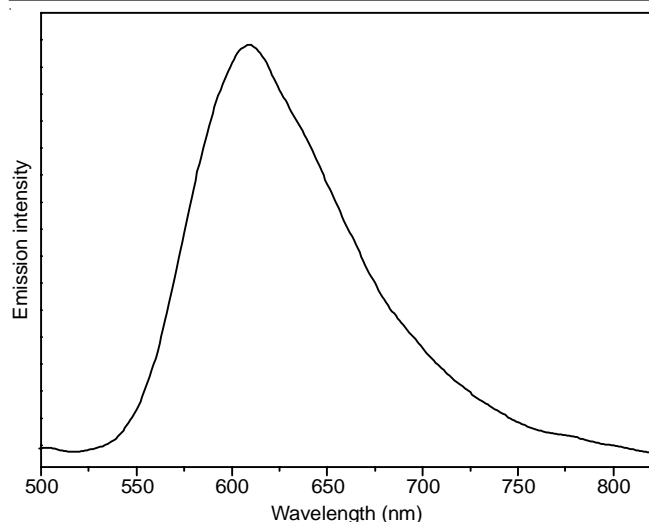


Fig. 3. Emission spectrum of $[\text{Ru}(\text{bpy})_2(\text{L})](\text{ClO}_4)_2$ in degassed CH_3CN at 298 K

ruthenium(II) diimine systems¹¹⁻¹³. But the complex showing a relatively lower luminescence quantum yield (0.014) in degassed acetonitrile comparing¹⁴ to that of $[\text{Ru}(\text{bpy})_3]^{2+}$, probably due to the electron-donating ability of the diaza group on the crown that was directly coordinated to the bipyridine unit, which would lead to quenching of the emissive ³MLCT state by photoinduced electron transfer.

The cation-binding ability of the complexes was studied by electronic absorption spectroscopic method. Upon addition of metal ions, such as Ca^{2+} , Zn^{2+} and Cd^{2+} to the CH_3CN (0.1 M $n\text{Bu}_4\text{NClO}_4$) solution of $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ induced large spectral changes in the UV-visible spectra. The band at about 360 nm experiences a blue shift in energy upon addition of Ca^{2+} ion providing resolution of the $d\pi(\text{Ru}) \rightarrow \pi^*$ (Schiff base) MLCT band. The shift was ascribed to the binding of the cations to the polyether cavity, as similar shifts were observed in the binding studies of other transition metal crown-containing complexes¹⁵. The spectral changes were ascribed to the binding of the cations to the polyether cavity, as similar shifts were observed in the binding studies of other transition metal crown-containing complexes¹⁵. Fig. 4 showed the UV-visible spectral changes obtained by monitoring the electronic absorption spectra of $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NClO}_4$) upon addition of Ca^{2+} ion. The binding constant could be obtained by a nonlinear least-squares fit⁹ of the absorbance vs. the concentration of the added metal ions (CM) according to eqn. 1, which was shown in Fig. 5. Similar results were obtained for the other metal ions such as Cd^{2+} and Zn^{2+} . The binding constants for different metal ions were summarized in Table-1. The results showed that $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ exhibited a higher binding affinity towards transition metal ions than alkaline earth metal ions.

Conclusion

In conclusion, we have successfully synthesized a ruthenium(II) bipyridine complex containing crown ether pedant with the synthetic route as shown in Fig. 1. The synthesis, photophysics and ion-binding studies are discussed. Addition of the alkaline earth metal ions and transition metal ions such as Ca^{2+} , Zn^{2+} and Cd^{2+} ions to an acetonitrile (0.1 M $n\text{Bu}_4\text{NClO}_4$)

Metal ion	Ca^{2+}	Zn^{2+}	Cd^{2+}
$\log K_s$	2.10	3.61	4.33

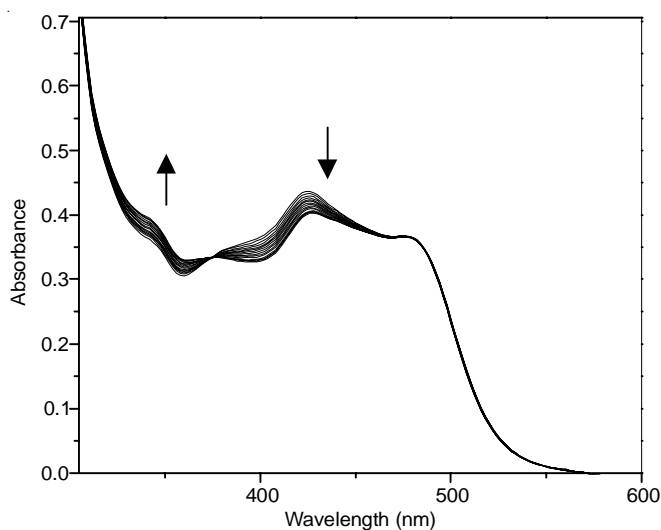


Fig. 4. UV-visible spectral changes of $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ in CH_3CN (0.1 M $n\text{Bu}_4\text{NClO}_4$) upon addition of $\text{Ca}(\text{ClO}_4)_2$

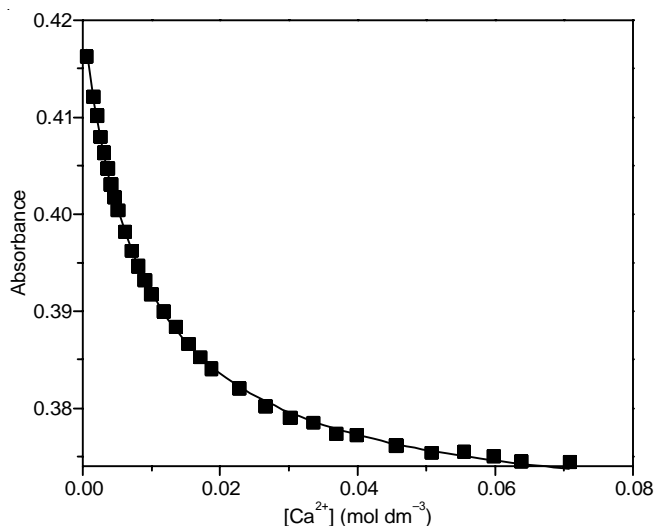


Fig. 5. A plot of absorbance at 414 nm (■) vs. $[\text{Ca}^{2+}]$ and its theoretical fit (—) for the binding study of $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ in acetonitrile (0.1 M $n\text{Bu}_4\text{NClO}_4$)

solution of $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ induced large changes in the UV-visible spectra with perfectly clean isosbestic points, which have been attributed to the good electron-donating nature of the nitrogen atoms directly attached to the bipyridine unit. The stability constants of the complexes with different metal ions were determined and that shows its binding ability is much stronger for transition metal ions than alkaline earth metal ions.

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REFERENCES

1. C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2. (a) J.D. Lamb, R.M. Izatt, J.J. Christensen and D.J. Eatough, in ed. G.A. Melson, *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press, New York, p. 145 (1979); (b) J.D. Lamb, R.M. Izatt, C.S. Swain and J.J. Christensen, *J. Am. Chem. Soc.*, **102**, 475 (1980).
3. (a) C.J. Pedersen, *Angew. Chem. Int. Ed. Engl.*, **27**, 1021 (1988); (b) J. Simon, M.K. Engel and C. Soulie, *New J. Chem.*, **16**, 287 (1992).
4. N. Kobayashi and Y. Nishiyama, *J. Chem. Soc. Chem. Commun.*, 1462 (1986).
5. P.D. Beer, O. Kocian, R.J. Mortimer and C. Ridgway, *J. Chem. Soc., Dalton Trans.*, 2629 (1993).
6. T. Lazarides, T.A. Miller, J.C. Jeffery, T.K. Ronson, H. Adams and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, 528 (2005).
7. K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano and T. Nagano, *J. Am. Chem. Soc.*, **126**, 12470 (2004).
8. B.P. Sullivan, D.J. Salmon and T.J. Meyer, *Inorg. Chem.*, **17**, 3334 (1978).
9. J. Bourson, J. Pouget and B. Valeur, *J. Phys. Chem.*, **97**, 4552 (1993).
10. G. Topal, N. Demirel, M. Togrul, Y. Turgut and H. Hosgoren, *J. Heterocycl. Chem.*, **38**, 281 (2001).
11. A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Von Zelewsky, *Coord. Chem. Rev.*, **84**, 85 (1988).
12. E.A. Seddon and K.R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam (1984).
13. R.A. Krause, *Struct. Bonding*, **67**, 1 (1987).
14. J.V. Caspar and T.J. Meyer, *J. Am. Chem. Soc.*, **105**, 5583 (1983).
15. Y.L. Pui, Ph.D. Thesis, *Syntheses, Luminescence Studies and Host-Guest Chemistry of d^{10} and d^6 Metal Complexes Containing Diimine and/or Chalcogenolate Ligands*, The University of Hong Kong (2000).