



Synthesis and Characterization of new Binuclear Chromium, Cadmium Complexes based on Terpyridine and Phenanthroline

ALIREZA OVEISIKEIKHA¹ and HAMIDEH SARAVANI^{2*}

^{1,2}Inorganic Chemistry Laboratory, Department of Chemistry, University of Sistan and Baluchestan, P. O. Box 98135-674, Zahedan, Iran.

*Corresponding author E-mail: saravani@chem.usb.ac.ir

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ABSTRACT

In this research, four binuclear complexes: [(phen)Cd(NO₃)₂(μ-phen-dion)Cr(NO₃)₂(phen)](NO₃)₂, [Cr(4-Ptpy)(μ-phen-dion)](NO₃)[Cd(4-Ptpy)(μ-phen-dion)](NO₃), [Cr(4-Ptpy)(μ-phen-dion)](NO₃)Cr(4-Ptpy)(μ-phen-dion)](NO₃), and [Cd(4-Ptpy)(μ-phen-dion)](NO₃)[Cd(4-Ptpy)(μ-phen-dion)](NO₃) were synthesized using reaction of chromium(III) nitrate nonahydrate, cadmium (II) nitrate tetrahydrate, phenidion, and 4-phenylterpyridine. The complexes were characterized using FT-IR spectroscopy, UV-Vis spectroscopy, ¹H NMR, elemental analysis, and cyclic voltammetry (CV). These complexes were found to be binuclear coordination complexes. The chromium and cadmium centers were achieved hexacoordination by coordinating with 4-phenylterpyridine groups, as tridentate chelating ligands and phenidion as bidentate chelating ligands.

Keywords: Binuclear complex, Phenidion, chromium, Cadmium, and terpyridine.

INTRODUCTION

Oligopyridines and their metal complexes have gained extensive attention in the last decades¹. The materials including the metal-coordinated 2,2':6':2''-terpyridines (tpy) with spacers at C(4') have opened up new opportunities for various applications in electronics, catalysis, energy, and medicine due to their electron transfer properties². The role of metal ions in the structure and function of binuclear complexes is essential, yet often unknown at the mechanistic and molecular level³. The hypotheses about principles governing selectivity and specificity

of oligopyridines for a given bridged metal are often based on theoretical assumption.

An attractive metal-binding ligand is tpy which has an exceptionally well understood coordination chemistry. Many substitutions at C(4') directly linked to the pyridine ring, such as hydroxyl,⁴ chloro,⁵ bromo,⁶ methylthiol,⁷ methylsulfonyl,⁸ dimethylamino,⁹ and phenyl have been prepared.

Recently, many efforts have been performed in the synthesis and characterization of the binuclear complexes¹⁰⁻¹³. The bridged dinuclear complexes,



in which the two metal centers are coupled each other in a conjugated system, are shown to be promising materials for new molecular electronic or magnetic materials¹⁴⁻¹⁹. Therefore, it is very important to investigate the synthesis and properties of these binuclear complexes. Hence, we decided to synthesize new binuclear complexes that can use as semiconductors.

EXPERIMENTAL

Materials and physical techniques

All synthetic work was performed at 60°C. The water was distilled and deionized. Cr(NO₃)₃·9H₂O, Cd(NO₃)₂·4H₂O, phendion, 4-phenylterpyridine were purchased from Merck Chemical Co. FTIR spectra were recorded as KBr pellets on a FT-IR JASCO 460 spectrophotometer and the UV-Vis spectra were taken at room temperature on a JASCO 7850 spectrometer. Cyclic voltammetry was performed at 20°C in an DMF solution with 0.1M TBAH as a supporting electrolyte at scan rate 100 mV s⁻¹. ¹H NMR spectra were recorded on a Bruker AM 300 MHz spectrophotometer.

Synthesis of [(4-Ptpy)Cr(NO₃)₃](μ-phen-dion)Cr(NO₃)₃(4-Ptpy)](NO₃)₄

To an aqueous solution containing chromium nitrate (1 mmol), phendion in ethanol (1 mmol) was added slowly and then the mixture was stirred at 60°C about 48 hours. After that, additional chromium nitrate (1 mmol) was then added to the solution and was stirred at the same temperature. Following After 24 h, 2 mmol of 4-Ptpy was added dropwise to the aqueous solution with continuous stirring for 3 days. Finally, solution filtered off and left to evaporate in beaker in air at room temperature, and green color crystals were formed. FT-IR (KBr) ν = 3391 m, 2477 m, 1705 m, 1613 s, 1453 m, 1333 s, 835 s, 665 s (cm⁻¹). CHN Anal., Found; C, 57.80; H, 3.15; N, 15.81. Calc.; 57.91; H, 3.27; N, 15.93. ¹H NMR (DMSO-d₆): δ = 9.06 (4H, m), 8.71 (4H, d, J = 17 Hz), 8.16 (4H, d, J = 19 Hz), 7.89 (4H, m), 7.64-6.98 (20H, m), 2.87 (1H, s), 2.64 (1H, s). UV (DMF): λ max = 570, 309, and 263 nm.

Synthesis of [(4-Ptpy)Cd(NO₃)₃](μ-phen-dion)Cr(NO₃)₃(4-Ptpy)](NO₃)₃

To prepare the [(4-Ptpy)Cd(NO₃)₃](μ-phen-dion)Cr(NO₃)₃(4-Ptpy)](NO₃)₃, chromium nitrate

(1 mmol), was added slowly to phendion (1 mmol) in ethanol, and then the mixture was stirred at 60°C for 48 h, and then a dark colour solution was obtained. After that, cadmium(II) nitrate tetrahydrate (1 mmol) was added dropwise to the reaction mixture and it was stirred. After 24 h, 2 mmol of 4-Ptpy was added to solution, and it turned to red colour. Then it was stirred for 3 days, and the solution was filtered. After 5 days, red crystals of [(4-Ptpy)Cd(NO₃)₃](μ-phen-dion)Cr(NO₃)₃(4-Ptpy)](NO₃)₃ were formed. FT-IR (KBr) ν = 3420 m, 3080 m, 2924 m, 1606 s, 1383s, 1161 m, 1033 m, 835 s, 766 m (cm⁻¹). CHN Anal., Found; C, 61.20; H, 3.15; N, 12.98. Calc.; 61.36; H, 3.40; N, 13.25. ¹H NMR (DMSO-d₆): δ = 9.06 (4H, m), 8.71 (4H, d, J = 17 Hz), 8.16 (4H, d, J = 19 Hz), 7.89 (4H, m), 7.64-6.98 (20H, m), 2.87 (1H, s), 2.64 (1H, s). UV (DMF): λ max = 570, 309, and 263 nm.

Synthesis of [(4-Ptpy)Cd(NO₃)₃](μ-phen-dion)Cd(NO₃)₃(4-Ptpy)](NO₃)₂

To an aqueous solution containing cadmium(II) nitrate tetrahydrate(1 mmol), phendion in ethanol (1 mmol) was added slowly and then the mixture was stirred at 60°C about 48 hours. After that, additional cadmium(II) nitrate (1 mmol) was then added to the solution and was stirred at the same temperature. Following After 24 h, 2 mmol of 4-Ptpy was added dropwise to the aqueous solution with continuous stirring for 3 days. Finally, solution filtered off and left to evaporate in beaker in air at room temperature, and red color crystals were formed. FT-IR (KBr) ν = 3420 m, 2923 m, 1617 s, 1565s, 1399s, 1158 m, 883 s, 795 s, 434 m (cm⁻¹). CHN Anal., Found; C, 57.87; H, 2.98; N, 12.35. Calc.; 58.04; H, 3.22; N, 12.54. ¹H NMR (DMSO-d₆): δ = 9.06 (4H, m), 8.71 (4H, d, J = 17 Hz), 8.16 (4H, d, J = 19 Hz), 7.89 (4H, m), 7.64-6.98 (20H, m), 2.87 (1H, s), 2.64 (1H, s). UV (DMF): λ max = 570, 309, and 263 nm.

Synthesis of [(phen)Cd(NO₃)₂](μ-phen-dion)Cr(NO₃)₂(phen)](NO₃)₂

To prepare the [(phen)Cd(NO₃)₂](μ-phen-dion)Cr(NO₃)₂(phen)](NO₃)₂, 1mmol chromium nitrate dissolved in water and 1mmol phendion in ethanol, then phendion added dropwise to the chromium nitrate, then the mixture was stirred at 60°C about 48 hours. After that, 1 mmol cadmium(II) nitrate was added to the solution and was stirred at the same temperature, and 2 mmol of 1,10phenanthroline

was added slowly to the mixture, after 24 h, mixture was filtered and a dark precipitate was formed. FT-IR (KBr) $\nu = 3420$ m, 3115 m, 2924 m, 1698 s, 1576s, 1441s, 839 s, 763 s, 557s (cm^{-1}). CHN Anal., Found; C, 56.70; H, 2.81; N, 11.21. Calc.; 56.93; H, 3.05; N, 11.95. ^1H NMR (DMSO-d_6): $\delta = 9.06$ (4H, m), 8.71 (4H, d, $J = 17$ Hz), 8.16 (4H, d, $J = 19$ Hz), 7.89 (4H, m), 7.64-6.98 (20H, m), 2.87 (1H, s), 2.64 (1H, s). UV (DMF): $\lambda_{\text{max}} = 572$, 305, and 252 nm.

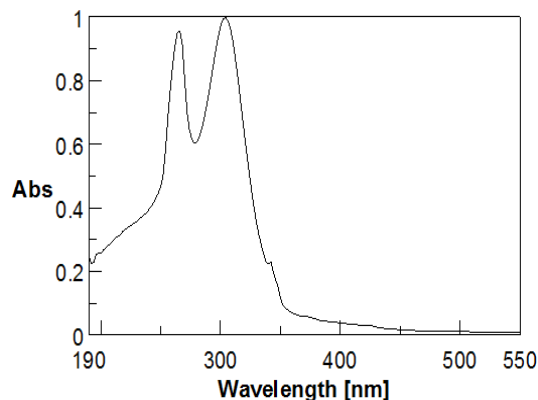
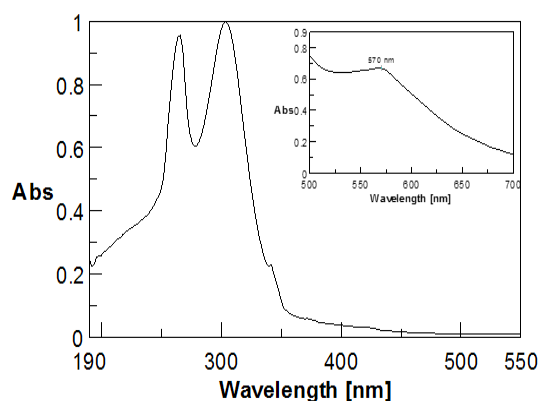
RESULTS AND DISCUSSION

The reaction of 4-Ptpy and phendion as ligand with chromium(III) nitrate nonahydrate, and cadmium(II) nitrate tetrahydrate result in the formation of four binuclear complexes. The FT-IR spectra of the $[(4\text{-Ptpy})\text{Cr}(\text{NO}_3)(\mu\text{-phen-dion})\text{Cr}(\text{NO}_3)(4\text{-Ptpy})](\text{NO}_3)_4$ shows absorption bands at $1300\text{-}400$ cm^{-1} that it is related to the coordination of carbonyl groups of the phendione ligand to the metal. The peaks at 419 and 451 cm^{-1} are assigned to the vibration of Cr-N and Cr-O bonds²⁰⁻²¹. The characteristic band of $[(\text{phen})\text{Cd}(\text{NO}_3)_2(\mu\text{-phen-dion})\text{Cr}(\text{NO}_3)_2(\text{phen})](\text{NO}_3)_2$ is the peak at 1400-1650 cm^{-1} that is attributed to the phenanthroline ligand. The peaks at about 434 and 590 cm^{-1} are related to the Cd-N and Cd-O bonds, confirming the formation of the binuclear complex. The peaks of C=C and C=N stretching modes at about 1585 and 1505 cm^{-1} , respectively, are moved to 1571 and 1500 cm^{-1} .

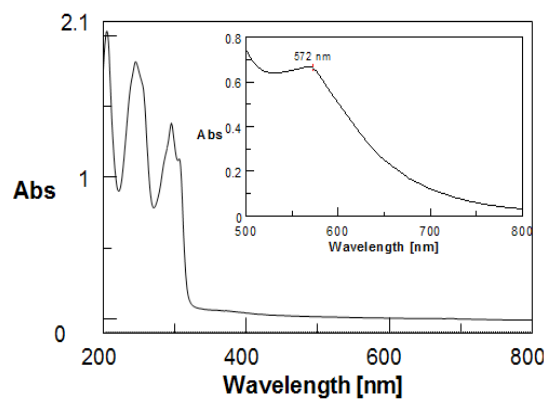
The UV-Vis absorption spectra of complexes in mixed solution (ethanol and water) is shown in Fig. 1a-b. The spectra exhibit characteristic $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ (phenanthroline and terpyridine) in the 263 and 309 nm. As observed in the fig, the peak at 570 nm is attributed to the charge transfer of Cr^{2+} .

Cyclic voltammetry was done in an DMF with 0.1M TBAH as a supporting electrolyte at scan rate 100 mV s^{-1} (Fig. 2a-c). In this voltammogram, two reversible oxidation-reduction and two irreversible reduction couples peaks at -1.2 to -1.6 V are assigned to the 4-Ptpy ligand²⁵⁻²⁶. The peaks of -1.6 to -0.9 could be assigned to phendion ligand and Cr metal²⁷⁻²⁸. The region between 0 and -1 might be related to phendion and 4-Ptpy ligands. In this voltammogram, two quasi-reversible reduction

couples at 0 and -1 V are assigned to the reduction of to phendion and 4-Ptpy ligands. In comparison with free ligands, the reduction couples shift to more positive potentials due to the coordination of ligands to the Cd center (Fig. 2c). Also, the figure showed no d-d electron transition for the Cd metal.



(a)



(b)

Fig. 1a, b. The UV-vis spectra of the $[(4\text{-Ptpy})\text{Cd}(\text{NO}_3)(\mu\text{-phen-dion})\text{Cr}(\text{NO}_3)(4\text{-Ptpy})](\text{NO}_3)_3$

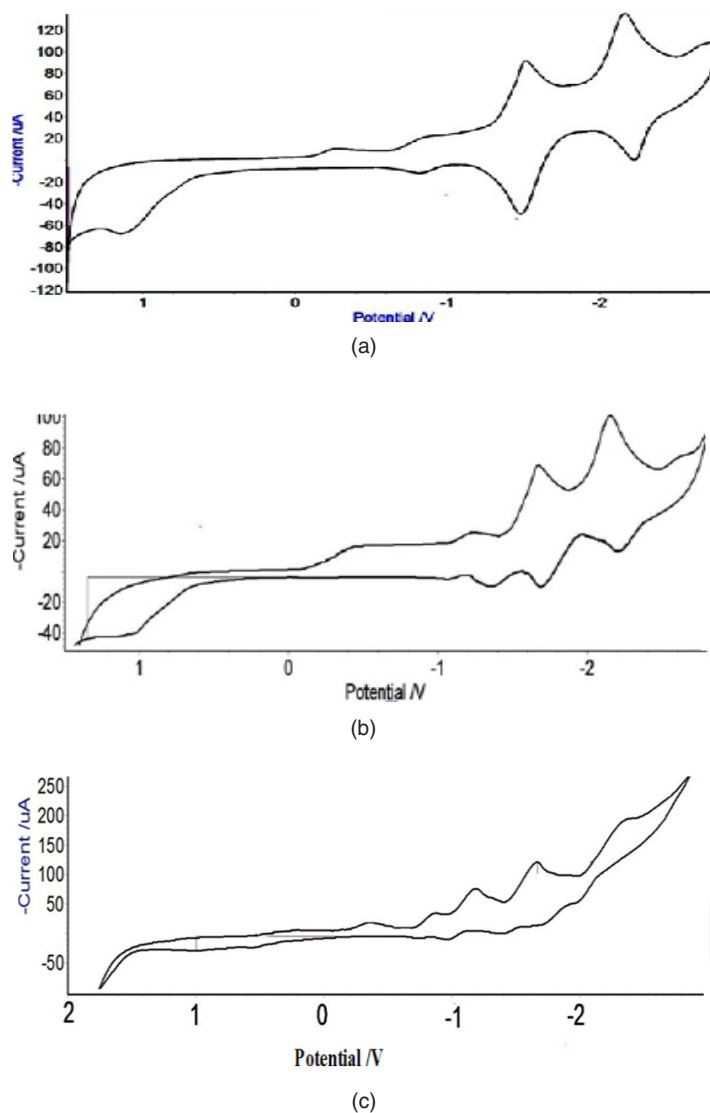


Fig. 2a, b, c The cyclic voltammety of the $[(4\text{-Ptpy})\text{Cd}(\text{NO}_3)_2(\mu\text{-phen-dion})\text{Cr}(\text{NO}_3)_2(4\text{-Ptpy})](\text{NO}_3)_3$

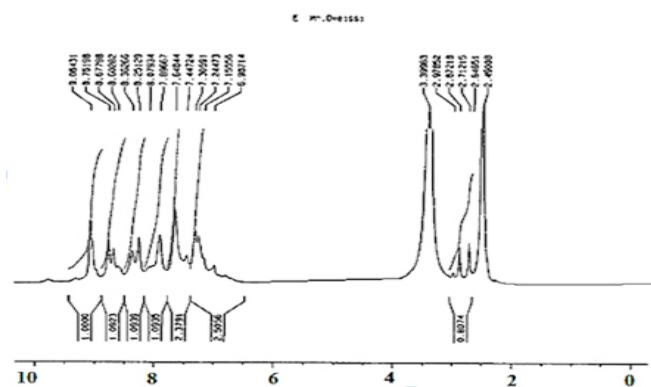


Fig. 3. The ^1H NMR spectra of the $[(4\text{-Ptpy})\text{Cd}(\text{NO}_3)_2(\mu\text{-phen-dion})\text{Cr}(\text{NO}_3)_2(4\text{-Ptpy})](\text{NO}_3)_3$

The ^1H NMR spectra of complexes were obtained in DMSO-d_6 as shown in Fig. 3. The peaks at 7-9 ppm were assigned to the aromatic compounds²⁹⁻³⁰. The hydrogens of the ligands were observed as doublet and triplet peaks. The peaks of spectra were broad, due to the paramagnetic characteristic of chromium metal³¹⁻³² (Figure 3).

Elemental analyses of the complexes were obtained, The values confirmed the successful syntheses of the bi-nuclear complexes.

CONCLUSION

Binuclear Cr(III) and Cd(II) complexes containing 4-phenylterpy and phenathroline ligands were synthesized conveniently and characterized by the various techniques. The complexes can further study and apply as semiconductors.

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