

SPECTROSCOPIC CHARACTERIZATION OF CROCONATE BRIDGING COMPLEX: CONVERSION OF RHODIZONATE (C₆O₆²⁻) TO CROCONATE BRIDGING LIGAND IN A PYRIDINE MODIFIED LARGE MACROCYCLIC METAL ARRANGEMENTS

MD. MAHBUBUL ALAM*, RAMKRISHNA SAHA, MD. REZWAN MIAH, BELAL AHMED AND IQBAL AHMED SIDDIQUEY¹

Department of Chemistry, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

ABSTRACT

Rhodizonic acid (H₂RHOD) was reacted with Co(PF₆)₂·6H₂O in the presence of pyridine modified large macrocyclic ligand (H₂Lopy) and triethylamine in N,N-dimethylformamide under argon atmosphere. Instead of [Co₄(RHOD)₂(Lopy)](PF₆)₂ (**1**), the main product of this reaction was a crystalline compound [Co₄(CROC)₂(Lopy)](PF₆)₂, which was isolated in low yield (< 25%). Based on the elemental analysis, ESI-mass spectroscopy, and infrared spectrum, the isolated compound was confirmed to be [Co₄(CROC)₂(Lopy)](PF₆)₂ (**2**), where CROC²⁻ is croconate anion C₅O₅²⁻.

Key words: Croconate bridging ligand, Macrocyclic metal arrangements, Rhodizonic acid

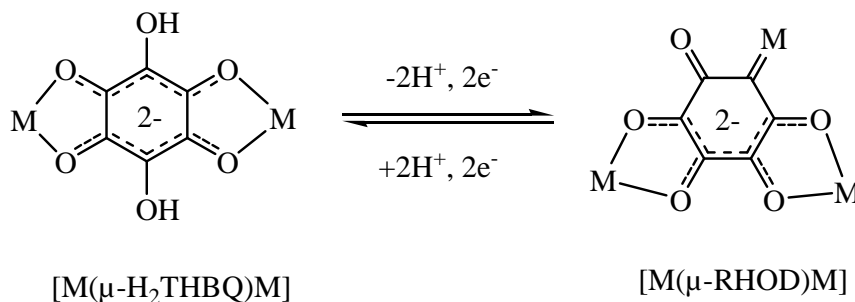
INTRODUCTION

Diverse functions of quinone derivatives in biology and industry appertain to their abilities of electron and proton transfer (Davidson 1992). This fascinating proton-coupled redox property has been stimulating synthetic coordination chemists to create an operative molecule-based material that consists of polynuclear transition metal complexes bearing quinone-frame ligand(s) (Masaoka *et al.* 2003). However, as *p*-benzoquinone has a very poor coordination ability, there is need to introduce coordinating functional groups onto the quinone frame to bridge two metals to yield polynuclear metal complexes. As a candidate for this type of quinone-based ligand, the authors planned to use rhodizonic acid in this report, as Asato *et al.* have very recently reported that the present quinone-based bridging ligand was successfully applied to create dinuclear metal complexes having [M(μ-H₂THBQ)M] structural motif (Asato *et al.* 2009 and Min *et al.* 2008). The most significant findings reported by Asato's group was that the [M(μ-H₂THBQ)M] unit quantitatively reacted with *p*-benzoquinone to give a [M(μ-RHOD)M] unit and hydroquinone, where H₂RHOD is rhodizonic acid. Another

*Corresponding author: <mahbubana-che@sust.edu>.

¹Department of Chemistry, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh.

important findings was the change in the bridging mode of the $C_6O_6^{2-}$ ligand before and after the $2H^+$, $2e^-$ -transfer process (Scheme 1).



Scheme 1

It is well known that super-exchange magnetic interaction between paramagnetic ions strongly depends on the bridging mode mediating the interaction. Thus, the similar change in the bridging mode induced by the $2H^+$, $2e^-$ acceptor process occurred on the $[M(\mu-RHOD)M]$ core can be theoretically applied to switch magnetic interaction between paramagnetic centers. Furthermore, a polynuclear transition metal complex which contains more than two units of $[M(\mu-RHOD)M]$ core could potentially show the redox-concerned catalytic activity, and so on. In order to create such a molecular system, the authors used a large macrocyclic ligand H_2Lopy that has already been reported to act as a tetranucleating ligand by Youshino *et al.* (2002) as shown in structure 1.

EXPERIMENTAL

All chemicals were purchased from Kanto Chemical Co., Ltd. and used with prior distillation. Elemental analyses were carried out using JM10 MICROCODER made by J. Science laboratory Co., Ltd. IR spectrum was recorded on IRPrestige-21 SHIMADZU spectrometer in the range 4000 – 400/cm as KBr pellets. UV-visible spectrum was measured on SHIMADZU-1800 UV-visible spectrophotometer. NMR spectrum was measured on Bruker Avance^{III}-400 with $CDCl_3$ as solvent. The positive-ion ESI-mass spectrum of complex was obtained with Quattro micro API spectrometer manufactured by Waters. All measurements were performed at room temperature ($25 \pm 2^\circ C$).

Synthesis of macrocyclic ligand (H_2Lopy) (Asato *et al.* 1999): Two hundred ml of methanol solution containing 13.082 g (0.074 mol) of 2-(chloromethyl) pyridine monohydrochloride was added to a solution of 11.94 g (0.0184 mol) of H_2L_{red} (Lindoy *et al.* 1998, Dwer *et al.* 1953, and Asato *et al.* 1995) and 13.150 g (0.157 mol) of $NaHCO_3$ dissolved in 250 ml of methanol. The reaction mixture was refluxed with stirring for 24

hours. After refluxing, the solution was evaporated into dryness and poured into 300 ml of water and extracted with 300 ml (100 ml \times 3) of chloroform. The combined organic layer was dried with anhydrous Na_2SO_4 , and then evaporated to dry. To the red sticky oil as the residue, a small quantity of acetone was added to give an off-white powder. The powder was washed with acetone and the yield was obtained, 5.184 g (28%). The structure of the ligand H_2Lopy was confirmed by ^1H NMR spectrum in CDCl_3 (Fig. 1).

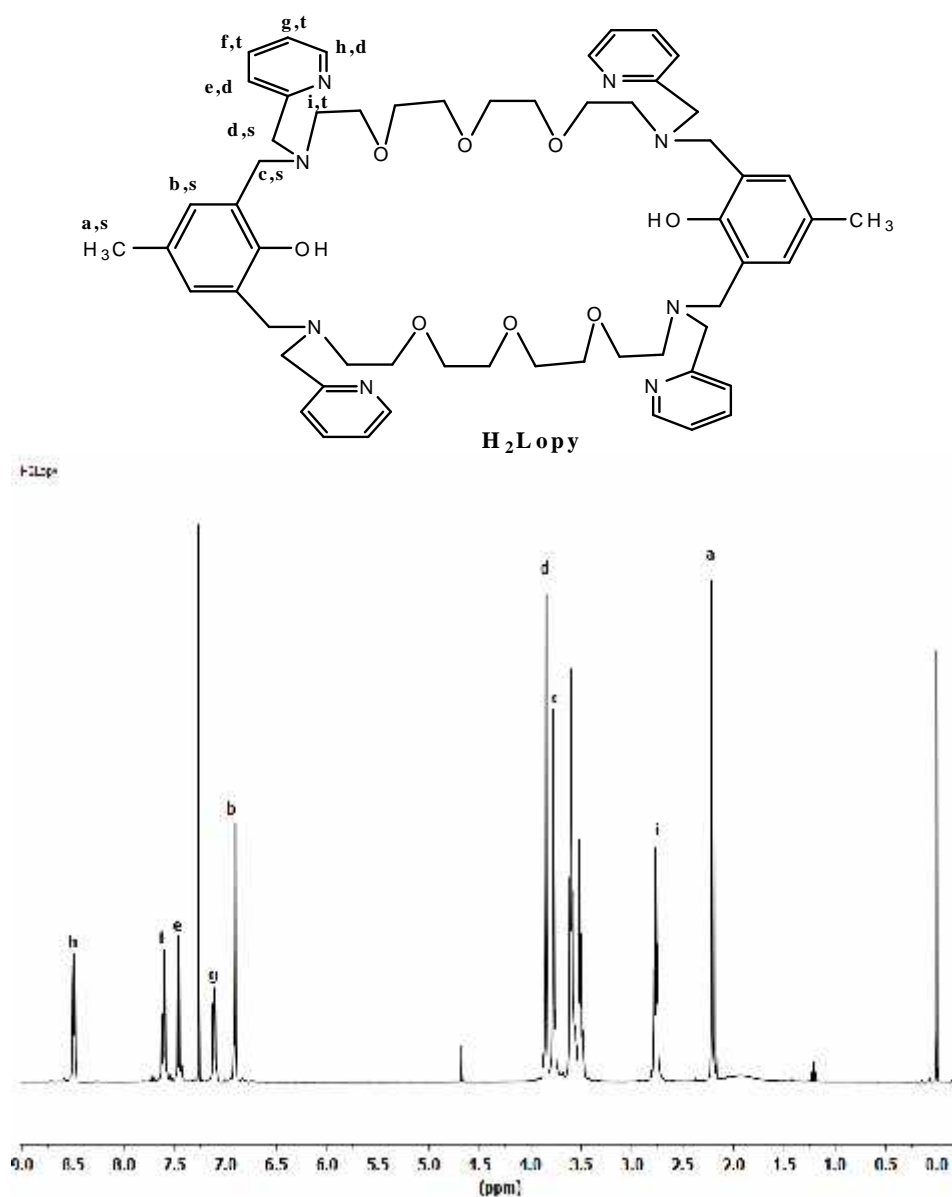


Fig. 1. ^1H NMR spectrum of H_2Lopy .

^1H NMR (400 MHz, CDCl_3 , 298K) (Fig. 1): 8.49 {d, 4H(h)}, 7.61 {t, 4H(f)}, 7.47 {d, 4H(e)}, 7.11 {m, 4H(g)}, 6.90 {s, 4H(b)}, 3.84 {s, 8H(d)}, 3.77 {s, 8H(c)}, 3.62-3.50 {m, 24H, $\text{CH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ }, 2.77 {t, 8H(i)}, 2.21 {s, 6H(a)} ppm.

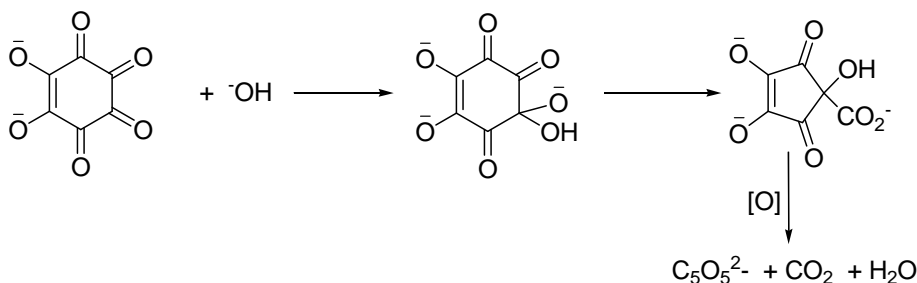
Synthesis of $[\text{Co}_4(\text{CROC})_2(\text{Lopy})](\text{PF}_6)_2$: In a 100 ml Schlenk tube, 0.162 g (0.355 mmol) of $\text{Co}(\text{PF}_6)_2 \cdot 6\text{H}_2\text{O}$ and 0.090 g (0.089 mmol) of H_2Lopy ligand were mixed in dry DMF (10 ml) under inert (argon) atmosphere. In another Schlenk tube, 10 ml of DMF solution containing 0.036 g (50 μl , 0.355 mmol) of triethylamine and 0.037 g (0.176 mmol) of rhodizonic acid (H_2RHOD) were mixed. The two solutions were mixed together under inert atmosphere. Very slow diffusion of diethyl ether gas into the solution gave brown crystals with 22% yield.

RESULTS AND DISCUSSION

With the aim of preparing $[\text{Co}_4(\text{RHOD})_2(\text{Lopy})](\text{PF}_6)_2$, $\text{Co}(\text{PF}_6)_2 \cdot 6\text{H}_2\text{O}$, macrocyclic ligand (H_2Lopy), triethylamine and H_2RHOD were reacted in DMF with a 4:1:4:2 stoichiometric ratio under inert atmosphere. Instead of $[\text{Co}_4(\text{RHOD})_2(\text{Lopy})](\text{PF}_6)_2$, the reaction mixture gave $[\text{Co}_4(\text{CROC})_2(\text{Lopy})](\text{PF}_6)_2$ by prolonged slow diffusion of diethyl ether gas with a low yield. The elemental analysis data obtained for the prepared complex are as follows:

$\text{C}_{68}\text{H}_{74}\text{Co}_4\text{F}_{12}\text{N}_8\text{O}_{18}\text{P}_2$ (FW 1817.02): Calculated: C, 44.95; H, 4.10; N, 6.17%, and Found: C, 43.52; H, 4.02; N, 5.97%.

Although tetrahydroxy-1,4-benzoquinone (Reinoso *et al.* 2007) and rhodizonate (Speier *et al.* 1997) anions are known to undergo ring contraction under aerobic basic condition to give $\text{C}_5\text{O}_5^{2-}$, CO_2 and water as shown in scheme 2, but the complex $[\text{Co}_4(\text{CROC})_2(\text{Lopy})](\text{PF}_6)_2$ was prepared under anaerobic condition. As the possibility of contamination by trace amount of oxygen cannot be excluded, reproducibility of the formation of the $\text{C}_5\text{O}_5^{2-}$ even under strict O_2 -free condition may suggest the mechanism for the reaction as shown in scheme 2.



Scheme 2. Change of rhodizonate ion into croconate ion.

The complex $[\text{Co}_4(\text{CROC})_2(\text{Lopy})](\text{PF}_6)_2$ is deep yellow in color, moderately crystalline, and air sensitive and becomes oily under exposure to open air within half an hour. This complex was identified by UV-visible, FT-IR and ESI-MS spectroscopic methods. Very strong bands appeared at 748 and 1527/cm in infrared spectrum were assigned to PF_6^- and C=O stretching of the croconate moiety, respectively. The moderate strong band at 1604/cm was assigned to pyridine C=N stretching (Fig. 2) (Nakamoto 2008).

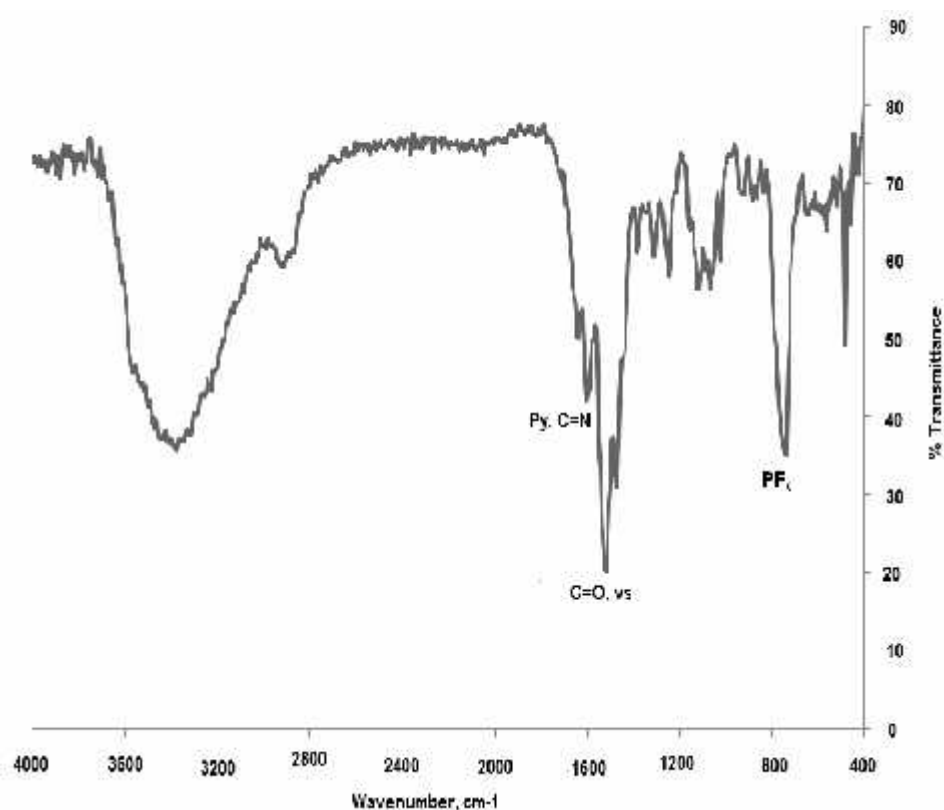


Fig. 2. Infrared spectrum of $[\text{Co}_4(\text{CROC})_2(\text{Lopy})](\text{PF}_6)_2$ complex.

The UV-visible spectrum (Fig. 3) was measured in acetonitrile which showed a characteristic band at 358 nm assigned to C_5O_5 -centered π - π^* absorption (Speier *et al.* 1997). In ESI-MS spectrum, a characteristic molecular ion $[\text{Co}_4(\text{CROC})_2(\text{Lopy})]^{2+}$ peak was detected at $m/z = 763.1$. The comparison of the measured isotope pattern for the molecular ion peak with its simulation is as shown in Fig. 4.

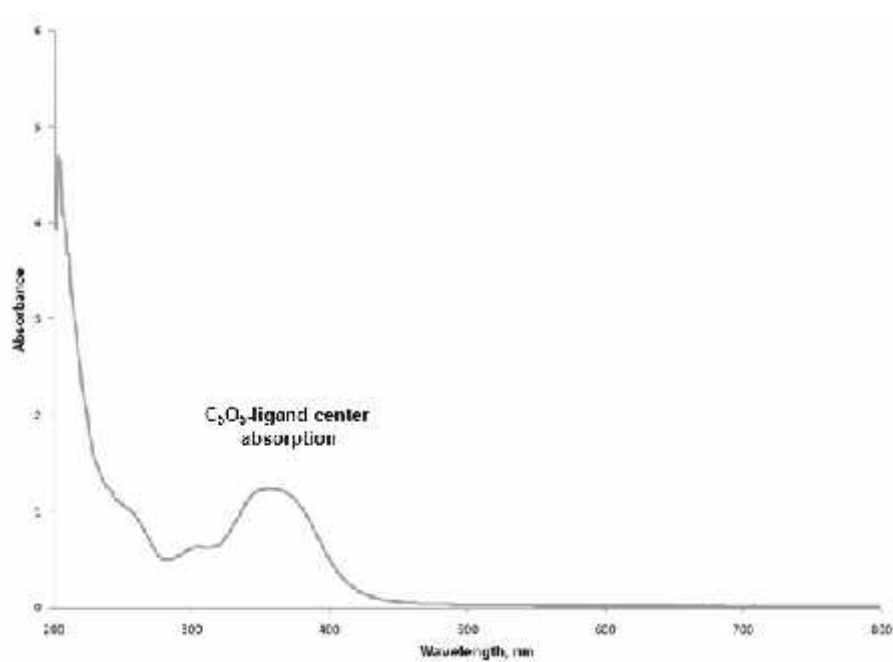


Fig. 3. UV-visible spectrum of $[\text{Co}_4(\text{CROC})_2(\text{Lopy})](\text{PF}_6)_2$ complex measured in MeCN.

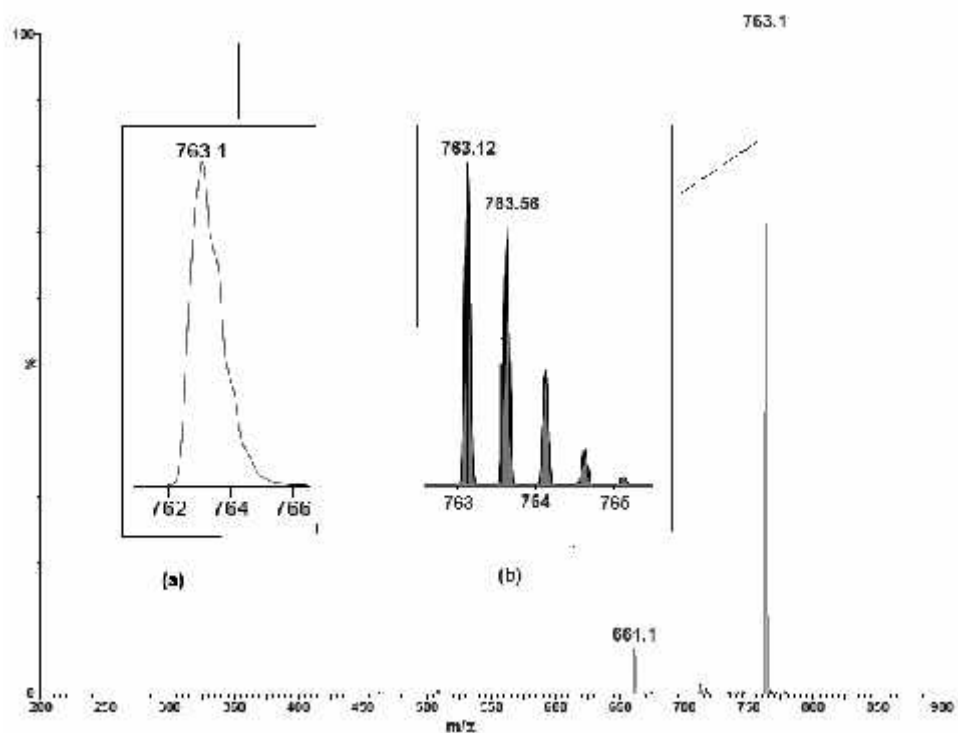
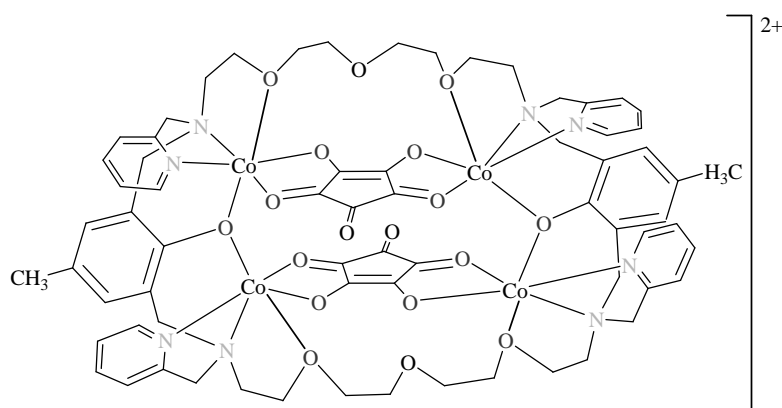


Fig. 4. ESI-mass spectrum of $[\text{Co}_4(\text{CROC})_2(\text{Lopy})]^{2+}$ measured in CH_3CN solution. (a) Measured and (b) calculated isotope patterns.

The possible tetranuclear structure is shown in structure 2. Each Co(II) ion has a similar six coordination attained by two nitrogen (amine-N and pyridine-N) and four oxygen (two from the $C_5O_5^{2-}$ chelation, one from phenoxy-O and the other from macrocyclic ligand) atoms.



Structure 2. Tetranuclear structure of $[Co_4(CROC)_2(Lopy)]^{2+}$ ion.

CONCLUSIONS

In this paper authors found the change of rhodizonate to bridging croconate ion in a tetranuclear macrocyclic arrangement. The reproducibility of the formation of the croconate ion even under strict O_2 -free condition suggested the mechanism occurring ring contraction under aerobic basic condition to give $C_5O_5^{2-}$, CO_2 . The cobalt croconate complex was confirmed by elemental analysis and ESI-MS spectroscopy. Infrared spectrum data supported the presence of PF_6^- , C=O, and C=N groups. Finally, based on the UV-visible and IR spectroscopic data, authors suggested the octahedral geometry of tetranuclear macrocyclic metal complex.

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