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Self-Assembly, Crystal Structure, and Spectroscopy Properties of Two New Complexes with 1,10-Phenanthroline-5,6-dione and SCN Ligands[1]

J. P. Song[a, b], Q. Ma[a, *], S. M. Shuang[b], Y. Guo[a], and C. Dong[b, *]

[a] *College of Chemistry and Environmental Engineering, Institute of the Applied Chemistry, Shanxi Datong University, Datong, Shanxi, 037009 P.R. China*

[b] *Institute of Environmental Science, Shanxi University, Taiyuan, 030006 P.R. China*

**e-mail: maqihx@163.com*

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Abstract—Two new complexes $[Co(Pdon)(SCN)_2(H_2O)_2]$ (**I**) and $[Hg(Pdon)_2Br_2]$ (**II**) (Pdon = 1,10-phenanthroline-5,6-dione) have been synthesized and characterized by element analysis, IR and single crystal X-ray diffraction (CIF files CCDC nos. 793904 (**I**) and 783209 (**II**)). Compounds **I** and **II** are mononuclear complexes obtained by the self-assembly of Pdon, SCN^- and metal ion Co^{2+} and Hg^{2+}, which are further in close contacted forming a two dimensional supramolecular framework via O–H···S and O–H···O hydrogen bonding interactions interactions between adjacent molecules.

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INTRODUCTION

1,10-Phenanthroline-5,6-dione (Pdon) is a versatile ligand for the assembly of metal organic materials [1, 2]. It may serve as a terminal or planar bridging ligand in the construction of multinuclear complexes and has the ability to form stable complexes with a wide variety of metal ions analogous to 1,10-phenanthroline (Phen) and carries an *o*-quinone moiety with pH-dependent electroactivity. So, metal complexes with the 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 [3, 4]. The diketone functionality can also easily be transformed to other chelating groups, such as diamine or dioxime [5, 6]. Moreover, it is also a versatile organic linker that can form bridges through amine condensation or a combination of coordination and condensation [7–9]. The SCN^- ligand is a linear ligand with two donor atoms and may coordinate through terminal modes or bridging modes or both, with great potential in building coordination network [10]. It can adopt end-to-end (EE) and end-on (EO) fashions via the nitrogen and sulfur atoms to build coordination networks as well as interlink the 1D or 2D molecules into frameworks via the non-covalent interactions [11, 12]. A series of new coordination polymers with interesting structures based on the bridging SCN^- ligand along with their magnetic properties have been reported [13]. The significance of this research work is to report the self-assembly synthesis of Pdon, SCN^- and d^{10} metal ion (Hg^{2+}).

Based on our interesting of the self-assembly of Pdon, SCN^- and different metal ions, in this research work, two complexes $[Co(Pdon)(SCN)_2(H_2O)_2]$ (**I**) and $[Hg(Pdon)_2Br_2]$ (**II**) were designed and synthesized. It is noted that two crystal structures exhibit different coordination forms comparable to the our reported similar complexes [14]. Herein, we report the synthesis, crystal structure and spectroscopy properties of complexes **I** and **II**.

EXPERIMENTAL

Materials and methods. All chemicals were of reagent grade and commercially available, and were used without further purification. The Infrared spectra were recorded as KBr pellets on a Shimadzu 8300 FT-IR spectrometer. Samples for elemental analysis were dried under vacuum, and the analysis was performed with a CHN-O-Rapid instrument.

Pdon was oxidated from its parent compound 1,10-phenanthroline. The processes of preparation and purify were easily followed to the literature [2]. Pure products were yellow-orange needles, m.p. = 257°C.

IR data (ν, cm^{-1}): 3457 s, 1689 s, 1559 s, 1460 m, 1415 s, 1291 m, 1206 w, 1115 w, 1063 w, 926 w, 808 w, 736 m, 671 w, 613 w, 541 w.

Synthesis of complex I. $CoCl_2$ (0.1 mmol) dissolved in 5.0 mL of aqueous solution was added to a methanol solution (10 mL) containing Pdon (0.021 g, 0.1 mmol) dropwise at room temperature and the mixture was reacted with stirring for 0.5 h. Then, KSCN (0.0195 g, 0.2 mmol) was slowly added dropwise with a constant

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Table 1. Crystallographic data and structural refinement details of complexes **I** and **II**

Parameter	Value	
	I	**II**
M	421.31	780.79
Temperature, K	298(2)	298(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$Fdd2$
a, Å	8.8845(11)	42.485(4)
b, Å	10.3264(14)	8.469(8)
c, Å	9.6862(13)	13.1831(12)
β, deg	96.817(1)	90
V, Å^3	885.5(2)	4744(5)
Crystal size, mm	0.43 × 0.32 × 0.19	0.40 × 0.37 × 0.13
Z	2	8
ρ_{calcd}, g cm^{-3}	1.299	1.552
μ, mm^{-1}	1.23	9.90
F(000)	426	1078
θ Range, deg	3.1–25.0	2.90–25.02
Limiting indices	$-6 \leq h \leq 6$, $-9 \leq k \leq 9$, $-14 \leq l \leq 15$	$-9 \leq h \leq 8$, $-15 \leq k \leq 14$, $-25 \leq l \leq 25$
GOOF(F^2)	1.08	1.13
Reflections measured	4402	5499
Reflections unique	2800	2030
R_{int}	0.028	0.057
Final R ($I > 2\sigma$, I)	$R_1 = 0.037$, $wR_2 = 0.087$	$R_1 = 0.0573$, $wR_2 = 0.1278$
R, all data	$R_1 = 0.045$, $wR_2 = 1.08$	$R_1 = 0.0691$, $wR_2 = 0.1373$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^3	0.53/−0.25	2.57/−1.86

stirring. The insoluble components were removed by filtration, and the filtrate was allowed to stand at room temperature. The orange red crystals were collected after slow evaporation at room temperature for about 2 weeks in a yield of 16.7%.

IR data (ν, cm^{-1}): 3444 s, 2073 s, 1695 s, 1571 s, 1470 w, 1421 s, 1298 w, 1121 w, 1027 w, 925 w, 834 w, 736 m, 697 w, 456 w.

For $C_{14}H_{10}N_4O_4S_2Co$

anal. calcd., %:	C, 39.91;	H, 2.39;	N, 13.30.
Found, %:	C, 39.32;	H, 2.35;	N, 13.33.

Synthesis of complex II was carried out by the same way as for **I**, using $HgBr_2$ instead of $CoCl_2$. The yield was 49%.

IR data (ν, cm^{-1}): 3444 s, 1703 s, 1579 m, 1467 s,1424 m, 1313 w, 1258 w, 1206 w, 1130 w, 1024 w, 823 w, 731 w 691 w, 626 w.

For $C_{24}H_{12}N_4O_4Br_2Hg$

anal. calcd., %:	C, 36.92;	H, 1.55;	N, 7.18.
Found, %:	C, 36.14;	H, 1.35;	N, 7.21.

X-ray diffraction study. The single crystal diffraction data of **I** and **II** were collected on a Bruker Smart Apex II diffractometer equipped with 1K CCD instrument by using a graphite monochromator utilizing MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were determined using SMART software [15]. Data reduction and corrections were performed using SAINTPlus. Absorption corrections were made via SADABS [16]. The structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least-squares methods on all F^2 data with SHELXL-97 [17]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached C were added theoretically and treated as riding on the concerned atoms. H atoms of coordinational water molecule in I were located from difference Fourier maps and refined their global U_{iso} value. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Details of the crystal parameters, data collection and refinement are summarized in Table 1. Selected bond lengths and bond angles were given in Table 2. The geometrical parameters of the hydrogen bonds are listed in Table 3.

Table 2. Selected bond distances (Å) and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
			I		
Co(1)–O(3)	2.223(4)	Co(1)–O(4)	2.116(4)	Co(1)–N(1)	2.154(4)
Co(1)–N(3)	2.061(4)	Co(1)–N(2)	2.154(3)	Co(1)–N(4)	2.083(4)
C(11)–O(1)	1.219(6)	C(12)–O(2)	1.215(6)		
			II		
Hg(1)–N(2)	2.501(14)	Hg(1)–N(1)	2.510(16)	Hg(1)–Br(1)	2.661(3)
C(11)–O(1)	1.19(3)	C(12)–O(2)	1.21(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
			I		
N(1)Co(1)N(2)	76.45(13)	N(3)Co(1)N(4)	93.82(17)	N(3)C(13)S(1)	179.3(5)
N(4)C(14)S(2)	178.3(5)				
			II		
N(2)Hg(1)N(1)	64.9(5)	N(2)Hg(1)Br(1)	91.5(3)	N(1)Hg(1)C(11)	105.8(4)

Table 3. Geometric parameters of hydrogen bonds for complex **I***

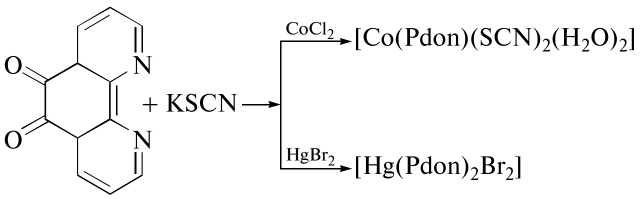
D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(4)–H(4*B*)···O(2)^{i}	0.85	2.63	3.049(5)	111.5
O(4)–H(4*B*)···O(3)^{ii}	0.85	2.15	2.994(5)	168.7
O(3)–H(3*B*)···S(1)^{iii}	0.85	2.47	3.283(4)	161.0
O(3)–H(3*A*)···O(2)^{iv}	0.85	2.05	2.867(5)	160.5

* Symmetry codes: ^{i} $-x + 1, y - 1/2, -z$; ^{ii} $-x + 1, y - 1/2, -z + 1$; ^{iii} $-x, y + 1/2, -z + 1$; ^{iv} $x, y, z + 1$.

Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 793904 and 783209, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

General method for the preparation of complexes **I** and **II** is given below:



The self-assembly process of **I** and **II** was achieved from three reacting reagents (Pdon, thiocyanate and $CoCl_2/HgBr_2$) in aqueous-ethanol solution at room temperature. The crystal structures of complexes **I** and **II** indicate that under synthesis condition of this work, Pdon acted only as a terminal ligand and occupied two coordinated sites of the metal ions. Despite this recipe adopted the same condition of synthesis, complexes **I** and **II** still exhibit different coordination mode. The architecture may relate to crystal and ionic radii (Å, C.N. 6) of metal ions, Co (0.79, 0.65) and Hg (1.16, 1.02) [18]. The infrared absorption spectrum shows a small shift to higher energy of C=O stretching of the pdon in **I**, **II** and the free ligand at 1703 and 1689 cm^{-1}, respectively. The C≡N stretching of thiocyanate in complex **I** was at 2073 cm^{-1}. The bond lengths of C=O ranging from 1.191 to 1.222(8) Å (Table 1) exhibit character of double bond, indicating Pdon participate in coordination mainly in the form of quinone. The products are further confirmed by elemental analyses.

X-ray crystallographic analysis revealed that complex **I** is a mononuclear species with one Pdon ligand, two coordinated water molecules and two *cis*-SCN^- anions, as shown Fig. 1a. The metal centre is six-coordinated in slightly distorted octahedron with a coordination environment of CoN_4O_2, in which four N atoms came from one Pdon ligand and two *cis*-SCN^-

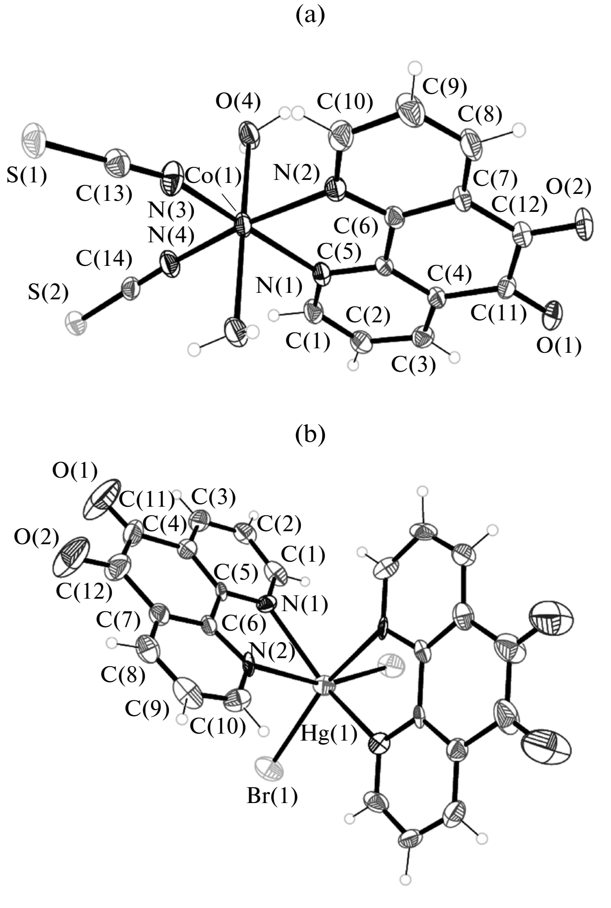


Fig. 1. ORTEP view of **I** (a) and **II** (b) with 30% thermal ellipsoids showing atom-labeling.

anions, two O atoms came from two coordination water molecules. The both Co-N(Pdon) distances are 2.154(4) Å, which are longer comparable to the corresponding bond distances in $[Co(Phen)_2(H_2O)_2](NO_3)_3 \cdot 2H_2O$ (1.934–1.952 Å) [19]. The Co–N(SCN^-) distances of **I** are 2.061(4) and 2.083(4) Å. The NCoN chelated angle formed by each Pdon is 76.45(13)°, which are slightly bigger than the corresponding angles found in *cis*-$[Co(Bipy)_2(SCN)_2]$ (75.4°) [20]. The NCoN angle formed by SCN^- is 93.82(17)°; NCS^- ligand acts as a terminal coordination mode. The Co(1)N(3)C(13) and Co(1)N(4)C(14) angles of 161.9(4)° and 174.3(4)°, respectively, indicate that the terminal NCS anions are coordinated in an almost linear fashion. The S(1)C(13)N(3) and S(2)C(14)N(4) angles of NCS (179.3(5)° and 178.3(5)°, respectively) are significantly in close to linear terminal NCS groups.

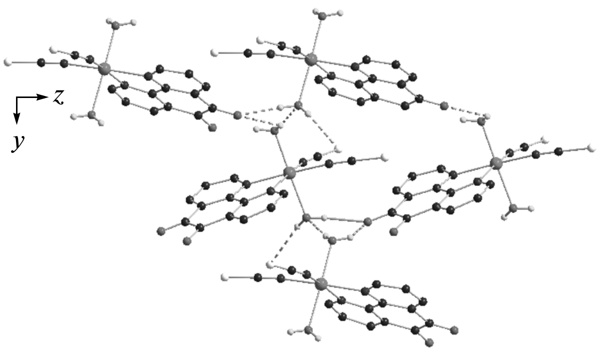


Fig. 2. Two dimensional supramolecular network formed by hydrogen bond interactions in complex **I**.

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architecture. There are persistent $O–H\cdots S$ and $O–H\cdots O$ hydrogen bonding interactions between crystal molecules (Fig. 2). The three kinds of the $O\cdots O$ distances are in the range of 2.867(5) to 3.049(5) Å and $O\cdots S$ bond distance is the 3.283(4) Å, which indicates that strong hydrogen bonds (Table 3) play an important role in stabilizing the network structure.

X-ray crystallographic analysis revealed that complex **II** is mononuclear species with two Pdon ligands and *cis*-Br^- anions (Fig. 1b). The metal centre is six-coordinated in slightly distorted octahedron with a coordination environment of HgN_4Br_2, in which four N atoms came from Pdon ligands and the other Br from anions. The Hg–N(Pdon) distances are appropriately in range of 2.501(14)–2.510(16) Å, which are longer than the corresponding bond distances in *cis*-$[Hg(Phen)_2(Br)_2]$ (2.340(8)–2.345(8) Å) [21]. The NHgN chelated angle of complex formed by each Pdon is 64.9(5)°, which are very smaller than the corresponding angles found in *cis*-$[Hg(Phen)_2(Br)_2]$ (71.2°) [21].

The crystal structure of complex **II** indicates that under synthesis condition of this work, Pdon acted only as a terminal ligand. The bond lengths of C=O ranging from 1.19(3) to 1.21(3) Å (Table 2) exhibit character of double bond, indicating Pdon participate in coordination mainly in the form of quinone. Supramolecular weak interactions are very usually important in the synthesis of supramolecular architecture. There are persistent $C–H\cdots Br$ (Fig. 3) and $C=O\cdots\pi$ supramolecular interactions (Fig. 4) between crystal molecules and chains. The $H\cdots Br$ distance is 2.93 Å, and $C=O\cdots\pi$ distances are in the range of the 3.163 to 3.476 Å, which indicates that strong $C–H\cdots Br$ hydrogen bonds and $C=O\cdots\pi$ interactions play an important role in stabilizing the network structure.

Figure 5 shows the UV-Vis absorption spectra of the ligand as well as complexes **I** and **II** in the aqueous-methanol solution. All of them exhibit two very strong absorption bands at 225–265 and 295–300 nm due to the $\pi–\pi^*$ transitions [22]. The peaks are similar to that in the reported compounds Pdon and $Co(Pdon)_3PF_6$ [23].

The emission spectra of complexes Pdon, **I** and **II** at room temperature are depicted in Fig. 6. The

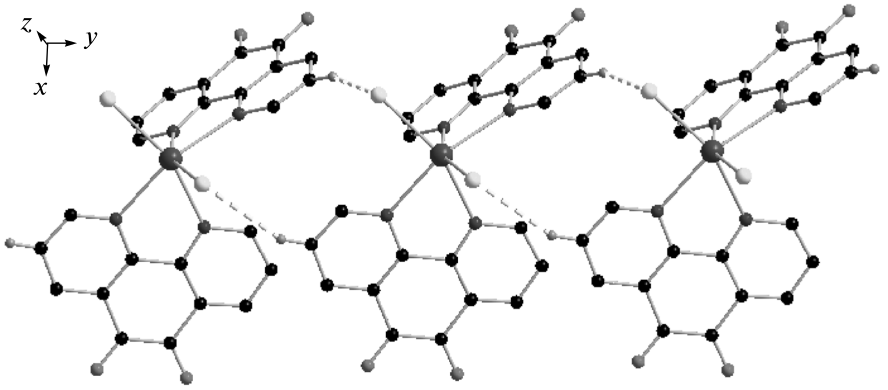


Fig. 3. Hydrogen bond interaction (C–H···Br, dashed lines) in complex **II**.

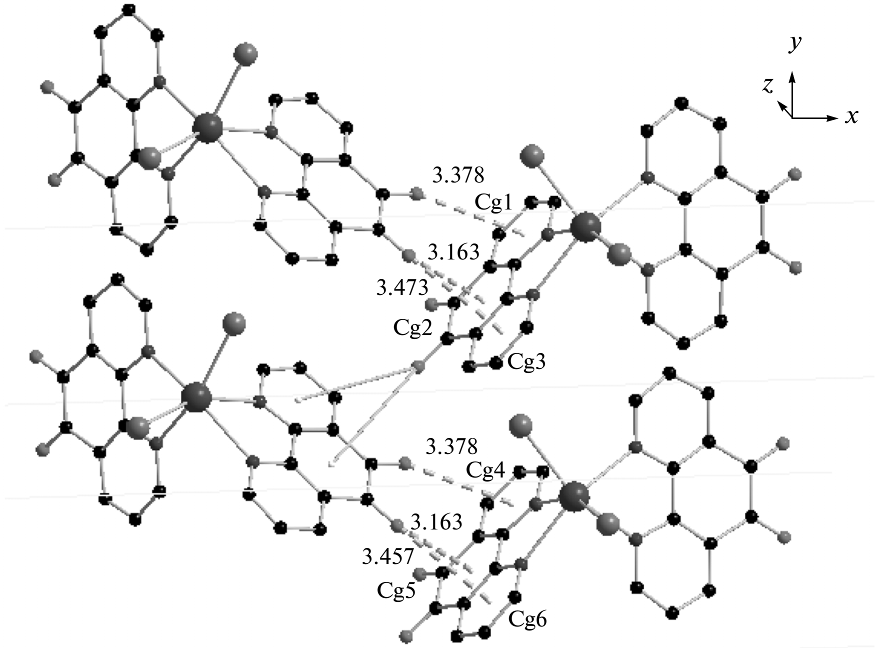


Fig. 4. ORTEP diagram and weak interactions (C=O···π, double dashed lines) in complex **II**, ring label: Cg1 N(1)/C(1)–C(5), Cg2 C(4)–C(7)/C(12)/C(11), Cg3 N(2)/C(6)–C(10).

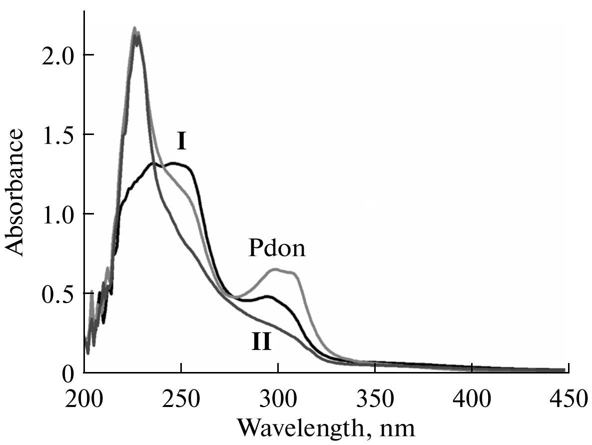


Fig. 5. UV-Vis spectra of Pdon and complexes **I** and **II** in the aqueous-methanol solution (methanol–H_2O = 2 : 1, $c = 1.0 \times 10^{-4}$ mol/L).

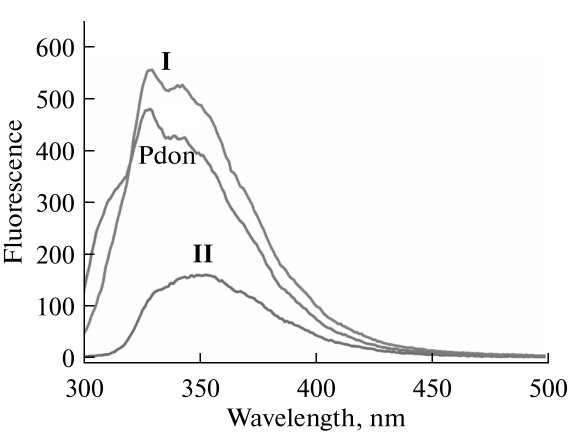


Fig. 6 The fluorescence spectra of **I** and **II** in the the aqueous-methanol solution at room temperature (methanol-H_2O = 2 : 1, $c = 1 \times 10^{-5}$ mol/L, $\lambda_{ex} = 279$ nm).

intense emissions occurred at 330 nm (λ_{ex} = 279 nm) for Pdon and **I**, while 350 nm (λ_{ex} = 279 nm) for **II**, can be attributed to the π–π^* intraligand transitions [24]. Complex **II** displays a 20 nm slight red shift compared with that of complex **I** and the free Pdon, probably due to the difference of metal ions and coordination environment [25]. In complex **II**, hydrogen-bonding interaction may also have an effect on the red shift [24]. Additionally, complex **II** shows obviously weaker fluorescence than that of free ligand and complex **I**, which may be attributed to the quenching effect of the Co^{2+} metal ion [26].

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