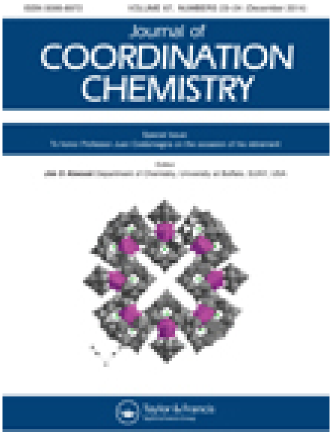

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Synthesis and crystal structure of an unexpected anionic trinuclear cobalt(III) complex with ferrocenyl-containing tridentate ONO donor Schiff base ligands

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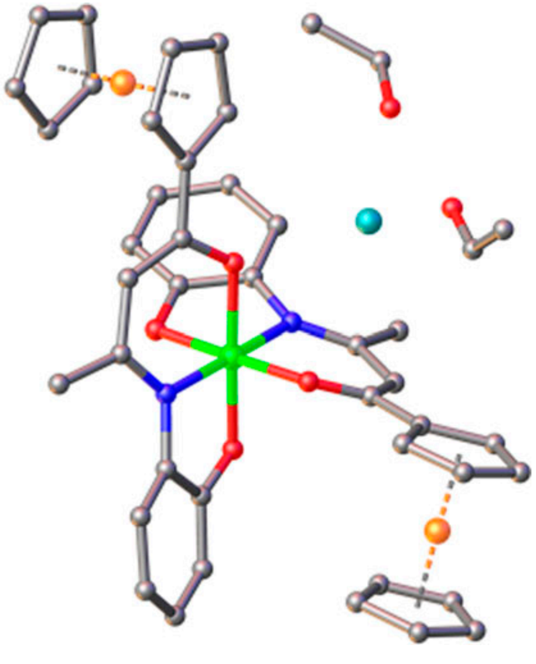

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Dedicated to our distinguished colleague and friend Prof. Juan Costamagna in recognition of his outstanding contribution to coordination chemistry.

Reaction of ferrocenyl-containing Schiff base ligand with Co(II) nitrate salt leads to the formation of an unexpected anionic trinuclear Co(III) complex with meridionally coordinated tridentate ONO metalloligand (O red, N blue, Co green, Fe orange, K sky-blue). The potassium cation binds assymmetrically the two metalloligands and the structure is retained in solution.

The tridentate ONO-donor Schiff base ligand derived from the condensation of 1-ferrocenyl-1,3-butanedione and 2-aminophenol, generated *in situ* and treated further with potassium *tert*-butoxide, reacted in THF with $Co(NO_3)_2{\cdot}6H_2O$ in the presence of pyridine to afford the ionic complex $[\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}C(O)CH{=}C(CH_3)N\text{-}C_6H_4\text{-}2\text{-}O\}_2Co(III)]^-[K(HOCH_2CH_3)_2]^+$ (**1**, 50% yield). Compound **1** was characterized by elemental analysis, FT-IR, and multidimensional ^1H and ^{13}C NMR spectroscopy. Single-crystal X-ray diffraction reveals that the two metalloligands are meridionally coordinated to a Co(III) ion that adopts a slightly distorted octahedral geometry. The doubly solvated potassium counter-ion is asymmetrically positioned with respect to the two metalloligands. Such an arrangement allows the observation by ^1H NMR of restricted rotation of the ferrocenyl units and the splitting of both carbonyl and imine carbons, thus suggesting that the structure observed in the solid state is retained in solution. Complex **1** exhibits in its cyclic voltammetry curve two anodic reversible waves attributed to the oxidation of Co(III)-phenolates into Co(III)-phenoxyl radical and that of the ferrocenyl fragment into its ferrocenium counterpart.

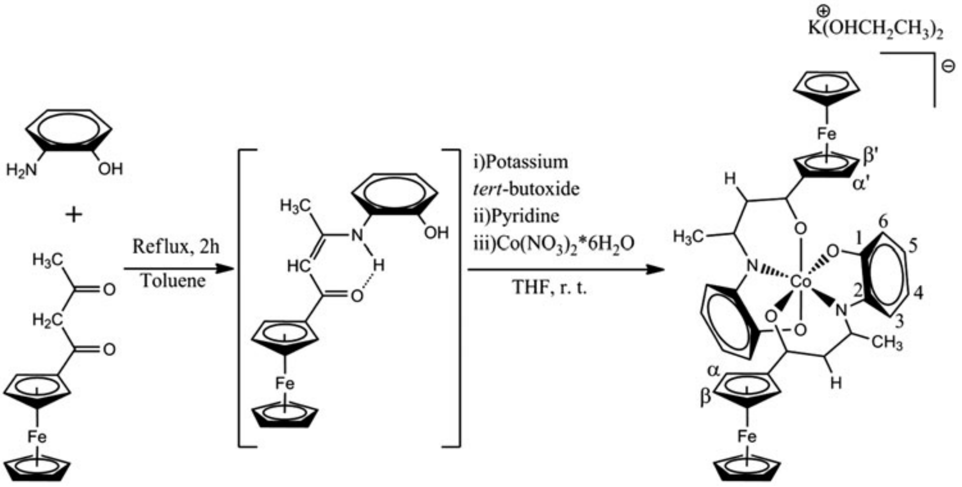
Keywords: Schiff base; ONO ligand; Ferrocenyl; Cobalt(III) complex; Crystal structure

1. Introduction

Schiff base compounds [1] constitute one of the most widely used families of organic substrates [2], not only as synthetic intermediates but also as polytopic ligands in coordination chemistry [3, 4], where they have been extensively studied due to their facile syntheses, thermal stability, and easily tunable electronic and steric properties. Among them, tridentate Schiff bases which combine O, N, and S donor atoms, derived from the mono-condensation of appropriate salicylaldehyde or β-diketone reagents and primary amine containing functional substrates [5] form, upon deprotonation, a group of anionic tridentate ligands that react readily with divalent transition metal ions to produce variable-nuclearity compounds depending on the coligand present [4–6].

Organometallic Schiff base ligands are also known since the disclosure [7] and structural characterization [8] of the parent ferrocenyl-containing ONN-metalloligand Fc-C(=O)CH=C(CH$_3$)N(H)CH$_2$CH$_2$NH$_2$ (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$), obtained-upon reaction of 1-ferrocenyl-1,3-butanedione with 1,2-diaminoethane. Recently, we disclosed the four-step synthesis of its ONO-hemiligand relative functionalized with the 4-hydroxyphenyl group at the imine carbon [9]. Related tridentate metalloligands exhibiting ONS-, ONO-, and ONN-donor sets were also prepared by single condensation of ferrocenoylacetone with S-benzyldithiocarbazate, 2-aminoethanol or variously substituted hydroxyanilines, and 2-(aminomethyl)pyridine, respectively [10]. In the late 2000s, we also reported on the synthesis and X-ray crystal structure of the ONN half-unit derivative resulting from the mono-condensation of ferrocenoylacetone and 1,2-phenylenediamine [11] that was used later on to synthesize new polymethylmethacrylate-anchored ferrocene-substituted unsymmetrical Schiff base complexes [12].

During the last few years, we were successful in using such ferrocenyl-containing tridentate ligands for the construction and the study of the non-linear optical (NLO) properties of both neutral binuclear and ionic trinuclear organometallic unsymmetrical Schiff base complexes [8, 13, 14]. As an extension of this work, we were interested in reacting a dianionic tridentate ONO-metalloligand and cobalt salts in the presence of nitrogenous base with the aim of obtaining and studying the electronic and NLO properties of neutral ternary cobalt



Scheme 1. Preparation of the trinuclear Schiff base complex **1** with the atom labeling for NMR assignments.

complexes containing two π-conjugated redox active centers. Indeed, since the seminal works of Werner and Jørgensen [15], cobalt complexes are known to possess interesting structural features for the development of coordination chemistry. The most common oxidation states of cobalt ions are +2 and +3, resulting in the formation of paramagnetic Co(II) and diamagnetic Co(III) complexes. In addition, the cobalt(III) complexes are kinetically non-labile, which make them ideal for spectroscopic study [16]. Cobalt(III) Schiff base complexes, mainly octahedral, are known in the literature either as their cationic [17], neutral [18], or anionic [19] forms, whereas their cobalt(II) Schiff base counterparts, which can also be anionic [20] or neutral [21] are scarcer. Herein, we report on the synthesis, analytical, spectral, and structural characterization of a new trinuclear anionic cobalt(III) compound formulated as *mer*-$[L_2Co(III)]^-$ isolated as its potassium salt (**1**), where H_2L is the mono-condensation product of 1-ferrocenyl-1,3-butanedione and 2-aminophenol (see scheme 1). The electrochemical behavior of **1** was also investigated using cyclic voltammetry (CV).

2. Experimental

2.1. *General experimental methods*

Reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under an atmosphere of nitrogen before use. All chemicals were purchased from commercial sources and used without purification. The metalloligand $Fc\text{-}C(O)CH_2C(O)CH_3$ was prepared according to our published method [13(a)]. FT-IR spectra were recorded on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the range 4000–450 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance III 400 spectrometer at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to the residual deuterated solvent peaks. Coupling constants (J) are expressed in Hertz (Hz). ^1H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^1H–^1H cozy, ^1H–^{13}C HMQC, and ^1H–^{13}C HMBC NMR experiments, and are given according to the numbering scheme in scheme 1. Microanalyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1, France. CV measurements were performed using a Radiometer Analytical model PGZ 100 all-in one potentiostat, using a three-electrode CEMM with platinum disk working electrode, Ag/AgCl reference electrode and platinum wire auxiliary electrode. The ferrocene/ferrocenium (Fc/Fc^+) couple was located at $E_{1/2} = 0.45$ V, where $E_{1/2}$ was calculated from the average of the oxidation and reduction peak potentials. Melting points were determined in evacuated capillaries on a Kofler Bristoline melting point apparatus and were not corrected.

2.2. Synthesis of $[\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}C(O)CH{=}C(CH_3)N\text{-}C_6H_4\text{-}2\text{-}O\}_2Co(III)]^-[K(EtOH)_2]^+$ (1)

A Schlenk tube was charged with a magnetic stir bar, 284 mg (1.05 mM) of 1-ferrocenyl-1,3-butanedione, 115 mg (1.05 mM) of 2-aminophenol, and 10 mL of toluene, and the mixture was refluxed for 2 h. After cooling, a red solid deposited. The precipitate was filtered off and washed with a petroleum ether: diethyl ether (1 : 1 v : v) mixture. Then, 354 mg (3.16 mM) of potassium *tert*-butoxide and 1.5 mL of THF were added and the reaction mixture was stirred at r.t. for 30 min, upon which time it turned dark red. Pyridine (400 µL, 5.20 mM) was then added and the solution was stirred for additional 10 min before dropwise addition of a solution of $Co(NO_3)_2{\cdot}6H_2O$ (437 mg, 1.5 mM) in 1.5 mL of THF. The solution was stirred for 15 min and turned dark brown. Vigorous stirring was continued overnight. The reaction was quenched with 10 mL of EtOH, giving a black solution. Then, 5 mL of diethyl ether was added and the solution was filtered and stored at −30 °C for five days, affording upon filtration 233 mg (50% yield) of **1** as dark black crystals. A suitable crystal from this crop was used for X-ray structure determination. M.p. 180–182 °C. Anal. Calcd for $C_{44}H_{46}N_2O_6Fe_2CoK{\cdot}H_2O$ (926.58 gM^{-1}): C, 57.03; H, 5.22; N, 3.02. Found: C, 56.77; H, 5.15; N, 2.92%. FT-IR (KBr, cm^{-1}): 3404(w) ν(O–H), 3096–3056(w) ν(C–H aryl), 2970–2923(w) ν(C–H alkyl), 1637(m), 1576(s), 1570(m) ν(C···O), ν(C···N) and/or ν(C···C). ^{1}H NMR (400 MHz, CD_3COCD_3): 1.12 (t, $^3J_{HH} = 7.0$ Hz, CH_3, Et_2O), 1.13 (t, $^3J_{HH} = 7.0$ Hz, CH_3, EtOH), 2.85 (s, 6 H, CH_3), 2.88 (br s, OH, EtOH), 2.91 (br s, OH, EtOH), 3.42 (q, $^3J_{HH} = 7.0$ Hz, CH_2, Et_2O), 3.58 (br q, $^3J_{HH} = 7.0$ Hz, CH_2, EtOH), 3.84 (s, 10 H, C_5H_5), 3.98 (sext, $^3J_{HH} = 2.4$ Hz, $^4J_{HH} = 1.3$ Hz, 2 H, H_β C_5H_4), 4.01 (sext, $^3J_{HH} = 2.4$ Hz, $^4J_{HH} = 1.3$ Hz, 2 H, $H_{\beta'}$ C_5H_4), 4.36 (quint, $^3J_{HH} = 2.4$ Hz, $^4J_{HH} = 1.3$ Hz, 2 H, H_α C_5H_4), 4.44 (quint, $^3J_{HH} = 2.4$ Hz, $^4J_{HH} = 1.3$ Hz, 2 H, $H_{\alpha'}$ C_5H_4), 5.61 (s, 2 H, CH=C), 6.37 (ddd, $^3J_{HH} = 8.0$ and 6.8 Hz, $^4J_{HH} = 1.8$ Hz, 2 H, H-4), 6.55 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.8$ Hz, 2 H, H-6), 6.59 (td, $^3J_{HH} = 8.0$ and 6.8 Hz, $^4J_{HH} = 1.3$ Hz, 2 H, H-5), 7.59 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.3$ Hz, 2 H, H-3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3COCD_3): 14.69 (CH_3, Et_2O), 17.95 (CH_3, EtOH), 24.49 and 24.56 (CH_3), 56.72 (CH_2, EtOH), 65.21 (CH_2, Et_2O), 66.73 ($C_{\alpha'}$ C_5H_4), 68.09 (C_α C_5H_4), 68.27 (C_β and $C_{\beta'}$ C_5H_4), 69.56 (C_5H_5), 83.35 (C_{ipso} C_5H_4), 97.65 (*C*H=C), 111.26 (C-5), 116.89 (C-3), 120.56 (C-6), 123.29 (C-4), 144.35 (C-2), 158.76 and 158.83 (CH=*C*), 168.71 (C-1), 174.55 and 174.59 (C=O).

2.3. X-ray crystal structure determination

X-ray data for a black single crystal of **1**, obtained as described above, were collected at 150 (2) K on a Bruker APEXII AXS diffractometer, equipped with a CCD detector, using MoKα radiation ($\lambda = 0.71073$ Å). The crystal of approximate dimensions 0.17 × 0.14 × 0.13 mm, was coated in Paratone-N oil and on a Kaptan loop, and transferred to the cold gas stream of the cooling device. The structure was solved by direct methods using SIR97 program [22], and then refined with full-matrix least-square methods based on F^2 (SHELXL-97) [23], with the aid of WINGX program [24]. The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm [25], implemented as the SQUEEZE option in PLATON [26]. A new data-set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All hydrogens were placed in their geometrically idealized positions and constrained to ride on their parent atoms. A summary of the details about crystal data, collection parameters, and refinement are documented below, and additional crystallographic details are in the CIF file. ORTEP and ball-and-stick views are generated using OLEX2 software [27].

Crystal data: $C_{44}H_{46}CoFe_2KN_2O_6$, $M_r = 908.56$, monoclinic, $P2_1/c$, $a = 15.2906(6)$ Å, $b = 17.9823(7)$ Å, $c = 16.7178(6)$ Å, $\beta = 111.880(2)°$, $V = 4265.6(3)$ Å^3, $Z = 4$, $\rho_{Calcd} = 1.415$ g cm^{-3}, $\mu = 1.201$ mm^{-1}, $F(0\,0\,0) = 1880$, 35,337 reflections measured, 9736 unique ($R_{int} = 0.062$), parameters refined: 523, R_1/wR_2 ($I > 2\sigma(I)$) = 0.0502/0.1169, R_1/wR_2 (all data) = 0.0860/0.1321, GOF = 1.015, $[\Delta\rho]_{min}/[\Delta\rho]_{max}$: −0.718/0.732 e Å^{-3}. CCDC deposition no. 992121.

3. Results and discussion

3.1. *Isolation and characterization*

The di-deprotonated ONO tridentate Schiff base metalloligand, $[Fc\text{-}C(O)CH{=}C(CH_3)N\text{-}o\text{-}C_6H_4\text{-}O]^{2-}$ (L^{2-}), was generated in a two-step one-pot reaction by facile condensation of 1-ferrocenyl-1,3-butanedione with 2-aminophenol, in 1 : 1 M ratio, in refluxing toluene for 2 h, followed by the double deprotonation of the red diprotic precipitate formed on cooling with an excess of potassium *tert*-butoxide in THF. The formed dark red product was then reacted with cobalt(II) nitrate salt in the presence of pyridine in an attempt to synthesize the ternary cobalt(II) complex $[(L)Co(NC_5H_5)]$. Instead, black crystals of the oxidized trinuclear Schiff base complex **1** were isolated in 50% yield upon crystallization from ethanol diethyl ether solution at –30 °C (scheme 1). The formation of **1** could result from the oxidation of an *in situ* generated cobalt(II) intermediate with adventitious oxygen to generate a cationic Co(III) species that would react with a second equivalent of dianionic metalloligand to form **1** in maximum yield of 50% as observed. However, all attempts to prepare $[(L)Co(NC_5H_5)]$ under strictly anaerobic conditions had proven unsuccessful, the isolated black crystals do not diffract and only a weak peak assignable to the metalloligand could be found in the mass spectrum.

Compound **1** is thermally stable, air and moisture insensitive on storage under ordinary conditions, exhibiting good solubility in common organic solvents such as dichloromethane, acetone or ethanol, but insoluble in diethyl ether and hydrocarbon solvents. Its composition and identity were deduced from FT-IR, and multinuclear 1-D and 2-D NMR spectroscopies. Analysis by ESI-MS did not give the parent ions or indeed any useful information, however, satisfactory analytical data on air dried powdered material demonstrates the purity of the compound (see section 2.2 for details). Additionally, the crystal and molecular structure of **1** was determined by single-crystal X-ray diffraction analysis (see below).

The solid-state FT-IR spectrum of **1** showed the characteristic set of medium to strong intensity bands at 1637–1570 cm^{-1} attributed to the ν(C···C), ν(C···N), and ν(C···O) stretching vibrations of the Schiff base skeleton [13, 14], suggesting that the imine nitrogen and carbonyl oxygen coordinate to Co(III). The spectrum shows also a weak broad absorption band at 3404 cm^{-1}, attributable to the ν(O–H) stretching mode of the free and coordinated ethanol molecules. On the other hand, the weak bands observed at 3096–3056 cm^{-1} are due to the aromatic ν(C–H) vibrations, while the bands found at 2970–2923 cm^{-1} are characteristic of aliphatic ν(C–H) vibrations.

From both the 1-D and 2-D NMR spectral data, **1** is characterized on the basis of chemical shift, coupling constants, and multiplicity and proton–proton connectivity. The ^{1}H NMR spectrum exhibits the expected resonance pattern consistent with the proposed structure, and clearly indicates the magnetic equivalency of the two ONO tridentate metalloligands. Thus, the ferrocenyl enaminoketonate entity is readily identified by its three sharp singlet resonances at 2.85, 3.84, and 5.61 ppm (integration ratio 6 : 10 : 2), respectively, due to the methyl, the free cyclopentadienyl ring, and the *pseudo*-aromatic methyne protons, while the *o*-phenylene ring gives four resonances, in agreement with four chemically non-equivalent protons (figure 1). They appear in the range 6.37–7.59 ppm as one double doublet (H-4) and three double doublets (H-3, H-5, H-6) multiplicity pattern with integration ratio of 2 : 2 : 2 : 2 (see scheme 1 for atom labeling).

Interestingly, the four multiplets, integrating each for 2 H, at 3.98, 4.01, 4.36, and 4.44 ppm were assigned to the four magnetically inequivalent H_β, $H_{\beta'}$, H_α, and $H_{\alpha'}$ protons of the substituted cyclopentadienyl ring, respectively (figure 1). The free rotation of the ferrocenyl moiety about the C_{ipso}–C bond is probably restricted by the steric hindrance caused by coordination of two metalloligands at the cobalt center. We have previously observed such a feature further to η^6-coordination of the bulky arenophile $[(\eta^5\text{-}C_5Me_5)Ru]^+$ onto the salicylidene ring of ferrocenyl-containing binuclear Schiff base complexes [8, 13(a), 14]. Compared with chemical shifts reported for ferrocenyl protons in such bi- and tri-nuclear Schiff base derivatives ($4.17 < \delta < 4.80$ ppm), it is worth nothing that the ferrocenyl protons in **1** undergo an upfield shift that presumably arises from the increased electron density in the complex anion.

In addition, the ^{1}H NMR spectrum of **1** shows also at 1.12, 1.13 and 3.42, 3.58 ppm, triplets and quartets (not depicted in figure 1) attributed to methyl and methylene protons of ethanol and diethyl ether co-crystallization solvents, respectively. From integration, the ratios of ethanol/complex and diethyl ether/complex were determined to be 5 and 2.5, respectively. The ethanol resonances are broader than those of diethyl ether, suggesting rapid exchange between free and potassium-coordinated ethanol molecules (see crystallographic section below).

The proton decoupled ^{13}C NMR spectrum of **1**, obtained at 25 °C in CD_3COCD_3, is fully consistent with the proposed structure, including the peaks of the solvate molecules (see section 2.2). For instance, the restricted rotation of the ferrocenyl moiety is highlighted with the five carbon atoms of the substituted cyclopentadienyl ring that give a total of four resonances at 66.73 ($C_{\alpha'}$), 68.09 (C_α), 68.27 (C_β and $C_{\beta'}$), and at 83.35 ppm for the quaternary carbon, while the five carbons of the free cyclopentadienyl ring show up at a sharp singlet at 69.56 ppm. As expected, six resonances are observed for the *o*-phenylene carbons with characteristic chemical shifts appearing at 144.35 and 168.71 ppm for the C-2 and C-1 carbons linked to N and O atoms, respectively (see scheme 1 for atom labeling). However, the most intriguing feature of this $^{13}C\{^1H\}$ NMR spectrum is the splitting of the carbonyl, imine, and methyl carbon signals into two closely spaced singlets at 174.55/174.59, 158.76/

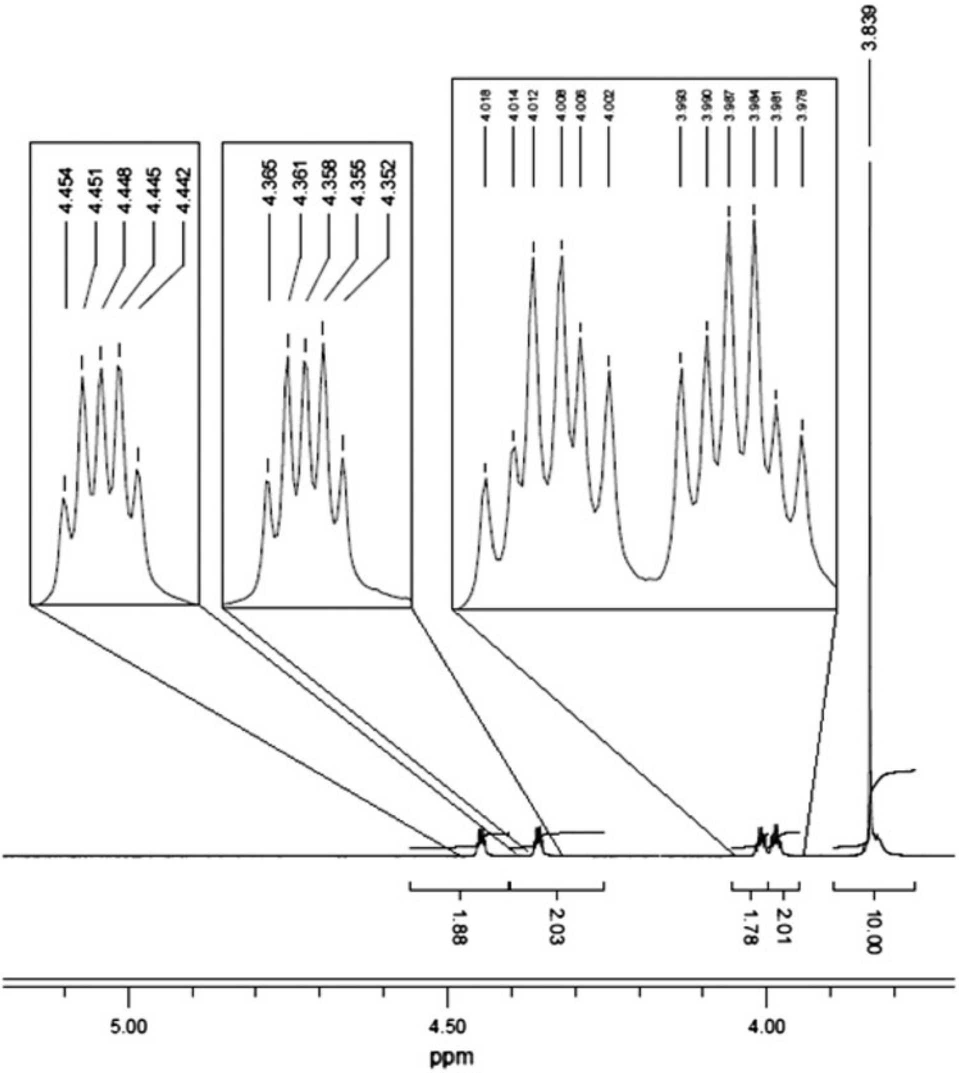


Figure 1. ^{1}H NMR spectrum of **1**, recorded at 400 MHz in CD_3COCD_3, showing the different proton resonance patterns and their chemical shifts (see scheme 1 for the atom numbering scheme). The insert shows an expansion of the multiplicity pattern of the substituted Cp-protons.

158.83, and 24.49/24.56 ppm, respectively, while the methyne carbon, which is part of the same six-membered metallocycle, resonates as a single line at 97.65 ppm. The crystal structure (see section 3.2 and figure 2) indicates a peculiar position of the solvated potassium ion that is close to O(1) and at a larger distance (~0.60 Å) from O(3), and its connected methyl-, carbonyl-, methyne-, and imine-carbon chain, making those carbons magnetically non-equivalent. The fact that the methyne carbon appears as a single resonance is probably due to accidental degeneracy. These findings strongly suggest that the structure of the ionic complex remains unchanged in solution and in the solid state.

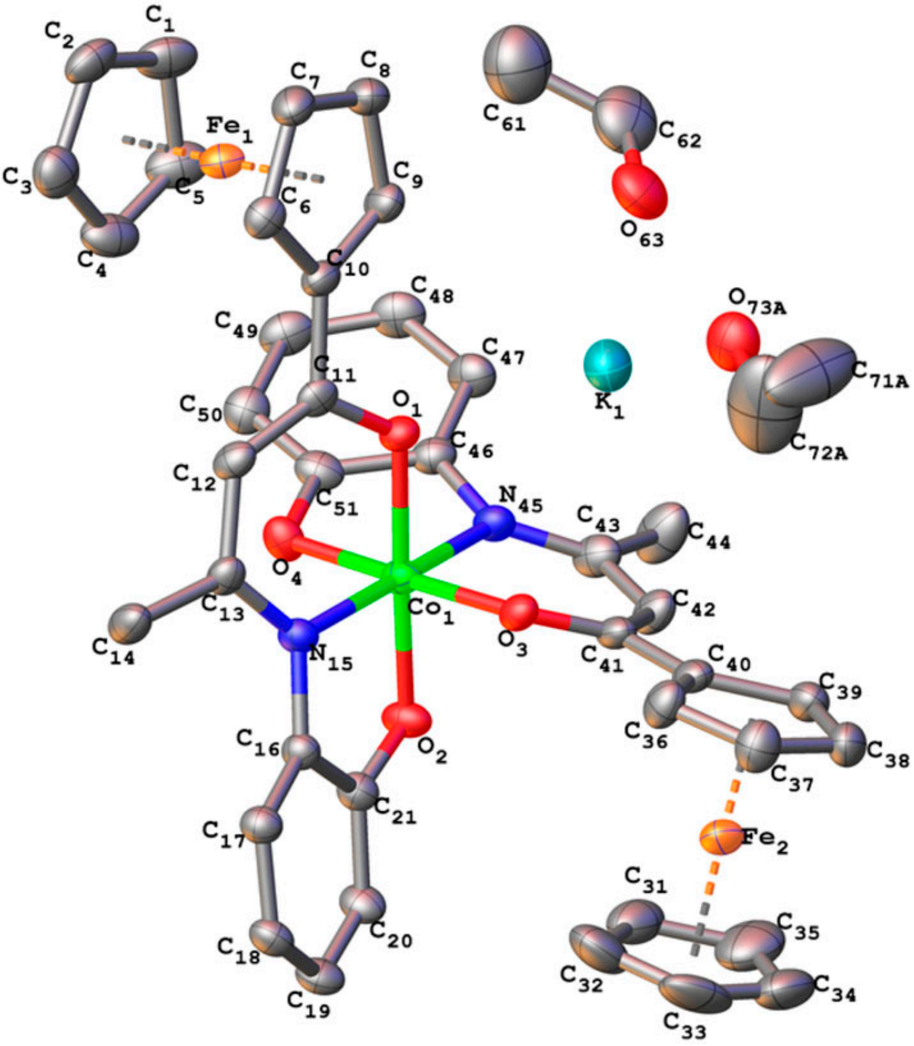


Figure 2. Molecular structure of **1** showing the atom numbering scheme. Thermal ellipsoids are drawn at 50% probability. Hydrogens have been omitted for clarity.

3.2. *X-ray diffraction study*

The molecular structure of **1** including the atom labeling scheme is depicted in figure 2 and selected bond lengths and angles are presented in table 1. The single-crystal X-ray study reveals that **1** crystallizes in the monoclinic space group $P2_1/c$. The complex consists of a mononuclear six-coordinate anionic metal center with a *pseudo*-octahedron, and one potassium cation, solvated by two ethanol molecules, to satisfy the uninegative charge of the complex anion, $[Co(III)(L)_2]^-$. The six coordination sites are occupied by four oxygens and two nitrogens from two dianionic metalloligands coordinated meridionally in a terdentate (O-carbonyl, N-imine and O-phenolic) fashion to the central cobalt(III) ion. The two imine nitrogens N(15) and N(45) are mutually *trans*, while the two carbonyl O(1), O(3), and the

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

Bond distances			
Co(1)–O(1)	1.894(2)	CO(1)–O(2)	1.895(2)
Co(1)–O(3)	1.905(2)	Co(1)–O(4)	1.895(2)
Co(1)–N(15)	1.922(3)	Co(1)–N(45)	1.916(3)
O(1)–C(11)	1.304(4)	O(3)–C(41)	1.297(4)
O(2)–C(21)	1.344(4)	O(4)–C(51)	1.341(4)
C(10)–C(11)	1.478(4)	C(40)–C(41)	1.479(5)
C(11)–C(12)	1.381(4)	C(41)–C(42)	1.387(5)
C(12)–C(13)	1.416(4)	C(42)–C(43)	1.409(5)
C(13)–N(15)	1.322(4)	C(43)–N(45)	1.328(4)
N(15)–C(16)	1.420(4)	N(45)–C(46)	1.415(4)
C(16)–C(21)	1.414(4)	C(46)–C(51)	1.418(5)
Fe(1)–C_{Cp} avg	2.046(4)	Fe(2)–C_{Cp} avg	2.037(4)
Fe(1)–$C_{Cp'}$ avg	2.035(3)	Fe(2)–$C_{Cp'}$ avg	2.037(4)
Angles			
O(1)–Co(1)–O(2)	178.29(10)	O(1)–Co(1)–O(3)	89.35(9)
O(1)–Co(1)–O(4)	89.58(9)	O(1)–Co(1)–N(15)	95.46(10)
O(1)–Co(1)–N(45)	87.77(10)	O(2)–Co(1)–O(3)	89.97(10)
O(2)–Co(1)–O(4)	91.09(10)	O(2)–Co(1)–N(15)	86.11(10)
O(2)–Co(1)–N(45)	90.72(10)	O(3)–Co(1)–O(4)	178.93(10)
O(3)–Co(1)–N(15)	90.03(10)	O(3)–Co(1)–N(45)	94.52(10)
O(4)–Co(1)–N(15)	90.11(10)	O(4)–Co(1)–N(45)	85.40(11)
N(15)–Co(1)–N(45)	174.46(11)	O(63)–K(1)–O(73)	107.36
O(1)–C(11)–C(12)	125.8(3)	O(3)–C(41)–C(42)	125.8(3)
C(11)–C(12)–C(13)	126.9(3)	C(41)–C(42)–C(43)	126.4(3)
C(12)–C(13)–N(15)	121.3(3)	C(42)–C(43)–N(45)	121.2(3)
C(16)–C(21)–O(2)	118.5(3)	C(46)–C(51)–O(4)	118.7(3)
Co(1)–O(1)–C(11)	121.70(19)	Co(1)–O(3)–C(41)	121.8(2)
Co(1)–O(2)–C(21)	110.72(19)	Co(1)–O(4)–C(51	110.10(19)
Co(1)–N(15)–C(13)	123.5(2)	Co(1)–N(45)–C(43)	123.6(2)
Co(1)–N(15)–C(16)	109.7(2)	Co(1)–N(45)–C(46)	110.1(2)

Abbreviations: Cp = C_5H_5, Cp′ = C_5H_4.

two phenolic O(2), O(4) oxygen atoms are mutually *cis*. The two tridentate ferrocenyl-containing Schiff base ligands are individually essentially planar and coordinate orthogonally to the cobalt metal ion. The acute dihedral angle between this pair of coordinating metal-organic ligands is 89.77°.

The anionic cobalt entity exhibits a slightly distorted octahedral geometry at the Co(III) center with two nitrogens (N(15) and N(45)) in axial positions and four oxygens (O(1), O (2), O(3), and O(4)) in equatorial positions. The Co(III)–N bond distances are 1.922(3) and 1.916(3) Å, while the Co(III)–O bond distances vary from 1.894(2) to 1.905(2) Å (table 1). The cisoid and transoid angles vary in the ranges 85.40(11)°–95.46(10)° and 174.46 (11)°–178.93(10)°, respectively (table 1). However, both the bond lengths and angles do not show any anomalies and agree with those measured in similar derivatives [17–19, 28].

In addition, the fused five- and six-membered heterometallacycles formed upon the Schiff base condensation of ferrocenoylacetone with 2-aminophenol and subsequent chelation of the Co(III) ion are essentially co-planar. Inspection of the bond length patterns and angles (table 1) suggests a significant electron delocalization within these chelating rings, as the O–C, C–C, and C–N bond distances fall between the measured values for related normal single and double bonds involving sp^2 hybridized atoms [29]. As a result of the asymmetric location of the potassium cation with respect to the inorganic moiety (see above), the dihedral angles between the six-membered metallacycle and its substituted cyclopentadienyl ring inside each metalloligand are different. The dihedral angle is 12.25° between the [O(1)C(11)

C(12)C(13)N(15)] and [C(6)–C(10)] planes (close contacts of K(1) with O(1) and C(9) of the C_5H_4 ring), whereas it is 3.65° between the corresponding planes of the second metal-organic Schiff base ligand.

The ferrocenyl fragments of the metalloligands, such as Fc1 and Fc2 feature linear sandwich structures with typical [η^5-Fe-η^5] coordination mode and eclipsed cyclopentadienyl rings. The iron is coordinated to the free and substituted cyclopentadienyl rings at ring centroid-iron distances of 1.654/1.684 Å for Fc1 and 1.645/1.636 Å for Fc2, with ring centroid-iron-ring centroid angle of 178.17° (Fc1) and 177.83° (Fc2), indicating that there is an Fe(II) oxidation state in each metallocene [30].

The potassium counter cation adopts a severely distorted nine-coordinate environment with a Co(1)–K(1) separation of 3.6707(9) Å. It is solvated by two molecules of ethanol with K(1)–O(63) and K(1)–O(73A) distances of 2.684 and 2.625 Å, respectively, forming a O(63)–K(1)–O(73A) angle of 107.36°. The potassium ion is asymmetrically located with respect to the two metalloligands with two very different oxygen–potassium bond lengths of 2.676(2) and 3.260(2) Å for O(1)–K(1) and O(3)–K(1), respectively. In addition, close contacts exist between the potassium cation and the C(9) atom (3.388(3) Å) of the substituted cyclopentadienyl ring of one metalloligand and C(41): 3.278(3) Å, C(42): 3.293(3) Å, C(43): 3.211(4) Å, and N(45): 3.126(3) Å of the second metalloligand.

Within the crystal structure of **1**, intermolecular O–H···O hydrogen bonds (see table 2) generate an infinite chain-type structure in the packing (figure 3). These interactions occur between the hydroxyl hydrogen of each solvating ethanol with the phenoxyl O(2) and O(4) of the neighboring complex anion.

3.3. *Electrochemical study*

The redox properties of **1** were investigated by CV in dichloromethane solution containing 0.1 M n-$Bu_4N^+PF_6^-$ as supporting electrolyte. Measurements were carried out in 10^{-3} M

Table 2. Hydrogen-bonding interaction parameters for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(63)–H(63A)···O(2)	0.84	1.987	2.698 (4)	141.7
O(73)–H(73A)···O(4)^i	0.84	1.841	2.670 (4)	169.2

i = x, y, z.

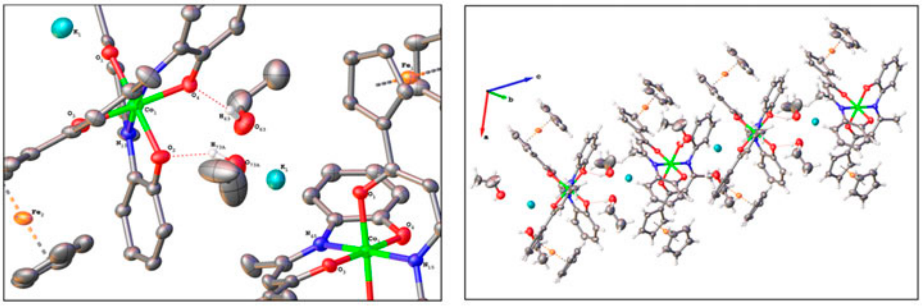


Figure 3. Packing diagram of **1** showing the molecular arrangement and hydrogen-bond interactions.

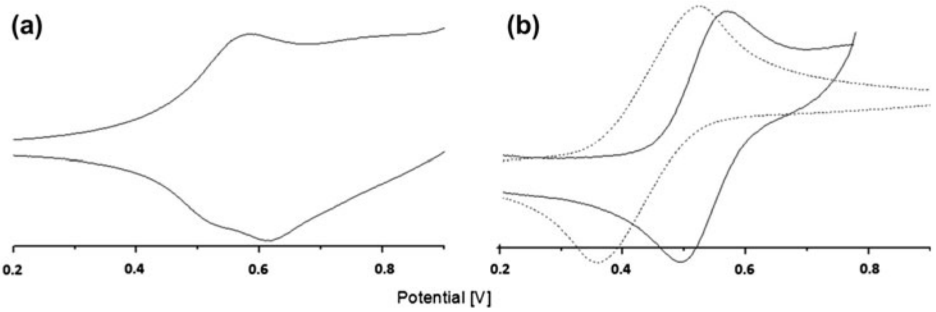


Figure 4. (a) Cyclic voltammogram of **1**, recorded in dichloromethane containing 0.1 M n-$Bu_4N^+PF_6^-$ as supporting electrolyte, at 293 K on a platinum disk working electrode, and scan rate = 0.1 V s^{-1}. (b) CV curve of the ferrocenium/ferrocene internal reference (dashed line, $E_{1/2} = 0.45$ V, $\Delta E_p = 170$ mV, arbitrary concentration) and the isolated CV curve (full line) of the ferrocenyl fragment upon reverse scan at $e_{pa} = +0.70$ V.

solutions at room temperature in the potential range +1.5 to –1.0 V with scan rate 100 mV s^{-1}. All the potential values are given relative to the ferrocenium/ferrocene reference electrode at 293 K [31]. The cyclovoltammogram of a solution containing **1** [figure 4(a)] shows two chemically reversible oxidation processes with current ratio i_{pa}/i_{pc} equal to unity, at $E_{1/2} = 0.53$ V ($\Delta E_p = 80$ mV) and $E_{1/2} = 0.69$ V ($\Delta E_p = 180$ mV), attributed to the Fe(II)/Fe(III) couple of the ferrocenyl fragments, and to the Co(III)-phenolate/Co(III)-phenoxyl radical couple [32], respectively. Interestingly, the $E_{1/2}$ value of the ferrocenyl units [figure 4(b)] is found to be 80 mV more anodic than that of free ferrocene, thus featuring some electron withdrawing ability of the Schiff base framework [8, 13, 14]. However, this value is somewhat smaller than those we have previously reported and this difference can be ascribed to changes in the global charge of the complexes; the negative charge in **1** does favor electron removal, making **1** easier to oxidize. One can also note that the $E_{1/2}$ value is of the same order as that obtained for related neutral and cationic cobalt derivatives [32]. Additionally, the CV curve shows an irreversible anodic wave (not shown on figure 4) at $E_{pa} = 1.07$ V which is presumably due to the irreversible oxidation of the Co(III)-phenoxyl moieties into phenoxonium cations with fast follow up decomposition reactions.

4. Conclusion

An unexpected ionic cobalt(III) Schiff base complex has been prepared, fully characterized analytically and by ^1H and ^{13}C NMR spectroscopy, and studied by single-crystal X-ray diffraction and CV. During the complexation reaction, the starting cobalt(II) reagent was oxidized to a cobalt(III) ion which adopts a slightly distorted octahedral geometry with two meridionally coordinated ferrocenyl-containing Schiff base dinegative ONO terdentate ligands. The crystal structure reveals also that the doubly solvated potassium counterion is asymmetrically located with respect to the two metalloligands. Such an arrangement allows the observation by NMR of restricted rotation of the ferrocenyl units, as well as the splitting of both carbonyl and imine carbons, suggesting that the structure observed in the solid state is retained in solution. An electrochemical study was performed to check the redox responses at both the cobalt and iron centers.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 992121 for **1**. Copies of this information may 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 www: http://www.ccdc.cam.ac.uk.

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