Introduction

The study of molecular complexes based on a redox-controllable metal center has been a hot topic in research because of the potential application in the field of redox shuttles for dye-sensitized solar cells (DSSC), anolytes for redox flow batteries, and as a redox mediator for water splitting and CO2 reduction. The function of such complexes has been proved to be strongly dependent on the electronic property of the N-donor ligands. Among these subjects, polypyridyl complexes containing iron and ruthenium metal centers have been widely investigated as efficient tools to tune the electrostatic effects of proximal nonredox active metal centers. For the purpose of potential applications, it is of paramount importance to tune the donor type and ligand field strength of the ligands available to form the cobalt coordination sphere. Just recently, Yang et al. reported the redox tuning and electronic effects of proximal nonredox active cations in cobalt Schiff-base complexes. The tunability in the reversible redox potential was ascribed to the control of the absolute energy of the molecular orbital participating in electron transfer. In the previous work, we investigated how the electronic effect of the ligand influences the spin crossover of Co(n) ion within a metallogrid complex. Based on the electrochemical results, modification of the ligand field strength would give rise to a variation in the electronic structure (or molecular orbitals) of the redox active cation. However, spin crossover in a multinuclear system is not easy to control due to the synthetic difficulty of modifying the ligand field of the bis-multidentate ligand. In contrast, the mononuclear system could provide a convenient tool to tune the electrostatic effect, which would uniformly shift the molecular orbitals on the redox active metal. To further elucidate the source of the change in redox potential and to optimize the spin crossover of the Co(n) ion starting from Schiff-base pyrazine ligands (Scheme 1, R1 = H; H: L1 = Me, R2 = H; L2Me, R1 = Me, R2 = NO2: L3NO2), we synthesized a series of mononuclear cobalt complexes, aiming at achieving control of the local spin state as well as the redox chemistry. The ligand environments with the N,O donor permitted facile comparisons of the electronic structure. In compound 1, ligand HL1 was deprotonated upon coordination and Co(n) was oxidized to Co(m). In other cases, L2Me and L3NO2 were not deprotonated, whereas HL4 in compound 4 was deprotonated, and divalent cobalt ion was stable. The ligand provided a coordination pocket of a transition-metal center, and thus could have a minimal effect on the coordination geometry of the cobalt center. Through this framework, a multielectron redox couple, such as Co(m)/Co(n), and ligand-based...
reduction were reversible, conveniently allowing systematic tuning of the electronic effect on the redox potential.

Although a handful of mononuclear 2,2′:6′,2′″-terpyridine-derivative Co(II)-center spin-crossover compounds have been previously investigated,20–25 other systems have been rarely reported and should be further developed.26–28 In the previous work, we investigated the deprotonation effects at the coordination pocket, such as how L1+ forms diamagnetic [Co(L1+)]X complexes irrespective of the counterion X and how the introduction of substituents at the imine position has an effect on the variation of the spin state.15 As a result, the cobalt(II) complex of 2,5-bis[1-[2-methyl-2-(pyridin-2-yl)-hydrazono]ethyl]pyrazine (L2Me), in which the methyl substituent was adopted to prevent deprotonation on the imine group, showed an incomplete spin crossover at higher temperature. In this paper we continue to expand the new ligand system and describe the synthesis of a number of ligands with modified substituents, aiming at achieving an enhanced spin crossover property of their Co(II) complexes, and also we discuss the effect of the substituents on the spin state of the cobalt(II) center.29

Experimental section
Materials and general procedures

All the reagents employed were commercially available and used without further purification. Methanol and acetonitrile were dried using standard procedures. Predeuterated dimethyl sulfoxide (DMSO-d₆) was purchased from Alfa Aesar Co. Ltd., while 2-hydrazinylpyridine, benzohydrazide, 2-Br-5-nitropyridyl, and 2-acetylpyrazine were obtained from a commercial source and used directly without any purification. 1-Methyl-1-pyridylhydrazine was prepared according to the revised literature method.30 To a round flask containing 2-Br-5-nitropyridyl (32 mmol, 6.5 g) was added excess 40% methylhydrazine (480 mmol, 55 g) under a nitrogen atmosphere, which was stirred for 3 h at boiling temperature. After cooling to room temperature, the mixture was evaporated under reduced pressure to dry. The residue was dissolved in ethyl acetate (250 mL), and washed with sodium carbonate (10% aqueous solution, 50 mL × 3) and saturated brine (50 mL × 3). The organic phase was dried with anhydrous Na₂CO₃ for 2 h and was then evaporated under vacuum to produce a yellow solid. Yield: 3.39 g, 63%. The solid was directly used for the synthesis of [LNO₂]₃ without NMR characterization.

Synthesis of 1-methyl-1-(4-nitropyridyl)hydrazine. The compound was synthesized according to the revised literature method.30 To a round flask containing 2-Br-5-nitropyridyl (32 mmol, 6.5 g) was added excess 40% methylhydrazine (480 mmol, 55 g) under a nitrogen atmosphere, which was stirred for 3 h at boiling temperature. After cooling to room temperature, the mixture was evaporated under reduced pressure to dry. The residue was dissolved in ethyl acetate (250 mL), and washed with sodium carbonate (10% aqueous solution, 50 mL × 3) and saturated brine (50 mL × 3). The organic phase was dried with anhydrous Na₂CO₃ for 2 h and was then evaporated under vacuum to produce a yellow solid. Yield: 3.39 g, 63%. The solid was directly used for the synthesis of [LNO₂]₃ without NMR characterization.

Synthesis of [1-2-(pyridin-2-yl)hydrazono]ethyl]pyrazine (HL1). A methanol solution mixture of 2-acetylpyrazine (1.2212 g, 0.01 mol) and 1-pyridylhydrazine (1.0913 g, 0.01 mol) was refluxed for 4 h, and after cooling to room temperature,
a pale-yellow crystal was obtained by filtration. The crude product was washed with cold methanol and dried in vacuo. Yield: 1.4721 g, 69%. 1H NMR (400 MHz, DMSO-d6): δ (ppm) = 2.37 (s, 3H), 6.88 (m, 1H), 7.4 (s, 0.5H), 7.47 (s, 0.5H), 7.71 (m, 1H), 8.20 (m, 1H), 8.52 (d, J = 2.64 Hz, 1H), 8.58 (m, 1H), 9.36 (d, J = 1.56 Hz, 1H), 10.22 (s, 1H). Elemental analysis (%) calculated for C11H11N5: C, 61.96; H, 5.20; N, 32.84. Found: C, 62.12; H, 5.12; N, 32.78. MS (m/z) [M + H]+ calcd for C11H11N5: 214.25, found 214.63.

Synthesis of [1-[2-methyl-2-(pyridin-2-yl)-hydrazono]ethyl]pyrazine (L2Me). A pale-yellow ligand L2Me was obtained by following the same procedure as that described for HL1 except that 1-methyl-1-pyridylhydrazine was used instead of 1-phenylhydrazine. Yield: 1.6798 g, 74%. 1H NMR (400 MHz, DMSO-d6): δ (ppm) = 2.49 (s, 3H), 3.49 (s, 3H), 6.89 (t, 1H), 7.18 (d, J = 8.40 Hz, 1H), 7.66 (t, 1H), 8.26 (d, J = 4.88 Hz, 1H), 8.68 (d, J = 7.04 Hz, 1H), 9.34 (s, 1H). Elemental analysis (%) calculated for C12H13N5: C, 63.42; H, 5.77; N, 30.82. Found: C, 63.34; H, 5.65; N, 30.93. MS (m/z) [M + H]+ calcd for C12H13N5: 228.27, found 228.84.

Synthesis of [1-[2-(5-nitropyridin-2-yl)-2-methylhydrazono]ethyl]pyrazine (L3NO2). A toluene solution containing 2-acetylpyrazine (1.2212 g, 0.01 mol) and 1-methyl-1-(4-nitropyridyl) hydrazine (1.9217 g, 0.01 mol) was refluxed for 24 h, and after cooling to room temperature, a yellow solid was obtained by filtration. The crude product was washed with cold methanol and dried in vacuo. Yield: 2.2032 g, 81%. 1H NMR (400 MHz, CDCl3): δ (ppm) = 2.57 (s, 3H), 3.65 (s, 3H), 7.03 (s, 0.5H), 7.06 (s, 0.5H), 8.30 (dd, 1H), 8.64 (m, 2H), 9.18 (d, J = 2.60 Hz, 1H), 9.46 (d, J = 1.40 Hz, 1H). Elemental analysis (%) calculated for C13H12N4O: C, 58.10; H, 4.13; N, 20.85. Found: C, 58.11; H, 3.72; N, 32.77.

Synthesis of complex [CoII(L1)2](ClO4)2 (1). A toluene solution containing 2-acetylpyrazine (4.8 mg, 20 μmol) in acetonitrile (5 mL) was dissolved in a 2 mL of ethyl acetate and added to a test tube. Finally, a 2 mL solution of Co(ClO4)2·6H2O (0.5 mg, 1.5 μmol in MeOH) was layered on top of the buffer layer. The tiny tube was kept in the dark and left undisturbed without protection from air. The course of two weeks, dark-red block-shaped crystals suitable for X-ray diffraction studies were obtained at the interface. Yield: 0.17 mg, 16%. IR (KBr pallet, cm−1): 625(w), 773(m), 850(w), 943(w), 1091(s), 1349(s), 1466(w), 1577(m), 1619(m). Elemental analysis (%) calculated for C25H28Cl2CoN12O13: C, 36.92; H, 3.12; N, 9.06. Found: C, 36.92; H, 3.12; N, 9.14.

Results and discussion

The non-symmetric ligands used in this work were prepared through reacting 1-phenylhydrazine and commercially available 2-acetylpyrazine. It should be noted that the reaction to produce L3NO2 was difficult to occur, possibly due to the relatively low electron density on the carbonylhydrazide nitrogen, which was unfavorable to nucleophilic attack, and so forcing conditions 780(m), 1092(s), 1316(m), 1472(m), 1621(m). Elemental analysis (%) calucalated for C25H28Cl2CoN12O13: C, 43.53; H, 3.46; N, 24.03. Found: C, 43.44; H, 3.35; N, 24.23.
were required, namely 120 °C in toluene for 1 day, to complete the reaction. This method, previously used to generate the symmetric pyrazine-bridged bis-tridentate ligand (L1)\(_3\),\(^{15}\) should open up access to a wide variety of non-symmetric pyrazine-based ligands. HL1 and HL4 were readily deprotonated so the complexes [Co\(^{III}\)(L1)\(_2\)ClO\(_4\)] (1) and [Co\(^{II}\)(L4)\(_2\)](ClO\(_4\))\(_2\) (4) were initially prepared by simply combining a 2 : 1 ratio of the ligand and [Co\(^{II}\)(H\(_2\)O)\(_6\)](ClO\(_4\))\(_2\) salt in methanol. However the oxidation solution for L2Me and HL4 and, on one occasion, of an ethyl acetate–MeOH solution for L2Me. However, the reaction between electron-deficient ligand L3\(^{NO2}\) and cobalt salt was not easy to occur at room temperature due to the dynamic inertia. Thus the syntheses of compounds 3\(^{ClO4}\) and 3\(^{BF4}\) were further optimized by holding the reaction suspension containing L3\(^{NO2}\) and cobalt salt in acetonitrile at 55 °C for 30 min, which was then diffused with ether vapor to produce higher-quality, more uniform single crystals suitable for X-ray diffraction analysis. It is necessary to note that the reaction to produce 1, 2, and 4 should be operated in a low concentration of reactants. The higher concentration was also attempted, but the diffusion reaction was so rapid that the precipitate with high impurity rather than crystals was obtained. Hence, to obtain spectroscopic, magnetic, and electrochemical data, we had to set up many reactions in parallel to accumulate enough sample.

The UV-vis absorption spectra of all the ligands and their cobalt complexes are shown in Fig. 1, where the features closely match those of the previously investigated [Co\(_4\)] complexes.\(^{15}\) For the complexes 1 and 4, two transitions appear at ~280 nm and ~320 nm that can also be observed in the free ligand spectra (see Fig. 1(a)). These could be expected to be ligand-based \(\pi \rightarrow \pi^*\) transition in nature. A similar transition was also observed in complexes 2 and 3. The transitions can be observed at ~390 nm for 1 and 415 nm for 4, and are red-shifted relative to the free ligand, and could possibly be assigned as a deprotonated ligand-based transition. The most striking point that can be observed in [Co\(^{III}\)(L1)]\(^+\) (1) is a strong absorption that spans from 450 to 650 nm, reminiscent of a similar feature in the [Co\(^{III}\)\(^{4+}\)] spectrum.\(^{15}\) This observation in solution at room temperature distinguishes these species into three categories: 1, 2 and 3, and 4 in view of the ground state electronic absorption spectra, which is consistent with the later analysis of the valence state.

X-ray diffraction data were collected for single crystals of the cobalt complexes at 298 K. In addition, the data at 150 K were collected for complex 3\(^{ClO4}\) considering the potential spin-state transition-induced structure changes. The structure refinement parameters are collected in Table 1. The cobalt(\(\text{III}\)) complex 1 crystallized in the monoclinic space group \(P2_1/c\). Here, the central cobalt atom is coordinated by two deprotonated \(L1\) ligands binding \textit{via} chelating in a \textit{mer} fashion the pyridyl nitrogens (N5 and N10), imide N8 and N3, and pyrazine nitrogens (N1 and N6) (Fig. 2(A)). Furthermore, the bond lengths of C7–N4 (1.312 Å) and N4–N3 (1.332 Å), as well as another pair of bond lengths (1.330 Å for C18–N9 and 1.310 Å for N9–N8) on the ligand, are intermediate between a normal single bond and a double one, suggesting that the protons on the N4 and N9 sites are lost upon metal binding. The lengths of the Co–N bonds are quite characteristic of the respective spin and oxidation states of the coordinated metal ion and, therefore, can be used as diagnostic tools for determining the electronic state of the metal ion.\(^{18}\) The Co–N bond distances range from 1.817(2) to 1.877(2) Å, typical of LS Co\(^{III}\)\(^{19}\) and the angular distortion parameter (\(\Sigma\), defined as the sum of deviation from 90° of 12 \textit{cis}-N–Co–N angles about the Co atom) is 76.68°. The resultant structural models of Co(\(\text{II}\)) complexes display geometries that are consistent with a singlet ground state for complex 1 at room temperature, while a quartet at the same temperature for complexes 3 and 4, highlighting the chemical modification of the electronic configuration of the metal-center orbitals.

The cobalt(\(\text{II}\)) complexes 3\(^{ClO4}\) and 3\(^{BF4}\) crystallized in the monoclinic space group \(P2_1/c\) and had similar structures except for the anions (Fig. 2(B) and Fig. S9, ESI†). Here, the binding mode of ligand L3\(^{NO2}\) to Co(\(\text{III}\)) is identical between complexes 3\(^{ClO4}\) and 3\(^{BF4}\) and so only the structure of 3\(^{ClO4}\) will be described herein. Single-crystal X-ray structures were determined at 296 K (3\(^{ClO4}\)\(^{−}\)) and 150 K (3\(^{ClO4}\)\(^{−}\)), respectively (Table 1). As in the case of 1, the coordination sphere of the Co(\(\text{III}\)) ion adopts a distorted octahedron with a CoN\(_6\) chromophore. Four equatorial N atoms, including N2, N3, N5, N9 with the average Co⋯N distance of 2.034(6) Å and two axial N atoms of N7 and N11 with Co⋯N distance of 2.114(4) and 2.122(3) Å that come from the pyrazine and pyridyl group of the individual ligand consist of an elongated octahedral environment, which is characteristic of Co\(^{III}\)–HS systems. In the crystal packing mode, some significant intermolecular weak interactions were found, such as \(\pi \cdots \pi\) stacking between two neighboring pyrazine rings with the shortest atom⋯atom distance of 3.317 Å (Fig. 2(D)).

![Fig. 1](image-url) UV-vis absorption spectra for all the ligands (a) and the corresponding cobalt complexes (b) in acetonitrile at room temperature.
addition, the intermolecular contacts through the nitro-group also support the framework, such as O⋯O contact of 2.952 Å and O⋯N contact of 3.001 Å.

In view of the spin-crossover behavior, we continued to determine the structure of 3ClO4 at low temperature (150 K). The coordination environment of the metal center was analogous to that observed in 3ClO4. However, the average Co⋯N bond lengths (Table 2) within the equatorial plane now shrink to 1.942(5) Å, and here the striking point is that the axial coordination bonds of 2.086(8) and 2.119(7) Å were not significantly changed, giving rise to more elongated octahedral as expected for a Jahn-Teller distorted low-spin octahedral d7 system. The observed distortion for the low-spin cobalt(II) complex was reminiscent of other low-spin mononuclear cobalt(II) complexes of 2,2′:6′,2″-terpyridine (terpy) and other N-donor complexes. The distortion situation is also consistent with our recently reported SCO CoIII metallogrid [CoII(HLMe)3][ClO4]3·4MeCN·H2O,13 but contrasts with that recently observed in the LS CoIV grid [CoII(HL3)4][ClO4]3·8H2O, where a compressed octahedron was observed.14 Alternatively, the distortion parameter, Σ, defined as the sum of the deviation from 12 cis-N–Co–N angles, is sensitive to the changes of the spin state of the center cobalt atom.14 In general, HS Co(n) compounds have a larger value of Σ than that in LS ones because HS metal complexes allow for more distorted coordination spheres. In the reported Co-terpy SCO compound,20–24 the values of Σ ranged from 92° corresponding to the LS state to 119° for the HS cobalt(n) center, respectively. For compound 3ClO4, the angular distortion parameters, Σ (deg), about the cobalt atom shrank from 113.2(1)° at room temperature corresponding to HS Co(n) to the value of 102.8(4)° at 150 K in a LS structure, indicating the heavier deviations from the ideal octahedral for the LS cobalt(n) center in this system. The low-spin Σ value was unusually large for this complex and, to the best of our knowledge, is at the high end among all cobalt(II) spin-crossover active complexes.20–24

Table 1 Data collection and structure refinement parameters for complexes 1–4

| Complex 1 | Complex 3ff4 | Complex 3ClO4 | Complex 4 |
|-----------|-------------|--------------|--------|
| Formula   | C24H24ClCoN10O4 | C24H24ClCoF8N12O4 | C24H24ClCoN10O4 |
| F.W.      | 582.86      | 793.12       | 830.39 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | P21/n      | P21/n       | P21/n  |
| a [Å]     | 8.6063(5)   | 14.713(8)    | 14.826(4) |
| b [Å]     | 9.7092(8)   | 13.235(7)    | 13.366(4) |
| c [Å]     | 28.092(2)   | 18.309(9)    | 18.433(5) |
| α [°]     | 90          | 90           | 90     |
| β [°]     | 98.083(2)   | 102.214(12)  | 102.714(7) |
| γ [°]     | 90          | 90           | 90     |
| Volume [Å³] | 2324.1(3)  | 3485(3)      | 3563.1(18) |
| Z         | 4           | 4            | 4      |
| Cal. Density (g cm⁻³) | 1.666 | 1.512 | 1.548 |
| μ/µm⁻¹    | 0.909       | 0.587        | 0.710  |
| f(000)    | 1192        | 1608         | 1636   |
| θ range [°] | 2.93–25.36  | 0.25–30.87   | 0.23–30.32 |
| Goodness of fit on F² | 1.132 | 1.035 | 1.055 |
| Final R indices | R₁ = 0.0466 | R₁ = 0.0903 | R₁ = 0.1001 |
| [I > 2σ(I)] | wR₁ = 0.0828 | wR₁ = 0.2357 | wR₁ = 0.2484 |
| R Indices (all data) | R₁ = 0.0801 | R₁ = 0.1508 | R₁ = 0.2189 |
| wR₁ = 0.0905 | wR₁ = 0.2621 | wR₂ = 0.2512 |

a R₁ = \sum(|F_o| - |F_c|)\sum|F_o|, b wR₂ = \left(\sum\left[w(F_o^2 - F_c^2)^2\right]\right)^{1/2}\sum[w(F_o^2)]

On the basis of X-ray diffraction data and electronic absorption spectra, magnetic susceptibility data of all the complexes were further collected in the studied temperature ranges in the solid state (Fig. 3(a)). As expected, complex 1 was diamagnetic over the measured temperature region, corresponding to the LS CoII ions. The room temperature \chiM/T value of compound 4 was equal to 2.34 cm³ K mol⁻¹, which was obviously higher than the expected values of 1.875 cm³ K mol⁻¹ corresponding to HS d⁷ (T_{2g}) ground state, reflecting the substantial orbital contribution to the magnetic moment. As
the temperature decreased, $\chi_M T$ did not significantly decrease until 40 K, then decreased more rapidly to reach a value of 1.8 cm$^3$ K mol$^{-1}$ at 5 K, due to zero field splitting effects on the resultant $^5A_2g$ state. However, the magnetic moment of complexes 2 and 3 with the different anions showed different results. The sample was first measured from room temperature to 5 K, followed by the sequential heating/cooling cycles. The temperature-dependent magnetic data showed the gradual spin-crossover phenomenon for all three compounds. Compared to compound 2, compound 3 evidenced the more complete transition from the spin state ($s = \frac{1}{2}$) at low temperature to high spin ($s = \frac{3}{2}$) at high temperature. As a representative, complex $3_{ClO_4}$ showed an initial $\chi_M T$ value of 2.08 cm$^3$ mol$^{-1}$ K at 400 K, corresponding to the main population of the HS Co$^{II}$ ground state, then a decrease in $\chi_M T$ occurred as the sample was cooled to 150 K where a $\chi_M T$ value of 0.88 cm$^3$ mol$^{-1}$ K was observed. Further cooling beyond this point gave rise to a sloping plateau in $\chi_M T$, reaching 0.58 cm$^3$ mol$^{-1}$ K at 5 K. The plot is typical of a gradual $S = \frac{1}{2}$ spin crossover. No obvious hysteresis occurred upon the sequential heating–cooling cycles in the temperature range of 5–400 K. The investigation of magnetic data for compound $3_{BF_4}$ gave a similar result. However, at low temperature, the compound showed a more complete spin transition. For

![Fig. 2](https://example.com/figure2.png)

**Fig. 2** Crystal structure of the Co-containing complexes in 1 (A), $3_{ClO_4}$ (B), 4 (C) and crystal packing mode in $3_{ClO_4}$ (D) with the selected atom labels with ball-and-stick representation. Co = pink ball, C = gray, N = blue, O = red. Hydrogen atoms have been removed for clarity.

![Fig. 3](https://example.com/figure3.png)

**Fig. 3** (a) Temperature dependence of the product $\chi_M T$ for solids 1–4 under an applied magnetic field of 2500 Oe. (b) Solid UV-visible absorption spectra of $3_{ClO_4}$ powder at temperatures between 77 K and 348 K.

| Comp. | 1 | $3_{ClO_4}$ | $3_{BF_4}$ | 4 |
|-------|---|------------|------------|---|
| Temp. | 150 K | 150 K | 298 K | 298 K | 296 K |
| Co–N$_{amine}$ | 1.866(3) | 1.884(9) | 2.020(7) | 2.007(6) | 2.047(5) |
| Co–N$_{pyrazine}$ | 1.871(3) | 1.962(9) | 2.053(6) | 2.038(6) |
| Co–N$_{pyridine}$ | 1.901(3) | 1.934(1) | 2.028(7) | 2.012(7) | 2.163(5) |
| Co–N/O$_{av}$ | 1.902(3) | 2.086(8) | 2.114(6) | 2.127(5) |
| $\Sigma$ (deg)$^c$ | 1.932(3) | 1.988(1) | 2.037(7) | 2.034(6) | 2.089(6)$^a$ |
| $\Sigma$ (deg)$^c$ | 1.934(3) | 2.119(7) | 2.122(5) | 2.143(5) |
| $\Sigma$ (deg)$^c$ | 1.901(3) | 1.996(1) | 2.061(3) | 2.067(3) | 2.100(2) |
| $\Sigma$ (deg)$^c$ | 66.4(5) | 102.8(4) | 113.2(1) | 111.6(5) | 131.4(8) |

$^a$ The value corresponds to the bond distance of Co–O. $^b$ av means the average bond distance. $^c$ $\Sigma$ (deg) is defined as the sum of deviation from 90° of twelve cis-N–Fe–N angles about the cobalt atom.
comparison, the magnetic data for the grid compound were aligned with the data of 3BF₄(Fig. S10, ESI†). In the reported tetranuclear cobalt grid complexes, the typical χₘT value at low temperature is ca. 2.2 cm³ mol⁻¹ K, corresponding to four low-spin states (s = 1/2). With increasing temperature, but the χₘT value could not reach the saturation value even at the highest temperature of 400 K, indicating the rather incomplete spin transition in the Co₄ grid complex. However, for 3BF₄, the high temperature χₘT value above 350 K almost plateaued at ca. 2.1 cm³ mol⁻¹ K, indicating the complete spin transition for the mononuclear complex.

Given the potential of temperature-dependent metal–ligand interactions occurring on the SCO complex 3ClO₄, there should be a partial population of the ligand-center ground state and concomitant π → π⁺ transition within a wide temperature range. To further check this point, we collected UV-vis absorption spectra in the solid state as a function of temperature over the range 77–348 K. As expected, the ultraviolet absorption feature increased in intensity as the sample was heated. On subsequent cooling to room temperature, the spectra could reversibly recover to the original one (Fig. 3(b)). This temperature-dependence recover to the original one (Fig. 3(b)).

This electrochemical switching provides an alternative stimuli for spin crossover from ca. 4 μM for CoIII-HS by oxidation to 0 μM for CoIII,LS. Cyclic voltammetric studies of a 0.1 mM solution of all the cobalt complexes under transient conditions were performed by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at 25 ± 2 °C in acetonitrile containing 0.05 M of [Bu₄N][PF₆] as the supporting electrolyte, and showed one to three well-separated processes labeled as I, II, and III, respectively, in Fig. 4 (Table 3). The formal reversible potentials (E(II) = (E氧化 p + E还原 p)/2) were –946 mV and –1010 mV versus [Fc]⁺ for complexes 1 and 2, which could be attributed to the one-electron reduction of Co(nii) to Co(ni) for process I. The peak current is proportional to the square root of the scan rates in the range of 0.05 V s⁻¹ to 0.5 V s⁻¹, indicating this process is diffusion controlled at the peak potential (Fig. S11–14, ESI†). A second potentially chemically reversible reduction process (II) with an approximate E(I) = –1706 and –1554 mV for 1 and 2, respectively, was observed when the potential was scanned to more negative values, which was associated with the reduction of the Co(ni) to Co(ni). The E氧化 p / E还原 p ratio at all scan rates studied was almost unity and ΔEₚ (ΔEₚ = E氧化 p – E还原 p , where the superscripts ox and red denote the oxidation and reduction peaks respectively) was close to the theoretical value of 57 mV at 25 °C for a simple one-electron process, indicating all the processes were one-electron chemically and electrochemically reversible. However, complex 3 evidenced only one redox process, II, with the formal potential of –1698 mV. Interestingly, an additional process, III, was observed for complex 4 with the formal potentials E(I) = –1510, and –510 mV. The current magnitude for processes I, II, and III were similar. Process III, (E₁/₂(III) = –2140 mV), exhibited a negative or reduction current, and hence was ascribed to a ligand-centered redox process on the basis of previous assignments of pyrazine-substituted cobalt complexes. From the electrochemical data, there existed a slight difference in the electronic behavior between complex 1 and 2 and the highest oxidation state corresponding to CoIII ion required a quite negative oxidation potential. In this situation, complex 2 was still isolated as CoIII species and did not induce any partial oxidation, as evidenced by magnetic characterization and X-ray diffraction analysis. However, the oxidation of the Co(ni) complex required the most negative potential in complex 2 compared to those in the cases of 1 and 4, suggesting that the ligand in 2 provided the most weak ligand field in the order of L₂M₄< L₁ < L₄. This is normal because deprotonation should render the delocalized aromatic system of the ligand as a weaker π acceptor, thus weakening the ligand strength in 1 and 4. This result is consistent with the observation of cobalt metallogrid complexes in the previous report.
CH$_3$CN [Co$^{III}$L$_1$$_2$]ClO$_4$ (1)  
[Co$^{III}$L$_2$Me$_2$]$_2$ (2)  
[Co$^{III}$L$_3$Me$_2$]$_2$CH$_3$OH (3ClO$_4$)  
[Co$^{III}$L$_4$]$_2$ (4)

DMF Co(salen–Me)  
Co(salen–Ome)

2Me$^d$  
[Co$^{III}$dpzca]$_2$$^e$

CH$_3$CN C1–C8  
[Co(BTSC) (L)$_2$]$^+$

CH$_3$CN  
[Co$^{III}$(L)$_3$]ClO$_4$$_x$  
[Co$^{III}$(L$_3$Me)$_3$]ClO$_4$$_x$  
[Co$^{III}$(L$_4$H$_3$)$_3$]ClO$_4$$_x$

Table 3  The potentials ($E_{1/2}$, V vs. Fe$^+/Fe^0$) of all the cobalt complexes in this work and the selected cobalt complexes

| Solvent Comp. | $E_{1/2}$ (V)$^a$ | Co$^{II/III}$ | Co$^{II/II}$ | Ligand-base |
|---------------|------------------|--------------|--------------|-------------|
| CH$_3$CN [Co$^{III}$L$_1$$_2$]ClO$_4$ (1) | −0.93 | −1.66 | −0.12 | This work$^d$ |
| CH$_3$CN [Co$^{III}$L$_2$Me$_2$]$_2$ (2) | −0.98 | −1.53 | −0.12 | |
| CH$_3$CN [Co$^{III}$L$_3$Me$_2$]$_2$CH$_3$OH (3ClO$_4$) | −0.49 | −1.52 | −0.12 ||
| CH$_3$CN C1–C8 | −0.22 | −0.82 to −1.92 | −1.61 to −2.49 | Ref. 10 |
| CH$_3$CN [Co(BTSC) (L)$_2$]$^+$ | −0.69 to −1.10 | −1.00 to −1.19 | −0.12 | Ref. 12 |
| DMF Co(salen–Me) | −0.22 | −1.46, −1.84 | −0.49, −0.49 | Ref. 24 |
| DMF Co(salen–Ome) | 2Me$^d$ | −1.38 to −1.41 | −0.12 | Ref. 14 |

$^a$ Scan rate = 100 mV s$^{-1}$.  
$^b$ Concentration in all cases = 0.1 mM.  
$^c$ Not observed.  
$^d$ M = Na$^+$, K$^+$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$.  
$^e$ The potential values were referenced against Ag/AgNO$_3$.

Conclusion

In conclusion, we prepared a series of new tridentate Schiff-base ligands bearing a variety of substituting moieties through a condensation reaction between 2-acetylpyrazine and different hydrazine derivatives. The corresponding cobalt complexes with bis-substitute were isolated and structurally characterized. The analysis of the crystal structures provided insights into understanding the differences in the Co–N bond lengths observed in the crystal structures, assigning them to differences in terms of the spin state and valence state. In particular, the Co–N bond length can be diagnostic for differentiating the low-spin doublet from the high-spin quartet state. In addition, we showed that the redox potential of the Co(ni)/Co(ni), Co(ii)/Co(i), and pyrazine-base couples could be easily modulated over a wide range by tuning the substituents on the ligands, allowing a broad range of potential applications. Study of the catalytic proton reduction by applying this class of complexes as a catalyst is currently ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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