Syntheses, Crystal Structures and Thermal Stability of Co(II) and Zn(II) Complexes with Ethyl Carbazate

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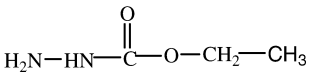
Cobalt(II) and zinc(II) complexes of ethyl carbazate (ECZ), $[Co(ECZ)_3](NO_3)_2$ and $[Zn(ECZ)_3](NO_3)_2$, were synthesized. Single crystals of these two compounds were grown from aqueous solutions using a slow evaporation method. Their structures have been determined by X-ray diffraction analysis. Both of them are monoclinic with space group $P2_1/n$. The complexes are further characterized by element analysis and IR measurements. Their thermal stabilities are studied by using TG-DTG, DSC techniques. When heated to 350 °C, only metal oxide was left for both complexes.

Key words: Cobalt(II) Complex, Zinc(II) Complex, Ethyl Carbazate, Crystal Structure, Thermal Stability

Introduction

Ethyl carbazate is an important chemical widely used in the syntheses of many medicines, herbicides, growth regulators of plants, germicides and insecticides. Ethyl carbazate has also been used to prepare various Schiff base metal complexes [1] with excellent antibiotic and anticarcinogenic activity. Recently, it has been considered as an energetic material for explosives due to its high enthalpy, incorrosiveness, low toxicity and good thermal stability [2]. The structural formula of ECZ is:



Since both hydrazine nitrogen atoms and the carbonyl oxygen atom in the molecule usually serve as electronic donor atom, ethyl carbazate can coordinate with some metal ions to form complexes with six coordination atoms and in octahedral configuration just like the compounds formed with carbohydrazide [3 – 6]. However, there are no published documents about ethyl carbazate complexes. In this paper, the preparation methods, crystal structural characterizations, and thermal decomposition mechanisms are presented for cobalt(II) and zinc(II) complexes.

Results and Discussion

Structures of title complexes

The molecular structures of $[Co(ECZ)_3](NO_3)_2$ and $[Zn(ECZ)_3](NO_3)_2$ are shown in Figs 1 and 2, respectively. Selected bond distances and angles around Co(II) and Zn(II) ions are given in Table 1.

As a bidentate ligand, ECZ coordinates to the metal cations with its carbonyl oxygen atom and the terminal nitrogen atom of hydrazine to form an almost planar five-membered chelating ring. Each centrosymmetric unit cell of both complexes contains two formula units in the asymmetric units. NO_3^- ligands do not coordinate at the metal center, but are connected with the coordination kernel by electrostatic interactions and hydrogen bonds. The coordination number at the metal ion is six and the configuration is octahedral [7]. Two slightly different conformations were found in the asymmetric unit of the centrosymmetric unit cell of each complex.

Two groups of C4-O4-C5-C6 and C7'-O6'-C8'-C9' are disordered in the molecule of $[Zn(ECZ)_3](NO_3)_2$ (as shown in Fig. 2). Both of the spatial occupancies of the groups of -O4-C5-C6 and -O4A-C5A-C6A are 0.5. For the groups of -O6'-C8'-C9' and -O6'B-C8'B-C9'B, the occupancies are 0.735 and 0.265, respectively.

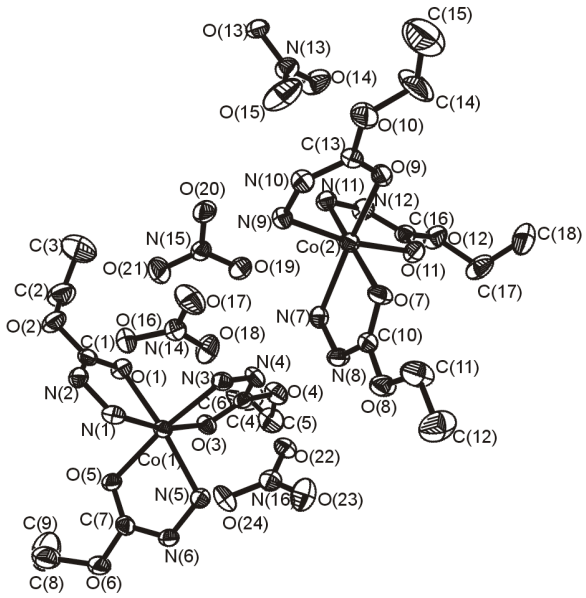


Fig. 1. The molecular structure of $[Co(ECZ)_3](NO_3)_2$.

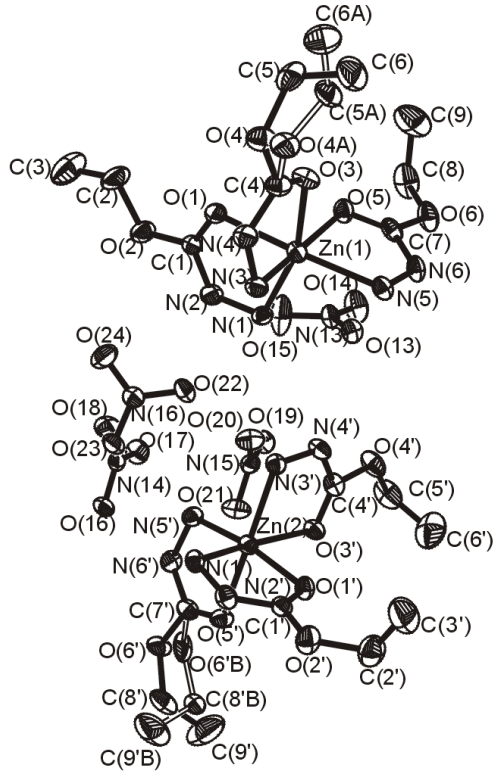


Fig. 2. The molecular structure of $[Zn(ECZ)_3](NO_3)_2$.

The two conformations in each complex molecule are similar. In the molecule of $[Zn(ECZ)_3](NO_3)_2$,

Table 1. Important bond distances (Å) and bond angles (°) for $[Co(ECZ)_3](NO_3)_2$ and $[Zn(ECZ)_3](NO_3)_2$.

Co(1)-O(1)	2.095(3)	Co(2)-O(7)	2.112(3)
Co(1)-O(3)	2.116(3)	Co(2)-O(9)	2.090(3)
Co(1)-O(5)	2.094(3)	Co(2)-O(11)	2.100(3)
Co(1)-N(1)	2.154(3)	Co(2)-N(7)	2.139(3)
Co(1)-N(3)	2.128(3)	Co(2)-N(9)	2.146(3)
Co(1)-N(5)	2.145(3)	Co(2)-N(11)	2.119(3)
O(5)-Co(1)-O(1)	94.81(11)	O(9)-Co(2)-O(11)	95.16(11)
O(5)-Co(1)-O(3)	99.42(11)	O(9)-Co(2)-O(7)	89.65(11)
O(1)-Co(1)-O(3)	90.58(10)	O(11)-Co(2)-O(7)	94.65(11)
O(5)-Co(1)-N(3)	173.04(12)	O(9)-Co(2)-N(11)	95.95(12)
O(1)-Co(1)-N(3)	91.81(11)	O(11)-Co(2)-N(11)	78.33(11)
O(3)-Co(1)-N(3)	78.34(11)	O(7)-Co(2)-N(11)	171.36(11)
O(5)-Co(1)-N(5)	77.75(11)	O(9)-Co(2)-N(7)	166.37(12)
O(1)-Co(1)-N(5)	172.02(12)	O(11)-Co(2)-N(7)	90.85(11)
O(3)-Co(1)-N(5)	87.86(11)	O(7)-Co(2)-N(7)	77.65(11)
N(3)-Co(1)-N(5)	95.53(12)	N(11)-Co(2)-N(7)	97.25(12)
O(5)-Co(1)-N(1)	88.51(11)	O(9)-Co(2)-N(9)	77.70(11)
O(1)-Co(1)-N(1)	78.01(11)	O(11)-Co(2)-N(9)	170.68(11)
O(3)-Co(1)-N(1)	166.66(11)	O(7)-Co(2)-N(9)	91.32(11)
N(3)-Co(1)-N(1)	94.97(12)	N(11)-Co(2)-N(9)	96.29(12)
Zn(1)-O(1)	2.152(2)	Zn(1)-N(1)	2.144(3)
Zn(1)-O(3)	2.098(2)	Zn(1)-N(3)	2.157(3)
Zn(1)-O(5)	2.118(2)	Zn(1)-N(5)	2.115(3)
Zn(2)-O(1')	2.117(2)	Zn(2)-N(1')	2.156(3)
Zn(2)-O(3')	2.136(2)	Zn(2)-N(3')	2.133(3)
Zn(2)-O(5')	2.110(2)	Zn(2)-N(5')	2.139(3)
O(3)-Zn(1)-N(5)	97.74(11)	O(5')-Zn(2)-O(1')	92.49(10)
O(3)-Zn(1)-O(5)	93.80(10)	O(5')-Zn(2)-N(3')	172.42(11)
N(5)-Zn(1)-O(5)	78.16(10)	O(1')-Zn(2)-N(3')	92.88(10)
O(3)-Zn(1)-N(1)	163.19(11)	O(5')-Zn(2)-O(3')	96.62(10)
N(5)-Zn(1)-N(1)	98.78(11)	O(1')-Zn(2)-O(3')	89.02(9)
O(5)-Zn(1)-N(1)	92.60(10)	N(3')-Zn(2)-O(3')	78.14(10)
O(3)-Zn(1)-O(1)	87.14(10)	O(5')-Zn(2)-N(5')	77.59(10)
N(5)-Zn(1)-O(1)	169.69(10)	O(1')-Zn(2)-N(5')	169.85(10)
O(5)-Zn(1)-O(1)	92.50(10)	N(3')-Zn(2)-N(5')	96.80(11)
N(1)-Zn(1)-O(1)	77.06(10)	O(3')-Zn(2)-N(5')	90.00(10)
O(3)-Zn(1)-N(3)	77.53(10)	O(5')-Zn(2)-N(1')	91.06(10)
N(5)-Zn(1)-N(3)	97.58(11)	O(1')-Zn(2)-N(1')	77.66(10)
O(5)-Zn(1)-N(3)	169.85(10)	N(3')-Zn(2)-N(1')	95.30(10)
N(1)-Zn(1)-N(3)	97.19(10)	O(3')-Zn(2)-N(1')	164.91(10)

the bond distances of Zn(1)-O(1) (2.152 Å) and Zn(2)-O(3') (2.136 Å) are longer than the other Zn-O bonds, of which the distances are about 2.11 Å. The average distance of Zn-O is 2.122 Å, which is longer than the corresponding Zn-O(1) (2.01(2) Å) and Zn-O(3) (2.09(3) Å) reported by Okawa in the molecule of $[ZnPb(L'')(ClO_4)_2(CH_3OH)]$ DMF (L''= $C_{24}H_{27}N_5O_2^{2-}$) [8]. As to the Zn-N bonds, the distance of Zn(1)-N(5) (2.115 Å) is much shorter than the others. The average distance is 2.141 Å, which is shorter than Zn-N(4) (2.193(4) Å) reported by Ibrahim *et al.* [9] in $[Zn(tren)(H_2O)](ClO_4)_2$. It is also shorter than the typical values (2.167 – 2.188 Å) of Zn-N bond

Table 2. Hydrogen bond distances (Å) and angles (°) for $[Co(ECZ)_3](NO_3)_2$ and $[Zn(ECZ)_3](NO_3)_2$.

D	H	A	D-H	H…A	D…A	D-H…A
$[Co(ECZ)_3](NO_3)_2$						
N1	H1BN	O16	0.90	2.61	3.455(5)	155.9
N1	H1AN	O18	0.90	2.32	3.080(4)	142.7
N3	H3AN	O21	0.90	2.56	3.450(5)	169.7
N3	H3BN	O22	0.90	2.16	3.013(4)	158.9
N5	H5BN	O24	0.90	2.01	2.905(4)	174.0
N5	H5AN	O20	0.90	2.17	3.063(4)	171.0
N7	H7AN	O16	0.90	2.19	3.003(4)	150.5
N7	H7BN	O13	0.90	2.17	3.071(4)	177.0
N9	H9BN	O17	0.90	2.25	3.042(4)	146.8
N9	H9AN	O20	0.90	2.36	3.137(4)	144.3
N11	H11B	O14	0.90	2.19	3.080(4)	167.9
N11	H11A	O19	0.90	2.13	2.969(4)	154.8
N2	H2N	O24	0.86	2.14	2.869(4)	142.2
N4	H4N	O13	0.86	2.11	2.949(4)	164.5
N6	H6N	O18	0.86	2.28	3.081(4)	154.4
N8	H8N	O22	0.86	2.18	2.951(4)	149.1
N10	H10N	O23	0.86	2.26	2.996(5)	143.4
N12	H12N	O13	0.86	2.11	2.951(4)	165.8
$[Zn(ECZ)_3](NO_3)_2$						
N1	H1NA	O13	0.90	2.17	3.071(4)	174.4
N1	H1NB	O17	0.90	2.17	2.999(4)	152.4
N2	H2N	O22	0.86	2.21	2.973(4)	148.5
N3	H3NA	O18	0.90	2.25	3.048(4)	148.1
N3	H3NB	O20	0.90	2.36	3.121(4)	142.2
N4	H4N	O24	0.86	2.26	2.989(4)	142.8
N5	H5NA	O14	0.90	2.18	3.073(4)	169.6
N5	H5NB	O19	0.90	2.13	2.966(4)	155.0
N6	H6N	O13	0.86	2.12	2.966(4)	166.0
N2’	H2’N	O23	0.86	2.17	2.887(4)	140.8
N4’	H4’N	O13	0.86	2.13	2.961(4)	161.6
N6’	H6’N	O16	0.86	2.31	3.090(4)	151.4
N6’	H6’N	O16	0.86	2.31	3.090(4)	151.4
N6’	H6’N	O16	0.86	2.31	3.090(4)	151.4

in an octahedral environment [10]. The average angles of N-Zn(1)-N and O-Zn(1)-O are 97.85° and 91.15°, respectively. The values of the N’-Zn(2)-N’ and O’-Zn(2)-O’ angles are 98.82° and 92.71°, respectively. In the molecule of $[Co(ECZ)_3](NO_3)_2$, the Co-O distances are all around 2.10 Å and the average distance is 2.101 Å for Co(1)-O and 2.102 Å for Co(2)-O. The distances Co(1)-N(1), Co(1)-N(5) and Co(2)-N(9) are all about 2.15 Å. The other three Co-N bonds are shortened to 2.125 Å, the average value is 2.142 Å for bond Co(1)-N and 2.135 Å for bond Co(2)-N. The mean Co-N and Co-O lengths in the title six-coordinate Co(II) bis-chelate compound is considerably longer than the corresponding lengths of 1.888 Å and 1.927 Å observed in the octahedral cobalt(III) complex, tris-{3-phenyl-3-hydroxypropan-2-oximiato} cobalt(III) [11], which is consistent with the difference in oxidation state. The mean Co-N and Co-O distances in the title six-coordinate Co(II) compound are also considerably longer than those in the five-coordinate cobalt(II) complex $[Co(L)_2(NO)]$ [12, 13] (where LH is the unsubstituted salicyladoxime ligand) of 1.863 Å and 1.871 Å, respectively, which may be attributed to the difference in the coordination number [14].

The N-H groups in the complexes are involved in hydrogen bonds, the geometric data of which are shown in Table 2. A recent study of amino acid structures suggested that three-center bonds tend to occur in ’proton deficient’ structures, *i.e.* structures that lack active protons (O-H, N-H) to satisfy the normal hydrogen bonding requirements of acceptor atoms [14]. Such acceptor atoms are present in these two compounds in the form of the nitrate oxygen atoms. At the same time, the terminal NH group of the hydrazine moiety acts as the donor. For example, in the molecule of $[Co(ECZ)_3](NO_3)_2$, between the terminal N(1)-H(1) and different O atoms [O(16), O(17), O(18)] four hydrogen bonds of N(1)-H(1AN)…O(16), N(1)-H(1AN)…O(17), N(1)-H(1BN)…O(16) and N(1)-H(1AN)…O(18) are found. The lengths of these hydrogen bonds range from 2.32 Å to 2.61 Å, a little longer than the normal hydrogen bond. Between the other terminal N-H groups N(3), N(5), N(7), N(9) and the nitrate oxygen atoms, there are only two kinds hydrogen bonds such as N(3)-H(3AN)…O(21) and N(3)-H(3BN)…O(22). Between the internal N-H groups (marked with even numbers: 2-12) and the nitrate oxygen atoms, only one kind hydrogen bonds like N(2)-H(2N)…O(24) exist. These hydrogen bonds play an important role in stabilizing the crystal structures. The same pattern of hydrogen bonds is found in the molecule of $[Zn(ECZ)_3](NO_3)_2$.

Thermal analysis

The DSC and TG-DTG curves of the title compounds are given in Figs. 3 – 6. The DSC analysis of $[Co(ECZ)_3](NO_3)_2$ indicates that there is only one acute exothermal peak which occurs at 216 – 218 °C, with an enthalpy change of 1405 kJ/mol. The TG-DTG measurement verifies that there is a sharp mass loss process in the range of 201 – 229 °C, corresponding to the exothermal process, with a mass loss of 84.2 wt-%. Due to vigorous exothermal decomposition process of $[Co(ECZ)_3](NO_3)_2$, the final residue is CoO according to the IR bands at 725 and 590 cm^{-1}, but formation of some Co_2O_3 is also indicated by the IR absorptions at 725, 664 and 563 cm^{-1} [15]. These observations verify

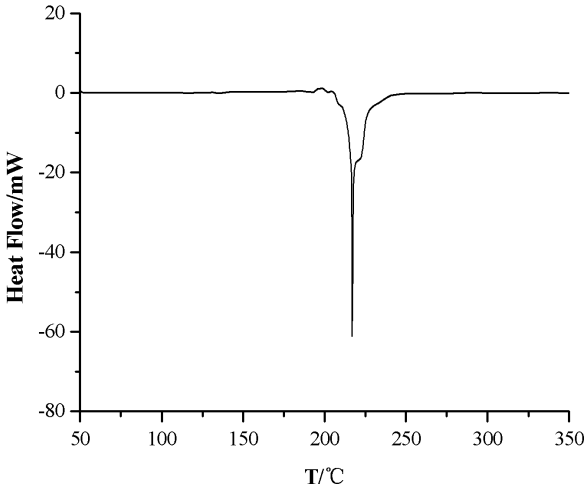


Fig. 3. DSC curve of $[Co(ECZ)_3](NO_3)_2$.

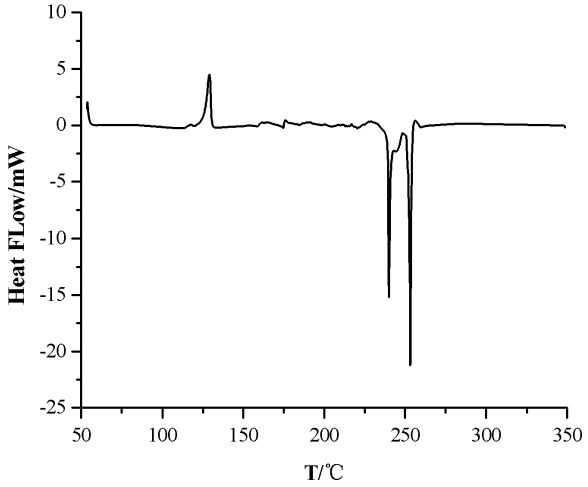


Fig. 4. DSC curve of $[Zn(ECZ)_3](NO_3)_2$.

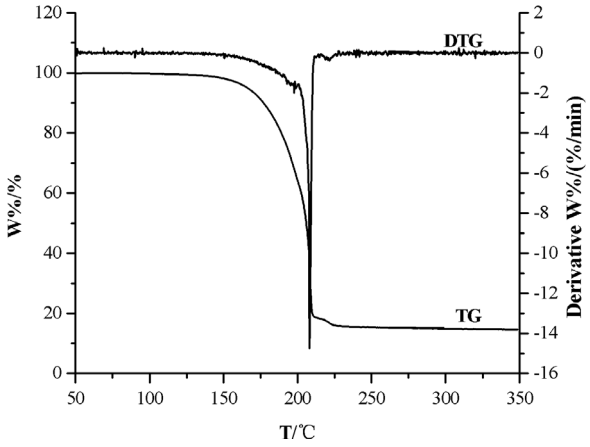


Fig. 5. TG-DTG curves of $[Co(ECZ)_3](NO_3)_2$.

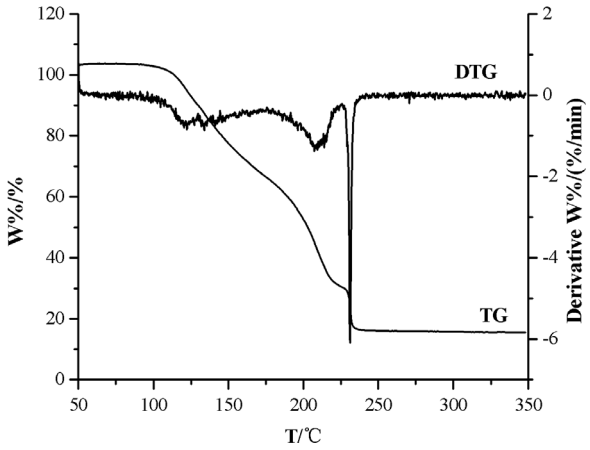


Fig. 6. TG-DTG curves of $[Zn(ECZ)_3](NO_3)_2$.

that $[Co(ECZ)_3](NO_3)_2$ can withstand temperatures up to 216 ℃. Decomposition of the molecule occurs in an explosion mode, and the final products are formed in one thermal step that is highly exothermic.

The DSC curve of $[Zn(ECZ)_3](NO_3)_2$ shows a small endothermic peak from 118 to 131 ℃ first, and the onset temperature is 125 ℃. Accordingly, its TG-DTG curves as shown in Fig. 6 confirm a small mass loss process of about 36.0 wt-% in the range 104–182 ℃. This acute endothermal process might be presumed as a melting process of the compound, and beginning slow decomposition as well the disappearance of vaporized material from the molten samples with the flowing nitrogen atmosphere. They account for the slow mass loss. Then, the DSC curve indicates two continuous exothermal decomposition processes from 199 to 264 ℃ with two acute peaks at 240 and 251 ℃. The total change of enthalpy from 238 to 255 ℃ is 410 kJ/mol. The corresponding mass loss processes also appear on TG-DTG curves continuously with two peaks at 217 and 233 ℃. The total mass loss is 47.9 wt-% in the range 182–250 ℃. The final residue is ZnO as verified by IR absorption peaks at 1350, 725 and 500 cm^{-1} [15]. The remaining material amounts to 16.1 wt-%, which agrees very well with the calculated value of 16.2 wt-%.

The obtained results confirm that $[Co(ECZ)_3](NO_3)_2$ is more stable than $[Zn(ECZ)_3](NO_3)_2$ when they endure a linear heating process. The thermal decomposition processes of $[Co(ECZ)_3](NO_3)_2$ is simpler than that of $[Zn(ECZ)_3](NO_3)_2$, which shows one endothermal and two exothermal processes. The re-

leased energy of $[Co(ECZ)_3](NO_3)_2$ is 3.4 times higher than that of $[Zn(ECZ)_3](NO_3)_2$, and this means that the cobalt complex is a more energy-rich material than the zinc complex. The exothermal decomposition of both complexes is very rapid, and the final residues are the corresponding metal oxides besides the gaseous products. Anyway, these two coordination compounds have some characteristics of explosives and they might be used as energetic materials or propellant components.

Experimental Section

Materials

Cobalt nitrate and zinc nitrate (analytical reagent) were commercial products and they were applied as aqueous solutions 15 wt-% for synthesis. Ethyl carbazate (m. p. 45 °C) was prepared as reported.

Physical techniques

The element analysis (C, H, N) was performed on an automatic element microanalyzer Flash EA 1112. The IR spectra were recorded in KBr pellets on a Bruker Equinox 55 FT-IR spectrometer, in the range of 4000 – 400 cm^{-1}. The metal element contents and thermal stability of both complexes were measured by using Perkin-Elmer Pyris1 TG-DTG and DSC instruments. The heating rate was 10 °C/min under the nitrogen atmosphere with a flow rate of 20 ml/min.

Synthesis of $[Co(ECZ)_3](NO_3)_2$ and $[Zn(ECZ)_3](NO_3)_2$

Ethyl carbazate (4.15 g, 0.04 mol) and distilled water (20 ml) were added to a reactor and heated to 60 °C with vigorously stirring. The aqueous solution of $Co(NO_3)_2 \bullet 6H_2O$ (2.95 g, 0.01 mol) for $[Co(ECZ)_3](NO_3)_2$ or $Zn(NO_3)_2 \bullet 6H_2O$ (2.97 g, 0.01 mol) for $[Zn(ECZ)_3](NO_3)_2$ was dripped into the ethyl carbazate solution within 20 min with continuous stirring. Then, the reacting mixture was kept at 60 °C for 20 min to complete the reaction. Finally, the solution was cooled to ambient temperature and no precipitates were formed. In order to get a pure solution, and to avoid bringing in some unknown impurity, the resulting solution was filtered and put into the culture utensil. After about 20 days in the oven at 25 °C, deep red sheet crystals of $[Co(ECZ)_3](NO_3)_2$ and colorless sheet crystals of $[Zn(ECZ)_3](NO_3)_2$ were obtained, which were collected and dried naturally in dehumidifier. *Since the products might lead to powerful explosion precaution must be paid during the treatment of these crystals.* – Yield of $[Co(ECZ)_3](NO_3)_2$: 4.00 g (80%); m. p. 216 °C. Analysis for $[Co(NH_2NHCO_2CH_2CH_3)_3](NO_3)_2$: calcd. C 21.83, H 4.88, N 22.62, Co 11.89; found C 22.82, H 4.92, N 22.61, Co 12.28. IR (KBr): ν = 3249(N-H), 1677, 1620 (C=O), 1376, 1544 (CH_3), 1312 (NO_3), 1029, 1114, 1202 (C-N) cm^{-1} [16]. Yield for $[Zn(ECZ)_3](NO_3)_2$: 3.75 g (75%); m.p. 125 °C. Analysis for $[Zn(NH_2NHCO_2CH_2CH_3)_3](NO_3)_2$(2): calcd. C 21.55, H 4.82, N 22.34, Zn 13.03; found C 22.60, H 4.94, N 22.38, Zn 12.94. IR (KBr): ν = 3251(N-H), 1679, 1623 (C=O), 1543 (CH_3), 1308 (NO_3), 1030, 1112, 1199 (C-N) cm^{-1} [16 – 18].

Table 3. Crystal data and structure refinement for $[Co(ECZ)_3](NO_3)_2$ and $[Zn(ECZ)_3](NO_3)_2$.

	$[Co(ECZ)_3](NO_3)_2$	$[Co(ECZ)_3](NO_3)_2$
Empirical formula	$C_9H_{24}CoN_8O_{12}$	$C_9H_{24}ZnN_8O_{12}$
Formula weight	495.29	501.73
Temperature [K]	288(2)	295(2)
μ(Mo-K$_\alpha$) [mm^{-1}]	0.902	1.258
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions [mm]	$0.52 \times 0.40 \times 0.16$	$0.44 \times 0.44 \times 0.24$
a [Å]	14.053(2)	14.094(2)
b [Å]	8.720(2)	8.692(1)
c [Å]	33.863(7)	33.907(6)
β [°]	92.29(2)	92.28(1)
V [Å^3]	4146.4(14)	4150.5(10)
Z	8	8
$D_{calcd.}$ [g cm^{-3}]	1.587	1.606
$F(000)$	2056	2080
θ [°]	1.20 to 25.00	1.20 to 25.25
h	0 to 16	0 to 16
k	0 to 10	0 to 10
l	−40 to 40	−40 to 40
Reflections measured	8645	8683
Independent reflections	7320 [$R_{int} = 0.0220$]	7518 [$R_{int} = 0.0240$]
Observed reflections $I > 2\sigma(I)$	3309	3691
Parameters	548	602
Reflections refined	7320	7518
R_1 (observed reflections)	0.0416	0.0383
wR_2 (all reflections)	0.0776	0.0714
Goodness-of-fit on F^2	0.744	0.800
Largest difference peak and hole [e Å^{-3}]	0.289 and −0.278	0.261 and −0.202

X-ray crystallography

The diffraction data collection were performed on a Siemens P4 four-circle diffractometer using Mo-K$_\alpha$ radiation (λ = 0.071073 nm) with a graphite monochromator, using ω-scans with θ limits $1.20° < \theta < 25.00°$ for $[Co(ECZ)_3](NO_3)_2$ and $1.20° < \theta < 25.25°$ for $[Zn(ECZ)_3](NO_3)_2$, respectively. Empirical absorption corrections were applied. Both structures were solved by direct methods and refined by least squares on F^2 using the SHELXS-97 program. Full-matrix least-squares anisotropic refinements for all non-hydrogen atoms were completed with the SHELXS-97 program. Hydrogen atoms were placed at their geometrically calculated positions and refined

isotropically. Crystal data and additional details regarding data collection and refinement are listed in Table 3.

Crystallographic data for the two structures have been deposited with the Cambridge Crystallographic Data Center as supplementary publication, CCDC No. for $[Co(ECZ)_3](NO_3)_2$: 213654, and for $[Zn(ECZ)_3](NO_3)_2$: 213655. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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