Deprotonation or Protonation: the coordination properties, crystal structures and spectra of cobalt (II) complex with 1-(2-pyridylazo)-2-acenaphthequinol ligand

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ABSTRACT

The reaction of 1-(2-pyridylazo)-2-acenaphthequinol (PAAL) with cobalt acetate in CHCl_3 gave the complex of $\text{Co}(\text{PAAL-H})_2$ (**1**), and $(\text{PAAL+H})_2[\text{CoCl}_4]\cdot 2\text{H}_2\text{O}$ (**2**) was isolated in the same system with ultraviolet light irradiation. Structures of both compounds were determined by X-Ray diffraction. The PAAL ligand was deprotonated in **1**, but it further protonated on N position at pyridine group in **2** and form cations. The spectra of these two compounds were also studied, as well as the fluorescence properties. Also, the redox property of **1** was preliminary investigated by cyclic voltammogram.

Keywords: Cobalt complex; fluorescence; redox-active, protonation

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1. Introduction

In the last decade, aromatic azo compounds were widely used as dyes in optical and color-changing materials, such as sunglasses, textiles, paints, cosmetics, and food additives. [1–16] Azo dyes account for 60–70% of all dyes produced in the world, and the azo group usually undergoes reversible *trans–cis* photoisomerization which can also be exploited in the design of photo-switches, molecular motors, *etc.* [17–21] In contrast to azo-benzenes, heterocyclic azo compounds are less well investigated, although they have shown rich structural diversity, as well as chromophoric strength. The aromatic heterocyclic azo compounds having hydroxyl groups in *ortho* positions may give rise to two distinct isomers: azo and hydrazine form, which could coexist under certain experimental conditions. [16] The intrinsic nature of the compounds could effect its coordination behavior and investigation of interconversion between azo and hydrazone isomers is still currently a topic of great interest from structures to properties, although azo to hydrazone tautomerism has been reported by pH control and coordination coupled proton transfer for several azo dyes. [22–25] Generally, the heterocyclic azo dyes deprotonated or further reduced to construct complex derivatives as poly-dentate ligand. [26] Several techniques such as IR, Raman and NMR method also have been employed to elucidate the structures of numerous azo compounds. However, the precise assignments of the spectroscopic signs of azo-enol or hydrazine-keto tautomers are still incomplete in the literature. [22] X-ray single crystal diffraction has been proved to be the most powerful tool to characterize various heterocyclic azo complexes, and the structural information is found to be related to the optical properties as well as to the technical properties of azo dyes and pigments. [27]

Detailed information such as location of ‘mobile’ protons on the structures and photochemical behavior of aromatic heterocyclic azo complexes is crucial for understanding their reactivity and applications. [2–3] In our previous work, the aromatic heterocyclic azo compound 1-(2-pyridylazo)-2-acenaphthequinol (PAAL) and its Zn complexes containing anionic (PAAL-H) have been reported. [28] While there are no published data concerning the synthesis and studies of metal complexes with PAAL in which the ligand exists in cationic form (PAAL+H). Herein, we further study coordination behavior of the PAAL with cobalt(II). Two new complexes $\text{Co}(\text{PAAL-H})_2$ (**1**) and $(\text{PAAL+H})_2[\text{CoCl}_4] \cdot 2\text{H}_2\text{O}$ (**2**) were synthesized, in which the PAAL ligands were deprotonated and protonated separately, and the spectra of the complexes were studied as well.

Scheme 1 Different protonation forms of the PAAL ligand.

2. Experimental

2.1 Materials and Instrumentation

All reagents and chemicals were purchased from commercial sources and use without further purifications. Syntheses of the complexes were done in open atmosphere. FT-IR spectra were obtained using a Perkin-Elmer 783 spectrophotometer. UV-Vis measurements were recorded on a Shimadzu 3600 UV-vis-NIR spectrophotometer in CHCl_3 solution using quartz colorimetricutensil. Cyclic voltammetry was carried out in anhydrous solvent (CH_3CN) that degased by sparging with N_2 gas for 10 min, using a three-electrode configuration (glassy carbon working electrode, platinum wire auxiliary electrode, Ag/AgCl reference electrode) and a PC controlled PAR model 273A electrochemistry system. Solution concentrations were approximately 10^{-3} M in analyte containing 0.5 M supporting electrolyte (Bu_4NPF_6). Fluorescence spectra were taken on fluorescence spectrophotometer F-7000. TG were obtained using a NETZSCH STA 449C. The heating rate is $10^\circ\text{C}/\text{min}$ in the range of $34\text{--}800^\circ\text{C}$ under argon atmosphere.

2.2 Synthesis of $\text{Co}(\text{PAAL-H})_2$ (1)

A solution of 1-(2-pyridylazo)-2-acenaphthequinol (0.273 g, 1.00 mmol) was dissolved in CHCl_3 (10 mL), adding the solution of CH_3OH containing $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1.245 g, 0.50 mmol), which was stirred for 4h at room temperature under sunlight irradiation and then filtered. The crystal was obtained by slowly evaporation of the solvent. Yield (66%). Elemental analysis (%) calc. for $\text{C}_{34}\text{H}_{20}\text{N}_6\text{O}_2\text{Co}$: C, 67.61; H, 3.31; N, 13.92; found: C, 67.84; H, 3.256; N, 13.81.

2.3 Synthesis of $(\text{PAAL+H})_2[\text{CoCl}_4] \cdot 2\text{H}_2\text{O}$ (2)

A solution of 1-(2-pyridylazo)-2-acenaphthequinol (0.273 g, 1.00 mmol) was dissolved in CHCl_3 (10 mL), adding the solution of CH_3OH containing $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1.245 g, 0.50 mmol), which was stirred for 2h under ultraviolet

light irradiation at room temperature, then filtered. The crystal was obtained by slowly evaporation of the solvent in the darkness. Yield(46%). Elemental analysis (%) calc. for $C_{34}H_{28}N_6O_4CoCl_4$: C, 52.00; H, 3.59; N, 10.7; found: C, 51.62; H, 3.81; N, 10.85.

2.4. X-ray crystallography

X-ray single crystal data of **1** and **2** were collected on a Bruker SMART APEX II CCD area detector equipped with a graphite monochromated Mo-K α radiation ($\lambda=0.71073$ Å) at room temperature using both θ - and ω -scan modes. The structures were obtained by direct methods and refined on F^2 by full matrix least squares using SHELXTL-97 crystallographic software package with anisotropic displacement parameters for all non-hydrogen atoms.[29] All H atoms were introduced in calculations using the riding model. The crystallographic data and structures refinement parameters of **1** and **2** were summarized in Table 1, and selected bond lengths and angles were listed in Table S1 (in ESI).

3. Results and discussion

3.1. Structural description

Complex $Co(PAAL-H)_2$ was synthesized by directly mixing $CHCl_3$ solution of the PAAL ligands and $Co(CH_3COO)_2 \cdot 4H_2O$ in CH_3OH . As shown in Fig. 1, the single crystal diffraction data indicate that the PAAL crystallized in the deprotonated form and the complex is pseudo-octahedral, featuring two coordinated tridentate PAAL anions binding through NNO donor sets. The four Co-N bonds with average bond length of 2.04(1) Å are significantly shorter than two Co-O bonds of 2.20(1) Å. The N=N bond length of the azo moiety is 1.30(1) Å, indicating significant double bond character. Also, the C-O [1.24 (1) and 1.25(1) Å] bond is a little shorter than that in similar complexes, demonstrating the bigger conjugated system has greater ability of attraction.[30-31]

Fig. 1 (left) Molecular structure of compound **1**; (right) Asymmetric unit of compound **2**

Alternatively, when the solution containing all the reactants were irradiate under ultraviolet light at room temperature,

the complex does not isomerize due to the steric effect of the acenaphthequinol group. Instead, the compound **2**, (PAAL+H)₂[CoCl₄]·2H₂O, was produced and isolated. The UV light decompose the CHCl₃ and generate HCl and CO₂ with the existence of residual water from the reactant Co(CH₃COO)₂·4H₂O, and the Co(II) coordinated with four Cl⁻ and form [CoCl₄]²⁻ anion. The PAAL was protonated as (PAAL+H)⁺ cations, which form a cation-anion complex with cobalt chloride that determined by X-Ray diffraction. As shown in Fig. **1** and Fig. S2, the anionic [CoCl₄]²⁻ tetrahedral with classic Co-Cl bond length 2.27(1) Å and bond the water molecules by Cl⁻⋯H Hydrogen bonds and form a super-molecular anionic chain. The cationic {PAAL+H} unit bond together by intermolecular $\pi\cdots\pi$ interaction with inter-planar spacing of about 3.50 Å and form the cationic part of the compound. The 3D supramolecular network was constructed by the ionic force between these two parts and the H-bond between the [PAAL+H]⁺ donor and water molecule accepters. Also, the structure indicated that the cationic protonation occurred on the N position at pyridine group. The azo–hydrazone tautomerism wasn't detected in this ionic compound and the hydrazone tautomer form was clearly displayed. The N-N bond and C=O bond length are 1.35(1) Å and 1.22 (1) Å, respectively.

Table 1

Crystallographic data and structure refinement parameters for 1 and 2.

Compound	1	2
Formula	C ₃₄ H ₂₀ N ₆ O ₂ Co	C ₃₄ H ₂₈ Cl ₄ N ₆ O ₄
Formula weight	603.49	785.35
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	C2/c
a/Å	9.2720(4)	15.6175(4)
b/Å	18.0887(8)	7.9385(2)
c/Å	18.3144(9)	27.8928(7)
α /°	90.00	90.00
β /°	117.715(3)	105.493(2)
γ /°	90.00	90.00
V/Å ³	2719.26(20)	3332.48(15)
Z	4	4
Dc/g·cm ⁻³	1.474	1.565
θ range(°)	1.69-25.00	1.52-26.00
Reflections collected / unique	18680 / 4724	12741 / 3281
R(int)	0.1203	0.0580
Data / restraints / parameters	4724 / 0 / 388	3281 / 0 / 230
R(all data)	^a R ₁ =0.2011 ^b wR ₂ =0.1347	R ₁ =0.1008 wR ₂ =0.0873
R[I>2 σ (I)]	R ₁ =0.0932 wR ₂ =0.1071	R ₁ =0.0408 wR ₂ =0.0716

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

$$^b wR_2 = [\sum w(FO^2 - Fc^2)^2 / \sum w(FO^2)^2]^{1/2}.$$

3.2. IR spectra and UV-vis absorption

Comparison of the IR spectra of polycrystalline compounds **1** and **2** show that the framework vibration Characteristic peaks of aromatic ring slightly shift (no more than 20cm^{-1}) to lower frequencies with simultaneous redistribution of their relatively intensity. As shown in Fig. S3, the N=N stretching vibration peak is located in 1415cm^{-1} in **1**, and the broad absorption peaks of 3435cm^{-1} , 3191cm^{-1} are attributable to O-H stretching vibration, NH group and H-bonded water molecules in **2**. Also, The UV-Vis absorption spectra of free ligand (PAAL), **1** and **2** in CHCl_3 are depicted in Fig. 2. Contrast to ligand, the conjugated system in **1** is larger, resulting in $\pi \rightarrow \pi^*$ transition blue shift to lower wavelength at 240 nm. Interestingly, both forming the complex and protonation of ligand leads peak split at 350nm to reduce the transition level differences, while the strong absorption peak at 440nm remain which assigned to the $n \rightarrow \pi^*$ absorption bands of the azo substituent, the acenaphthylenequinone moiety and the pyridyl ring together. The transitions in **1** are essentially ligand centered charge transfer bands, and a new peak observed at 510 nm due to the form of complex, which is consisted with the previous observation in its zinc complex.[28]

Fig. 2 UV-Vis absorption spectra of free ligand (PAAL) **1**, and **2** in CHCl_3 .

3.3. Photoluminescence investigation

Both of these compounds do not show obvious fluorescence under the 440nm and 510nm light irradiation, while the $\text{Zn}(\text{PAAL-H})_2$ has shown strong red fluorescence. Instead, strong emission of multiple peaks around 390nm and weak emission at 620nm was detected when the excited light shift to 320nm, which is produced by the conjugated Aromatic system in both case. The coordination with cobalt or protonation of the ligands does not show apparent effect on the luminesce nature of the ligand.[28]

Fig 3. Emission spectra of **1** and **2** in CHCl_3 at excited wavelength 310 nm and 320 nm

3.4. Redox properties

The electrochemical properties of both compounds were preliminary investigated by cyclic voltammetry (CV). As shown in Fig. 4, compound **1** shows rich redox response in nature. Two most likely reversible redox processes of the ligand with $E_{1/2} = 0.242\text{V}$ and 0.522V are observed, which indicate that the form of radical species and consisted with the previous report of similar system.[32-33] Also, the oxidation peak of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ is observed at -0.45V at 100mV/s scan rate, while the relevant reduction process is not clearly recognizable in the data. In contrast, the redox processes which in compound **2** system are more complicated due to the deprotonation of the cation and the existence of water molecules. Only a few irreversible redox processes are observed, and further exploring the redox properties is ongoing.

Fig 4. Cyclic voltammogram of a 5mM solution $\text{Co}(\text{PAAL-H})_2$ in CH_3CN containing 0.1M Bu_4NPF_6 with the scan rate of 100mV/s .

4 Conclusions

In summary, we have developed a facile protocol for generation of new azo compound cationic derivatives from the reaction of PAAL with transition metals. The further protonated form of PAAL ligand, $[\text{PAAL}+\text{H}]^+$ cation was detected in isolated for the first time and two new complexes **1** and **2** were synthesized and characterized. Also, the Uv-Vis and fluorescence spectra studies of the compounds show that the protonation or deprotonation does slightly changed molecular orbital energy, but does not significantly affect the fluorescence properties. Further, the CV study further confirmed these PAAL complexes are a promising functional radical precursor. The results obtained anticipate the possibility of improvement of the luminescence and redox properties of this type complex by further chemical modifications of the metals. Studies aiming at the use of these compounds in light emitting devices or sensors are in due course.

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