

Synthesis, structure, spectroscopic, magnetic and electrochemical studies of Ni^{II} phen-dione complex

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Abstract

The first crystal structure of Ni^{II} phen-dione complex is reported. This compound is [Ni(bpy)₂(phen-dione)](PF₆)₂ (bpy = 2,2'-bipyridine and phen-dione = 1,10-phenanthroline-5,6-dione). The complex has been characterized by elemental analysis, IR and electronic absorption spectroscopy and cyclic voltammetry. The electrochemical behavior and electronic spectrum of [Ni(bpy)₂(phen-dione)](OAc)₂ has also been studied in buffered solutions at pH between 1 and 8. ORTEP drawing of [Ni(bpy)₂(phen-dione)](PF₆)₂ · 2CH₃CN shows that the coordination geometry around the Ni^{II} is a distorted octahedron, with bite angles of 78.1–78.8° for all three bidentate ligands and the two pyridyl rings of the bpy ligands are nearly co-planar, as are the two pyridyl rings of phen-dione.
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Keywords: Ni^{II} complex; Phenanthroline derivatives; Crystal structure; Metal-to-ligand charge-transfer; Cyclic voltammetry; Magnetic moment

1. Introduction

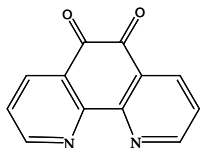
1,10-Phenanthroline and its derivatives such as 5,6-diamino-1,10-phenanthroline, 1,10-phenanthroline-5,6-dione, 2,9-dimethyl-1,10-phenanthroline-5,6-dione and 1,10-phenanthroline-5,6-dioxime play important roles as molecular scaffolding for supramolecular assemblies, building block for the synthesis of metallo-dendrimers, thin films of luminescent complexes and ligand for synthesis of ring-opening metathesis polymerization (ROMP) monomer [1–8]. One especially important and desirable class of derivatives are those which retain the twofold symmetry of this ligand and thereby avoid some of the stereochemical problems associated with their tris chelated metal complexes, namely formation of *mer* and *fac* isomers. 5,6-Diamino-1,10-phenanthroline is particularly important in that it can either

directly bridge two metal centers or be condensed with a variety of *ortho*-quinones to form addition derivatives. For example, the useful bridging ligand, tetrapyrrodo[3,2-a:2',3'',2''-h:2''',3'''-j]phenazine, is readily formed upon condensation of phen-diamine with 1,10-phenanthroline-5,6-dione [3,9].

The focus is on complexes of 1,10-phenanthroline-5,6-dione (Scheme 1) because this ligand has the ability to form stable complexes with a wide variety of metal ions and carries an *o*-quinone moiety with pH-dependent electroactivity [10,11]. Metal complexes of this ligand potentially allow for the variation and control of redox properties over a wide range as well as the fine tuning of potentials through pH changes [12].

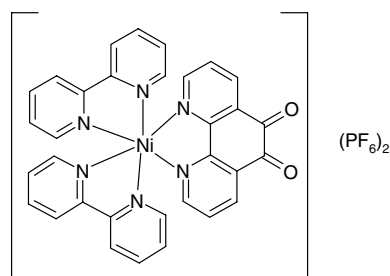
Metal complexes of the type [M(LL)₃]ⁿ⁺, where LL is either 1,10-phenanthroline or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA. The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an

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1,10-phenanthroline-5,6-dione
(phen-dione)

Scheme 1.



$[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{PF}_6)_2$

Scheme 2.

individual application, thus providing an easy access for the understanding of details involved in DNA-binding and cleavage [13–16]. Clearly, further studies using various phen-dione complexes such as $[\text{M}(\text{phen-dione})_3]^{n+}$, $[\text{M}(\text{phen-dione})_2\text{tpphz}]^{n+}$ and $[\text{M}(\text{phen-dione})_2(\text{LL}')^{n+}$ complexes are needed to evaluate the influence of metal-ion-induced geometry, charge, spin-state, redox potential, etc. changes on the DNA binding and cleavage mechanisms in this important class of complexes as was the case with the previously reported metalloderivatives ($\text{M} = \text{Ru}^{\text{II}}$, Rh^{III} , Pt^{II} , Pd^{II} , Co^{III} , Cr^{III} , etc.) of phen or modified phen ligands [13–23].

We now report the preparation, crystallography, electrochemical and magnetic characterization of $[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{PF}_6)_2$ (Scheme 2).

2. Experimental

2.1. Materials and general methods

All reagents and solvents used were reagent grade. 1,10-Phenanthroline-5,6-dione was synthesized according to the literature [10]. The buffers used at different pH were $\text{H}_2\text{SO}_4 + \text{NaOH}$ (for pH 1), $\text{H}_3\text{PO}_4 + \text{NaOH}$ (for pH 2–3), acetate buffer (for pH 4–6) and $\text{NaH}_2\text{PO}_4 + \text{NaOH}$ (for pH 7–8). All buffers were prepared in bidistilled water by reagent grade chemicals with ionic strength adjusted at 0.3 M.

Elemental analyses were performed by Heraeus CHN-O-Rapid elemental analyzer. IR spectra were recorded as KBr pellets on a FTIR JASCO 460 spectrophotometer and electronic spectra on a JASCO 7850 spectrophotometer. ^1H NMR spectra were recorded on a Bruker DRX-

500 MHz, Avance spectrometer at ambient temperature in $\text{DMSO}-d_6$. Cyclic voltammograms were recorded by using a Metrohm 694 apparatus. Three electrodes were utilized in this system, a platinum disk working electrode (RDE), a platinum wire auxiliary electrode and $\text{Ag}|\text{AgCl}$ reference electrode. The platinum disk working electrode was manually cleaned with 1- μm diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol–water (1/1) and vacuum-dried at 110 °C overnight. Acetonitrile was distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by bubbling with Ar for 15 min.

2.2. Synthesis of $[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{OAc})_2 \cdot 2\text{H}_2\text{O}$

A mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (475 mg, 2 mmol) and 2,2'-bipyridine (625 mg, 4 mmol) dissolved in 50 ml 1-butanol was stirred at reflux temperature for 1 h. The blue precipitate, $[\text{Ni}(\text{bpy})_2\text{Cl}_2]$, which formed was collected and washed with 1-butanol and ether. This product was dissolved in 50 ml CH_3CN and refluxed for 10 min. To the solution was then added TIOAc (1054 mg, 4 mmol) and stirred at reflux temperature for 30 min. The solution was cooled to -5 °C overnight and filtered through Celite to remove the fine white TiCl precipitate. To the filtrate was then added 1,10-phenanthroline-5,6-dione (420 mg, 2 mmol) and the resulting solution was stirred with heating (40–45 °C) for 10 h. The solution was evaporated to dryness. The crude orange solid was dissolved in a small amount of water and left at room temperature for several days to yield orange crystals of $[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. Yield: 1352 mg, 92%. Anal. Calc. for $\text{C}_{36}\text{H}_{32}\text{NiN}_6\text{O}_8$: C, 58.82; H, 4.40; N, 11.43. Found: C, 59.11; H, 4.45; N, 11.57%.

2.3. Synthesis of $[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{CN}$

$[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (735 mg, 1 mmol) was dissolved in 25 ml water and precipitated from solution as a hexafluorophosphate salt by the addition of NH_4PF_6 (625 mg, 4 mmol). The product, $[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{PF}_6)_2$, was collected by suction filtration, washed with cold water and ether, and then air dried. Diffusion of ether into an acetonitrile solution of the complex gave orange crystals suitable for crystallography. Yield: 757 mg, 80%. Anal. Calc. for $\text{C}_{36}\text{H}_{28}\text{F}_{12}\text{NiN}_8\text{O}_2\text{P}_2$: C, 45.36; H, 2.96; N, 11.75. Found: C, 45.63; H, 3.00; N, 11.93%.

2.4. X-ray crystallographic study of $[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{CN}$

Orange crystals of $[\text{Ni}(\text{bpy})_2(\text{phen-dione})](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{CN}$ were grown by ether diffusion into an acetonitrile solution of the complex. Single-crystal X-ray diffraction measurements were carried out with a Siemens P4 diffractometer

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