两个含草酸根及硫氰酸根的新型三脚架钴(Ⅱ)配合物的合成、晶体结构及光谱性质

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摘要:本文合成了两个新型 Co(Ⅱ)配合物,$[LCo(\mu\text{-}C_2O_4)CoL]\cdot(ClO_4)_2\cdot 2CH_3CN$ (**1**)和$[CoL(SCN)]\cdot ClO_4$ (**2**),其中,L 即三(3,5-二甲基吡唑甲基)胺。在配合物 **1** 中,Co 与来自三脚架配体的 4 个氮和草酸根桥联配体的 2 个氧原子配位,处于扭曲八面体配位环境。由草酸根桥联两套 LCo,构成了一个双核结构。在单核配合物 **2** 中,Co(Ⅱ)处于三角双锥配位构型,SCN^-通过 N 配位与中心离子 Co(Ⅱ)键联。在同一晶胞中有两个构型略微不同的分子,两个分子之间通过 SCN 的 S 原子有弱相互作用。对化合物 **1** 和 **2** 在溶液中的光谱性质做了进一步的研究和讨论。

关键词:钴(Ⅱ)配合物;三(3,5-二甲基吡唑甲基)胺;草酸根桥联;晶体结构;光谱
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Synthesis, Crystal Structures and Spectral Properties of Two New Cobalt Complexes of Tripodal Ligand with Oxalate and Thiocyanate

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Abstract: Two novel cobalt complexes, $[LCo(\mu\text{-oxalate})CoL)\cdot(ClO_4)_2\cdot 2CH_3CN$ (**1**) and $[CoL(SCN)]\cdot ClO_4$ (**2**) have been synthesized, and their structures have been determined by X-ray crystallography, where L is tris[(3,5-dimethylpyrazol-l-yl)methyl]amine. In compound **1**, Co(Ⅱ) is in a distorted octahedron environment with four nitrogen atoms from the tripodal ligand and two oxygen atoms from the bridged oxalate, and the molecule is a dimmeric structure consisting of two LCo unites linked by bridging oxalate. In the monomer **2**, Co(Ⅱ) center is in trigonal bipyrimad coordination configuration, a thiocyanate group is bonded to the metal center through the nitrogen atom. There are two somewhat different configurations of **2** in the unit cell, and there is a weaker interaction between two molecules of **2** at sulphur atoms. The title complexes were generated by a precursor mononuclear cobalt (Ⅱ) complex $[CoL(N_3)]\cdot ClO_4$ (**3**). Their spectral properties in solution have been further studied and discussed. CCDC: 244798, **1**; 244799, **2**.

Key words: Cobalt (Ⅱ) complex; tris [(3,5-dimethylpyrazol-l-yl)methyl]amine; oxalate bridging; crystal structure; spectra

0 Introduction

The molecular structures and coordination configurations of metal complexes can be changed and modified by introducing of smaller ions that are namely second ligands. The second ligands usually can be divided into two kinds of types: One is terminal ligand, another is bridging ligand. The second ligands not only provide a second chemical bond, such as hydrogen bond or other weaker interactions, to assemble

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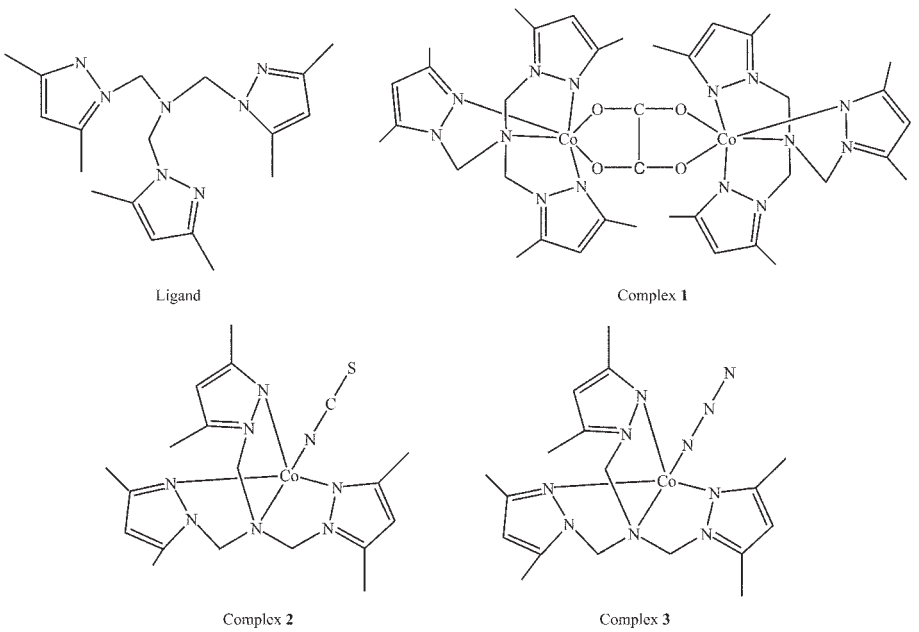
multinuclear metal complexes, but also modify the structures and configurations of metal complexes. Therefore, the metal complexes involved smaller donors have been extensively studied as the functional materials and model compounds of bio-enzymes[1~3].

Oxalate group is a versatile ligand that can adopt a large range of coordination modes. Among those, the bis (bidentate) bridging one is the most interesting and extensively studied[4~6]. Other smaller donors, such as azido[7], thiocyanate[8], are also studied extensively.

In our group, we have isolated serial metal complexes of some tripodal ligands with various second donors, such as azido group [9], chloride ion [10], and squarate ion [11]. In order to study further the affecting rule of the second ligands on the coordination configuration and properties of the metal complexes, we herein report the synthesis, crystal structures and spectral properties of two cobalt (Ⅲ) complexes of tris [(3,5-dimethylpyrizol-l-yl)methyl] amine (L) (Scheme Ⅰ) with bridging oxalate and terminal thiocyanate group.



Scheme Ⅰ Molecular structures of the compounds used in this paper

1 Experimental

1.1 Materials and general methods

All starting materials and solvents for syntheses were obtained commercially and purified by standard methods. The tripodal ligand, tris[(3,5-dimethylpyrazol-l-yl)methyl] amine (L), was synthesized according to the modified literature methods[12]. FTIR absorption spectra were recorded on a Nicolet170 SX FTIR spectrophotometer using KBr discs in the range of 4 000~400 cm^{-1}. UV-Vis spectra were recorded on a Shimadzu Uv-2401 spectrophotometer in methanol solution.

1.2 Synthesis

The precursor complex **3**, was synthesized according to the method which have been reported previously[13]. For compound **1**, $Na_2C_2O_4$ (6.7 mg, 0.05 mmol) aqueous (5 mL) was added dropwise into the solution of the precursor complex **3** (54 mg, 0.10 mmol) in methanol (15 mL) with continuous stirring for 0.5 h at room temperature. The reaction mixture was filtered. After solvent was evaporated, the red powders were generated. The red powders were dissolved in CH_3CN (5 mL) again, and it was left to stand for one month, the red crystals of **1** suitable for X-ray diffraction analysis were obtained. Elemental analyses: (Found (%): C, 42.86; H, 5.57; N, 18.89. $C_{42}H_{60}Co_2N_{16}O_{12}Cl_2$ Calcd. (%): C, 43.08; H, 5.13; N, 19.15). IR (cm^{-1}): 3 450, 2 965, ν(CN) 2 072; ν(C=O) 1 649; 1 555, 1 397, 1 276, $\nu(ClO_4)$ 1 096; 796, 624.

For compound **2**, an aqueous (5 mL) of KSCN (68 mg, 0.05 mmol) was added dropwise into a methanol solution (10 mL) of **3** (54 mg, 0.10 mmol) with continuous stirring for 0.5 h at room temperature. After two weeks, purple block crystals of **2** suitable X-ray analysis were obtained. (In our original purpose, we are going to make the dimmer compound by thiocyanate bridged, but it did not get success). Elemental analyses

(Found (%): C, 40.41; H, 5.36; N, 19.88. $C_{19}H_{27}N_8SCoClO_4$ Calcd. (%): C, 40.89; H, 4.88; N, 20.08). IR (cm^{-1}): 3 441, 2 959, ν(CNS) 2 065; 1 636, 1 554, 1 471, 1 389, 1 250, $\nu(ClO_4)$ 1 091; 798, 623.

1.3 Crystal structures determination

Crystals of **1** (0.20 mm × 0.25 mm × 0.30 mm) and **2** (0.22 mm × 0.18 mm ×0.14 mm) were mounted on respective glass fibers using epoxy resin. Data collection was performed on a Siemens SMART diffractometer equipped with a CCD detector (Mo $K\alpha$ radiation). The data of **1** and **2** were collected up to 2θ maximum of 50.04° using the ω-scan technique.

The intensities were corrected for Lorentz-polarization effects, absorption and intensity decay, respectively. The crystal structures were solved by the direct methods and by subsequent difference Fourier syntheses. Anistropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by the use of geometrical restrains. The SHELXTL-PC program packages[14] were used for computations. All pertinent crystallographic data for **1** and **2** are summarized in Table 1.

CCDC: 244798, **1**; 244799, **2**.

Table 1　Crystallographic data and processing parameters for 1 and 2

Molecular formula	$C_{42}H_{60}Cl_2Co_2N_{16}O_{12}$ (**1**)	$C_{38}H_{54.5}Cl_2Co_2N_{16}O_{8.25}S_2$ (**2**)
Formula weight	1 169.82	1 120.36
Crystal color and habit	Red, block	Blue purple block
Crystal dimension / mm	0.20 × 0.25 × 0.30	0.22 × 0.18 × 0.14
System space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a / nm	1.094 49(12)	0.898 9(3)
b / nm	1.189 36(12)	1.444 3(4)
c / nm	1.215 77(13)	2.035 5(6)
α / (°)	78.998(2)	92.012(6)
β / (°)	71.374(2)	100.936(6)
γ / (°)	65.153(2)	90.328(6)
V / nm^3	1.357 9(2)	2.592 8(14)
Z	1	2
D_c / ($kg \cdot m^{-3}$)	1.430	1.435
μ / (mm^{-1})	0.781	0.886
F(000)	608	1 161
θ range / (°)	1.77~25.02	1.02~25.01
Measured refl. number	5 686	13 543
Independent refl. number	4 764 (R_{int}=0.015 9)	9 103 (R_{int}=0.076 6)
R [$I>2\sigma(I)$]	R_1=0.044 5, wR_2=0.125 4	R_1=0.066 6, wR_2=0.156 2
R (all data)	R_1=0.056 3, wR_2=0.135 1	R_1=0.137 3, wR_2=0.194 1
GOF	1.037	0.956
Data/ restrait / parameters	4 764 / 0 /334	9 103/190/712
Largest diff. peak and hole ($e \cdot nm^{-3}$)	407 / −455	1 027 / −452

2 Results and discussion

2.1 Synthesis

In order to study the affecting rule of the second ligands on configuration of Co(Ⅱ) complexes, a precursor compound **3** was prepared at first, and then the second donor, $C_2O_4^{2-}$ or SCN^-, was added into the methanol and acetonitrile mixture (v∶v=1∶1) of **3** with the molar ratio of **3**: C_2O_4 (or SCN)=2∶1. The dimmer 1 and monomer **2** were isolated from the reaction mixture, respectively.

It has been ever tried by using the mole ratio of 2∶2∶1 of cobalt (Ⅱ) salt to tripodal ligand to oxalate ion to make complex **1**, but we did not get success. While an extra amount of oxalate was added into the reaction mixture of metal salt and tripodal ligand, and a six-

coordinated octahedron monomer metal complex incorporated as a 1,2-bis-dentate terminal coordinated oxalate has been isolated in our group[11].

From the fact of synthesis, it can be seen that the order of coordination ability of the second ligands is: $C_2O_4^{2-} > SCN^- > N_3^-$ in this reaction condition. The oxalate is easier to generate dimmer with six-coordinated configuration because the longer distance of two C=O sets bridging groups. The SCN^- group coordinated to the metal center through nitrogen, and it does not seem to have any binuclearing tendency toward cobalt (Ⅱ) due to the electronic and stereo inhibiting effect. It is obvious that the configurations of metal complexes of tripodal ligand can be affected by different second ligands. While for the complexes of same ligand, the molar ratio of metal salt to ligand and second donor is more important, and the configuration of metal complex can be changed by proper molar ratio selected.

2.2 Crystal structures

The structure of **1** is shown in Fig.1, and the selected bond distances and angles are listed in Table 2. The binuclear cation consists of two LCo unites bridged by a bis-bidentate oxalate anion. As can be seen in Fig.1, in the complex **1**, the tripodal ligand binds at both metals by *cis*-α form, and in which the pyrizol rings of ligand are trans. There is a crystallographic inversion center in the middle of the bridged oxalate, bisecting the C(19)-C(19A) bond and relating the left side of the molecule to the right side in Fig.1. Consequently, the coordination geometries of the two center cobalt(Ⅱ)s are identical, and each metal cation presents a distorted octahedral coordination configuration with the four nitrogen atoms of the tris [(3,5-dimethylpyrazol-l-yl)methyl]amine ligand and two oxygen atoms of the bridging oxalate. The $C_2O_4^{2-}$ ion is approximately planar and the two Co atoms lie only -0.005 96 nm out of this plane. The C-O bond lengths of 0.125 1(3) and 0.124 3(3) nm in the oxalate ion are normal for bidentate coordination. The C-C bond of 0.156 3(6) nm is longer than that of normal C-C bond, which is similar to those of binulear metal complexes by oxalate bridged[15]. The bond length of Co(1)-O(2) is 0.212 3 (2) nm, which is slightly longer than that of Co(1)-O(1) [0.205 1(19) nm]. The Co(1)···Co(1A) separation is 0.539 7 nm, again shorter than bis (bidentate) oxalate Co(Ⅱ)-Co(Ⅱ) complex reported by literature[15].

The axial bond lengths Co-$N_{pyrizol}$, Co (1)-N (1)= 0.210 2(2) nm and Co(1)-N(3)=0.214 3(2) nm, are longer than that of the equatorial one, Co (1)-N (3)= 0.207 8(2) nm which is in the trans positions of the oxalate group. While the Co-N_{amne} of 0.223 2 (2) nm is longer than those of Co-$N_{pyrizol}$. The Co-N_{amine} of complex **1** is shorter than that of the precursor complex **3**, it might be due to coordinated ability of oxalate with cobalt(Ⅱ) is stronger than that of azide group.

The angle of N_{amine}-Co(1)-$N_{pyrazol}$ are slightly various from 76.86(9)° to 79.02(8)° to 79.40°. Thus, deviating significantly from the ideal coordination angle of 90° was observed, which is similar to that of complex with tripodal tetradentate amine[16].

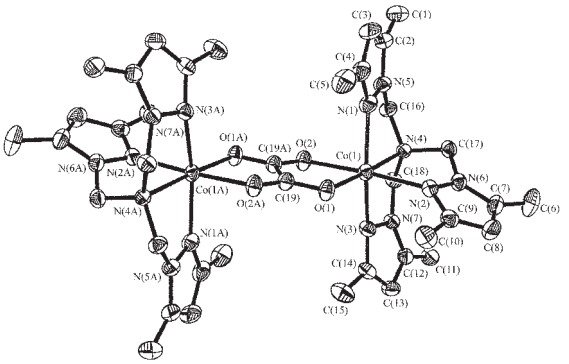


Fig.1 Molecular structure of complex **1**
Hydrogen atoms are omitted.

Table 2 Selected bond lengths (nm) and bond angles (°) of 1

Bond length			
Co(1)-O(1)	0.205 10(19)	N(1)-N(5)	0.135 6(4)
Co(1)-N(1)	0.210 2(3)	N(2)-N(6)	0.136 6(3)
Co(1)-N(2)	0.207 8(2)	N(3)-N(7)	0.136 4(3)
Co(1)-O(2)	0.212 3(2)	N(4)-C(17)	0.146 4(4)
Co(1)-N(4)	0.223 2(2)	N(4)-C(18)	0.147 3(3)
O(1)-C(19)	0.125 1(3)	N(1)-C(4)	0.133 3(4)
O(2)-C(19A)	0.124 3(3)	N(2)-C(9)	0.133 6(4)
Bond angle			
O(1)-Co(1)-N(2)	102.27(9)	O(2)-Co(1)-N(3)	87.97(9)
O(1)-Co(1)-N(1)	100.27(9)	O(1)-Co(1)-N(4)	177.07(8)
N(2)-Co(1)-N(1)	99.39(10)	N(2)-Co(1)-N(4)	79.40(9)
O(1)-Co(1)-O(2)	80.37(8)	O(2)-Co(1)-N(4)	98.17(8)
N(2)-Co(1)-O(2)	174.62(8)	N(3)-Co(1)-N(4)	79.02(8)
N(1)-Co(1)-O(2)	84.64(10)	C(19)-O(1)-Co(1)	113.60(18)
O(1)-Co(1)-N(3)	103.41(9)	C(19)-O(2)-Co(1)	111.22(18)
N(2)-Co(1)-N(3)	86.85(9)	C(4)-N(1)-Co(1)	140.8(2)
N(1)-Co(1)-N(3)	153.46(10)	N(5)-N(1)-Co(1)	113.82(17)
C(9)-N(2)-Co(1)	136.2(2)	N(6)-N(2)-Co(1)	112.23(17)

A perspective view of **2** and a packing diagram are shown in Fig.2 and Fig.3, respectively. Selected bond lengths and bond angles are given in Table 3. There are two independent configurations that are somewhat different in the same unit cell. Each cobalt atom lays a distorted trigonal bipyramidal environment composed of three pyrizol nitrogen atoms and one amine nitrogen from L and one thiocyanate nitrogen atom which is in the axial position. The CNS^- group is almost linear [N(8)-C(19)-S(1)=176.5(8)°, and N(16)-C(38)-S(2)=179.0(9)°]. The distance of Co-$N_{pyrazol}$ [average bond length of Co-$N_{pyrazol}$ is 0.204 2(6) nm or 0.204 6(6) nm] is longer than that of Co-$N_{thiocyanate}$ bond length [0.196 6(7) nm or 0.197 0(7) nm] due to the stereo inhibiting from substituted methyl groups on the pyrizol ring, while it is slightly shorter than that of Co-N_{azido} of **3** [0.198 1(4) nm], which might be due to the electronic delocation on S atom of SCN^- leading to the slightly increase of electronic densities on nitrogen of SCN^- group and coordinated abilities increase. The distance of Co-N_{amine} [0.228 5(5) nm] is much longer than those of Co-$N_{pyrizol}$ because of the stronger para-effect of the coordinated thiocyanate group, which is similar to the coordination mode of same ligand in the mononuclear compounds.

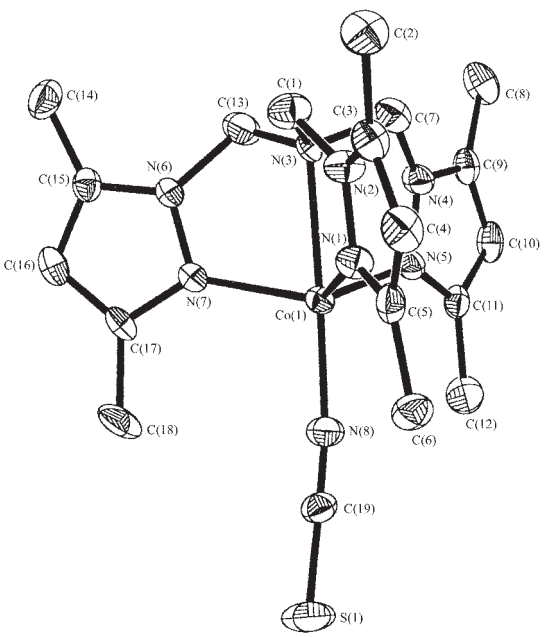


Fig.2　Molecular structure of complex **2**

Fig.3 shows a perspective drawing of the molecular stacking of **2** in the unit cell. It is obvious that there is a weaker interaction of two molecules of **2** at the thiocyanate sulphur atom. The S(1)⋯S(2) distance is 0.360 2 nm.

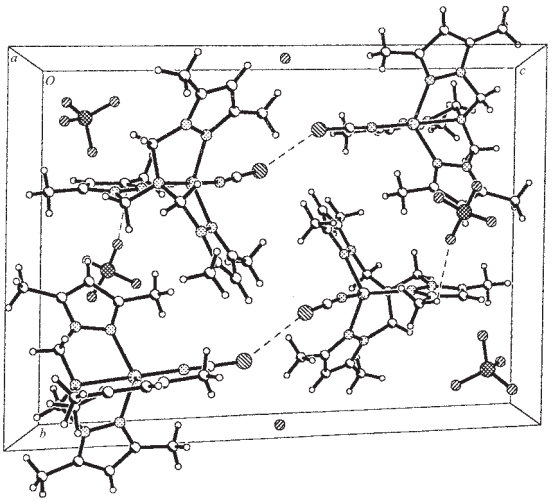


Fig.3　Perspective view of molecular stacking of **2** in unit cell

Table 3　Selected bond lengths (nm) and bond angles (°) of 2

Bond length			
Co(1)-N(8)	0.196 6(7)	N(1)-C(5)	0.132 8(9)
Co(1)-N(5)	0.201 3(6)	N(7)-C(17)	0.133 1(8)
Co(1)-N(1)	0.205 3(6)	N(5)-C(11)	0.133 6(8)
Co(1)-N(7)	0.205 9(6)	N(3)-C(13)	0.142 4(9)
Co(1)-N(3)	0.228 5(5)	N(3)-C(1)	0.144 5(9)
Co(2)-N(16)	0.197 0(7)	S(2)-C(38)	0.159 8(9)
Co(2)-N(9)	0.203 3(6)	N(11)-C(20)	0.144 5(8)
Co(2)-N(11)	0.227 6(5)	N(15)-C(36)	0.133 1(8)
Co(2)-N(13)	0.205 6(6)	N(13)-C(30)	0.132 7(9)
Co(2)-N(15)	0.204 8(6)	N(14)-C(34)	0.134 4(8)
S(1)-C(19)	0.160 5(8)	N(3)-C(3)	0.143 8(9)
Bond angle			
N(8)-Co(1)-N(5)	106.2(3)	N(1)-Co(1)-N(7)	115.9(2)
N(8)-Co(1)-N(1)	101.3(3)	N(8)-Co(1)-N(3)	176.5(2)
N(5)-Co(1)-N(1)	112.0(2)	N(5)-Co(!)-N(3)	77.2(2)
N(8)-Co(1)-N(7)	103.0(3)	N(1)-Co(1)-N(3)	76.3(2)
N(5)-Co(1)-N(7)	116.4(2)	N(7)-Co(1)-N(3)	76.1(2)
N(8)-C(19)-S(1)	179.0(9)	N(16)-C(38)-S(2)	178.7(8)
N(16)-Co(2)-N(9)	104.8(3)	N(15)-Co(2)-N(13)	116.9(2)
N(16)-Co(2)-N(15)	103.5(3)	N(16)-Co(2)-N(11)	178.2(3)
N(9)-Co(2)-N(15)	114.4(2)	N(9)-Co(2)-N(11)	76.7(2)
N(16)-Co(2)-N(13)	102.3(3)	N(15)-Co(2)-N(11)	76.5(2)
N(9)-Co(2)-N(13)	112.7(2)	N(13)-Co(2)-N(11)	76.2(2)

2.3　Spectroscopic properties

The spectra data of the title complexes are shown in Table 4, and the data of **3** were shown for comparison.

Table 4 Spectra data of 1 and 2, the data of 3 were shown for comparison

Spectra	Ligand	Complex **1**	Complex **2**	Complex **3**	Assignment
UV-Vis λ / nm		247(4 120)	325(1 200)	299 (171)	L → Co
(ε / (mmol^{-1}·L·cm^{-1}))		593(35)	578(92)	516(94)	*d* → *d*
		496(113)			
		467(101)		604(861)	
IR / cm^{-1}		1 097, 1 052	1 091	1 107, 1 059	ClO_4^-
			2 065 (SCN)	2 102	N_3^-
		1 650			C=O

2.3.1 IR spectra

The IR spectra of the title complexes show that $\nu_{C=O}$ model exhibits very strong absorption band at 1 650 cm^{-1} and strong band of N_3^- at 2 102 cm^{-1} disappeared contrasting to that of the precursor **3**, which has been shown that incorporated azide group of **3** has been replaced by oxalate, a weaker absorption band at 2 073 cm^{-1} is assigned to C≡N vibration from the solvent CH_3CN. A strong absorption band at 1 096~1 052 cm^{-1} is assigned to the perchlorate ion[17]. All of these are consistent with the results of the X-ray structure analysis.

In IR spectra of **2**, there is a very strong band at 2 065 cm^{-1} assigned to CN stretching vibration[18] of thiocyanate group. The δ NCS value of 484 (w) and 442 cm^{-1} (m) in compound **2** indicates that NCS group is bonded to the cobalt ion through the nitrogen atom because N-bonded group absorbs in the range 440~490 cm^{-1}, S-bonded group absorbs in the range 400~440 cm^{-1} [19]. The stronger absorption band at 1 091 cm^{-1} of ClO_4^- is observed.

2.3.2 Electronic spectra

The electronic spectra of **1** in methanol solution show that a broad band of moderate intensity with a shoulder at 470 nm (101 mol^{-1}·dm^3·cm^{-1}) appears at 496 nm (113 mol^{-1}·dm^3·cm^{-1}), and another is at 590 nm (35 mol^{-1}·dm^3·cm^{-1}) which assigned to *d-d* band. The *d-d* band was much red-shifting compared with that of **3** (516 nm, 94 mol^{-1}·dm^3·cm^{-1}). It indicates that **1** might change slightly from octahedron to a tetrahedron geometry in acetonitrile solution due to incorporating oxalate[20]. The electronic spectra of **2** in methanol show that the d-d band is at 578 nm (92 mol^{-1}·dm^3·cm^{-1}), which is also red-shifting compared with that of **3** due to the electronic effect on sulphur atom of the coordinated NCS^- group.

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