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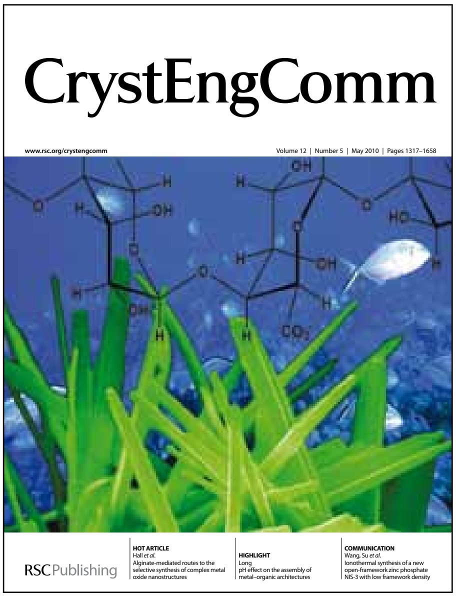

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PAPER

Synthesis and Characterization of Cobalt(Ш) Cyanide Complexes: Cobalt Participate in the Decomposition of Radical Anion of TCNQ

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Reaction of $Co(CH_3COO)_2•4H_2O$, KTCNQ (TCNQ =7,7,8,8-Tetracyanoquinodimethane) with the racemic or chiral H_2salency (N,N'-Bis(salicylidene)-1,2- cyclohexanediamine) ligand afforded three Co(Ш) complexes $K[Co(salency)(CN)_2]•CH_3OH$ (1), $K[Co(S,S\text{-}salency)(CN)_2]•H_2O$(**1S**) and $K[Co(R,R\text{-}salency)(CN)_2]•CH_3OH$ (**1R**), which have been fully characterized. The cyanide groups in these three complexes are generated from the in situ decomposition of the radical anion of TCNQ with the participation of cobalt(II). Single-crystal X-ray diffraction analysis reveals that complex **1** exhibits infinite double stair-like chain structure. However, the chiral complexes **1S** and **1R** show chain structures consisting of two independent sub-chains. And all of these chains are bridged by the K^+ ions, with the cyanides interacting with K^+ in the end-on and unusual side-on π-type mode. Second-order nonlinear optical effect studies in the solid state revealed that **1S** and **1R** are SHG active.

Introduction

Nonlinear optical materials play a major role in the field of photonics including optical information processing, sensor protector applications, data storage, laser technology and so on.[1-13] It has been reported that some chiral coordination complexes exhibit large NLO response, several orders of magnitude larger than widely known inorganic materials. Meanwhile, the chiral coordination complexes show intriguing variety of architectures and topologies.[14-17] Thus the synthesis and characterization of chiral inorganic-organic materials have received considerable attention in recent years.

The two most often used methods to obtain chiral species are by stereoselective synthesis using chiral species or by spontaneous resolution upon crystallization without any chiral auxiliary.[18-21] To prepare new chiral complexes, we focus our attention on TCNQ-based complexes incorporated organic auxiliary ligands H_2salency(N,N'-Bis(salicylidene)-1,2-cyclohexanediamine) with optical activity. TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) is a well-known multi-redox active ligand.[22-24] The four C≡N groups allows variable coordination to a transition metal in mono-, bi-, tri-, and tetra-dentate binding modes, offering great flexibility in the self-assembly of interesting clusters and extended networks. While the electron affinity enables facile reduction by electron-rich metal complexes to form related radical anions and dianions. Moreover, it has been found that certain primary and secondary amines can react with TCNQ to give products in which one or two cyanide groups are replaced by the amine. In addition to the displacement of cyanide groups of TCNQ with amines, chemists also discovered that the cyanide group can be displaced by nitrite ion or (H_2O/O_2) to give an orange-red salt.[22, 25-34] With all this in mind, we tried to synthesis NLO materials with intriguing architectures by the reaction of KTCNQ, $Co(CH_3COO)_2•4H_2O$ and H_2salency. However, we got three unexpected complexes with the cyanide groups other than the TCNQ ligands, $K[Co(salency)(CN)_2]•CH_3OH$ (**1**), $K[Co(S,S\text{-}salency)(CN)_2]•H_2O$ (**1S**), $K[Co(R,R\text{-}salency)(CN)_2]•CH_3OH$ (**1R**). The three complexes maybe resulted from the redox reaction of Co^{2+} and $TCNQ^{-\cdot}$ as well as the consequent decomposition of $TCNQ^{-\cdot}$ [28, 35-38]. These are the first examples of cobalt cyanide complexes obtained from the lost cyanide groups of TCNQ and these also can put a new insight into the decomposition of TCNQ. All these complexes exhibit infinite chain structures which are bridged by K^+ ions and second-order nonlinear optical effect studies in the solid state revealed that chiral complexes **1S** and **1R** are SHG active with a weak signal. Herein, we report the details of the syntheses, structures and properties of the three complexes.

Experimental section

Materials and methods

All chemicals were reagent grade and used without further purification. H_2salency[39, 40] and KTCNQ[28] were prepared as reported procedures. Elemental analyses of C, H and N were performed with a Vario MICRO CHNOS Elemental Analyzer. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum

One Spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. Powder X-ray diffraction data were collected using a MiniFlexII powder diffractometer equipped with Cu Kα radiation (λ = 1.54056 Å). Circular dichroism (CD) spectra were conducted on a Jasco J-810 spectrodichrometer. Electrospray ion mass spectra (ESI−MS) were performed on DECAX-30000 LCQ Deca XP Ion Trap Mass Spectrometry. The ESR spectra were acquired on a Bruker ER-420 spectrometer.

Synthetic procedures

Resolution of (±)trans-1,2-Diaminocyclohexane

L-(+)-tartaric acid 15 g (0.1 mmol) in 50 ml distilled water was stirred at 70 °C for 15 mins, then (±)trans-1,2-diaminocyclohexane 24 ml (0.2 mol) was added in 30 mins. After 2 h, 10 ml glacial acetic acid was added in the resulting solution and a white precipitate formed immediately. The slurry was vigorously stirred for 2 h and cooled to room temperature. The precipitate was collected by filtration, washed with ice water, methanol, diethyl ether and dried in air. Yield: 19.9 g (79.0%).

(R,R)-N,N'-Bis(salicylidene)-1,2-cyclohexanediamine

The above mentioned product (5.947 g, 0.0225 mol), K_2CO_3 (6.216 g, 0.0450 mol) were dissolved in 30 ml distilled water. Salicylaldehyde (4.74 ml, 0.0225 mol) in 20 ml ethanol was added in 30 mins. The resulting yellow slurry was stirred at reflux for 6 h and then cooled slowly. The product was collected by filtration, washed with ice water and ethanol. This crude solid was dissolved in CH_2Cl_2 and washed with water. After drying over Na_2SO_4, the solvent was removed under vacuum and yellow oil was obtained. Yield: 3.52 g, 48.6%. The ligands H_2salency and (S, S)-H_2salency are prepared in a similar way.

K[Co(salency)(CN)$_2$]•CH$_3$OH (1)

A mixture of $Co(CH_3COO)_2$•$4H_2O$ (0.0498 g, 0.2 mmol), H_2salency (0.0644 g, 0.2 mmol), KTCNQ (0.0408 g, 0.2 mmol) and CH_3OH (8 mL) was stirred at room temperature for 1 h and placed in a Teflon-lined stainless container. The mixture was heated at 80 °C for 3 days, and then cooled to room temperature for 33 h. Red block-shaped crystals suitable for X-ray analysis were obtained, washed with distilled water and dried in the air. Yield: 49.8 mg (49.6% based on Co). $C_{23}H_{24}CoKN_4O_3$ (502.49): Calcd. C 54.98, H 4.81, N 11.15; found C 54.96, H 4.36, N 11.70. IR (KBr): 3478 (br), 2948 (m), 2863 (w), 2144 (w), 2118 (m), 1638 (s), 1599 (s), 1538 (m), 1466 (m), 1452 (s), 1385(w), 1348 (m), 1320 (m), 1220 (w), 1195 (w), 1150 (w), 1126 (w), 1044 (w), 906 (w), 756 (s), 738 (w)，694 (w), 567 (m) cm^{-1}.

K[Co(S,S-salency)(CN)$_2$]•H$_2$O (1S)

This complex was prepared by the similar method as for **1**. Yield: 35.6 mg (36.5% based on Co). $C_{22}H_{22}CoKN_4O_{33}$ (488.47): Calcd. C 54.10, H 4.54, N 11.47; found C 54.84, H 4.52, N 11.47. IR (KBr): 3482 (br), 2943 (m), 2864 (w), 2141 (w), 2118 (m), 1639 (s), 1600 (s), 1538 (m), 1469 (m), 1453 (s), 1384 (w), 1347 (m), 1321 (m), 1223(w), 1196 (w), 1151 (w), 1126 (w), 1046 (w), 906 (w), 757 (s), 738 (w)，694 (w), 567 (w) cm^{-1}.

K[Co(R,R-salency)(CN)$_2$]•CH$_3$OH (1R)

This complex was prepared by the similar method as for **1**. Yield: 34.9 mg (34.7% based on Co). $C_{23}H_{24}CoKN_4O_3$ (502.49): Calcd. C 54.98, H 4.81, N 11.15; found C 55.13, H 4.48, N 11.75. IR (KBr): 3470 (br), 2945 (m), 2866 (w), 2147 (w), 2121 (m), 1639 (s), 1595 (s), 1533 (m), 1469 (m), 1450 (s), 1387 (w), 1348 (m), 1320 (m), 1225 (w), 1197 (w), 1150 (w), 1126 (w), 1044 (w), 907 (w), 756 (s), 739 (w)，695 (w), 564 (m) cm^{-1}.

X-ray crystallography

Single crystals for **1**, **1S** and **1R** were mounted on glass fibers. Cell constants and data collections were performed on a Rigaku Mecury CCD diffractometer equipped with graphite-monochromated Mo-K*α* radiation source (*λ* = 0.71073 Å) by *ω* scan mode. The structures were solved by the direct method using the SHELXTL Version 5 package of crystallographic software, and refined with a full-matrix least-squares refinement on F^2. Metal atoms were located from the E-maps and refined anisotropically. The other non-hydrogen atoms were located by the difference Fourier maps basing on these atomic positions and refined anisotropically. Hydrogen atoms were added according to the theoretical models. Pertinent crystal data and structure refinement results are summarized in Table 1, and their selected bonds lengths and angles are provided in Tables S1–S3, respectively.

Results and discussion

Description of the structure

Complexes **1**, **1S** and **1R** were fully characterized by X-ray crystallography. Single-crystal X-ray structural analysis reveals that complex **1** exhibits a 1D chain structure. The selected bond lengths and angles for complexes **1** are given in Table S1, Complex **1** consists of the units of $[Co(salency)(CN)_2]^-$, K^+ ions and methanol molecules. The Co(III) ion in the octahedral monoanion $[Co(salency)(CN)_2]^-$ is low-spin and sixcoordinated by two equatorial nitrogen atoms and two equatorial oxygen atoms from the tetradentate Schiff-base ligand, and two axial carbon atoms from the two cyanide groups. The Co-N distances are 1.892(3) Å for Co1-N1, 1.894(3) Å for Co1-N2. The Co1-O1 and Co1-O2 distances are 1.915(3) and 1.910(3) Å, respectively. The bond lengths of Co-C are 1.944(4) and 1.932(4) Å, respectively, which are slightly longer than the Co-O and Co-N bond lengths, indicating the slightly distorted octahedron coordination sphere of the Co(III) ion. The C-N distances in the axial cyanide groups are 1.136(5), 1.148(5) Å. The Co1-C21≡N3 and Co1-C22≡N4 are in a good linear conformation with the angles of 178.6(4) and 178.5(4) °.

It is notable that the kalium ions are linkers playing an important role for the 1D double-stair like chain structure of complex **1**. Each kalium ion interacts with three discrete $[Co(salency)(CN)_2]^-$ units. Consequently, all the $[Co(salency)(CN)_2]^-$ units are held together by the bridging K^+

Table 1 Crystal data and structure refinements for **1**, **1S** and **1R**.

Polymer	**1**	**1S**	**1R**
Empirical formula	$C_{23}H_{24}CoKN_4O_3$	$C_{22}H_{22}CoKN_4O_3$	$C_{23}H_{24}CoKN_4O_3$
Formula weight	502.49	488.47	502.49
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1$
a (Å)	13.449(5)	13.873(15)	13.969(10)
b (Å)	21.788(8)	8.124(9)	8.164(5)
c (Å)	8.202(3)	19.53(2)	19.974(13)
α (°)	90.00	90.00	90.00
β (°)	101.794(7)	91.96(2)	92.823(13)
γ (°)	90.00	90.00	90.00
V (Å^3)	2352.8(15)	2200(4)	2275(3)
Z	4	4	4
T (K)	293(2)	293(2)	293(2)
D_c (g/cm^3)	1.419	1.475	1.467
μ (mm^{-1})	0.938	1.000	0.970
F(000)	1040	1008	1040
2θ range [°]	2.09–27.47	2.51–27.39	4.01-26.01
Unique reflections (R_{int})	4268	5498	6560
	(0.0359)	(0.0422)	(0.0407)
GOF (F^2)	1.122	1.024	0.968
Flack parameter		-0.04(2)	0.04(3)
Final R indices [$I > 2\sigma(I)$]^a	R_1 = 0.0604, wR_2 = 0.1749	R_1 = 0.0676, wR_2 = 0.1789	R_1 = 0.0583, wR_2 = 0.1303
Final R indices (all data)^a	R_1 = 0.0746, wR_2 = 0.1845	R_1 = 0.1018, wR_2 = 0.2144	R_1 = 0.0932, wR_2 = 0.1523
CCDC	859524	859525	859526

^{a} $R_1 = \sum(F_o - F_c)/\sum F_o$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

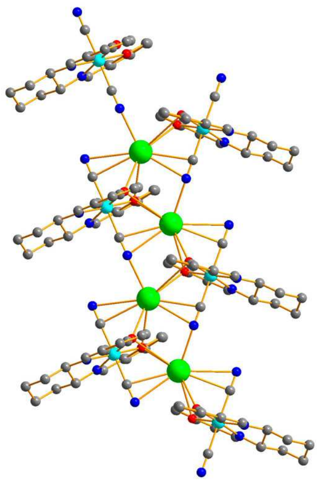


Fig. 1 view of double-stair like chain structure of complex **1** (Ni turquoise, K green, O red, N blue, C gray).

atoms (Fig.1). Interestingly, although the Schiff-base ligands possess the same coordination mode, they are arranged in different geometry configurations. The pair of enantiomers are situated alternately in the chain (Fig.2).

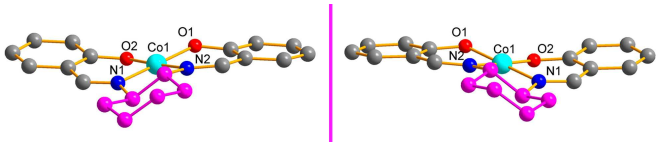


Fig. 2 The pair of enantiomers in complex **1**.

As shown in figure 3, the K^+ ion interacts with a pair of cyanide groups in a side-on manner, a N atom from the end-on cyanide, four O atoms from the Schiff-base ligands. The K-N, K-O and K-C average separations in this interaction are 3.032, 2.951 and 3.042 Å, respectively, comparable to those observed in the few other K^+ complexes of this type.[41-45]

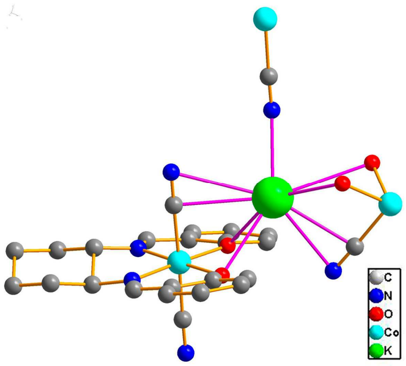


Fig. 3 Asymmetric unit of complex **1,** with some additional symmetry-equivalent atoms included to complete the coordination spheres around the metal atoms.

Complexes **1S** and **1R** are enantiomers and crystallized in the chiral space group $P2_1$. Since **1S** and **1R** are a pair of enantiomers (Fig.4), only the crystal structure of **1S** is described in detail here (The structure of complex **1R** is shown in Fig. S1 and S2). Some important bond parameters and angles for complexes **1S** and **1R** are listed in Table S2-S3. For complex **1S**, the C-N distances in the axial cyanide groups are in the range of 1.153-1.190 Å, the Co1-C21$\equiv$N6, Co1-C22$\equiv$N5, Co2-C44$\equiv$N7 and Co2-C45$\equiv$

N8 are in a good linear conformation with the angles of 177.9(8), 178.0(9), 175.3(1) and 178.9(9)° respectively. Similarly, for complex **1R**, the C-N distances in the axial cyanide groups range from 1.125 to 1.146 Å, the Co1-C21≡N6, Co1-C22≡N5, Co2-C44 ≡ N7 and Co2-C45 ≡ N8 are also in a good linear conformation with the angles of 174.6(7), 177.3(9), 175.0(9) and 178.7(8)°, respectively. All the distances and angles are in the normal range.[39, 40]

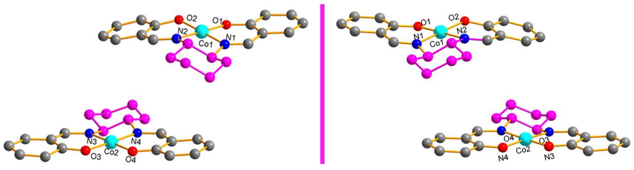


Fig. 4 The pair of enantiomers in complexes **1S** (left) and **1R** (right). The axial cyanide groups, bridging K$^+$ ions and hydrogen atoms have been omitted for clarity.

The crystal structure of complex **1S** is shown in Fig.5. The Co(III) ion similar to that in complex **1**, is also low-spin and sixcoordinated with a Schiff-base ligand and two axial cyanide groups, with normal bond distances and angles. Unlike complex **1**, the asymmetry unit of complex **1S** consists of two monoanion [Co(S,S-salency)(CN)$_2$]$^-$, two K$^+$ ions and two water molecules. It should be noted that the bridging interactions around the K$^+$ ions are different. K1 and K2 each interact with two side-on cyanides, one water molecule, four oxygen atoms in Schiff-base ligand and one additional cyanide ligand via the N atoms only, with the K-N and K-C side-on interactions averaging 3.250 and 3.135 Å for K1, 3.215 and 3.118 Å for K2 respectively. The combination of multiply bridging cyanide ligands, as well as the bridging oxygen atoms between the K$^+$ ions, results in propagation of the structure into a 1-D chain with two sub-chains (Fig.6). Meanwhile, the interaction between the K$^+$ ions and the surrounding atoms in complex **1R** are almost the same as that of complex **1S** except the absence of water molecules. And the K-N and K-C separations in the side-on interactions average 3.295 and 3.147 Å for K1, 3.225 and 3.097 Å for K2 respectively, and all these interactions between the K$^+$ ions and the side-on cyanides are also comparable to those in previous reports.[41-45]

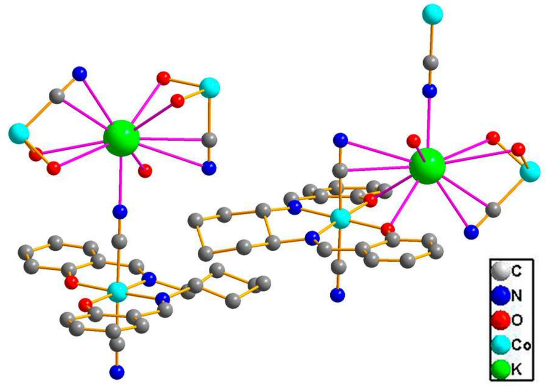


Fig. 5 Asymmetric unit of complex **1S,** with some additional symmetry-equivalent atoms included to complete the coordination spheres around the metal atoms.

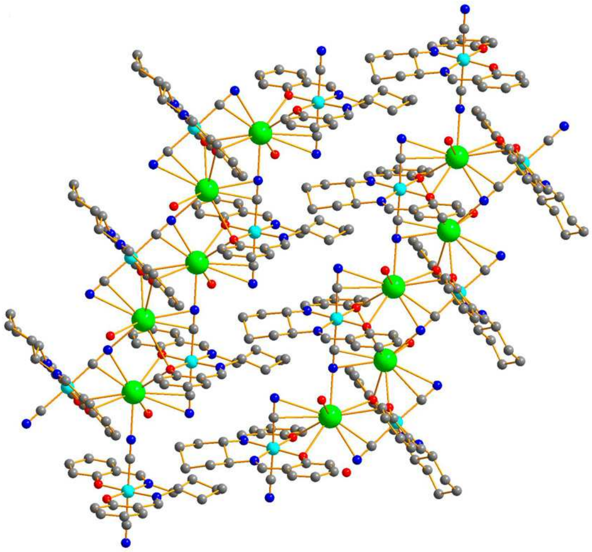


Fig. 6 view of chains in complex **1S** (Ni turquoise, K green, O red, N blue, C gray).

Optical spectra and NLO properties

The infrared spectrum of **1** shows two ν(C≡N) stretches at 2144 and 2118cm^{-1}, consistent with the presence of both the terminal and bridging cyanide groups.[41, 46-49] Complexes **1S** and **1R** show no significant difference in the infrared spectrum and they have similar absorption in the same region as complex **1**.

Complexes **1S** and **1R** crystallize in the chiral monoclinic space group with flack parameters of -0.04(2) and 0.04(3) respectively.The circular dicrhrosim (CD) spectra in KBr pellets were mearsured to confirm the optical activity and the enatiomeric nature of these complexes. The CD spectrum for **1S** shows a mirror image of that for **1R** at a similar wavelength confirming that complexes **1S** and **1R** are enantiomers of each other (Fig.7). The outcomes are in accord with the structures obtained by single crystal X-ray diffraction. Besides, complexes **1S** and **1R** exhibit second-order nonlinear optical (NLO) effect as expected. Powdered samples of **1S** and **1R** are SHG active with a weak signal.

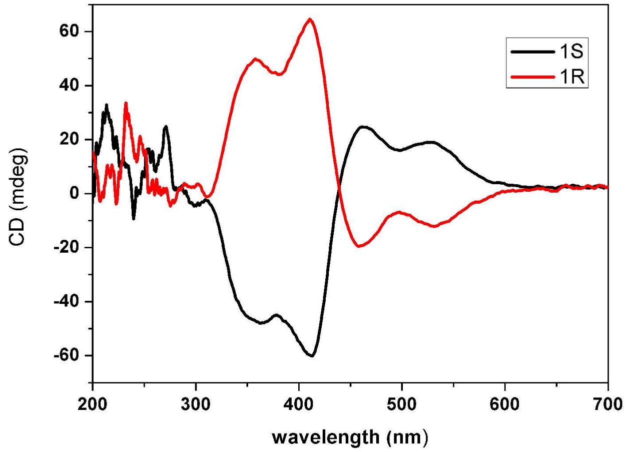
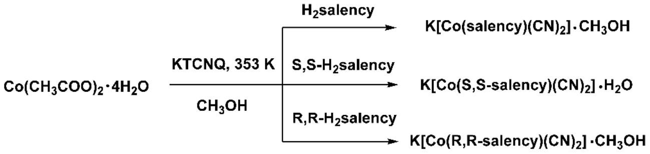


Fig. 7 The solid-state CD spectra of bulk samples 1S and 1R.

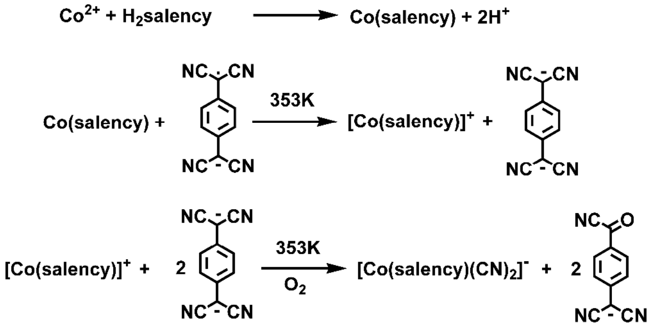
About in situ synthesis

The reaction of KTCNQ, $Co(CH_3COO)_2{\cdot}4H_2O$ and H_2salency in methanol provided an unexpected different result and three novel complexes containing $[Co(CN)_2(salency)]^-$ units linked by K^+ ions were produced (scheme 1).



Scheme 1 The synthetic route of **1**, **1S** and **1R**.

Considering the typically similar reactivity of TCNQ molecule, the reaction here is quite different. In the absence of amines and nitrite ions, the participation of cobalt put a new insight into the route of TCNQ decomposition. The possible mechanism of the unusually reaction is illustrated by scheme 2. The electron-rich coordination complex Co(salency) with the equatorial inplane tetradentate Schiff-base ligand was formed at first. While TCNQ is a well-known multi-redox active ligand and KTCNQ can proceed redox reaction with Co(salency). $TCNQ^{-\bullet}$(KTCNQ) was reduced by Co(salency) and further formed its dianion $TCNQ^{2-}$. Meanwhile, the Co^{2+} was oxidized into Co^{3+}, this was confirmed by the fact that all the final complexes **1**, **1S** and **1R** show no EPR signals. And then, in the presence of O_2, $TCNQ^{2-}$ lost the CN^- groups which were transferred to the Co^{3+} center and turned into the stable product $DCTC^-$ (α,α-dicyano-*p*-toluoylcyanide anion).[22, 28, 29, 31, 46, 50-53] The existent of CN^- groups in complexes **1**, **1S** and **1R** was supported by the typical infrared absorption of -CN in the IR spectra and the element analyses of the three complexes. The orange-red powder by-product $DCTC^-$ salt formed in the reactions was confirmed by the MS analysis (m/z for $C_{11}N_3OH_4$ calcd 194.2, found 194.8) and the infrared study revealed both the existence of the carbonyl group (1640 cm^{-1}) and the cyanide group (2133-2194 cm^{-1}) of $DCTC^-$ [32, 39] Thus, the reaction of Co^{2+}, H_2salency and CN^- from KTCNQ provided anion $[Co(CN)_2(salency)]^-$. Furthermore, the counter K^+ cations help to self-assemble complexes into a 1D chain structures.



Scheme 2 Schematic representation of the in situ reactions.

Conclusions

In summary, we got three cobalt(III) cyanide complexes which are obtained from the cyanide groups of $TCNQ^{-\bullet}$. The study of these reactions throws new light on the dicompositon of radical anion of TCNQ and provides a new method to synthesize metal cyanide complex. Complex **1** exhibits infinite double stair-like chain structure. However, the chiral complexes **1S** and **1R** show novel chain structures consisting of two independent sub-chains. And all of these chains are bridged by K^+ ions with unusual interations. Second-order nonlinear optical effect studies in the solid state revealed that **1S** and **1R** are SHG active with a weak signal.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: supplementary figures, tables and XRD. CCDC 849524-849526. For ESI and crystallographic data in CIF or other electronic format, See DOI: 10.1039/b000000x/

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Synthesis and Characterization of Cobalt(Ш) Cyanide Complexes: Cobalt Participate in the Decomposition of Radical Anion of TCNQ

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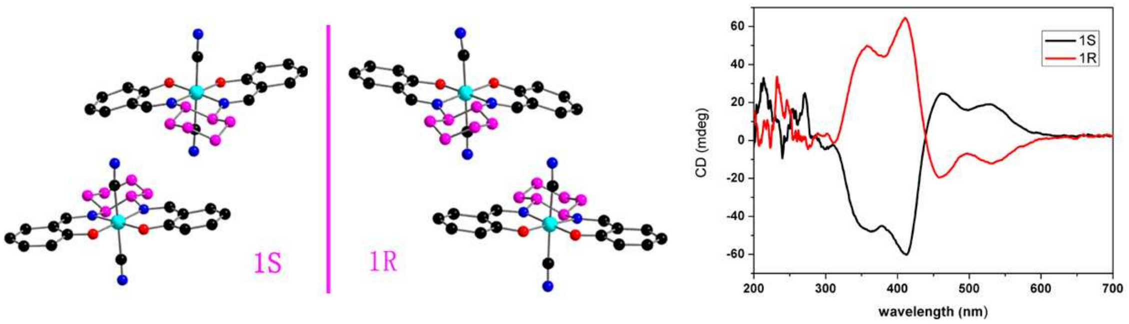

A racemic and two chiral cobalt(Ш) cyanide complexes were synthesized by the in situ decomposition of the radical anion of TCNQ with the participation of cobalt(II)