

Synthesis, characterization and structure of mononuclear cobalt(III) carbonato complexes containing a tailored tetradentate amine as an end-capping ligand

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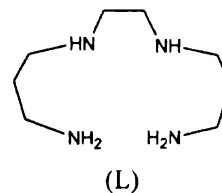
Abstract : Two hexacoordinated mononuclear compounds of the type $[\text{Co}(\text{L})(\text{CO}_3)]\text{ClO}_4/\text{PF}_6$ (1/2) [L = *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine] have been synthesized and characterized using microanalytical, spectroscopic and other physicochemical results. Single crystal X-ray structural analysis shows that the metal center in 1 adopts a distorted octahedral geometry with a CoN_4O_2 chromophore. Hexacoordination of cobalt(III) is attained by binding with four N atoms of L and two O atoms of a chelated carbonate ion. Multiple intermolecular N-H...O hydrogen bondings in 1 result in a 2D sheet structure. In MeCN solutions, the diamagnetic compounds show a nearly reversible one-electron reductive response corresponding to cobalt(III)-cobalt(II) couple.

Keywords : Cobalt(III) carbonato, polyamine, X-ray structure, redox behaviour.

Introduction

The study of mono-, di- and polynuclear complexes of cobalt in its varied oxidation states has been the center of current research because of their interesting synthetic, structural, spectroscopic, magnetic and optoelectronic features¹⁻⁵. The essential prerequisites for such research are the judicious choice⁶ of organic spacers and inorganic/organic terminals/bridges that may lead to directed properties. Recently, we are interested⁷⁻¹¹ in the construction of different coordination molecules through variation of ligand backbones and metal coordination environments; in this regard, tailored polyamine/Schiff base spacers and pseudohalide terminals/bridges have been widely used. Polyamines¹²⁻¹⁴ are bifunctional ligands with potential donor centers to form metal-ligand covalent bonds and hydrogen bond donor/acceptor sites resulting supramolecular entities. Carbonate is known to function as a versatile ligand with a variety of coordination modes¹⁵. Many metal carbonato complexes¹⁶⁻²⁰ are formed through fixation of atmospheric CO_2 and transformation into its hydration products such as HCO_3^- and CO_3^{2-} . The present work stems from our interest to build new molecular and

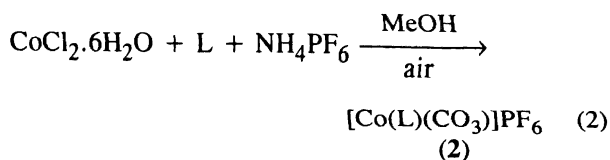
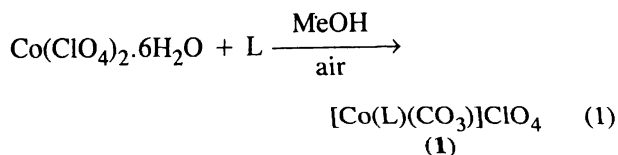
crystalline aggregates of cobalt(III) in combination with a tailored polyamine, *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine (L) and carbonate. Successfully, we have isolated two mononuclear cobalt(III) complexes of the type $[\text{Co}(\text{L})(\text{CO}_3)]\text{ClO}_4/\text{PF}_6$ (1/2). The details of syntheses, characterizations, structures and properties of these complexes are described below.



Results and discussion

The hexacoordinated mononuclear compound 1 was obtained in good yield through reaction of a 1 : 1 molar ratio of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and L in open air at room temperature as shown in eq. (1). For preparation of 2, one equivalent of NH_4PF_6 was added to the reaction mixture containing a 1 : 1 molar ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and L [eq. (2)].

The formation of carbonato complexes **1** and **2** may presumably¹⁷ be due to intake of CO₂ from atmosphere by the reactive cobalt(III) amine moiety that leads to transformation of CO₂ into CO₃²⁻ in MeOH solutions followed by its coordination to the metal ion in a *cis* chelating fashion. **2** was also isolated by metathesis of **1** with NH₄PF₆ in MeOH solution [eq. (3)]:

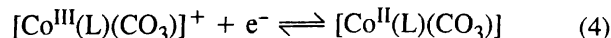


The complexes are characterized by elemental analyses, spectroscopic studies and other physicochemical results. The microanalytical data are in good conformity with formulations **1** and **2**. The compounds are air-stable and moisture-insensitive, and are soluble in water and in common organic solvents such as methanol, acetonitrile, dimethylformamide and dimethylsulphoxide. In MeCN solutions, they show conductivity values [$\Lambda_M = 120$ and $125 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for **1** and **2**, respectively] corresponding to a 1 : 1 electrolytic behavior²¹. Room temperature solid-phase magnetic susceptibility measurements show that the compounds are diamagnetic [singlet ground state ($S = 0$) with t_{2g}^6 configuration]. In IR, $\nu(\text{N-H})$ stretching frequencies of the -NH₂ groups of L in **1** and **2** are observable at ~ 3325 and $\sim 3270 \text{cm}^{-1}$. Several bands in the range $2930\text{--}2980 \text{cm}^{-1}$ are assigned to the aliphatic $\nu(\text{C-H})$ stretching vibration of the ligand. Four strong absorption bands at ~ 1660 , ~ 1640 , ~ 1595 and $\sim 1440 \text{cm}^{-1}$ are indicative of the presence of $\nu(\text{CO}_3)$ ²². The bands corresponding to the $\nu(\text{ClO}_4)$ stretches at 1100 and 627cm^{-1} in **1** and the $\nu(\text{PF}_6)$ bands at 837 and 558cm^{-1} in **2** are in line with non-coordination²³ of the counter anions to the metal centers. Pink DMF solutions of **1** and **2** show two main bands at ~ 525 and $\sim 360 \text{nm}$ characteristic of octahedral cobalt(III); the transitions are assign-

able to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ types, respectively. The band at 268nm in both compounds may be assigned to a ligand based transition²⁴. The solid state reflectance spectra [**1** : 523 , 362 and 268nm ; **2** : 526 , 363 and 268nm] of the complexes show good correspondence to the solution spectra suggesting similar gross geometric and electronic structures both in solid state and in solution.

To examine thermal stabilities of the compounds, thermogravimetric and differential thermal analyses (TG-DTA) were made between $40\text{--}755 \text{ }^\circ\text{C}$ in a static atmosphere of N₂. The TG curves (Fig. 1) indicate that the complex **1** is stable up to $190 \text{ }^\circ\text{C}$ and then releases the polyamine (L) moiety (weight loss : observed 40.7% and calcd. 44.4%) in the temperature range $190\text{--}300 \text{ }^\circ\text{C}$ with an exothermic effect at $242 \text{ }^\circ\text{C}$ and the remaining carbonate (weight loss : observed 14.2% and calcd. 15.2%) in the temperature range $300\text{--}500 \text{ }^\circ\text{C}$ with an exothermic effect at $417 \text{ }^\circ\text{C}$, whereas compound **2** shows thermal stability up to $172 \text{ }^\circ\text{C}$ before starting to decompose with release of the polyamine (L) moiety (weight loss : observed 37.3% and calcd. 39.8%) in the temperature range $172\text{--}260 \text{ }^\circ\text{C}$ with an exothermic effect at $200 \text{ }^\circ\text{C}$ and the carbonate (weight loss : observed 16.2% and calcd. 13.7%) in the temperature range $260\text{--}475 \text{ }^\circ\text{C}$ with an exothermic effect at $450 \text{ }^\circ\text{C}$. In summary, thermal analyses show greater thermal stability of compound **1** over compound **2**.

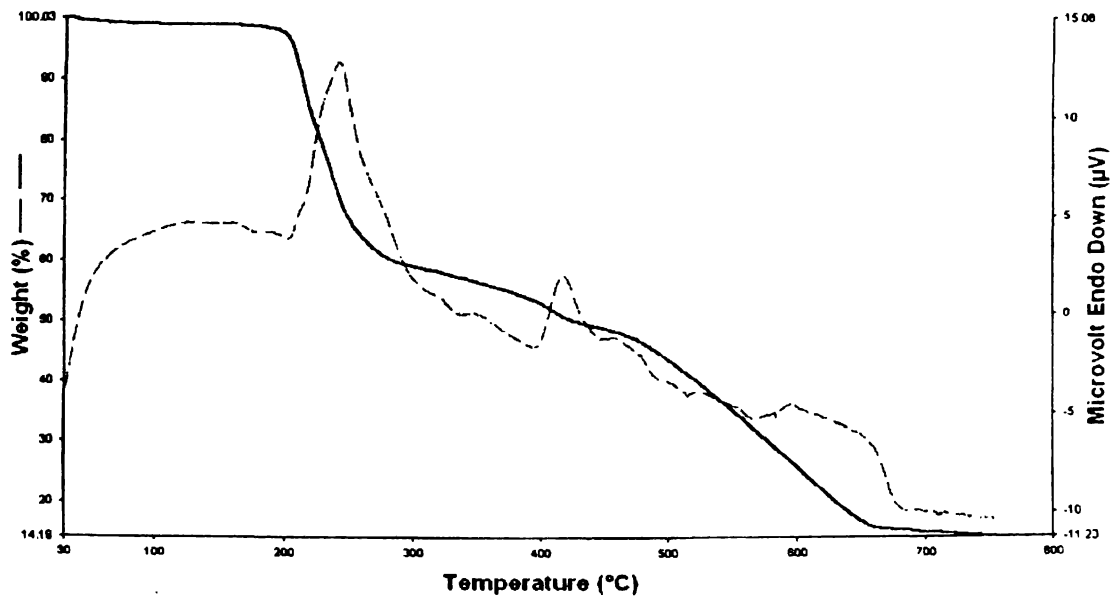
The electroactivity of the compounds was examined in MeCN solutions using cyclic voltammetry (CV) at a platinum working electrode. The complexes show a nearly reversible ($\Delta E_p = 110 \text{ mV}$) reductive response presumably due to the Co^{III}-Co^{II} couple [eq. (4)]:



The response is reproducible with no trace of decomposition after a number of cycles. The formal potential is $\sim 0.3 \text{ V}$ versus non-aqueous Ag/AgCl electrode. The one-electron nature of the couple was verified by comparison with a standard sample²⁵.

In order to define the coordination sphere conclusively, single-crystal X-ray diffraction study in one case, namely, **1** was made. An ORTEP diagram with atom numbering scheme of the cation in **1** is shown in Fig. 2. Selected interatomic bond lengths and bond angles are listed in Table 1. Significant hydrogen bonding data are set in Table 2. Structural analyses reveal the crystal lattice of **1**

(a)



(b)

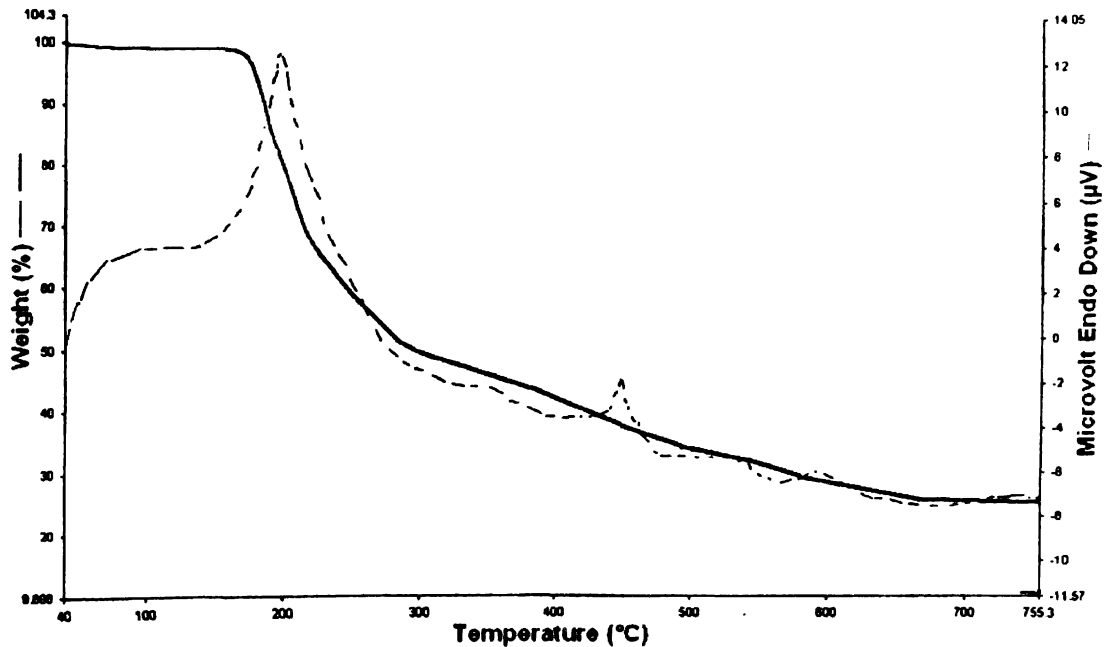


Fig. 1. Thermal behaviours of : (a) compound 1 and (b) compound 2.

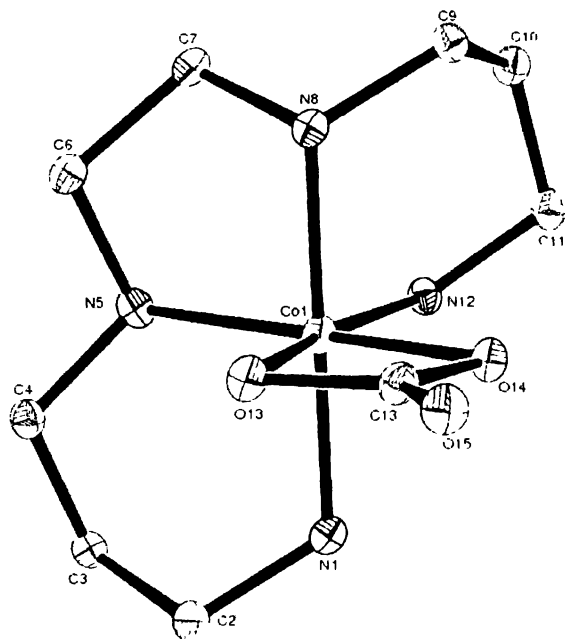


Fig. 2. ORTEP diagram of $[\text{Co}(\text{L})(\text{CO}_3)]^+$ in **1** with atom labeling scheme and 20% probability ellipsoids for all non-hydrogen atoms.

Table 1. Selected bond distances (Å) and bond angles ($^\circ$) for **1**

Bond distances :			
Co(l)-O(14)	1.916(6)	Co(l)-N(1)	1.980(9)
Co(l)-O(13)	1.928(6)	O(13)-C(13)	1.333(11)
Co(l)-N(8)	1.967(8)	O(14)-C(13)	1.298(11)
Co(l)-N(5)	1.979(8)	O(15)-C(13)	1.262(11)
Co(l)-N(12)	1.981(8)		
Bond angles :			
O(14)-Co(l)-O(13)	69.3(3)	N(8)-Co(l)-N(5)	86.2(3)
O(14)-Co(l)-N(8)	90.5(3)	N(8)-Co(l)-N(12)	90.9(3)
O(13)-Co(l)-N(8)	88.6(3)	N(5)-Co(l)-N(12)	93.9(3)
O(14)-Co(l)-N(5)	168.3(3)	N(8)-Co(l)-N(1)	177.6(3)
O(13)-Co(l)-N(5)	99.4(3)	N(5)-Co(l)-N(1)	94.9(3)
O(14)-Co(l)-N(12)	97.4(3)	N(12)-Co(l)-N(1)	91.1(3)
O(13)-Co(l)-N(12)	166.6(3)	O(15)-C(13)-O(14)	125.8(9)
O(14)-Co(l)-N(1)	88.0(3)	O(15)-C(13)-O(13)	122.0(8)
O(13)-Co(l)-N(1)	89.2(3)	O(14)-C(13)-O(13)	112.2(8)

Table 2. Hydrogen bond distances (Å) and angles ($^\circ$) for **1**

D-H...A	D-H	H...A	D...A	D-H...A
N(1)-H(1A)...O(2) ^a	0.98(2)	2.30(3)	3.267(12)	171(11)
N(1)-H(1B)...O(4) ^b	0.97(2)	2.12(5)	3.048(11)	160(10)
N(5)-H(5A)...O(15) ^b	0.98(2)	1.90(4)	2.816(10)	154(6)
N(8)-H(8A)...O(3)	0.98(2)	2.25(2)	3.225(12)	176(7)
N(12)-H(12A)...O(15) ^b	0.98(2)	2.00(3)	2.968(10)	170(9)

^a $x + 1, y, z$; ^b $-x + 1/2, y + 1/2, 3/2 - z$.

to consist of $[\text{Co}(\text{L})(\text{CO}_3)]^+$ cation and ClO_4^- anion. The coordination polyhedron around the metal center is best described as a distorted octahedron with a CoN_4O_2 chromophore. Four amine nitrogen atoms [N(1), N(5), N(8), N(12)] of L along with two oxygen atoms [O(13), O(14)] of *cis* chelating carbonate complete the octahedral coordination around cobalt(III). The equatorial positions are occupied by two nitrogen atoms [N(5), N(12)] of the tetradentate amine and two oxygen atoms [O(13), O(14)] of the carbonate ion while the other two remaining nitrogen atoms [N(1), N(8)] of L are in the axial positions. The degrees of distortion of the coordination sphere are reflected in the *cisoid* [69.3(3)–99.4(4) $^\circ$] and the *transoid* [166.6(3)–177.6(3) $^\circ$] bond angles. L forms one five-membered and two six-membered puckered chelate rings with subsequent bite angles N5-Co1-N8 86.2(3) $^\circ$, N1-Co1-N5 94.9(3) $^\circ$ and N8-Co1-N12 90.9(3) $^\circ$. The carbonate creates a small chelated²⁶ four membered loop with bite angle 69.3(3) $^\circ$. Among the three C–O distances C13–O13 and C13–O14 bond lengths are similar and larger than the remaining C13–O15 distance (Table 1), which shows chelation mode²⁶ of the carbonate.

In the crystalline state, mononuclear units of **1** are associated by bifurcated weak intermolecular N–H...O hydrogen bonds (Table 2) involving uncoordinated O atom (O15) of carbonate and H atoms (H5a and H12a) of –NH– and –NH₂ groups of L forming in a 1D chain along crystallographic *b*-axis. The chains are further engaged in multiple interwoven N–H...O hydrogen bondings along crystallographic *a*-axis with the perchlorate ions embedded between the chains resulting in a 2D sheet structure parallel to *ab*-plane (Fig. 3).

Two mononuclear cobalt(III) carbonate complexes in combination with a tailored polyamine are isolated. Structure of one representative member, **1**, is solved by X-ray diffraction measurement to establish the coordination sphere. Several attempts to grow single crystals of **2** failed; however, available spectroscopic, electrochemical and other physicochemical properties strongly suggest that structure **2** is congnate with **1**.

Experimental

Materials and methods :

High purity *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine (Lancaster, UK), cobalt(II) chloride hexahydrate

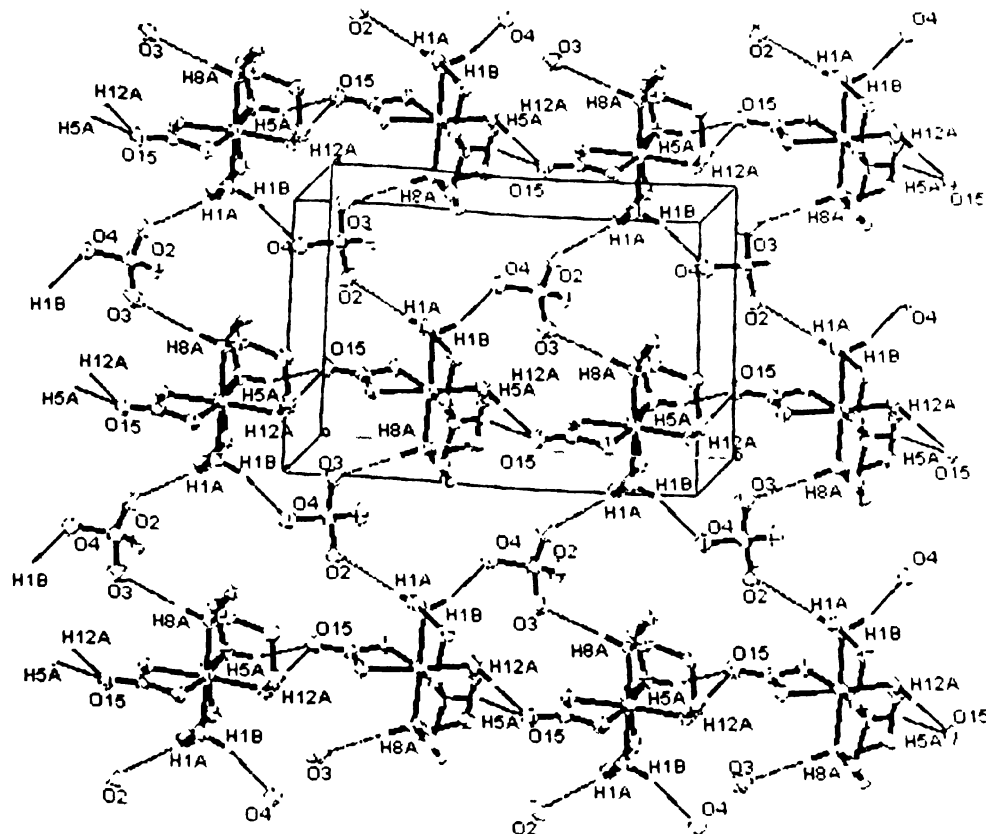


Fig. 3. Perspective view of 2D sheet structure in $[\text{Co}(\text{L})(\text{CO}_3)]\text{ClO}_4$ (1) formed through multiple interwoven N-H...O (carbonate) and N-H...O (perchlorate) hydrogen bonds in *ab*-plane.

(E. Merck, India) and ammonium hexafluorophosphate (Fluka, Germany) were purchased from respective concerns and used as received. Cobalt(II) perchlorate hexahydrate was prepared²⁷ by treatment of the cobalt(II) carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on a steam-bath, filtration through a fine glass-frit and preserved in a desiccator containing concentrated sulfuric acid (E. Merck, India) for subsequent uses. All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in open air.

Caution! Perchlorate salts of metal ions are potentially explosive²⁸ especially in the presence of organic ligands. Only a small amount of these materials should be prepared and handled with care.

Elemental analyses (C, H and N) were done using a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–300 cm^{-1}) were recorded using a

Perkin-Elmer FTIR model RX1 spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01 M KCl solution and dry MeCN was used as solvent. Room temperature magnetic susceptibilities were measured on a CAHN electroblance 7550 with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as reference and diamagnetic corrections were made using Pascal's constants²⁹. Thermal behaviors were investigated with a Perkin-Elmer Diamond TG/DT analyzer heated from 40–755 °C under nitrogen. Ground state absorption measurements (in DMF) were made with a Shimadzu model UV-2450 UV-Vis spectrophotometer. Electrochemical experiments were examined with a computer controlled Sinsil (model CHI1120A) electrochemical instrument using a platinum disk working electrode. The following parameters and relations were used : scan rate (v), 50 mV s^{-1} ; formal potential $E^0 = 0.5 (E_{\text{pa}} + E_{\text{pc}})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_{p} ,

the peak-to-peak separation. The potentials were referenced to a non-aqueous Ag/AgCl electrode.

Preparation of complexes :

[Co(L)(CO₃)]ClO₄/PF₆ (1/2) : L (174 mg, 1 mmol) in MeOH (10 ml) was added slowly to a pink solution (10 ml) of Co(ClO₄)₂.6H₂O (365 mg, 1 mmol) in the same solvent. After filtration through a fine glass-frit, the supernatant red solution was kept in open air for slow evaporation. Pink rectangular crystals of **1** that deposited within a week, were separated by filtration and dried *in vacuo* over silica gel indicator. Yield, 270 mg (70%). Compound **2** was prepared similarly using CoCl₂.6H₂O (237 mg, 1 mmol) instead of Co(ClO₄)₂.6H₂O followed by addition of an MeOH solution of NH₄PF₆ (163 mg, 1 mmol). The resulting red solution was processed as in **1**. Yield, 285 mg (65%). **2** was also prepared by metathesis of **1** with NH₄PF₆ in 1 : 1 molar ratio in an MeOH solution (20 ml) with constant stirring for 45 min at room temperature. The resulting red solution was filtered and left undisturbed in air for slow evaporation. Red shining compound **2** was obtained in almost quantitative yield. Found : C, 27.7; H, 5.8; N, 14.5. Calcd. C₉H₂₂N₄O₇ClCo (**1**) : C, 27.5; H, 5.7; N, 14.3%. IR (KBr, cm⁻¹) : ν(N-H) 3327, 3271; ν(C-H) 2979, 2934; ν(CO₃) 1661, 1638, 1594, 1441; ν(ClO₄) 1100, 627. Λ_M (MeCN, Ω⁻¹ cm² mol⁻¹) : 120. UV-Vis (λ, nm) : 524, 361, 268; E⁰ (MeCN) : 0.29 V; Found : C, 26.8; H, 5.2; N, 12.5. Calcd. C₉H₂₂N₄O₃F₆PCo (**2**) : C, 26.6; H, 5.0; N, 12.7%. IR (KBr, cm⁻¹) : ν(N-H) 3323, 3267; ν(C-H) 2975, 2930; ν(CO₃) 1658, 1642, 1597, 1438; ν(PF₆) 837, 558. Λ_M (MeCN, Ω⁻¹ cm² mol⁻¹) : 125. UV-Vis (λ, nm) : 527, 362, 268; E⁰ (MeCN) : 0.31 V.

X-Ray crystallographic analysis :

X-Ray crystal data for **1** were collected using a Rigaku MM007 High brilliance RA generator/confocal optics (Mo Kα radiation λ = 0.71073 Å) and Mercury CCD system at 125(2) K. CrystalClear software was used for data reduction³⁰ and data intensity was corrected with multi-scan mode³¹. The structure was solved by direct methods, and refined by full-matrix least-squares methods based on |F|² using SHELXL-97³². All non-hydrogen atoms were refined anisotropically. The NH hydrogen atoms of L were located from a difference map and refined

isotropically subject to a distance restraint. Other hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. All the calculations were carried out using SHELXS-97³², SHELXL-97 and SHELXTL³² programs. The crystallographic data for the complex **1** are summarized in Table 3.

Table 3. Crystallographic data for [Co(L)(CO₃)]ClO₄ (**1**)

Crystallographic parameter	1
Empirical formula	C ₉ H ₂₂ N ₄ O ₇ ClCo
Formula weight	392.69
Temperature (K)	125(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
D (calcd.) (g/cm ³)	1.636
Volume (Å ³)	1594(3)
Z	4
Unit cell dimension :	
a (Å)	8.974(9)
b (Å)	13.414(12)
c (Å)	13.675(14)
α (°), β (°), γ (°)	90, 104.42(3), 90
F (000)	816
μ (mm ⁻¹)	1.282
θ range for data collection (°)	2.16, 26.32
h/k/l	-10,11/-16,16/-17,14
Reflections collected	12157
Independent reflections	3186
Data/restraints/parameters	3186/6/224
Goodness-of-fit on F ²	1.118
Final R indices [I > 2σ(I)]	0.1174
R indices (all data)	0.1431
Largest peak and hole (eÅ ⁻³)	0.712, -0.769
$R = \sum F_o - F_c / \sum F_o $, $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, calcd. $w = 1/[\sigma^2(F_o^2) + (0.1449P)^2 + 6.7513P]$; where $P = (F_o^2 + 2F_c^2)/3$.	

Supplementary data :

Crystallographic data (excluding structure factors) for **1** has been deposited with the Cambridge Crystallographic Data Centre No. CCDC 798729. Copies of this information can be obtained, free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax : +44-1223-336033; E-mail : deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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