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E-mail: bjsir07@gmail.com

Mononuclear cobalt(III) azido complex containing a tetradentate amine: one pot synthesis, structure and thermal behavior

Sumitava Khan

Department of Chemistry, Burdwan Raj College, Purba Bardhaman 713104, West Bengal, India

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Abstract

One hexacoordinated mononuclear complex *trans*-[Co(L)$(N_3)_2$]PF_6(**1**)[L = N,N′-bis(3-aminopropyl)-1,2-ethanediamine] is prepared by using one-pot reactions of the building units and characterized. X-ray analysis shows that cobalt center in **1** adopts a distorted octahedral geometry with CoN_6 chromophore ligated through four N atoms of tetradentate amine (L) and the two N atoms of terminal azides in mutual *trans* orientation. In the crystalline state, double N-H…N and multiple N-H…F hydrogen bondings result in 2D sheet structure. The compound has a thermal stability up to 193°C.

Keywords: Cobalt(III) azido; Polyamine synthesis; Thermal study; X-ray structure

Introduction

Extensive research is being conducted on the design and construction (Cornils *et al*., 2000; Miller and Drillon, 2005; Petty, 2008; Marder, 1996) of metal-organic coordination frameworks for the preparation of functional materials (Comba and Hambley, 2009; Lalena and Cleary, 2010). Using various organic ligands and bridging units, different networks can be accessed by leveraging the veracity of coordination geometry around metal ion templates. Self-assembly is the most efficient method of preparing such materials (Yang *et al*., 2008). There have been active approaches (Khan *et al*., 2011; Choubey *et al*., 2014; Maji *et al*., 2017; Chatterjee *et al*., 2019) for construction of different coordination molecules through variation of ligand backbones and metal-ion coordination environments; in this regard, different transition and non-transition metal-ions are used as geometry setters, tailored polyamine as an end-capping units and pseudohalides terminals/bridges have been widely used.

Because of their intriguing synthetic, structural, spectroscopic, magnetic and catalytic properties, cobalt complexes in their various oxidation states have been the focus of current research (Murrie, 2010; Bhar *et al*., 2012; Mitra *et al*., 2015; Maji *et al*., 2017). Metal-ligand covalent bond and hydrogen bond donor/acceptor sites can be obtained by the potential donor centre of polyamines resulting in superstructure (Khan *et al*., 2011). Pseudohalide, like homoatomic azide, is known for its versatile coordination modes, which allow for a wide range of monomeric, dimeric, and polymeric complexes (Ribas *et al*., 1999; Khan *et al*., 2013). Herein, the reaction behavior of a tailored amine, N,N′-bis(3-aminopropyl)-1,2-ethanediamine (L, Scheme 1) towards cobalt(II) salt and azide has been examined. A similar complex with *cis* geometry and a different ligand but same metal ion and counter anion was reported by Khan *et al.* in 2011. However the new complex is superior compared to the previously reported one by the fact that it is water soluble due to the presence of amine moiety in the ligand structure. Our future endeavor would be to check the biological activities of this synthesized complex and if successful, check the biological activities *in vivo*. One mononuclear cobalt(III) complex of the type *trans*-[Co(L)$(N_3)_2$]PF_6 which are engaged in intermolecular N-H···N and N-H···F hydrogen bondings to afford 2D sheet structure has been successfully synthesized and X-ray crystallographically characterized. The details of synthesis, molecular and crystalline architectures, and properties of this new complex have been reported in this study.

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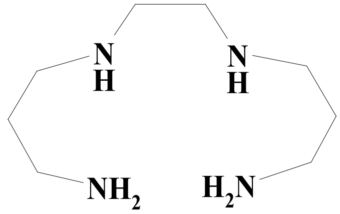
*Corresponding author e-mail: mynamesumitavakhan@gmail.com



Scheme 1. N,N′-bis(3-aminopropyl)-1,2-ethanediamine (L)

Materials and methods

Materials

High purity N,N′-bis(3-aminopropyl)-1,2-ethanediamine (Lancaster, UK), cobalt(II) chloride hexahydrate (E. Merck, India), sodium azide (E. Merck, India) and potassium hexaflurophosphate (Fluka, Germany) were purchased from respective concerns and used as received. All other chemicals and solvents employed were AR grade. The synthesis was carried out in open air.

Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000-400 cm^{-1}) were recorded by a Perkin-Elmer FTIR model RX1 spectrometer. Molar conductance was measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01M KCl solution and dry acetonitrile (MeCN) was used as solvent. Room temperature magnetic susceptibilities was measured on a CAHN electroblance 7550 with $Hg[Co(SCN)_4]$ as reference and diamagnetic corrections were made using Pascal's constants. (Carlin, 1986). Ground state absorption measurement (in methanol, MeOH) was conducted with a Shimadzu model UV-2450 UV-VIS spectrophotometer. Thermal behavior was investigated with a Perkin-Elmer Diamond TG/DT analyzer under heating scans from 30-780 °C under nitrogen atmosphere using alumina sample pans.

General synthesis of the complex 1

A methanolic (MeOH) solution (10 mL) of L (174 mg, 1 mmol) was added slowly to a pink solution (10 ml) of $CoCl_2.6H_2O$ (237 mg, 1 mmol) in the same solvent. To this solution mixture a H_2O solution (20 mL) of NaN_3 (130 mg, 2 mmol) followed by addition of KPF_6 (184 mg, 1 mmol) in MeOH solution (20 mL) were added. The resulting wine-red solution was filtered and left undisturbed in air for slow evaporation. After four days, green rectangular shaped crystals were separated and were collected in pure form and dried in *vacuo* over silica gel.

Yield, 340 mg (75%). Found: C, 20.9; H, 4.8; N, 30.6.Calcd. $C_8H_{22}N_{10}F_6PCo$ (1): C, 20.7; H, 4.8; N, 30.8%. IR (KBr, cm^{-1}): ν(N-H) 3313, 3243;ν(C-H) 2979, 2924;ν(N_3) 2054; ν(PF_6) 838, 558. Λ_M (MeCN, Ω^{-1} cm^2 mol^{-1}): 125. UV-Vis (λ, nm): 573, 344, 265, 221.

X-ray crystallographic study

X-ray crystal data of 1 was collected using a Rigaku MM007 rotating anode/confocal optics and a Mercury CCD at 125(2) K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). CrystalClear software was used for data reduction (Rigaku, 2004) and data intensity was corrected with multi-scan mode (Jacobson, 1998). The data were corrected for Lorentz polarization and absorption effect. The structure was solved by direct methods, and refined by full-matrix least-square methods based on $|F|^2$ using SHELXL-97 (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. The NH hydrogen atoms of L were placed in idealised positions and refined with riding thermal parameters 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 outusing SHELXS-97, SHELXL-97 and SHELXTL programs (Sheldrick, 2008). The crystallographic data for the complex is summarized in Table I.

Crystallographic data (excluding structure factors) for 1 has been deposited with the Cambridge Crystallographic Data Centre No. 2109140. 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).

Results and discussion

Synthesis and formulation

The hexacoordinated mononuclear compound **1** was initially formed as a green crystalline product through reaction of a 1:1:1 molar ratio of $CoCl_2.6H_2O$, L and NaN_3 in MeOH-H_2O mixed solvent followed by the addition of one equivalent KPF_6 at room-temperature. Such reactant ratio would be expected to yield either a diazido bridged compound of the composition $[(L)Co^{II}(N_3)_2Co^{II}(L)](PF_6)_2$ or a monoazido bridged coordination polymer of the type

Table I. Crystallographic data for $[Co(L)(N_3)_2]PF_6$ (1)

Empirical formula	$C_8H_{22}N_{10}F_6PCo$
Formula weight	462.84
Temperature (K)	125(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	P6(1)
D (cal) [g/cm^3]	1.794
Volume (Å^3)	2568(2)
Z	6
Unit cell dimension	
a (Å)	9.358(4)
b (Å)	9.358(4)
c (Å)	33.85(2)
α (°), β(°), γ (°)	90, 90, 120
F (000)	1416
μ (mm^{-1})	1.176
θ range for data collection (°)	2.51, 25.33
h/k/l	-11,10/-11,11/-40,40
Reflections collected	14756
Independent reflections	3115
Data/restraints/parameters	3115/34/237
Goodness-of-fit on F^2	2.151
Final R indices [$I>2\sigma(I)$]	R = 0.1593 and wR = 0.4138
R indices (all data)	R = 0.1598 and wR = 0.4146
Largest peak and hole (eÅ^{-3})	2.664, -1.325
Weighting scheme: $R = \Sigma\|Fo\| - \|Fc\|\|/\Sigma\|Fo$, $wR = [\Sigma w(F_o^2 - F_c^2)_2/\Sigma w(F_o^2)^2]^{1/2}$, calcd $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2 + 0.0000P]$; where $P = (F_o^2 + 2F_c^2)/3$.	

$[Co^{II}(L)(N_3)]_n(PF_6)_n$. Though, microanalyses showed a 1:1:2:1 ratio of metal ion, L, azide and hexaflurophosphate. Room temperature solid-phase magnetic susceptibility measurements showed that 1 is diamagnetic [singlet ground state (S = 0) with t_{2g}^6 configuration]. Reactants ratio corresponding to the product stoichiometry afforded better yields of 1 as shown in Equation 1.

The air-stable and moisture-insensitive compound 1 is soluble in water and in common organic solvents such as methanol, acetonitrile, dimethylformamide and dimethylsulphoxide. In MeCN solution, 1 shows conductivity value (Λ_M: 125 Ω^{-1} cm^2 mol^{-1}) corresponding to 1:1 electrolytic behavior (Geary, 1971). In IR,ν(N-H) stretching frequencies of the NH_2 groups of L are observable at 3313 and 3243 cm^{-1}. Several bands in the range 2920-2980 cm^{-1} are assigned to the aliphatic ν(C-H) stretching vibration of L. A strong absorption band at 2054 cm^{-1} is assignable to the stretching vibration of the terminal azides and also with non distinct splittings indicating mutual *trans* alignment of the two azides. The bands corresponding (Nakamoto, 2009) to the ν(PF_6) stretches at 838 and 558 cm^{-1} are also observed as expected. Green MeOH solution of **1** exhibits two distinct strong and broad absorption bands at 573 and 344 nm owing to the spin allowed transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively which are characteristic of octahedral cobalt(III) ion in the complex (Lever, 1984). The bands at 265 and 221 nm may be assigned to a ligand based transition.

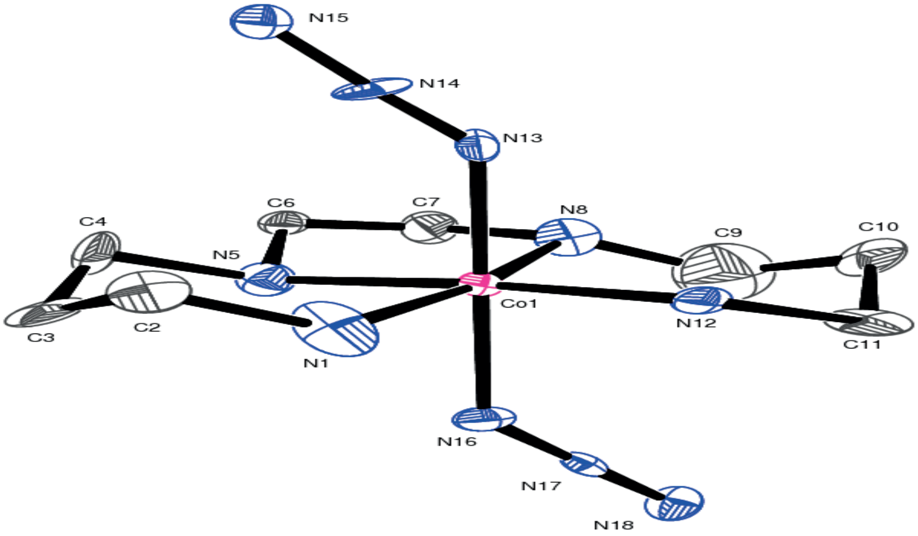


Fig. 1. ORTEP representation of $[Co(L)(N_3)_2]^+$ (1)

Table II. Selected bond distances (Å) and bond angles (°) for 1

Bond distances			
Co(1)-N(8)	1.945(4)	Co(1)-N(13)	1.975(8)
Co(1)-N(16)	1.955(9)	Co(1)-N(12)	2.013(8)
Co(1)-N(1)	1.975(4)	Co(1)-N(5)	2.004(9)
Bond angles			
N(8)-Co(1)-N(16)	96.2(4)	N(8)-Co(1)-N(5)	81.4(3)
N(8)-Co(1)-N(1)	168.83(13)	N(16)-Co(1)-N(5)	84.8(4)
N(16)-Co(1)-N(1)	86.0(3)	N(1)-Co(1)-N(5)	87.9(3)
N(8)-Co(1)-N(13)	88.0(3)	N(13)-Co(1)-N(5)	97.5(4)
N(16)-Co(1)-N(13)	175.5(5)	N(12)-Co(1)-N(5)	174.0(4)
N(1)-Co(1)-N(13)	90.2(3)	N(14)-N(13)-Co(1)	128.2(7)
N(8)-Co(1)-N(12)	104.1(4)	N(13)-N(14)-N(15)	169.5(11)
N(16)-Co(1)-N(12)	92.1(4)	N(17)-N(16)-Co(1)	133.1(7)
N(1)-Co(1)-N(12)	86.7(4)	N(18)-N(17)-N(16)	178.4(11)
N(13)-Co(1)-N(12)	85.2(4)		

Crystal structure of 1

An ORTEP representation with atom numbering scheme of 1 is shown in Fig. 1. Selected bond distances and bond angles relevant to the metal coordination sphere are listed in Table II. The bond angle and bond distance are important for the assignment of geometry to the molecule. Significant hydrogen bonding data are set in Table III. Structural analyses reveal that 1 consists of *trans*-$[Co(L)(N_3)_2]^+$ cation and PF_6^- as counter anion. The cobalt(III) center is best described as a distorted octahedron with a CoN_6 chromophore, which is obtained from a calculation involving bond angle and bond distance. Distortion from the ideal octahedral geometry is due to the asymmetric nature of the bound tetradentate amine (L) and the deviations of the refine angles (90º/180º) formed at the metal center (Table II). The coordination includes four amine N atoms [N(1), N(5), N(8) and N(12)] of L and two N atoms [N(13) and N(16)] of two terminal azides. The equatorial sites are occupied by four amine N atoms of L and two azide N atoms are placed at the

Table III. Hydrogen bond distances (Å) and angles (°) for 1

D-H…A	D-H	H…A	D…A	D-H…A
N(1)-H(1A)…N(15)[a]	0.98	2.14	2.993(11)	145.0
N(1)-H(1B)…F(5)[b]	0.98	2.37	3.199(8)	142.4
N(5)-H(5A)…F(1)[c]	0.98	2.18	3.130(14)	161.8
N(8)-H(8A)…F(3)[d]	0.98	2.32	3.268(10)	161.5
N(12)-H(12A)…N(18)[e]	0.98	2.13	3.013(13)	149.7
N(12)-H(12A)…F(2)	0.98	2.25	3.193(18)	160.7
N(12)-H(12B)…F(4)	0.98	2.42	3.243(15)	140.9

Symmetry code: a =y, -x+y+1, z-1/6; b =x-y+1, x+1, z+1/6; c = x+1, y, z; d = x-y+1, x, z+1/6; e = x-y, x, z+1/6.

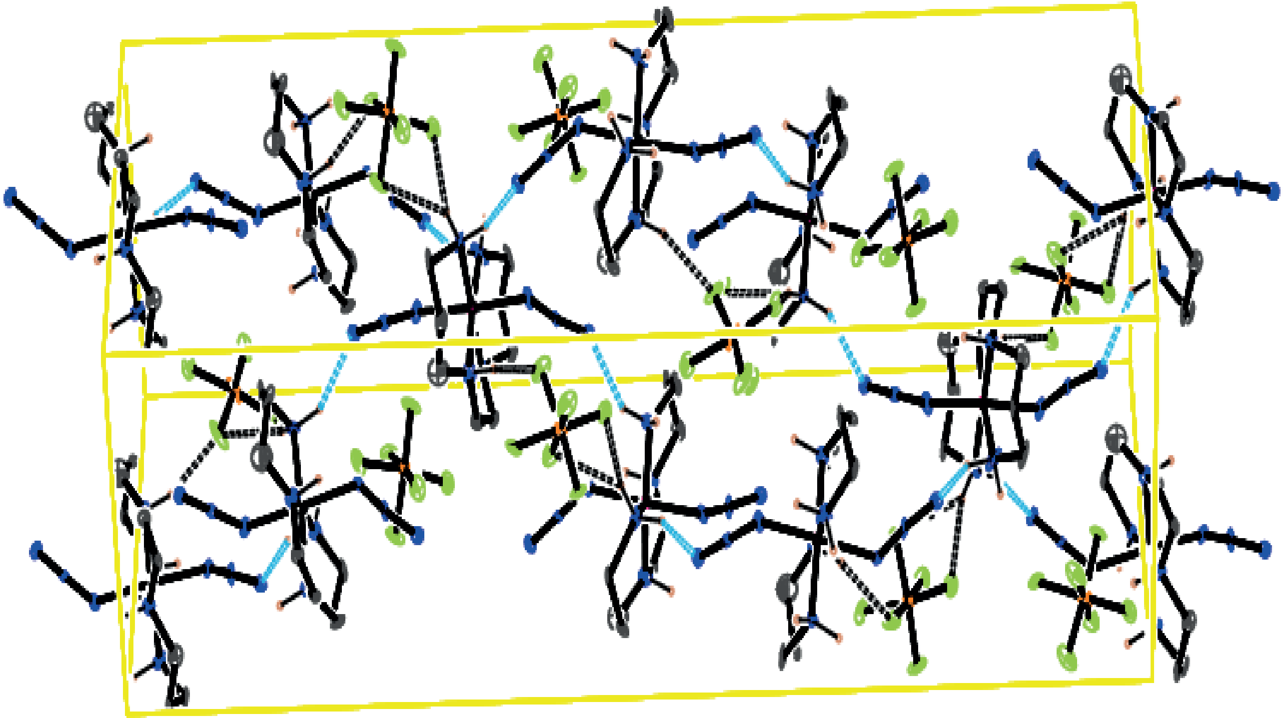


Fig. 2. Packing view of 2D sheet structure in 1 formed through double N-H…N and multiple N-H…F hydrogen bonds

axial positions. The degrees of distortion of the coordination sphere are reflected in the *cisoid* [81.4(3)-104.1(4)°] and the *transoid* angles [168.83(13)-175.5(5)°]. The sum (360.1°) of the equatorial angles [N(1)-Co(1)-N(12) 86.7(4)°, N(8)-Co(1)-N(12) 104.1(4)°, N(8)-Co(1)-N(5) 81.4(3)° and N(1)-Co(1)-N(5) 87.9(3)°] are almost close to 360.00°. So the N(1), N(5), N(8), N(12) and Co(1) atoms are almost on a same plane. The azides are almost linear [N(13)-N(14)-N(15) 169.5(11)° and N(16)-N(17)-N(18) 178.4(11)°] and mutually in trans alignment with N(13)-Co(1)-N(16) angle 175.5(5).

In the crystalline state, mononuclear 0D units of 1 packs through double N-H…N and multiple N-H…F hydrogen bondings (Table III) leading to 2D sheet structure (Fig. 2).

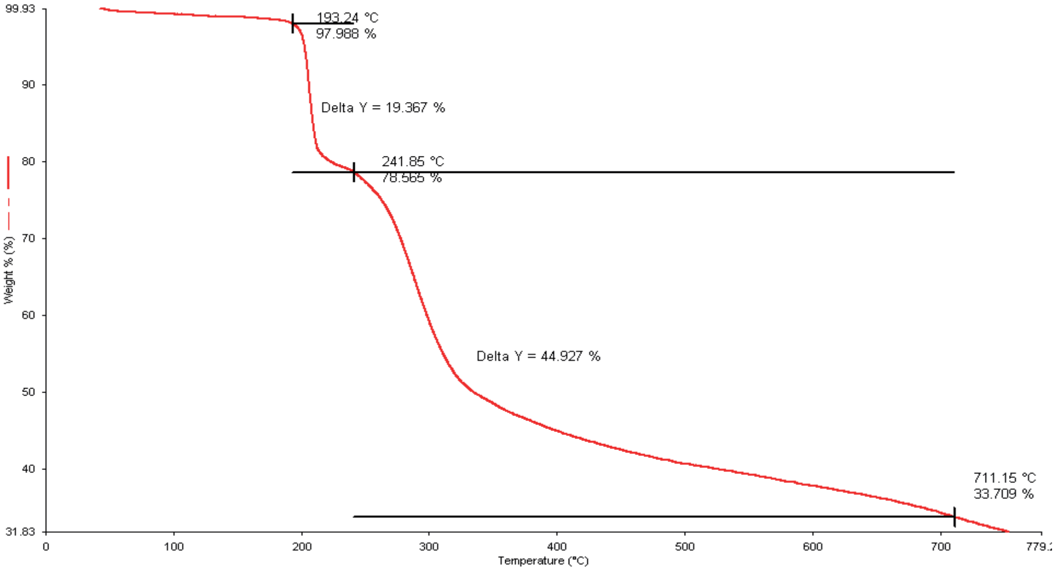


Fig. 3. Thermal behavior of 1

Thermogravimetric studies

To examine thermal stabilities of the complex**,** thermogravimetric analyses (TGA) was made between 30 and 780 ºC in a static atmosphere of N_2. Complex **1** is stable up to 193 ºC (Fig. 3) and this decomposes in two successive steps in the temperature range 193-711 ºC. The first weight loss is associated with the simultaneous removal of two azide unit (obs.: 19.3%, calcd.: 18.2%) in the temperature range 193-241 ºC. The second weight loss (obs.: 44.9%; calcd.: 37.6%) in the range of 241-711 ºC is associated with decomposition of the remaining polyamine (L).

A similar work reported by Khan *et al.* 2011, shows the presence of same metal ion, same counter anion but with different ligand system. However, this work is significantly different from the reported work since in case of the previously reported *cis*-$[Co(L)(N_3)_2]PF_6$ the molecule consists of two mononuclear *cis*-$[Co(L)(N_3)_2]PF_6$ moieties (molecules A and B) whereas the newly synthesized *trans*-$[Co(L)(N_3)_2]PF_6$ consists of one mononuclear *trans*-$[Co(L)(N_3)_2]PF_6$ moiety is present. The ligand in the previously reported work is Schiff base so, *cis*-$[Co(L)(N_3)_2]PF_6$ is water insoluble but *trans*-$[Co(L)(N_3)_2]PF_6$ water soluble as the ligand is amine. For the previously reported *cis*-$[Co(L)(N_3)_2]PF_6$, two azide nitrogen atoms along with one pyridine nitrogen atom and one imine nitrogen atom occupy the equatorial position while remaining pyridine nitrogen and imine nitrogen atoms are placed at the axial position. But for this *trans*-$[Co(L)(N_3)_2]PF_6$, four nitrogen atoms of tetradentate amine occupy the equatorial position and two azide nitrogen atoms are placed at the axial position. The reported compound *cis*-$[Co(L)(N_3)_2]PF_6$ is stable up to 213 ºC due to the fact that it consists of two mononuclear moieties whereas compound *trans*-$[Co(L)(N_3)_2]PF_6$ is stable up to 193 ºC.

Conclusion

One molecular and crystalline architecture based mononuclear cobalt(III) azido complex was prepared using a tailored polyamine prepared through single-pot reaction of the molecular building units in preassigned molar ratio. The product was isolated and crystallographically characterized. The compound was found to have thermal stability up to 193°C. Our future endeavor would be to check the biological activities of this synthesize complex.

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