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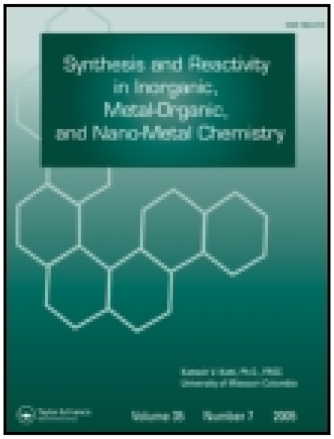

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Synthesis, Crystal Structure, and Antioxidant Property of a New Co(Ⅲ) Coordination Polymer Based on Ligand (E)-2-{2-[1-(1-methyl-1H-benzo[d]imidazol-2-yl)ethylidene]hydrazinyl}benzo[d]thiazole

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Synthesis, Crystal Structure, and Antioxidant Property of a New Co(Ш) Coordination Polymer Based on Ligand (E)-2-{2-[1-(1-methyl-1H-benzo[d]imidazol-2-yl)ethylidene]hydrazinyl} benzo[d]thiazole

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A new Co(Ш) complex, $[CoL_2](ClO_4)(CH_3CN)$ (1) (HL = (E)-2-{2-[1-(1- methyl- 1H-benzo[d]imidazol-2-yl)ethylidene]hydrazinyl} benzo[d]thizole), has been prepared by solvent evaporation method, and characterized by single-crystal X-ray diffraction, bond valence sum, and elemental analysis. The result of single-crystal X-ray diffraction analysis indicates that each Co(Ш) ion is six-coordinated by six nitrogen atoms from two L^- to form distorted octahedral geometry. The hydrogen bonds and $\pi\ldots\pi$ stacking interactions ensure the cohesion of crystal lattice in a 3D supramolecular framework in the solid state. The antioxidant activities of HL and 1 were also studied.

Keywords: Co(III) complex, crystal structure, antioxidant activity

Introduction

Over the past several decades, the self-assembled coordination polymers (CPs) have received considerable attention due to their interesting functions in catalysis, gas storage, luminescence, chemical sensors, biological activity, and so on.[1–10] In particular, with the increasing attention of people against oxidative and aging, CPs have been extensive used in biological activity, especially for the oxidative activity. There are several key factors to influence biological activity of CPs, such as metal ions and ligands. Among these factors, Co(Ш) ion shows significant effects on biological activity,[11–13] while thiazole derivatives exhibit perfect biological properties as well,[14] which can also applied in medicine.[15] Up to now, the reports of CPs based on thiazole Schiff base ligand have been prepared.[16–18] However, the study of Co(Ш) coordination polymer containing thiazole group and its biological property is still very limited. With this background information, we herein report a new Co(Ш) complex, namely, $[CoL_2](ClO_4)(CH_3CN)$ (**1**), derived form ligand (E)-2-{2-[1-(1-methyl-1H-benzo[d]imidazol-2-yl)ethylidene]hydrazinyl}benzo[d]thizole (**HL**). The antioxidant activities of **HL** and **1** were also described.

Experimental

General Remarks

All solvents and reagents were used directly without further purification as commercially analytical grade. Elemental analyses of C, H, and N were recorded on a VaRio EL Instrument. X-ray diffraction analysis data of **1** was collected with a Bruker SMART APEX II diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) by θ scan mode. The structure was solved by direct methods with *SHELXS-97* and refined with the full-matrix least-squares technique using the *SHELXL-97* program.[19] All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were fixed geometrically at calculated distances and refined isotropically. The detailed crystallographic data and structure refinement for **1** are given in Tables 1 and 2.

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Table 1. Crystal data and structure refinement of **1**

Complex	**1**
Identification code	950220
Empirical formula	$C_{38}H_{35}ClCoN_{11}O_4S_2$
Formula weight	868.27
Temperature	293(2)
Crystal system	Triclinic
	P-1
Space group	$a = 9.8419(15)$ Å
	$b = 14.343(2)$ Å
	$c = 14.532(2)$ Å
Unit cell dimensions	$\alpha = 88.\ 88.361(2)°$
	$\beta = 89.327(2)°$
	$\gamma = 74.679(2)°$
Volume	1977.6(5) $Å^3$
Z	2
Density (calculated)	1.458 $Mg{\cdot}m^{-3}$
F(000)	896
Crystal size	0.24 × 0.23 × 0.21 mm
Theta range for data collection	2.26–28.04°
Limiting indices	$-11 \le h \le 11$
	$-17 \le k \le 9$
	$-17 \le l \le 17$
Reflections collected / unique	6900 / 6034
	$[R(int) = 0.0207]$
Data/restraints/parameters	6900 / 0 / 521
Goodness of fit on F^2	1.048
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0454$
	$wR_2 = 0.1286$
R indices (all data)	$R_1 = 0.0513$
	$wR_2 = 0.1359$
Largest diff. peak and hole	0.591 and –0.312 $e{\cdot}A^{-3}$

Table 2. Selected bond lengths (Å) and bond angles (°) and valence sum calculations of **1**

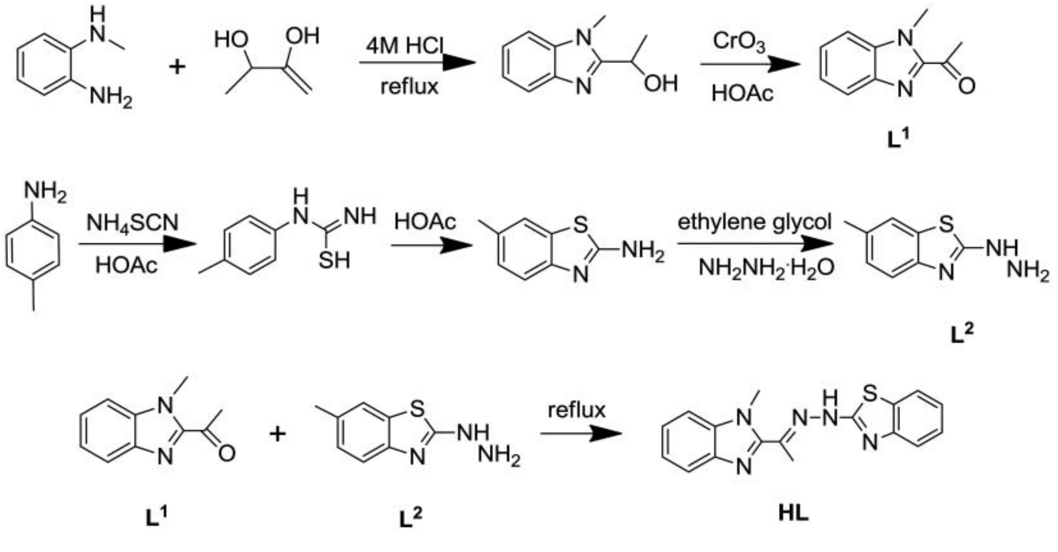
Co1-N2 = 1.932(2)	N4-Co1-N11 = 101.60(9)
Co1-N4 = 1.898(2)	N6-Co1-N8 = 91.40(9)
Co1-N6 = 1.930(2)	N6-Co1-N9 = 100.57(9)
Co1-N8 = 1.934(2)	N6-Co1-N11 = 89.89(9)
Co1-N9 = 1.899(2)	N8-Co1-N9 = 82.07(9)
Co1-N11 = 1.921(2)	N8-Co1-N11 = 163.08(9)
N2-Co1-N4 = 81.86(9)	N9-Co1-N11 = 81.12(9)
N2-Co1-N6 = 162.85(9)	N4-Co1-N6 = 81.25(10)
N2-Co1-N8 = 93.13(9)	N4-Co1-N8 = 95.27(9)
N2-Co1-N9 = 96.43(9)	N4-Co1-N9 = 176.77(9)
N2-Co1-N11 = 90.56(9)	$\sum S(Co) = 2.89$

Synthesis of L^1, L^2, and HL

1-(1-methyl-1H-benzo[d]imidazol-2-yl)ethanone (**L^1**), 2-hydrazinyl-6-methylbenzo [d]thiazole (**L^2**) and (E)-2-{2-[1-(1-methyl-1H-benzo[d]imidazol-2-yl)ethylidene] hydrazinyl} benzo[d]thizole (**HL**) were prepared according to published procedures.[20–23] The synthesized steps are given in Scheme 1.

Synthesis of 1

HL (0.2 mmol, 0.065 g) was dissolved into a mixed solution of 20 mL methanol and 10 mL acetonitrile. After stirring for 0.5 h, $Co(ClO_4)_2{\cdot}6H_2O$ (0.2 mmol, 0.0724 g) was added in the solution. The mixture was further stirred for another 0.5 h and then filtered at ambient temperature. After one month, purple block-shaped crystals of **1** suitable for X-ray diffraction were obtained. Yield, 32%. Elemental Anal. Calcd. for $C_{38}H_{35}CoClN_{11}O_4S_2$: C, 52.56%; H, 4.06%; N, 17.74%; Found: C, 52.46%; H, 4.16%; N, 17.49%.



Sch. 1. The synthesized steps of **HL**.

Scavenger Measurements of Superoxide Radical and Hydroxyl Radical

The superoxide radicals were measured in the test system using $VitB_2$/NBT /MET.[24] **HL** and **1** dissolved in DMF ($C_{i\,(1-5)}$ = 0.2, 1.0, 2.0, 3.0, 4.0 μM), respectively, were add to solution containing NBT (4.6×10^{-5} mol·L^{-1}), MET (0.01 mol·L^{-1}), $VitB_2$ (3.3×10^{-6} mol·L^{-1}), and phosphate buffer (0.067 mol·L^{-1}). After incubating the mixture solution at 30°C for 10 min and illuminating with a fluorescent lamp for 3 min, the absorbance (A_i) of these samples were measured at 560 nm. The results are shown in the following section. The suppression ratio was calculated by using following equation[25]:

$$\text{Suppression ratio}(\%) = [(A_0 - A_i)/(A_0)] \times 100\%$$

Where, A_i is the absorbance in the presence of **HL** and **1**, and A_0 is the absorbance in the absence of **HL** and **1**.

The hydroxyl radical scavenging study was prepared through Fenton reaction.[26] **HL** and **1** were dissolved in DMF ($C_{i(1-5)}$ = 2.0, 4.0, 6.0, 8.0, 10.0 μM). Then, 1 mL 945 μM EDTA-Fe(II), 0.5 mL 114 μM safranine, 1 mL 3% H_2O_2, and 2.5 mL 0.15 M phosphate buffer (pH = 7.4) were added to the 30 μL previously tested solution. The sample without the tested compounds was used as the control. The resulting mixture was incubated for 1 h at 37°C. Then UV spectrophotometer was used to measure the absorbance at 520 nm (A_i, A_0, A_c). The results are presented in and Figure 6b. The suppression ratio was calculated by using following equation[27]:

$$\text{Suppression ratio}(\%) = [(A_i - A_0)/(A_c - A_0)] \times 100\%.$$

Where, A_i is the absorbance in the presence of **HL** and **1**; A_0 is the absorbance in the absence of **HL** and **1**; and Ac is the absorbance in the absence of **HL** and **1**, EDTA-Fe(II) and H_2O_2.

The antioxidant activity was described as the 50% inhibitory concentration (*IC_{50}*). *IC_{50}* values were calculated from regression lines where: x was the concentration of **HL** and **1** in μM and y was the percent inhibition of **HL** and **1**.

Results and Discussion

Structural Description of 1

Perspective view of complex **1** together with atom numbering scheme is shown in Figure 1. In this structure, the Co-N bond lengths in the range of 1.898–1.934 Å give a basic evidence for **1** being a Co(III) complex,[28] which is also confirmed by the result of bond valence sum (BVS) analysis[29–31] (shown in Table 2). The asymmetric unit of **1** contains one

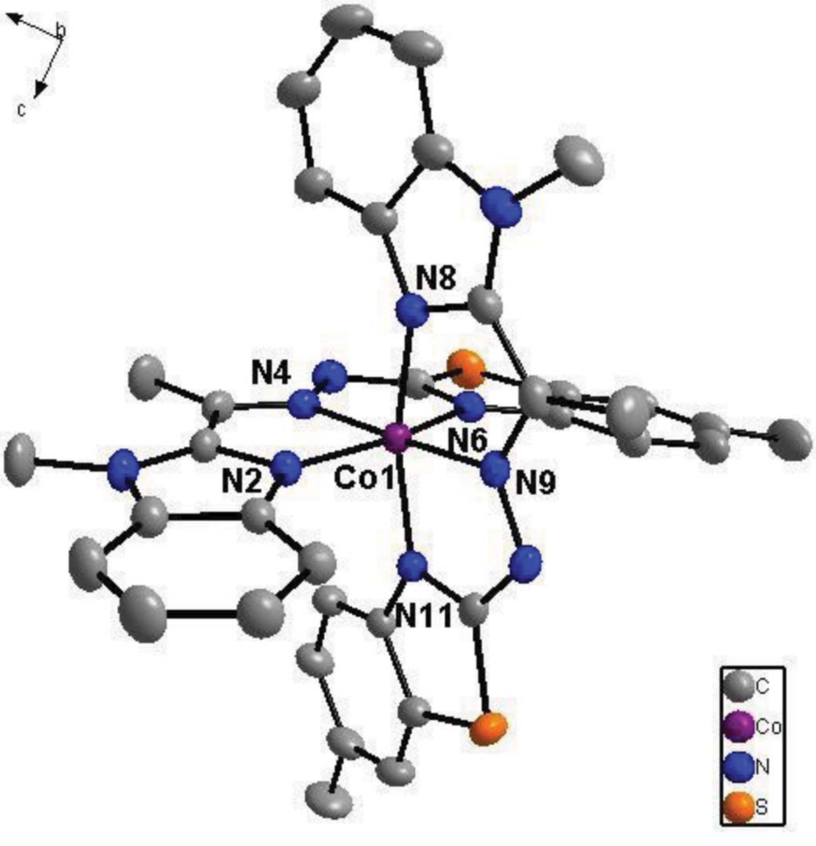


Fig. 1. Crystal structure of **1** with 30% thermal ellipsoids probability. All hydrogen atoms, free acetonitrile molecule, and free ClO_4^- ion are ignored for clarity.

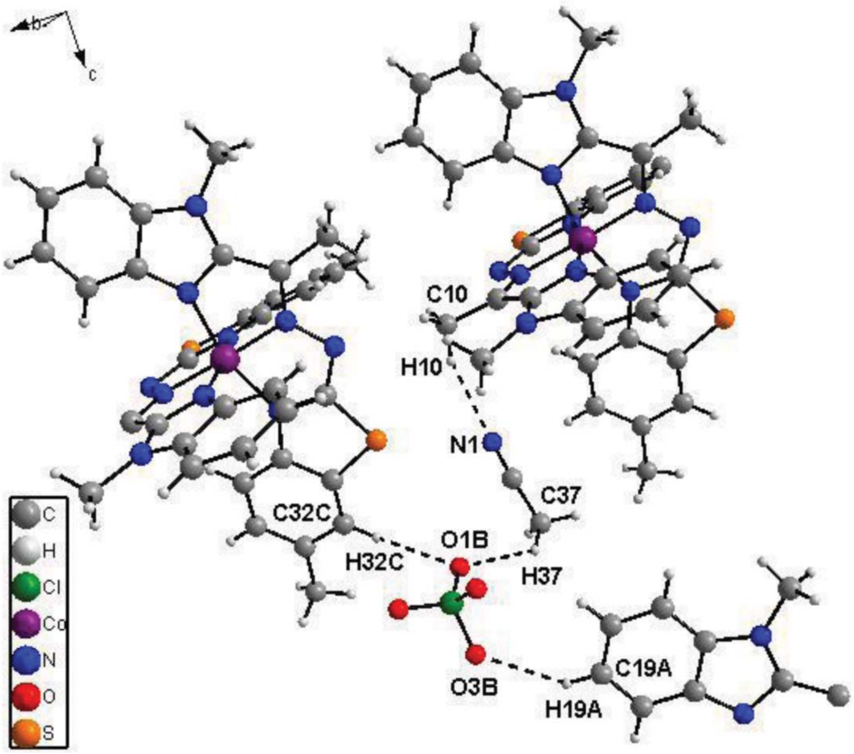


Fig. 2. The hydrogen-bonds (C-H. . .O and C-H. . .N) in **1**.

crystallographically unique Co(III) cation, two **L**$^-$, one free perchlorate ion, and one free acetonitrile molecule. Each Co (III) ion is coordinated by six nitrogen atoms of two **L**$^-$ to form a distorted octahedral geometry. The degree of distortion compared to an ideal octahedral geometry can be reflected by the bond angles around the central metal ion from 81.25(10)° to 176.77(9)° (Table 2). It is interesting to note that the distances of Co-N(benzimidazoyl) [1.932(2) and 1.934(2) Å] exhibit slightly shorter than those of Co-N (thiazoyl) [1.921(2) and 1.930(2) Å], which can be ascribed to the more electron-rich coordination site of the benzimidazoyl group than the thiazoyl unit. Within one asymmetric unit, two ligands are aligned nearly perpendicular to each other. Finally, as shown in Figures 2 and 3, the asymmetric units [Co**L**$_2$](ClO$_4$)(CH$_3$CN) are connected by the hydrogen-bonds (C-H. . .O and C-H. . .N, the detailed geometrical parameters of hydrogen bonding shown in Table 3) and offset $\pi\ldots\pi$ stacking: Cg-Cg^I (Cg = ligand plane, the centroid-centroid

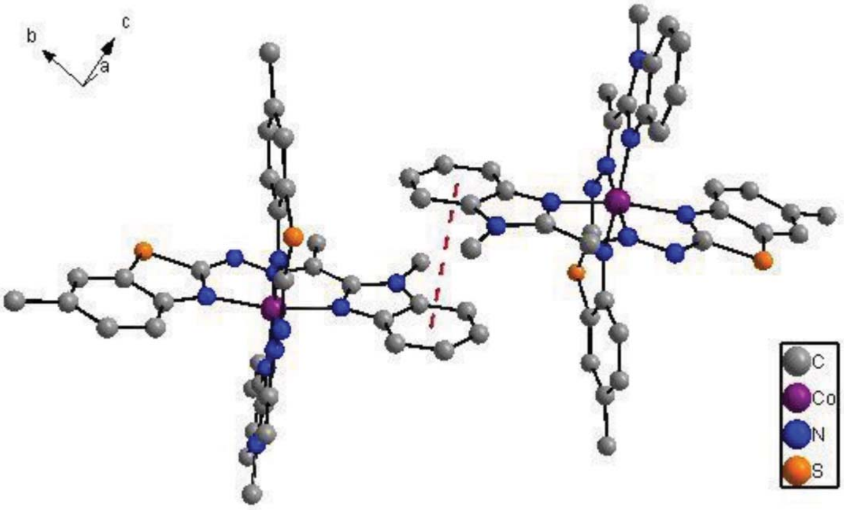


Fig. 3. The offset $\pi\ldots\pi$ stacking in **1**.

Table 3. The geometrical parameters of hydrogen bonding of **1**

D-H. . .A	D-H (Å)	H. . .A (Å)	D. . .A (Å)	D-H. . .A (°)	Symmetry code
C32C-H32C. . .O1B	0.93	2.56	3.39	149	A: x, y, 1 + z
C37-H37C. . .O1B	0.96	2.58	3.29	131	B: 1 – x, 1 – y, 1 – z
C19A-H19A. . .O3B	0.93	2.60	3.29	132	C: 1+ x, y, z
C10-H10. . .N1	0.96	2.47	3.39	160	

distance: 4.07 Å, the dihedral angle: 0.00°, the interplanar distance: 3.70 Å, symmetry code: ^{I}: 1 – x, –y, 1 – z), to generate a 3D supramolecular network in the solid state.

Antioxidant Activity of HL and 1

Figure 4 displays and compares the inhibitory effects of **HL** and **1** based on $O_2^{\cdot -}$ (Figure 4a) and $^{\cdot}OH$ (Figure 4b). It can be seen that increasing inhibitory effects against $O_2^{\cdot -}$ and $^{\cdot}OH$ are shown with the increasing concentration of the tested compounds, while the suppression ratio increases with the increasing sample concentration in the region of tested concentration. As shown in Figure 4(a), IC_{50} value of the inhibitory effects of **HL** and **1** against $O_2^{\cdot -}$ are 3.98 and 1.46 μM, respectively, which obviously display higher superoxide dismutase activities than that of standard antioxidants, such as vitamin C (IC_{50}: 852 mM).[32] Among the studied **HL** and **1** show higher superoxide scavenging ability of 50% and 67% at concentration of 4 μM. As illustrated in Figure 4b, the observed IC_{50} values of the inhibitory effects of **HL** and **1** based on $^{\cdot}OH$ are 10.12 and 5.58 μM, respectively. **HL** and **1** also showed considerably good scavenging activity with 49% and 63% at concentration of 10 μM. Especially, 1 show better antioxidants than those of **HL**. It was believed that the information of this work would afford a new possible for potential antioxidants and therapy some diseases.

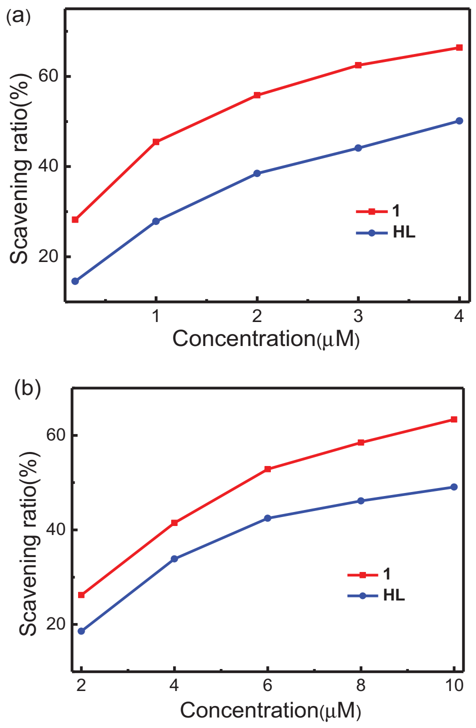


Fig. 4. Scavenging effects of **HL** and **1** on $O_2^{\cdot -}$ (a) and $^{\cdot}OH$ (b).

Conclusion

In summary, a new Co(Ⅲ) complex, [CoL_2](ClO_4)(CH_3CN), has been synthesized under solvent evaporation method based on the schiff base ligand (E)-2-{2-[1-(1-methyl-1H-benzo[d]imidazol-2-yl)ethylidene]hydrazinyl}benzo[d]thizole (**HL**). The result of single-crystal X-ray diffraction analysis reveals that **1** is a mononuclear complex. The hydrogen bonds (C-H. . .O and C-H. . .N) and $\pi. . .\pi$ interactions further extend the mononuclear units into a 3D supramolecular structure. In addition, the antioxidant activities of **HL** and **1** were also studied to afford a guiding role for potential antioxidant resistance.

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Supplementary Material

CCDC 950220 contains the supplementary crystallographic data for complex **1**. The specific information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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