

Synthesis, crystal structures and spectral properties of cobalt(II) complexes: $[\text{CoL}(\text{N}_3)] \cdot \text{ClO}_4$ and $\text{CoL}(\text{N}_3)_2$ [L = tris((3,5-dimethylpyrazol-1-yl)methyl)amine]

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Two monomeric cobalt(II) complexes, $[\text{CoL}(\text{N}_3)] \cdot \text{ClO}_4$ (1) and $\text{CoL}(\text{N}_3)_2$ (2), where L is tris((3,5-dimethylpyrazol-1-yl)methyl)amine, were synthesized and their crystal structures were determined by X-ray diffraction technique. Complex 1 is five coordinated with one azide nitrogen atom and four nitrogen atoms of the tris((3,5-dimethylpyrazol-1-yl)methyl)amine ligand, and the metal center is in distorted trigonal bipyramidal environment. Complex 2 is six coordinated distorted octahedron with the two azide nitrogen atoms and four nitrogen donors of the tris((3,5-dimethylpyrazol-1-yl)methyl)amine ligand. The solution behaviors of the title complexes have been further investigated by UV-Vis, and ^1H NMR analysis. It is found that the formation of 1 and 2 depends on the molar ratio of the azide ion to metal salt and ligand. Complex 1 attached with one azide group is more stable and easy to generate than complex 2 incorporated with two azide groups, and the reasons were well discussed.

Keywords Tripodal ligand, cobalt(II) complex, crystal structure, spectroscopic properties, azide ligand

Introduction

The metal complexes of some tripodal ligands as some bioenzyme models have been studied extensively.¹⁻³ Among them, the ligands containing imidazoles and its derivatives, such as pyrazole and its derivatives, have attracted much attention for the understanding of the relationship between structural features and the bio-

logical properties. Tris((3,5-dimethylpyrazol-1-yl)methyl)amine (L) is tripodal in shape and a potential tetradentate ligand to a variety of metal ions, and it is a strong base and acts as a bulky group (Chart 1). The metal complexes of this ligand have made great contributions.⁴⁻⁶ Among them, the cobalt(II) complexes of L with various second coordinated groups, such as BPh_4 and H_2O , have been investigated as the model complexes for cobalt-substituted carbonic anhydrase.⁷⁻⁹

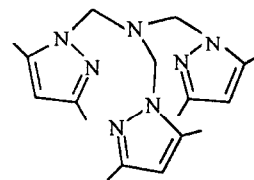


Chart 1 Molecular structure of ligand L.

The participation of the second coordinating group not only changes the properties of the metal complexes, such as solubility, but also modifies the configuration of the metal complexes. Thus, using various small donors for assembling ideal configuration is a good method in molecular construction. Azide group is a useful one for this purpose because it can link metal centers by different fashion,¹⁰ either simple monomer as a terminal coordinated ligand or bridging end-to-end or end-on modes.¹¹

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In order to further explore the effect of the second coordinating group on the coordination configuration and the properties of the metal complexes, we herein report the crystal structures of the cobalt(II) complexes of tm-pza incorporated azide ions and their spectroscopic properties.

Experimental

General methods

IR absorption spectra were recorded on a Nicolet 170 SX FT-IR spectrophotometer using KBr discs. UV-Vis spectra were recorded on a Shimadzu UV-240 spectrophotometer in methanol solution. ^1H NMR analysis was performed on a Bruker AC-P200 spectrometer (200 MHz, 25°C) in CD_3CN . Chemical shifts (in ppm) are referenced to the residual protonic solvent peaks.

Syntheses

Tripodal ligand All reagents were of reagent grade. Tris((3, 5-dimethylpyrazol-1-yl) methyl) amine (L) was synthesized according to the modified literature methods.¹² Ammonium acetate (3.08 g, 40 mmol) and *N*-(hydroxymethyl)-3, 5-dimethylpyrazole (5.0 g, 120 mmol) were dissolved in acetonitrile (60 mL) and stirred for 24 h at room temperature. Then, the solvent was removed by a vacuum rotary evaporator, rendering colorless oily product to be recrystallized with 10 mL of water and kept cooling in a freezer to obtain the white crystalline product. ν_{max} (KBr pellets, cm^{-1}): 3427, 2984, 2920, 2880, 1555 (pyrazol ring), 1458, 1312, 775. δ_{H} (CD_3CN): 1.82(9H, s, 3- CH_3), 2.16(9H, s, 5- CH_3), 4.94(6H, s, CH_2), 5.75(3H, s, 4-CH of pyrazol ring). Anal. $\text{C}_{18}\text{H}_{27}\text{N}_7$. Calcd.: C, 63.30; H, 7.98; N, 28.72. Found: C, 62.95; H, 8.30; N, 28.48.

$[\text{CoL}(\text{N}_3)] \cdot \text{ClO}_4$ **1** The solution of Co(ClO_4)₂·6H₂O (36.6 mg, 0.1 mmol) in methanol (10 mL) was added dropwise into the solution of L, (34.1 mg, 0.1 mmol) in methanol (20 mL). To this reaction mixture, a methanol solution (ca. 5 mL) of NaN_3 (13 mg, 0.2 mmol) was added with continuous stirring for 1 h. The final mixture was filtered and the filtrate was left to stand over two weeks until blue crystals of complex **1** deposited. Yield 80%. ν_{max} (KBr pellets,

cm^{-1}): 3432, 2998, 2044 (N_3), 1557 (pyrazol-ring), 1467, 1103 (ClO_4), 624 (ClO_4). δ_{H} (CD_3CN): 1.98 (9H, s 3- CH_3), 2.27(9H, s 5- CH_3), 7.48(3H, br, 4-CH of pyrazol ring), 22.70—22.77(6H, m, CH_2). Anal. $\text{C}_{18}\text{H}_{27}\text{N}_{10}\text{-CoClO}_4$. Calcd: C, 39.86; H, 5.02; N, 25.84. Found: C, 39.30; H, 4.80; N, 26.01.

$\text{CoL}(\text{N}_3)_2$ **2** Except for increasing the amount of NaN_3 and choosing the molar ratio of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to L to NaN_3 as 1:1:5. The similar procedures to that of **1** were run, and two kinds of crystals were obtained, in which the blue crystal of **1** as the major species and the red purple crystal of **2** as the minor one deposited. Suitable red purple crystal of **2** was picked out for X-ray analysis. Yield 10%. ν_{max} (KBr pellets, cm^{-1}): 3425, 2922, 2054 (N_3), 2029 (N_3), 1556 (pyrazol-ring), 1469, 1397, 1041, 796. δ_{H} (CD_3CN): 1.99(9H, s, 3- CH_3), 2.60(9H, s, 5- CH_3), 7.71(3H, br, 4-CH of pyrazolring), 22.82—22.96(6H, m, CH_2). Anal. $\text{C}_{18}\text{H}_{27}\text{N}_{13}\text{Co}$. Calcd.: C, 44.61; H, 5.62; N, 37.59. Found: C, 44.45; H, 5.16; N, 37.44.

Caution: Metal perchlorate salts containing organic ligands and azido salts are potentially explosive and should be handled with great care.

X-Ray crystallography

All pertinent crystallographic data for **1** and **2** are summarized in Table 1. Crystals **1** and **2** were mounted on glass fibers using epoxy resin. Data collection proceeded on an Enraf-Nonius CAD-4 diffractometer for **1** and a Siemens SMART diffractometer equipped with a CCD detector (Mo K_α) for **2**, respectively. The data for **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, for absorption and also for intensity decay. The crystal structures were solved by direct methods and by subsequent Fourier analysis. Anisotropic displacement parameters were applied to non-hydrogen atoms in full-matrix least-squares refinements based on F for **1** and F^2 for **2**, respectively. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by the use of geometrical restraints. The SHELXTL-PC¹³ program packages were used for computations.

Table 1 Crystallographic data and processing parameters for 1 and 2

Compound	1	2
Molecular formula	C ₃₆ H ₅₄ Co ₂ N ₂₀ (ClO ₄) ₂	C ₁₈ H ₂₇ CoN ₁₃
Formula weight	1083.74	484.46
Crystal color and habit	blue, block	red purple, block
Crystal dimension (mm)	0.20 × 0.30 × 0.40	0.35 × 0.30 × 0.25
System space group	triclinic, <i>P</i> -1	Orthorhombic, <i>Pbca</i>
<i>a</i> (nm)	0.8979(2)	1.7414(11)
<i>b</i> (nm)	1.4658(3)	1.2908(8)
<i>c</i> (nm)	2.0248(4)	1.9962(13)
α (°)	108.98(3)	90
β (°)	94.76(3)	90
γ (°)	90.80(3)	90
<i>V</i> (nm ³)	2.509(1)	4.487(5)
<i>Z</i>	2	8
<i>D_c</i> (kg/m)	1.434	1.434
μ (mm ⁻¹)	0.8312	0.800
<i>F</i> (000)	1124	2024
θ range (°)	2–25	2.04–25.02
Measured refl. number	9004	17747
Independent refl. number	7239 (<i>R</i> _{int} = 0.055)	3957 (<i>R</i> _{int} = 0.0648)
Observed refl.	3924 (<i>I</i> ≥ 3 σ (<i>I</i>))	3011 (<i>I</i> ≥ 2 σ (<i>I</i>))
<i>R</i>	0.068	0.041
<i>R_w</i> ^a	0.074	0.108
GOF	1.06	1.039
Data/restraint/parameters	3924/0/591	3957/0/289
Largest diff. peak and hole e/nm × 10 ³	0.5/–0.43	0.373/–0.322

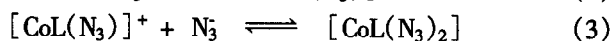
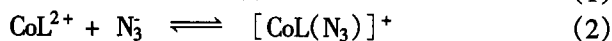
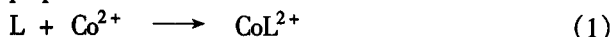
$$^a R_w = [\sum w(|F_o| - |F_c|)^2], w = 1/(\sigma^2(F) + 0.0001F^2)$$

Results and discussion

Syntheses of 1 and 2

The reaction of cobalt(II) ions and tris((3,5-dimethyl-pyrazol-1-yl)methyl)amine (L) in the presence of azide ions in methanol media afforded the title complexes 1 and 2. The outcome is dependent on the molar ratio of the azide salt to the ligand. Employing the azide salt to L to cobalt(II) in 2:1:1 molar ratio only gave blue block of complex 1. When the amount of azide salt was increased and the molar ratio of azide to L to cobalt perchlorate in 5:1:1 was kept, there was a mixture of 1 and 2 formed, in which the amount of the blue crystal of 1 was much more than that of the red purple of 2. Attempts to obtain azide-bridged dimer complex were not successful under the conditions mentioned above. It is illustrated that 1 is more stable and easy to generate than 2 because Co(II) is favorable to form a five-coordinated configuration than six-coordination. After one azide

group is coordinated, another azide group is more difficult to insert into the bulky adduct complex of L with cobalt(II) perchlorate due to the steric effect from the substituted methyl groups on sites 1 and 3 of the pyrazole rings. From the experimental phenomena, a possible formation reaction mechanism of the complexes could be proposed as follows:



Crystal structure

Structure of 1

There are two different molecules of complex 1 in a unit cell. The perspective views for both molecules are shown in Fig. 1 and Fig. 2, respectively. Selected bond lengths and bond angles of the two molecules are summarized in Table 2. From the Fig. 1, it can be seen that

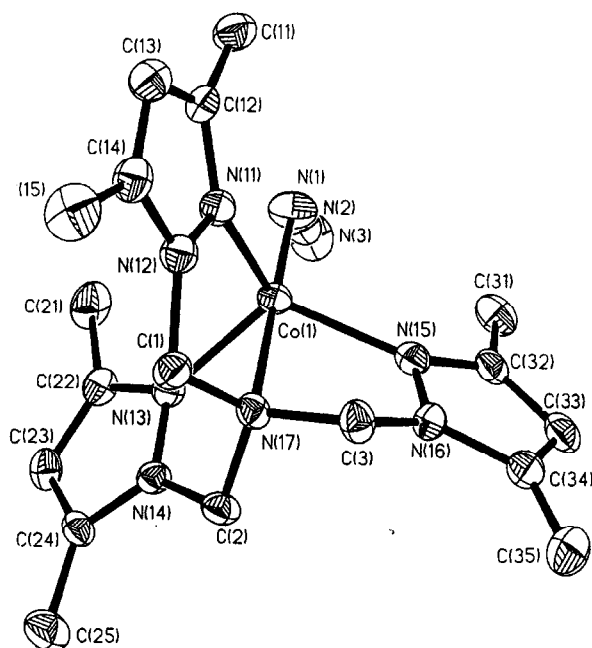


Fig. 1 Molecular structure of $[\text{CoL}(\text{N}_3)] \cdot \text{ClO}_4$ (1).

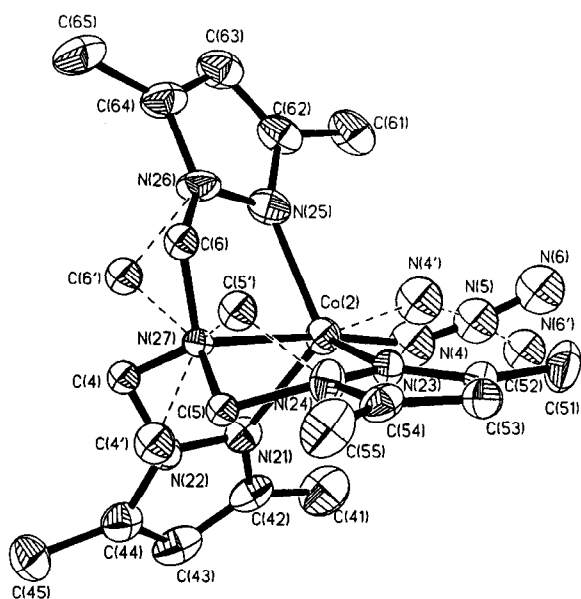


Fig. 2 Another molecular structure of $[\text{CoL}(\text{N}_3)] \cdot \text{ClO}_4$ (1).

$[\text{CoLN}_3]^+$ cation is in a five-coordinated environment formed by three pyrazol nitrogen atoms and one amine nitrogen from L and one azido nitrogen atom. The geometry is best described as distorted trigonal bipyramid with the amine nitrogen and the azide nitrogen in the axial sites. Similar coordination geometry has been encoun-

tered for cobalt complexes with the same ligand.^{14,15} The cobalt to amine nitrogen distance is somewhat longer than that of the cobalt to pyrazol nitrogen, and they can be regarded as normal for this class of complexes.¹⁶ The distance of $\text{Co}(1) - \text{N}_{\text{amine}}$ [0.2303(4) nm] is much longer than that of $\text{Co}(1) - \text{N}_{\text{azido}}$ [0.1981(4) nm].

The coordinated angles around $\text{Co}(1)$ are very similar: the angle of $\text{N}_{\text{amine}} - \text{Co}(1) - \text{N}_{\text{pyrazol}}$ varies from 75.5 to 76.3°, thus, deviating significantly from the ideal coordination angle of 90° was observed, which is a character of tripodal pyrazol complexes.¹⁷ The tertiary amine nitrogen to cobalt to azide nitrogen angle is nearly 180°.

In another molecule of complex 1 in the unit cell, there are two somewhat different configurations arisen from some atoms being in disordered state. As shown in Fig. 2, the occupancy of C(4), C(5), C(6) is 70%, respectively, while the occupancy of N(4), N(6) is 50%, respectively. The molecular structure is shown by solid line. The occupancy of C(4'), C(5'), C(6') is 30%, respectively, while the occupancy of N(4'), N(6') is 50%, respectively. The molecular structure is shown by dashed line. The ClO_4^- is in disordered state.

Structure of 2

A plot and atom numbering scheme of complex 2 is shown in Fig. 3. Selected bond lengths and bond angles are given in Table 3. Two single azide anions coordinate to the central metal ion as the terminal ligand and show *cis*-configuration. The cobalt(II) is in a distorted octahedral environment with two azide nitrogen atoms and four nitrogen atoms from L. The distances of $\text{Co}-\text{N}(11)$ [0.2271(3) nm] and $\text{Co}-\text{N}_{\text{amine}}$ [0.2268(2) nm] are much longer than those of $\text{Co}-\text{N}_{\text{pyrazol}}$ due to the stronger *para*-effect of the coordinated azide groups.

The pyrazole rings of L in this complex are divided into two types: two pyrazole rings of L are *trans* to each other, namely equatorial, and the other one is *trans* to the terminal azido group, namely axial. The two equatorial pyrazole arms cause distortion of the octahedron of the cobalt center with a bond angle $\text{N}(1) - \text{Co} - \text{N}(11) = 165.79(10)^\circ$. The distances of $\text{Co}-\text{N}_{\text{azido}}$ in complex 2 [0.2123(3), 0.2021(3) nm] are much longer than the distance of $\text{Co}-\text{N}_{\text{azide}}$ in complex 1 [0.1981(4) nm] because the coordination number of $\text{Co}(\text{II})$ in 2 is higher than that of $\text{Co}(\text{II})$ in 1 with the same ligand. While the

distance of Co—N_{aziido} being in axial site, Co(1)—N(1) [0.2123(3) nm] is longer than that of Co—N(4) [0.2021(3) nm] due to the stronger *trans* influence of

the 3,5-dimethyl pyrazole than that of the tertiary amine group,¹⁷ and this case is quite similar to that of other tripodal ligand complexes.¹⁸

Table 2 Selected bond lengths ($\times 10^{-1}$ nm) and bond angles ($^{\circ}$) of the complex **1**

Bond length			
Co(1)—N(1)	1.981(4)	N(2)—N(3)	1.143(6)
Co(1)—N(11)	2.028(5)	N(15)—N(16)	1.376(6)
Co(1)—N(13)	2.041(4)	N(11)—C(12)	1.339(8)
Co(1)—N(17)	2.303(4)	N(13)—C(22)	1.332(6)
Co(1)—N(15)	2.054(5)	N(15)—C(32)	1.337(6)
N(11)—N(12)	1.373(5)	N(17)—C(1)	1.463(6)
N(1)—N(2)	1.182(6)	N(17)—C(3)	1.477(6)
Co(2)—N(4)	1.955(7)	N(4)—N(5)	1.154(8)
Co(2)—N(4')	1.954(7)	N(4')—N(5')	1.148(8)
Co(2)—N(21)	2.049(4)	N(5)—N(6)	1.201(8)
Co(2)—N(23)	2.023(5)	N(5)—N(6')	1.217(8)
Co(2)—N(25)	2.052(5)	N(21)—N(22)	1.341(7)
Co(2)—N(27)	2.308(4)	N(21)—C(42)	1.320(6)
Bond angles			
N(1)—Co(1)—N(11)	103.4(2)	N(4')—Co(2)—N(25)	91.2(2)
N(1)—Co(1)—N(13)	105.2(2)	N(21)—Co(2)—N(25)	114.7(2)
N(11)—Co(1)—N(13)	107.6(2)	N(23)—Co(2)—N(25)	113.3(2)
N(1)—Co(1)—N(15)	103.4(2)	N(4)—Co(2)—N(27)	171.5(2)
N(11)—Co(1)—N(15)	118.5(2)	N(4')—Co(2)—N(27)	166.3(2)
N(13)—Co(1)—N(15)	117.0(2)	N(21)—Co(2)—N(27)	75.8(2)
N(11)—Co(1)—N(17)	76.3(2)	N(23)—Co(2)—N(27)	76.4(2)
N(13)—Co(1)—N(17)	75.5(1)	N(25)—Co(2)—N(27)	75.8(2)
N(15)—Co(1)—N(17)	76.2(1)	C(4)—N(22)—C(44)	128.6(4)
N(1)—Co(1)—N(17)	179.3(2)	C(4')—N(22)—C(44)	117.4(5)
Co(1)—N(1)—N(2)	131.7(5)	C(5)—N(24)—C(54)	125.0(5)
Co(1)—N(11)—N(12)	137.4(3)	C(5')—N(24)—C(54)	121.4(5)
Co(1)—N(13)—N(14)	116.6(3)	C(6)—N(26)—C64	125.1(5)
Co(1)—N(15)—N(16)	115.7(3)	C(6')—N(26)—C64	117.7(4)
Co(1)—N(17)—C(1)	108.7(3)	N(4)—Co(2)—N(23)	108.6(2)
N(4)—Co(2)—N(4')	20.5(2)	N(4')—Co(2)—N(23)	105.6(2)
N(4)—Co(2)—N(21)	95.8(2)	N(21)—Co(2)—N(23)	115.0(2)
N(4')—Co(2)—N(21)	114.4(2)	N(4)—Co(2)—N(25)	107.6(2)

Spectral characters

IR spectra The IR spectra of the title complexes show that $\nu_{\text{asym.}}(\text{N}_3^-)$ model exhibits very strong absorption bands. In complex **1**, a single band at 2069 cm^{-1} is consistent with one incorporated azide group, whereas two bands at 2054 and 2029 cm^{-1} can be attributed to the two terminal coordinated azide groups in

complex **2**. These spectral data are typical for coordinated azide complexes and consistent with those of reported azide complexes.¹⁹ In complex **1**, there is a strong absorption band at 1090 cm^{-1} assigned to the perchlorate ion.

Electronic spectra The electronic spectra of **1** and **2** are measured in methanol solution, and the spectral data

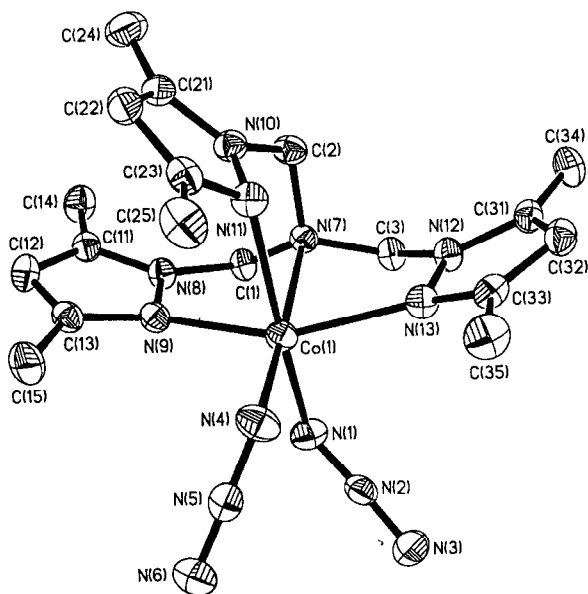


Fig. 3 Molecular structure of $\text{CoL}(\text{N}_3)_2$ (**2**).

and assignment are summarized in Table 4. From Table 4, it can be seen that the d-d transition of **1** or **2** appeared as a broad band at 516 ($94 \text{ M}^{-1} \cdot \text{cm}^{-1}$) or 520 ($70 \text{ M}^{-1} \cdot \text{cm}^{-1}$), respectively. There are slightly red

shifts for the corresponding bands of **2** toward those of **1**. This can be illustrated that the increasing of the azide ligands raises the base property of the medium which is consistent with some reported results.¹⁷ The spectral feature of **2** is similar as that of $\text{Co}(\text{II})$ -substituted hemerythrin which has a high-spin six-coordinated $\text{Co}(\text{II})$ complex.²⁰

¹H NMR spectra The ¹H NMR spectra of **1** and **2** in CD_3CN were recorded and shown in Fig. 4. The spectrum of the free ligand consists of four signals of intensities 1:2:3:3 at $\delta 5.86$, 4.96 , 2.17 and 1.92 , respectively, which are assigned to the 4-C proton of pyridyl rings, $-\text{CH}_2^-$, 5- CH_3 and 3- CH_3 of pyridyl ring. In the middle spectrum for complex **1**, the peak of 4-C proton shifted toward down-field (it is shifted from $\delta 5.86$ to 7.46), and CH_2 proton peaks shifted from $\delta 4.96$ of free ligand to $\delta 22.73$ and it obviously became broad because of the formation of coordination bonds of $\text{N}_{\text{pyridyl}}$ with Co^{II} atom. The bottom spectrum for complex **2** is quite similar to that of the middle one, and the signal of 4-C proton of pyridyl ring and $-\text{CH}_2$ peak slightly shifted to down-field compared with those of complex **1** due to the second azide group coordinated.

Table 3 Selected bond lengths ($\times 10^{-1} \text{ nm}$) and bond angles ($^\circ$) of the complex **2**

Bond length			
Co—N(4)	2.012(3)	N(2)—N(3)	1.162(4)
Co—N(1)	2.123(3)	N(4)—N(5)	1.201(4)
Co—N(13)	2.130(2)	N(5)—N(6)	1.156(4)
Co—N(9)	2.160(2)	N(8)—N(9)	1.361(3)
Co—N(7)	2.268(2)	N(10)—N(11)	1.376(3)
Co—N(11)	2.271(3)	N(12)—N(13)	1.370(3)
N(1)—N(2)	1.178(4)		
Bond angle			
N(4)—Co—N(1)	95.93(11)	N(1)—Co—N(11)	165.79(10)
N(4)—Co—N(13)	103.20(11)	N(13)—Co—N(11)	87.14(9)
N(1)—Co—N(13)	92.58(10)	N(9)—Co—N(11)	83.24(9)
N(4)—Co—N(9)	104.14(11)	N(7)—Co—N(11)	77.55(8)
N(1)—Co—N(13)	0.50(10)	N(2)—N(1)—Co	122.1(2)
N(13)—Co—N(9)	152.00(9)	N(5)—N(4)—Co	122.3(2)
N(4)—Co—N(7)	175.51(10)	N(3)—N(2)—N(1)	178.0(3)
N(1)—Co—N(7)	88.56(9)	N(6)—N(5)—N(4)	177.5(3)
N(13)—Co—N(7)	76.50(8)	N(8)—N(9)—Co	112.75(17)
N(9)—Co—N(7)	75.77(8)	N(10)—N(11)—Co	104.87(17)
N(4)—Co—N(11)	97.97(11)	N(12)—N(13)—Co	112.80(17)

Table 4 Electronic spectra data of complexes 1 and 2

Compd.	Solvent	λ_{\max} (nm ($\epsilon/M^1 \cdot \text{cm}^{-1}$))	Assignment
1	methanol	299(171)	L→Co
		516(94)	d→d
		604(861)	
2	methanol	340(520)	L→Co
		520(70)	d→d
			$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$
		604 (130)	

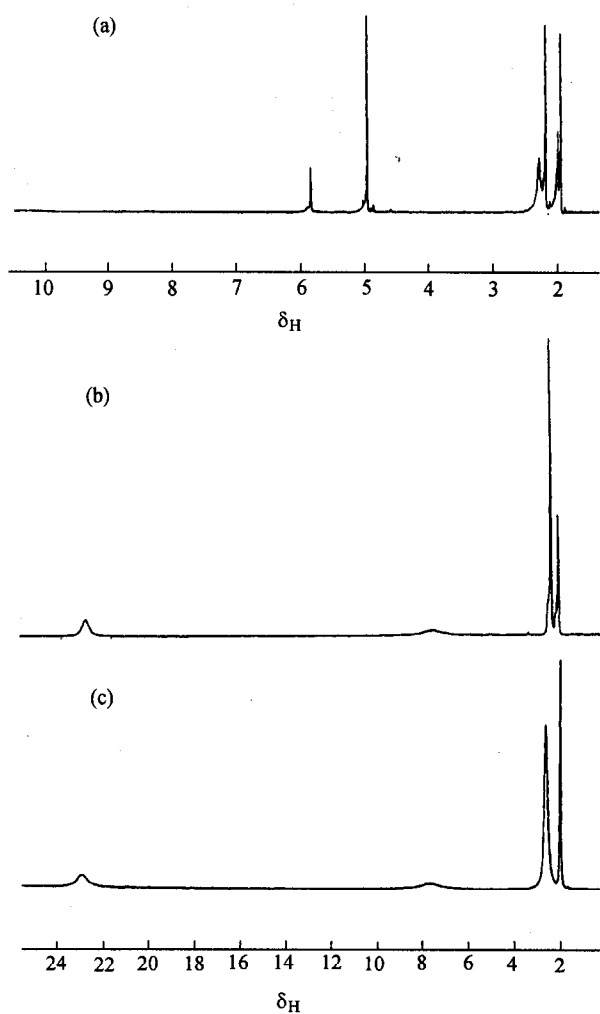


Fig. 4 ^1H NMR spectra: (a) free ligand; (b) $[\text{CoL}(\text{N}_3) \cdot \text{Cl}_4]$ (1); (c) $\text{CoL}(\text{N}_3) \cdot \text{Cl}_2$ (2).

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