

Novel linear hexanuclear cobalt string complexes (Co_6^{12+}) and one-electron reduction products (Co_6^{11+}) supported by four bpyany $^{2-}$ ligands

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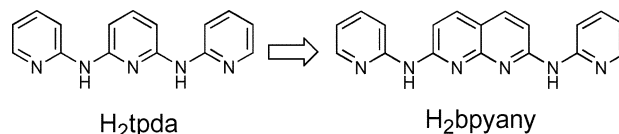
The new ligand, 2,7-bis(α -pyridylamino)-1,8-naphthyridine (H_2bpyany), was synthesized by the reaction of 2,7-dichloro-1,8-naphthyridine with 2-aminopyridine in the presence of *t*-BuOK under palladium(0)-catalyzed conditions. The preparation and characterization of novel hexacobalt string complexes, $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_n$ ($n = 1$ (**1**); $n = 2$ (**2**)) and $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2](\text{OTf})_n$ ($n = 2$ (**3**); $n = 1$ (**4**)) are presented. The crystal structures for compounds **1–4** have been determined by X-ray crystallography. Compounds **1** and **4** have the Co_6^{11+} configurations and are air-stable. Compounds **2** and **3** with Co_6^{12+} configurations are structurally similar to **1** and **4**, respectively. The electrochemistry of **1** displays four redox couples at $E_{1/2} = -0.55, +0.38, +0.91,$ and $+1.18$ V (vs. Ag/AgCl). The magnetic data show that compounds **1** and **4** are in a spin state of $S = 1/2$, and **2** and **3** in a spin state of $S = 1$. The results of the EHMO calculations on compounds **1** and **2** are in agreement with their magnetic measurements.

Introduction

Owing to their fascinating bond nature, the metal–metal multiple bonds in dinuclear metal complexes have been an interesting and vital research topic.^{1–4} Recently, various linear multinuclear metal complexes and infinite one-dimensional metal complexes have been synthesized and investigated due to their promising applications as nanoscale electronic devices.^{5–15} During the past decade, our seminal and systematic approach on the all-*syn* oligo-(α -pyridyl)amido ligands coordinated metal ions has successfully opened up a new chapter, extending this territory from dinuclear to linear oligo-nuclear metal complexes.^{16–20} An STM study of one-dimensional metal string complexes revealed the potential applications as molecular wires and molecular switches.²¹ A similar concept of extended metal atom chain (EMAC) has been proposed by Cotton.^{22–25} On the basis of the electrochemistry of the multinuclear metal complexes with oligo-(α -pyridyl)amido ligands, these complexes are stable in various oxidation states. Indeed, numerous oxidized forms of these complexes have been synthesized and structurally characterized.^{18,25} However, the reduced forms of these complexes are generally unstable to be isolated and characterized.

A variety of di- or multinuclear metal complexes coordinated with 1,8-naphthyridine (ny) or its derivatives have been synthesized and their structures, chemical, and physical properties have been extensively investigated.^{26,27} The dinuclear nickel compound $[\text{Ni}_2(\text{ny})_4\text{Br}_2](\text{BPh}_4)$ is a mixed-valence complex with average charges of +1.5 on each nickel ion.²⁷ In order to obtain the reduced forms of linear multimetal complexes, one of our approaches is to modify the ligands by replacing some of the pyridyl groups in the

ligands with naphthyridyl units. For example, the ligand H_2tpda (tripyridyldiamine) can be modified by substitution of the central pyridyl group with a naphthyridyl group to form the new ligand 2,7-bis(α -pyridylamino)-1,8-naphthyridine (H_2bpyany).



In this paper, we report the synthesis of the novel ligand H_2bpyany and its hexanuclear cobalt string complexes. The crystal structures, magnetic properties, electrochemistry and qualitative molecular orbital calculations of these hexanuclear cobalt string complexes are discussed in this work.

For clarity, the complexes described in this paper are listed as follows: $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)$ (**1**), $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_2$ (**2**), $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2](\text{OTf})_2$ (**3**), $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2](\text{OTf})$ (**4**).

Results and discussion

Syntheses

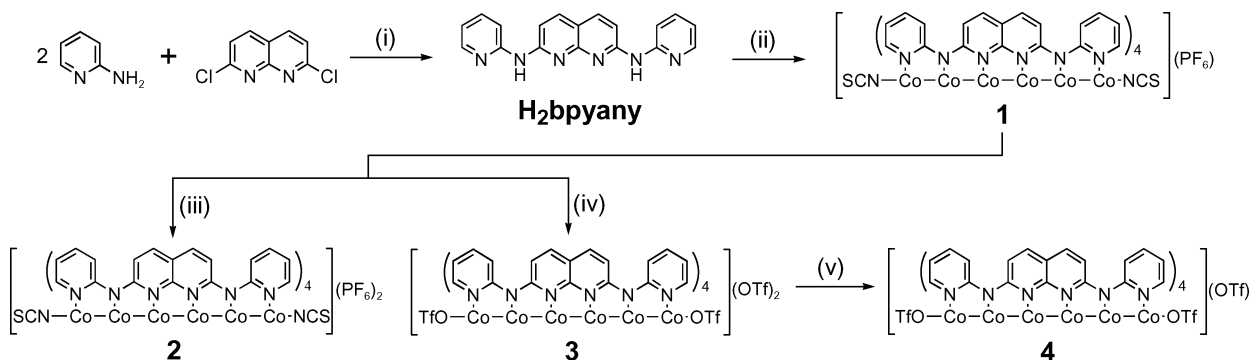
The preparation of the novel ligand, H_2bpyany , is similar to that of oligo- α -pyridylamino ligands we have previously reported.¹⁹ The new ligand can be readily synthesized in 66% yield by the palladium-catalyzed cross coupling reaction of 2,7-dichloro-1,8-naphthyridine²⁸ with 2-aminopyridine in the presence of *t*-BuOK (Scheme 1).

The preparation of the oligopyridylamine-based metal string complexes was carried out in refluxing naphthalene. Under modified conditions, the hexanuclear cobalt string complexes can be obtained in high yields. The mixture of H_2bpyany ligand with *t*-BuOK in the melting naphthalene and DMF co-solvent were heated at *ca.* 130–140 °C to form presumably the corresponding

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Scheme 1 The synthetic routes of H₂bpyany and its hexanuclear cobalt complexes: (i) Pd₂(dba)₃, dppp and *t*-BuOK in refluxing toluene at 120 °C; (ii) (1), *t*-BuOK in melting naphthalene/DMF. (2), CoCl₂ in DMF (3), NaSCN in CH₂Cl₂/MeOH (4), KPF₆ in CH₂Cl₂/MeOH; (iii) [Cp₂Fe](PF₆) in CH₂Cl₂/MeOH; (iv) (1), NaOTf in CH₂Cl₂/MeOH (2), 3 eq. AgOTf in CH₂Cl₂/MeOH; (v) (1), N₂H₄·H₂O in CH₂Cl₂. (2). Anhydrous MgSO₄(s).

potassium salt K₂bpyany. Addition of CoCl₂ in DMF followed by KPF₆ afforded the desired product [Co₆(μ₆-bpyany)₄(NCS)₂](PF₆) (1). One-electron oxidation product [Co₆(μ₆-bpyany)₄(NCS)₂](PF₆)₂ (2) was prepared by reacting compound 1 with [Cp₂Fe](PF₆) in a mixture of CH₂Cl₂ and MeOH. The axial ligand exchange was accomplished by reacting compound 2 with excess NaOTf and 3 eq. AgOTf to form compound 3. The reaction of compound 3 with hydrazine gave compound 4. These complexes 1–4 have been characterized by various spectrometry. The IR active C≡N stretching vibrations of compound 1 and 2 were observed at 2058 and 2060 cm⁻¹, respectively.

Crystal structures

The crystal data for compounds 1–4 are listed in Table 1. Compounds 1, 3 and 4 crystallize in the space groups *Pna*2₁, *C2/c* and *P2*₁/*n*, respectively, with the hexacobalt chains locating at general positions. Compound 2 crystallizes in the tetragonal

system with space group *P4*₁2₁2 residing on a special position of 2-fold symmetry perpendicular to the hexacobalt axis. Fig. 1–4 show

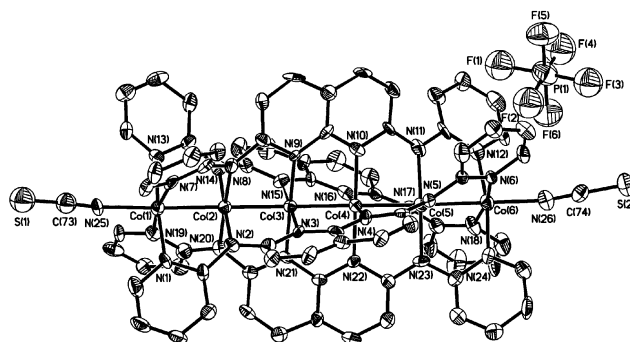


Fig. 1 ORTEP drawing of 1. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1 Crystal data for compounds 1–4

	1·6CH ₂ Cl ₂ ·H ₂ O	2·4CH ₂ Cl ₂	3·6CH ₂ Cl ₂	4·5CH ₂ Cl ₂ ·O(C ₂ H ₅) ₂ ·0.75H ₂ O
Formula	C ₈₀ H ₆₂ Cl ₁₂ Co ₆ F ₆ N ₂₆ OPS ₂	C ₇₈ H ₅₆ Cl ₈ Co ₆ F ₁₂ N ₂₆ P ₂ S ₂	C ₈₂ H ₆₀ Cl ₁₂ Co ₆ F ₁₂ N ₂₄ O ₁₂ S ₄	C ₈₄ H _{69.50} Cl ₁₀ Co ₆ F ₉ N ₂₄ O _{10.75} S ₃
Formula weight	2391.63	2348.73	2708.76	2562.40
Temperature/K	150(1)	150(1)	150(1)	150(1)
Diffractometer	NONIUS, Kappa CCD	NONIUS, Kappa CCD	NONIUS, Kappa CCD	NONIUS, Kappa CCD
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Tetragonal	Monoclinic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P4</i> ₁ 2 ₁ 2	<i>C2/c</i>	<i>P2</i> ₁ / <i>n</i>
<i>a</i> /Å	27.3324(4)	17.3930(2)	48.8644(4)	12.9988(2)
<i>b</i> /Å	12.9324(2)	17.3930(2)	16.9122(1)	28.3349(5)
<i>c</i> /Å	25.6423(4)	28.0060(5)	24.1983(2)	26.0264(3)
<i>a</i> /°	90	90	90	90
<i>β</i> /°	90	90	96.5410(4)	93.2970(8)
<i>γ</i> /°	90	90	90	90
<i>V</i> /Å ³	9063.9(2)	8472.3(2)	19867.4(3)	9570.2(2)
<i>Z</i>	4	4	8	4
Absorption coefficient/mm ⁻¹	1.566	1.578	1.481	1.452
Crystal size/mm	0.45 × 0.35 × 0.15	0.18 × 0.15 × 0.12	0.40 × 0.40 × 0.30	0.25 × 0.20 × 0.15
<i>θ</i> range for data collection/°	1.49–27.50	1.38–25.00	1.27–27.50	1.06–25.00
Reflection collected	60692	46542	91642	100270
Independent reflections	18376 (<i>R</i> _{int} = 0.0517)	7470 (<i>R</i> _{int} = 0.0761)	22806 (<i>R</i> _{int} = 0.0493)	16872 (<i>R</i> _{int} = 0.0672)
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0722, 0.1943	0.0502, 0.1229	0.0560, 0.1552	0.0891, 0.2599
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0937, 0.2117	0.0778, 0.1369	0.0896, 0.1731	0.1200, 0.2924
GOF	1.041	1.019	1.075	1.029

^a *R*₁ = Σ||*F*_o| - |*F*_c|| / Σ|*F*_o|; *wR*₂ = [Σ*w*(*F*_o² - *F*_c²)² / Σ*w*(*F*_o²)²]^{1/2}; *w* = 1/σ²(*F*_o²) + (*aP*)² + *bP*, where *P* = [max(0 or *F*_o²) + 2(*F*_c²)]/3.

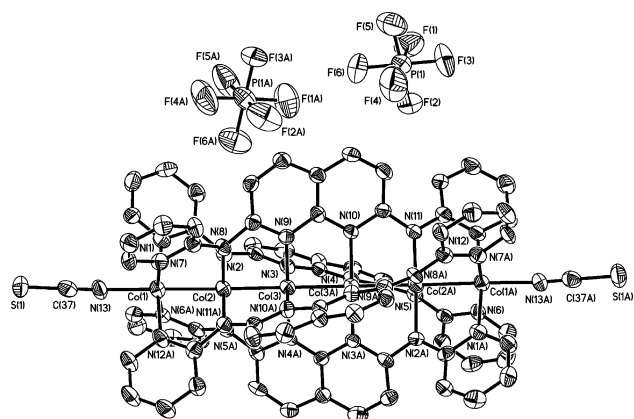


Fig. 2 ORTEP drawing of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

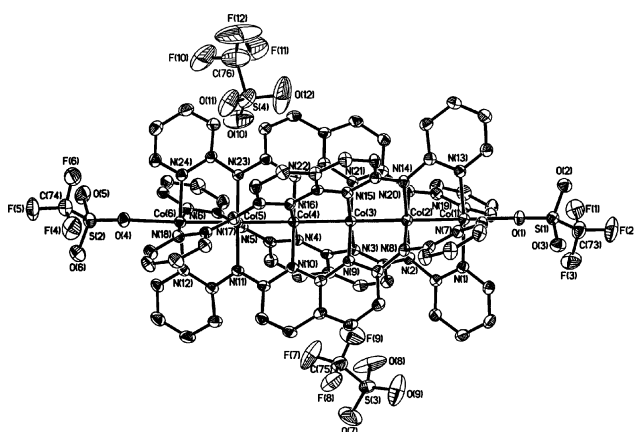


Fig. 3 ORTEP drawing of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

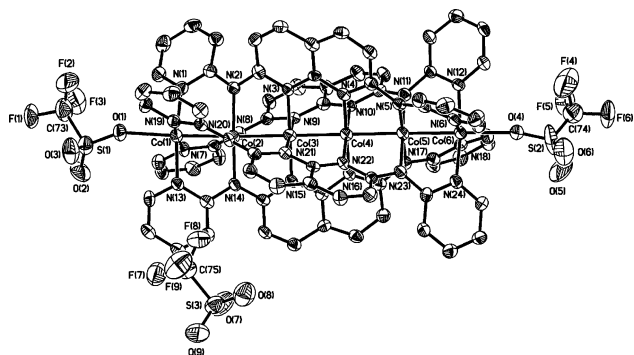
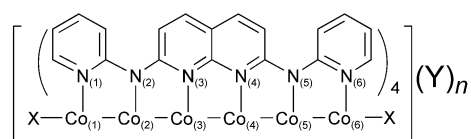


Fig. 4 ORTEP drawing of **4**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

the ORTEP drawings of compounds **1–4**, respectively. The crystal structures of these compounds have much in common except that the axial ligands or the oxidation states are different. Compounds **1–4** all have roughly D_4 symmetry without considering axial ligands. Therefore, average bond distances (Å) and torsion angles ($^\circ$) for compounds **1–4** are calculated in terms of D_4 symmetry, as shown in Table 2. In all these complexes, the hexacobalt chains are

Table 2 Average bond distances (Å) and torsion angles ($^\circ$) for compounds **1–4**^a



X=NCS, Y=PF₆⁻: $n=1$ (**1**), 2 (**2**)

X=Y=OTf⁻: $n=1$ (**4**), 2 (**3**)

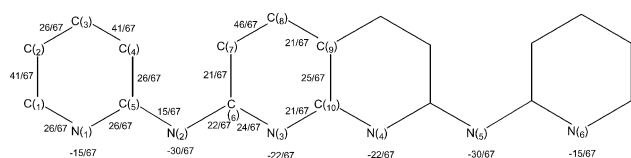
	1	2	3	4
Co(1)–Co(2)	2.313(1)	2.313(1)	2.283(1)	2.284(1)
Co(2)–Co(3)	2.273(1)	2.255(1)	2.243(1)	2.249(1)
Co(3)–Co(4)	2.256(1)	2.245(2)	2.267(1)	2.251(1)
Co(1)–N(1)	1.981(7)	1.984(5)	1.970(3)	1.972(7)
Co(2)–N(2)	1.917(6)	1.910(5)	1.911(3)	1.911(7)
Co(3)–N(3)	1.932(6)	1.936(5)	1.934(3)	1.935(6)
Co(1)–X ^b	2.070(7)	2.034(6)	2.223(3)	2.244(5)
N(1)–C(1)	1.353(11)	1.354(8)	1.353(5)	1.354(10)
N(1)–C(5)	1.366(10)	1.361(8)	1.362(5)	1.360(10)
N(2)–C(5)	1.370(9)	1.374(8)	1.380(5)	1.378(10)
N(2)–C(6)	1.359(10)	1.375(8)	1.362(5)	1.363(10)
N(3)–C(6)	1.354(9)	1.358(8)	1.358(5)	1.358(10)
N(3)–C(10)	1.375(10)	1.365(8)	1.364(5)	1.371(10)
C(1)–C(2)	1.359(13)	1.368(10)	1.368(6)	1.366(12)
C(2)–C(3)	1.387(14)	1.387(10)	1.388(7)	1.393(13)
C(3)–C(4)	1.367(12)	1.357(10)	1.373(6)	1.372(12)
C(4)–C(5)	1.409(11)	1.407(9)	1.400(6)	1.405(12)
C(6)–C(7)	1.425(11)	1.414(9)	1.421(6)	1.425(11)
C(7)–C(8)	1.366(12)	1.363(10)	1.358(6)	1.359(12)
C(8)–C(9)	1.405(12)	1.414(9)	1.409(6)	1.413(12)
C(9)–C(10)	1.408(11)	1.403(9)	1.407(5)	1.401(11)
Co(1)⋯Co(6)	11.429(1)	11.381(2)	11.318(1)	11.317(1)
$\phi(1)^c$	21.05	19.88	22.18	21.87
$\phi(2)^c$	16.23	17.58	16.66	16.74
$\phi(3)^c$	14.20	15.86	14.37	15.18

^a D_4 symmetry is used to calculate average bond distances and torsion angles. ^b X = axial ligand. ^c Torsion angle $\phi(k)$ ($^\circ$) is defined as N(k)–Co(k)–Co($k+1$)–N($k+1$), $k=1, 2$, or 3.

helically wrapped by four bpyany²⁻ ligands with smaller average torsion angle $\phi(3)$ N_{py}–Co(3)–Co(4)–N_{py} of 14.20–15.86 $^\circ$ relative to the average N_{py}–Co(n)–Co($n+1$)–N_{amido} angle of 22.5 $^\circ$ for the pentacobalt string complex [Co₅(tpda)₄(NSC)₂] (tpda = dianion of tripyridyldiamine).^{17,18b} The average Co–Co distances of **1** from outer to inner are 2.313(1), 2.273(1) and 2.256(1) Å, respectively. Similar to those of **1**, the average Co–Co distances of **2** are 2.313(1), 2.255(1) and 2.245(2) Å, respectively. The average Co–N_{axial} distances are 2.070(7) Å for **1** and 2.034(6) Å for **2**. The average Co–N distances of **1** are 1.980(7), 1.917(6), and 1.932(6) Å, comparable to those of **2**. It should be noted that addition of one electron to compound **2** does not show significant structural changes. When weak axial ligands (OTf⁻) are coordinated to Co₆ chain, no obvious structural changes are observed for compounds **3** and **4**. For example, the respective Co–Co distances of **3** are 2.283(1), 2.243(1) and 2.267(1) Å whereas those of **4** are 2.284(1), 2.249(1) and 2.251(1) Å. In all these compounds, the outer Co–Co distances, in general, are slightly longer than the inner three Co–Co distances due to square-pyramidal environment for Co(1) and Co(6). On the basis of structural analysis of compounds **1–4**, the reduction of compounds **2** and **3** occurs on the delocalized hexacobalt chain.

Resonance analysis

To examine the qualitative electronic effects of the deprotonated bpyany²⁻ ligand, the charge distributions and π bond orders were analyzed by the resonance structures. The negative charges are assumed to resonate only on the nitrogen atoms. As illustrated in Scheme 2, the bpyany²⁻ ligand has a C_2 axis passing through the C(9)–C(10) bond and the negative charges symmetrically reside on the nitrogen atoms. The charge distributions from outer to inner nitrogens are $-15/67$, $-30/67$ and $-22/67$, respectively. The amido position has larger negative density than the nitrogens on pyridyl and naphthyridyl groups, indicating that the ligand field of the amido nitrogens is stronger than those on the pyridyl and naphthyridyl groups. Thus, the Co(2)–N(2) distances (1.910–1.917 Å) are the shortest among the Co(k)–N(k) bond distances ($k = 1, 2$ and 3 , respectively). On the contrary, the outer nitrogen of the pyridyl groups have the least charge distribution ($-15/67$). Hence, the Co(1)–N(1) distances (1.970–1.984 Å) are the longest. The C–C and C–N π bond orders are also shown in Scheme 2. It is well-known that bond order is inversely proportional to the bond distance. The C(7)–C(8) bond has a π character of 46/67 which is the largest among all C–C bonds. In compounds 1–4, the respective C(7)–C(8) bond distances of 1.366(12), 1.363(10), 1.358(6) and 1.359(12) are shorter as compared to other C–C bond lengths in the ligands. As expected for the smallest π bond character (21/67) of the C(6)–C(7) and C(8)–C(9) bond, longer bond distances are observed in the structures. The C–N bond orders and distances can also be analyzed by such a method. For instance, the N(2)–C(5) bond is of the smallest bond order (15/67), consistent with the longer C–N bond distances of 1.370(9), 1.374(8), 1.380(5) and 1.378(10) Å for compounds 1–4, respectively.



Scheme 2 Charge distributions on nitrogen atoms and π bond orders on C–C and C–N bonds of the bpyany²⁻ ligand.

Electrochemistry

Similar to the tri- and pentanuclear cobalt complexes,^{18b,25c} compound 1 displays rich redox chemistry as evinced by its cyclic voltammogram (Fig. 5). Compound 1 exhibits four reversible redox couples at $E_{1/2} = -0.55$, $+0.38$, $+0.91$ and $+1.18$ V

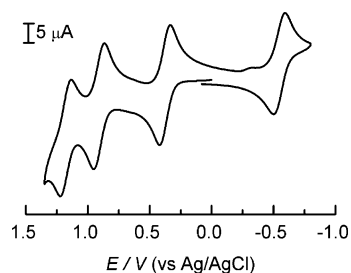


Fig. 5 The cyclic voltammogram of compound 1 in CH_2Cl_2 containing 0.1 M TBAP with scan rate = 100 mV s^{-1} .

(vs. Ag/AgCl). All electrochemical reactions undergo one-electron transfer, which is confirmed by spectroelectrochemistry.²⁹ Fig. 6 illustrates spectral changes of compound 1 at applied potentials from $+0.20$ to $+0.46$ V in CH_2Cl_2 containing 0.1 M TBAP. The peaks at 298, 412, 629 and 798 nm decrease in their absorption intensity whereas those at 273, 572 and 745 nm increase with clear isosbestic points at 235, 290, 330, 350, 485, 580, 705 and 845 nm. The resulting spectrum is analogous to that of complex 2 obtained by chemical method, indicating that the oxidation occurred predominantly at the hexacobalt core. The second 1-e^- oxidation was continuously performed at applied potentials from $+0.46$ to $+0.95$ V as shown in Fig. 7. The peaks at 273, 335, 412 and 572 nm decrease in their intensity and those at 700 and 880 nm increase when the applied potential is increased from $+0.46$ to $+0.95$ V. The presence of clear isosbestic points at 270, 320 and 620 indicates the formation of only one product during the process of electrolysis. The spectral changes of the third 1-e^- oxidation process of 1 were depicted in Fig. 8. The peaks at 270

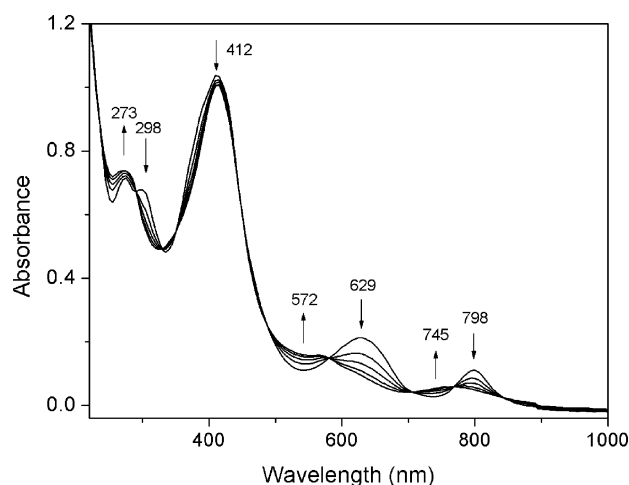


Fig. 6 Electronic absorption spectral changes for the first oxidation of compound 1 in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials from $+0.20$ to $+0.46$ V.

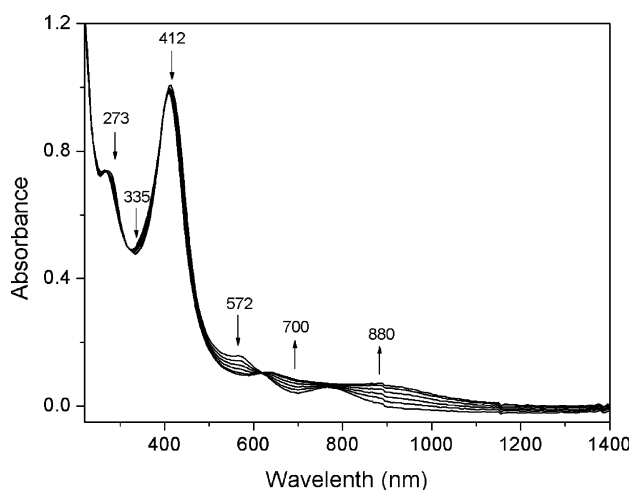


Fig. 7 Electronic absorption spectral changes for the first oxidation of compound 1 in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials from $+0.46$ to $+0.95$ V.

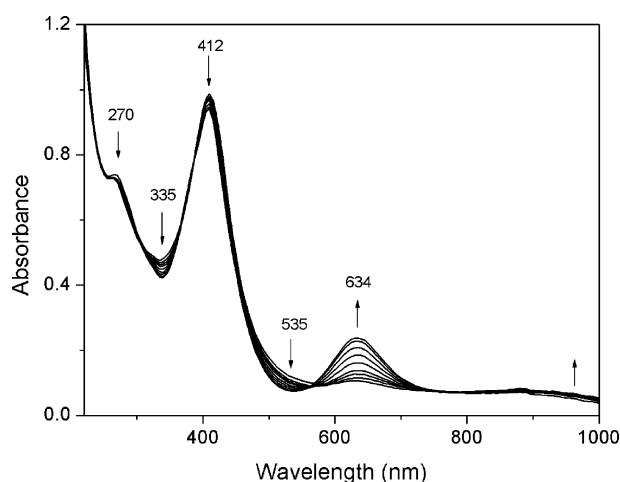


Fig. 8 Electronic absorption spectral changes for the first oxidation of compound **1** in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials from +0.95 to +1.3 V.

and 412 nm decrease whereas those at 634 nm increase in intensity with isosbestic points at 250, 365 and 385 nm. All the oxidation processes are reversible at the time scale of spectroelectrochemistry (about 2 h). However, attempts to isolate and crystallize the two- and three-electron oxidation products were unsuccessful because of poor quality and stability of the crystals.

Magnetic properties

The plots of effective magnetic moments (μ_{eff} , B.M.) vs. temperature (K) for compounds **1** and **2** are shown in Fig. 9. Compound **1** with Co_6^{11+} configuration has effective magnetic moments of 2.06 B.M. at 300 K, which can be considered as a spin state of $S = 1/2$, although it is slightly higher than the spin-only μ_{eff} of 1.73 B.M. Compound **2** with Co_6^{12+} configuration is expected to be diamagnetic and has a $S = 0$ ground state if the linear combinations of the six d^7 cobalt ions (each $S = 1/2$) are considered by simple MO treatments. However, compound **2** has a magnetic moment of 2.79 B.M. at 300 K, indicating a spin state of $S = 1$. The well-known compound $[\text{Co}_2(\text{triza})_4]$ (triza = anion of di-*p*-tolyltrizenate) was reported to be diamagnetic with $\sigma^2\pi^4\delta^2\delta'^2\pi^*4$

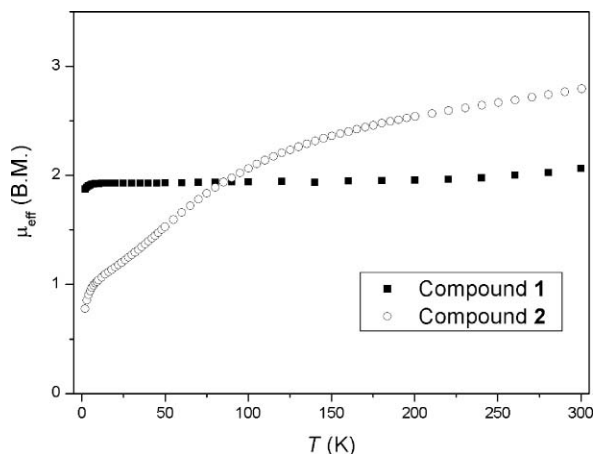


Fig. 9 Temperature-dependent effective magnetic moments for compounds **1** and **2**.

configuration.³⁰ In the case of our hexacobalt complexes, the d electrons are considered to be delocalized over the Co_6 chain. If the energy gap between HOMO and LUMO is small enough, one of the paired electrons in HOMO would fill in LUMO, resulting in a spin state of $S = 1$ (e.g. compounds **2** and **3**). Magnetic moments for compounds **3** and **4** are of 3.30 and 2.25 B.M., respectively, at 300 K, suggesting compounds **3** and **4** being in $S = 1, 1/2$ configurations, respectively.

EHMO calculation

To further study the electronic properties for the Co_6 species, the extended Hückel molecular orbital (EHMO) method using the free software CACAO³¹ was performed on the dication of the compound **2**. The crystal data of the dication of **2** were used as the input file. The default values for Co, C, N, H and S are used for the calculations without considering the solvents and counter anions, PF_6^- . The z axis direction passes through the hexacobalt chain. The qualitative molecular orbital diagram is shown in Fig. 10.

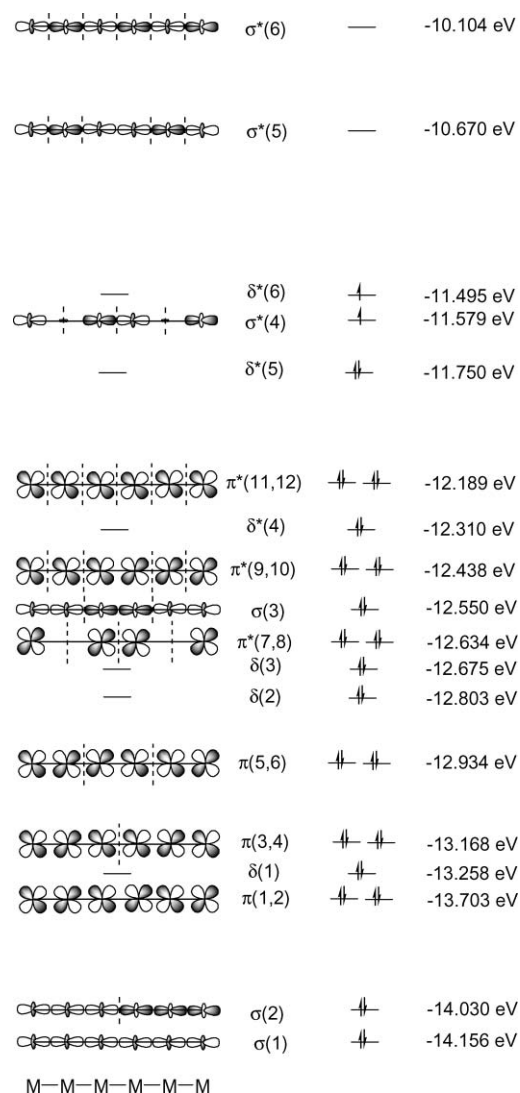


Fig. 10 The qualitative molecular orbital diagram of the linear six cobalt(II), $\text{Co}^{\text{II}}\text{-Co}^{\text{II}}\text{-Co}^{\text{II}}\text{-Co}^{\text{II}}\text{-Co}^{\text{II}}\text{-Co}^{\text{II}}$ system for dication of compound **2**.

The σ bonds are formed mainly from cobalt d_{z^2} orbitals, and d π bonds are mostly contributed by cobalt d_{xz} or d_{yz} atomic orbitals. The weak δ bonds are constructed from cobalt $d_{x^2-y^2}$ or d_{xy} atomic orbitals. The M–L σ bonds predominantly formed from $d_{x^2-y^2}$ or d_{xy} atomic orbitals are not shown in Fig. 10 because they offer weak or no metal–metal bondings. The MO calculations suggest that there are two unpaired electrons filled in the $\sigma^*(4)$ and $\delta^*(6)$ orbitals. The small energy difference of 0.084 eV between these SOMOs ($\sigma^*(4)$ and $\delta^*(6)$) results in paramagnetism rather than diamagnetism for compound **2**. The average Co–Co bond order is 0.6 on the basis of MO calculations. When reduction is performed on Co_6^{12+} compound, the extra electron would fill into $\sigma^*(4)$ orbitals to afford the complex with a spin state of $S = 1/2$ and the one unpaired electron occupies in the $\delta^*(6)$ orbital. The calculations also reveal the sum of Co–Co bond orders for compounds **1** and **2** are of 2.5 and 3.0, respectively. The separations for $\text{Co}(1) \cdots \text{Co}(6)$ are of 11.429(1) and 11.381(2) Å, inversely proportional to the corresponding bond orders for **1** and **2**.

Conclusion

We have synthesized the novel ligand, H_2bpyany , containing naphthyridyl group and its corresponding hexacobalt complexes. On the basis of magnetic measurements, the one-electron reduction species **1** and **4** have a spin state of $S = 1/2$ whereas compounds **2** and **3** (Co_6^{12+}) are in a spin state of $S = 1$. The EHMO calculations are consistent with the magnetic measurements for compound **1** and **2**. Attempts to synthesize other types of hexanuclear metal complexes are underway in this laboratory.

Experimental

Materials

All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. CH_2Cl_2 used for electrochemistry was dried over CaH_2 and freshly distilled prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized twice from ethyl acetate and dried under vacuum. The precursor, 2,7-dichloro-1,8-naphthyridine was prepared according to the literature.²⁸

Physical measurements

Absorption spectra were performed on a Varian Carry 50 spectrophotometer. IR spectra were obtained from a Nicolet Fourier Transform in the range 500–4000 cm^{-1} . FAB mass spectra were taken on a JEOL HX-110 HF double-focusing spectrometer operating in the positive ion detection mode. Magnetic susceptibility was collected by a Quantum external magnetic field 10 000 G. Electrochemistry was carried out on a CH Instruments, (Model 750A) using CH_2Cl_2 solvent with 0.1 M TBAP and 1 mM analytes. Cyclic voltammetry was recorded with a home-made three-electrode cell equipped with a BAS glassy carbon (0.07 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a home-made Ag/AgCl (saturated) reference electrode. The reference electrode is separated from the bulk solution by a double junction filled with electrolyte solution. Potentials are reported vs. Ag/AgCl (saturated) and referenced to the ferrocene–ferrocenium ($[\text{Cp}_2\text{Fe}]/[\text{Cp}_2\text{Fe}]^+$) couple which

occurs at $E_{1/2} = +0.54$ V vs. Ag/AgCl (saturated). The working electrode was polished with 0.03 μm alumina on Buehler felt pads and was subjected to ultrasound for 1 min prior to each experiment. The reproducibility of individual potential values was within ± 5 mV. Optical thin layer electrochemical (OTTLE) spectra were accomplished with the use of a 1 mm UV cell, a 100 mesh platinum gauze as working electrode, a platinum wire as auxiliary electrode, and a Ag/AgCl (saturated) reference electrode.

Syntheses

2,7-Bis(α -pyridylamino)-1,8-naphthyridine (H_2bpyany). To a flame-dried flask under argon were placed 2,7-dichloro-1,8-naphthyridine (1.98 g, 10 mmol),²⁸ 2-aminopyridine (2.16 g, 23 mmol), *t*-BuOK (2.81 g, 25 mmol), $\text{Pd}_2(\text{dba})_3$ (183 mg, 0.20 mmol), and dppp (165 mg, 0.40 mmol). The mixture was stirred and refluxed in toluene (100 mL) for 48 h and turned to deep brown. The solvent was removed under reduced pressure. The mixture was poured into water and the precipitate was filtered to obtain the solid. Column chromatography was performed on silica gel using ethyl acetate as the eluent affording the bright yellow product, H_2bpyany . Yield: 2.09 g, 66%. $^1\text{H NMR}$ (400 MHz; $\text{DMSO}-d_6$): δ 10.16 (2 H, s), 8.29 (2H, m), 8.26 (2H, $J = 8.4$ Hz, d), 8.02 (2 H, $J = 8.4$ Hz, d), 7.77 (2 H, m), 7.64 (2H, $J = 8.4$ Hz, d), 6.96 (2H, m); $^{13}\text{C NMR}$ (100 MHz; $\text{DMSO}-d_6$): δ 155.5, 154.6, 153.7, 147.3, 137.5, 137.2, 116.5, 113.2, 112.4, 110.6; IR (KBr) $\nu/\text{cm}^{-1} = 3260, 3189$ (NH), 1619, 1582, 1522, 1481, 1458, 1435, 1404, 1379, 1348, 1323, 1304 (py); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 262 (4.47), 363 (3.84), 381 (5.62), 414 (0.524), 440 (0.116); MS(FAB) m/z 315 ($[\text{M} + \text{H}]^+$); EA (%) H_2bpyany : calcd. C 68.78, H 4.49, N 26.74; found C 68.53, H 4.52, N 26.90.

$[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)$ (1**).** The mixture of H_2bpyany (251 mg, 0.80 mmol), naphthalene (25 g), and DMF (5 mL) placed in an Erlenmeyer flask was heated at *ca.* 100 °C and then *t*-BuOK (224 mg, 2.0 mmol) was slowly added. The color immediately changed to dark brown. After heating the solution at about 130–140 °C for 15 h followed by 15 min at refluxing (*ca.* 200 °C), a clear orange solution was formed, and then a solution of anhydrous CoCl_2 (182 mg, 1.4 mmol) in DMF (5 mL) was added dropwise. After refluxing for another 30 min, NaSCN (32 mg, 0.40 mmol) was added slowly. The color changed from dark brown to dark green. The mixture was refluxed for further 3 h, and then concentrated to the amount of *ca.* 5 mL, followed by cooling to about 70 °C. The residue was treated with hexane to precipitate the metal complexes. The precipitates were collected by suction filtration, and rinsed with hexane to remove the residual naphthalene and DMF. The solid was extracted with CH_2Cl_2 (50 mL) and filtered. After the CH_2Cl_2 solution was treated with excess KPF_6 in MeOH (25 mL) and stirred overnight, the solvent was removed under vacuum. The residual solid was extracted with CH_2Cl_2 (50 mL) and filtered. Dark purple crystals were obtained by slow diffusion of *n*-pentane vapor into the filtrate. Yield 50 mg, 30%. IR (KBr) ν/cm^{-1} : 2058 ($\text{C}\equiv\text{N}$), 1711, 1608, 1585, 1556, 1508, 1467, 1436, 1363, 1340(py), 849, 839(P–F); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 306 (6.28), 415 (11.2), 628 (2.55), 799 (1.38); MS(FAB) m/z 1718 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2]^+$), 1660 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})]^+$); EA

(%) $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)\cdot\text{CH}_2\text{Cl}_2$: calcd. C 46.22, H 2.59, N 18.69; found C 46.74, H 2.73, N 18.95.

$[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_2$ (2). To a solution of compound **1** (93 mg, 0.05 mmol) in a mixture of CH_2Cl_2 (25 mL) and MeOH (1 mL) was added $[\text{Cp}_2\text{Fe}](\text{PF}_6)$ (23 mg, 0.07 mmol) under argon atmosphere. The resulting solution turned to dark brown immediately. After stirring for 30 min, the solvent was removed under vacuum. The residual solid was rinsed with ethyl acetate to remove excess $[\text{Cp}_2\text{Fe}](\text{PF}_6)$ and the byproduct $[\text{Cp}_2\text{Fe}]$. The remaining solid was dissolved in a mixture of CH_2Cl_2 (50 mL) and MeOH (2 mL) and then filtered. Deep brown crystals were obtained by slow diffusion of ether into the filtrate. Yield: 73 mg, 73%. IR (KBr) ν/cm^{-1} : 2060 ($\text{C}\equiv\text{N}$), 1709, 1610, 1602, 1554, 1508, 1468, 1437, 1365, 1346(py), 843 (P–F); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 276 (9.28), 412 (11.49), 572 (2.02), 757 (0.94); MS(FAB) m/z 1718 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2]^+$), 1660 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})]^+$); EA (%) $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{NCS})_2](\text{PF}_6)_2\cdot 2\text{CH}_2\text{Cl}_2$: calcd. C 41.89, H 2.41, N 16.71; found C 42.06, H 2.51, N 16.88.

$[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2](\text{OTf})_2$ (3). To a solution of compound **1** (93 mg, 0.05 mmol) in a mixture of CH_2Cl_2 (25 mL) and MeOH (25 mL) was added excess NaOTf. After the solution was stirred overnight, solvent was removed under vacuum. The residual solid was extracted with CH_2Cl_2 (50 mL) and AgOTf (38 mg, 0.15 mmol) in MeOH (2 mL) was added under argon atmosphere. The resulting solution turned to dark brown gradually. After stirring for 30 min, the solution was filtered through Celite. Deep brown crystals were obtained by slow diffusion of ether into the filtrate. Yield: 62 mg, 56%. IR (KBr) ν/cm^{-1} : 1613, 1558, 1472, 1439, 1369, 1353, 1363, 1344(py), 1033(C–F); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 274 (8.77), 413 (12.4), 566 (1.39), 799 (1.38); MS(FAB) m/z 1900 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2]^+$), 1751 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})]^+$); EA (%) $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2](\text{OTf})_2\cdot 3\text{CH}_2\text{Cl}_2$: calcd. C 38.67, H 2.22, N 13.70; found C 49.08, H 2.43, N 13.60.

$[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2](\text{OTf})$ (4). To a solution of compound **3** (55 mg, 0.03 mmol) in CH_2Cl_2 (25 mL) was added two drops of hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$). The resulting solution turned to dark green immediately. Before anhydrous $\text{MgSO}_4(\text{s})$ was added the solution was stirred for 2 h. The mixture was filtered through Celite. Deep greenish brown crystals were obtained by slow diffusion of ether into the filtrate. Yield: 47 mg, 92%. IR (KBr) ν/cm^{-1} : 1707, 1610, 1602, 1560, 1508, 1468, 1437, 1363, 1344(py), 1033(C–F); UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 305 (6.17), 413 (10.7), 629 (2.21), 800 (1.29); MS(FAB) m/z 1900 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2]^+$), 1751 ($[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})]^+$); EA (%) $[\text{Co}_6(\mu_6\text{-bpyany})_4(\text{OTf})_2](\text{OTf})$: calcd. C 42.75, H 2.36, N 15.74; found C 42.67, H 2.58, N 15.85.

X-Ray crystallographic determinations

The crystals were mounted on a glass fiber. Crystal data were collected on a NONIUS Kappa CCD diffractometer with monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150(1) \text{ K}$. Cell parameters were retrieved and refined using *DENZO-SMN* software on all observed reflections. Data reduction was performed with the *DENZO-SMN* software.³² An empirical absorption was based on the symmetry-equivalent reflections and

absorption corrections were applied with the SORTAV program.³³ All the structures were solved by using the *SHELXS-97*³⁴ and refined with *SHELXL-97*³⁵ by full-matrix least squares on F^2 values. Hydrogen atoms were fixed at calculated positions and refined using a riding mode.

CCDC reference numbers 283614–283617.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515311e

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