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# Syntheses and coordination isomerism of heteroleptic divalent-metal (M = Co, Zn) carbazate complexes

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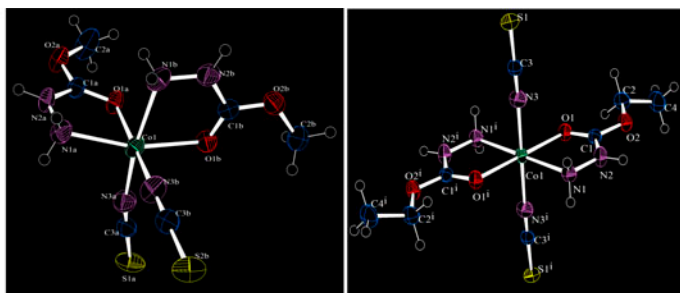
Three heteroleptic divalent-metal alkyl-carbazate-thiocyanate complexes, [M(NCS)$_2$(NH$_2$NHCO-OR)$_2$] [M = Co and R = CH$_2$CH$_3$ (**1**); M = Co and R = CH$_3$ (**2**); M = Zn and R = CH$_3$ (**3**)], have been prepared and characterized, and their crystal structures determined. In **1**, Co(II) adopts a fairly regular centrosymmetric *trans*-CoO$_2$N$_4$ octahedral geometry arising from its coordination by two N, O-bidentate ethylcarbazate ligands and two *trans* N-bonded thiocyanates. In isostructural **2** and **3**, the metals adopt distorted *cis*-MO$_2$N$_4$ octahedral geometries arising from two N,O-bidentate methylcarbazate ligands with *cis* N-bonded thiocyanates. The crystal structures feature N–H⋯O and N–H⋯S interactions. Thermal analysis data show that these compounds begin to decompose at temperatures between 130 and 160 °C. Crystal data: **1**, CoC$_8$H$_{16}$N$_6$O$_4$S$_2$, M_r = 383.32, $P2_1/n$ (No. 14), a = 5.2599(3) Å, b = 7.4209(4) Å, c = 20.1948(12) Å, β = 94.070(1)°, V = 786.28(8) Å^3, Z = 2, $R(F)$ = 0.028, $wR(F^2)$ = 0.073; **2**, CoC$_6$H$_{12}$N$_6$O$_4$S$_2$, M_r = 355.27, $P2_1/n$ (No. 14), a = 7.8663(3) Å, b = 10.5804(3) Å, c = 17.6313(5) Å, β = 102.019(10)°, V = 1435.26(8) Å^3, Z = 4, $R(F)$ = 0.036, wR (F^2) = 0.097; **3**, ZnC$_6$H$_{12}$N$_6$O$_4$S$_2$, M_r = 361.71, $P2_1/n$ (No. 14), a = 7.8883(2) Å, b = 10.5756(3) Å, c = 17.5827(5) Å, β = 101.676(1)°, V = 1436.46(7) Å^3, Z = 4, $R(F)$ = 0.031, $wR(F^2)$ = 0.084.

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1. Introduction

A variety of functional materials have been synthesized containing different types of molecular and supramolecular architectures incorporating strong metal–ligand covalent bonds and weak non-covalent interactions [1, 2]. Extensive investigations have been made in the roles of different types of organic and inorganic ligands in establishing these networks [3, 4]. An important strategy for the generation of new supramolecular architectures involves the use of neutral ligands having both hydrogen bond donor and acceptor capabilities [5, 6].

In this context, alkyl carbazates, the alkyl esters of hydrazine carboxylic acid ($NH_2NHCOOH$), are of interest. These molecules contain NH_2 and NH donor groups, potential N- and O-hydrogen-bond acceptors, and at the same time, they can act as N,O-chelating ligands. The coordination chemistry of alkyl carbazates has not been much explored, but recently, we have reported various complexes and coordination polymers using ethyl carbazate ($NH_2NHCOOCH_2CH_3$, Ec), as a co-ligand [7]. The SCN^- thiocyanate anion, in combination with different chelating and bridging ligands, has been used to construct numerous molecular and extended crystalline structures [8]. Complexes of the type $[M(NCS)_2(L)_2]$ (L = unsymmetrical bidentate, chelating ligand) can, in principle, give rise to 15 distinct structures when considering geometrical and linkage isomerism [9].

In this manuscript, we describe the syntheses, characterization, and crystal structures of three divalent-metal complexes of general formula $[M(NCS)_2(L)_2]$, where M = Co and Zn and L = methyl and ethyl carbazate (Mc and Ec), namely $[Co(NCS)_2(Ec)_2]$ (**1**), $[Co(NCS)_2(Mc)_2]$ (**2**), and $[Zn(NCS)_2(Mc)_2]$ (**3**).

2. Experimental

2.1. *Materials and methods*

All chemicals were of analytical grade and used as received. The hydrazine and thiocyanate contents were determined titrimetrically using standard KIO_3, and metal contents were determined using EDTA solutions [10, 11]. Elemental analyses were carried out using a Perkin-Elmer-240B CHN analyzer. IR spectra were recorded as KBr pellets with a Perkin-Elmer Pyris Diamond spectrophotometer from 4000 to 400 cm^{-1}. UV/visible spectra were recorded in methanol solution on a Shimadzu UV-168 spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker 400 MHz instrument. Magnetic susceptibility measurements for **1** and **2** were made using a Lakeshore VSM 7410 vibrating sample magnetometer. Thermogravimetric analyses were carried out under oxygen on a Pyris Diamond thermal analyzer with a heating rate of 20 °C min^{-1} and ~5 mg of sample used for each experiment.

2.2. *Syntheses*

A 10 mL aqueous solution of the appropriate metal nitrate (0.001 M) was added to 10 mL of an aqueous solution containing 0.002 M of ammonium thiocyanate and 0.002 M of Mc or Ec. The total volume was increased to 60 mL by adding distilled water. The resulting solutions (pale pink for **1** and **2**; colorless for **3**) of pH ~6 were concentrated on a water bath to about one-third of their initial volumes and left for crystallization at room

temperature. After a few days, the solid products formed were filtered off, washed with ethanol, and dried in air. All three syntheses yielded single crystals suitable for diffraction studies. The same products arise if the corresponding metal chlorides are used as starting materials.

Compound **1**: pink, 97% yield. Anal. Calcd for $C_8H_{16}N_6O_4S_2Co$: N_2H_4, 16.70, NCS^-, 30.80; Co, 15.33; C, 25.04; H, 4.17; N, 21.91%. Found: N_2H_4, 16.50; NCS^-, 30.31, Co, 16.40; C, 24.90; H, 4.30; N, 22.10%.

Compound **2**: violet, 82% yield. Anal. Calcd for $C_6H_{12}N_6O_4S_2Co$: N_2H_4, 18.03; NCS^-, 32.65; Co, 16.60; C, 20.27; H, 3.38; N, 23.64%. Found: N_2H_4, 18.70 (18.03), NCS^-, 32.10; Co, 15.40; C, 20.60; H 3.60; N, 23.30%.

Compound **3**: colorless, 70% yield. Anal. Calcd for $C_6H_{12}N_6O_4S_2Zn$: N_2H_4, 17.71; NCS^-, 32.07; Zn, 18.09; C, 19.91; H, 3.32; N, 23.22%. Found: N_2H_4, 17.10; NCS^-, 31.50; Zn, 17.40; C, 20.20; H, 3.10; N, 23.40%. ^1H NMR (400 MHz, D_2O, δ in ppm): 3.67 (s, 3H). ^{13}C NMR (400 MHz, D_2O, δ in ppm): 53.49 ($-OCH_3$), 161.39 ($-C=O$); 133.23 ($-N=C=S$).

2.3. X-ray crystallography studies

Single-crystal X-ray diffraction data for **1**, **2**, and **3** were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Selected crystal, data collection, and refinement parameters are listed in table 1. Multi-scan absorption corrections were performed using SADABS [12] during data reduction. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least squares against F^2 using SHELXL-97 [13]. Hydrogens were located in different maps, relocated to idealized geometries, and refined as riding (N–H = 0.86–0.90 Å; C–H = 0.97–0.98 Å) with $U_{iso}(H) = 1.2U_{eq}$(N atom) or $1.5U_{eq}$(C atom). The methyl groups were allowed to rotate, but not to tip, to best fit the electron density.

Table 1. Crystal, data collection, and refinement parameters for **1–3**.

Empirical formula	$CoC_8H_{16}N_6O_4S_2$ (**1**)	$CoC_6H_{12}N_6O_4S_2$ (**2**)	$ZnC_6H_{12}N_6O_4S_2$ (**3**)
M_r	383.32	355.27	361.71
T (K)	223(2)	296(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	5.2599(3)	7.8663(3)	7.8883(2)
b (Å)	7.4209(4)	10.5804(3)	10.5756(3)
c (Å)	20.1948(12)	17.6313(5)	17.5827(5)
β (°)	94.070(1)	102.019(10)	101.676(1)
V (Å^3)	786.28(8)	1435.26(8)	1436.46(7)
Z	2	4	4
ρ_{Calcd} (g cm^{-3})	1.619	1.644	1.673
μ (mm^{-1})	1.380	2.018	2.018
$F(000)$	394	724	736
R_{Int}	0.020	0.063	0.025
Data/restraints/parameters	1788/0/98	3577/0/174	6072/0/175
Goodness-of-fit on F^2	1.085	1.073	1.005
$R(F)$	0.028	0.036	0.031
$wR(F^2)$	0.073	0.097	0.084
$\Delta\rho$ limits (e Å^{-3})	−0.25 to +0.39	−0.56 to +0.59	−0.67 to +0.87

3. Results and discussion

3.1. Synthesis

The reaction of divalent Co and Zn salts with ammonium thiocyanate and Mc or Ec in water led to compounds of the general formula $[M(NCS)_2(L)_2]$. All the compounds are highly soluble in water. The following general scheme represents the synthesis of **1**, **2**, and **3**:

$$MX_2 \cdot nH_2O + 2NH_4SCN + 2L \rightarrow [M(NCS)_2(L)_2] + 2NH_4X + nH_2O$$
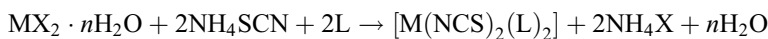
where $X = Cl^-$ or NO_3^-: $M = Co^{2+}$, $L = Ec$ (**1**); $M = Co^{2+}$, $L = Mc$ (**2**); $M = Zn^{2+}$, $L = Mc$ (**3**).

3.2. Spectroscopic studies

IR spectra of **1**, **2**, and **3** (see Supplementary material) each show a strong band at 2100 cm^{-1}, which can be assigned to ν_{asym}(CN) stretch of the thiocyanate. The peak position strongly suggests N-coordination of this anion in these complexes [14]. The spectra also exhibit a band at 1670–1690 cm^{-1}, which is characteristic of coordinated C=O stretching frequency of carbazate ligands, compared to 1735 and 1724 cm^{-1} in the spectra of Ec and Mc, respectively [7]. Absorptions around 3180–3250 cm^{-1} and 1120 cm^{-1} for all three complexes are in accord with N–H and N–N stretching vibrations, respectively, of carbazate ligands, signifying coordination of nitrogen to the metal.

The UV/visible spectra of **1** and **2** show broad absorptions with $\lambda_{max} = 510$ nm (19,600 cm^{-1}) and 515 nm (19,400 cm^{-1}), respectively. These can both be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ d–d electronic transition of an octahedral Co^{2+} d^7 system [15], although the colors perceived by the eye are distinctly different for the two compounds, which can be ascribed to the different λ_{max} values arising from the different dispositions of the ligands in **1** and **2**.

In the ^{1}H NMR spectrum of the Mc ligand, the methoxy protons are a singlet at $\delta = 3.72$ ppm, whereas the ^{13}C{^{1}H} NMR spectrum shows two peaks at $\delta = 52.52$ and 159.45 ppm due to the methoxy and carbonyl carbon, respectively. In both the ^{1}H and ^{13}C{^{1}H} NMR spectra of **3**, the downfield shift of all these peaks indicates coordination of the carbonyl O of Mc to Zn. In addition, the ^{13}C{^{1}H} spectrum shows a peak at 133.23 ppm, which can be assigned to the carbon of coordinated thiocyanate.

The room temperature magnetic susceptibility measurements showed that the effective magnetic moments for **1** and **2** are 4.9 and 4.1 μ_B, respectively, which are higher than the spin-only value of 3.88 μ_B. This may be ascribed to the orbital angular momentum contribution in d^7 systems and is typical of distorted octahedral cobalt(II) complexes.

3.3. Thermogravimetry

The simultaneous TG–DTA traces (Supplementary material) showed that **2** is stable to 160 °C, whereas **1** and **3** start to decompose at 145 and 130 °C, respectively. All these compounds decomposed in multi-step processes over a wide temperature range; the total mass losses indicate the eventual formation of CoO at 800 °C (obs. 80 wt%, Calcd 80.20 wt%) and ZnO at 820 °C (obs. 78 wt%, Calcd 77.5 wt%) from **1** and **3**, respectively. The mass-loss calculation (obs. 76 wt%, Calcd 76.6 wt%) for **2** suggests the formation of Co$_2$O$_3$ at

~820 °C. **1–3** showed about a 40–60% mass loss around 200 °C. This rapid weight loss may be due to the exothermic decomposition of the hydrazinic moiety (Calcd 54.10 wt% for **1**; 50.66 wt% for **2**; 49.80 wt% for **3**).

3.4. *X-ray crystal structures of 1–3*

The molecular structures of **1**, **2**, and **3** are depicted in figures 1, 2, and 3, respectively; selected geometrical data are given in tables 2, 3, and 4, respectively. All these complexes consist of neutral mononuclear units, viz [Co(NCS)$_2$(Ec)$_2$] (**1**), [Co(NCS)$_2$(Mc)$_2$] (**2**), and [Zn(NCS)$_2$(Mc)$_2$] (**3**). In **1**, the cobalt is located on a crystallographic inversion center, whereas in isostructural **2** and **3**, all the atoms lie on general positions.

The thiocyanate ions in **1** are mutually *trans*-coordinated, whereas they are *cis*-oriented in **2** and **3**; oxygens of the carbazate ligands are mutually *trans* in **1,** but are *cis* in **2** and **3**.

The metal coordination polyhedron in **1** is defined by a pair of N and O atoms of two N, O-chelated bidentate Ec ligands lying in a common plane and a pair of nitrogens from the *trans*-thiocyanate ions perpendicular to this plane. In **2** and **3**, N3b and O1a, which have the largest *trans* bond angle [174.88(6)° for **2** and 173.82(5)° for **3**], may be defined as the axial atoms and the other bonded atoms as equatorial. Based on bond-valence-sum (BVS) calculations by the Brown–Altermatt method [16], Co(II) ions in **1** and **2** appear to be distinctly under-bonded, with BVS values of 1.76 and 1.74, respectively (expected = 2.00). The valence of Zn(II) in **3**, on the other hand, is satisfied (observed = 1.95, expected = 2.00).

The Ec ligand in **1** bites Co1 with a N1–Co1–O1 angle of 77.92(5)°. The resulting five-membered chelate ring forms a shallow envelope, with Co1 as the flap, displaced by 0.128 (3) Å from the essentially coplanar ligand atoms (rms deviation = 0.006 Å). The corresponding bite angles for the two Mc are 76.64(6)° and 75.98(6)° in **2** and 75.10(4)° and 75.62 (4)° in **3**. In each case, the chelate ring also forms a shallow envelope with the metal as the flap. In **2**, Co1 deviates from the mean planes of the N1a-containing Mc ligand (rms
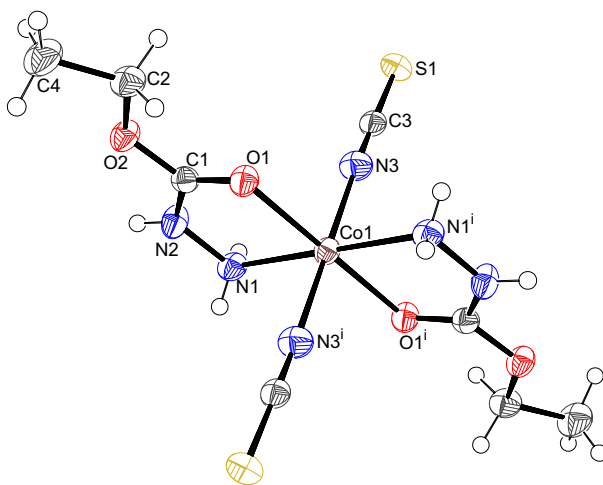

Figure 1: The molecular structure of **1** showing 50% displacement ellipsoids. Symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*.
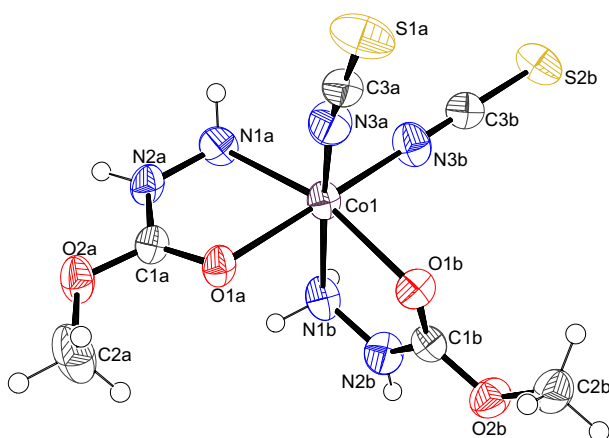
Figure 2:   The molecular structure of **2** showing 50% displacement ellipsoids.
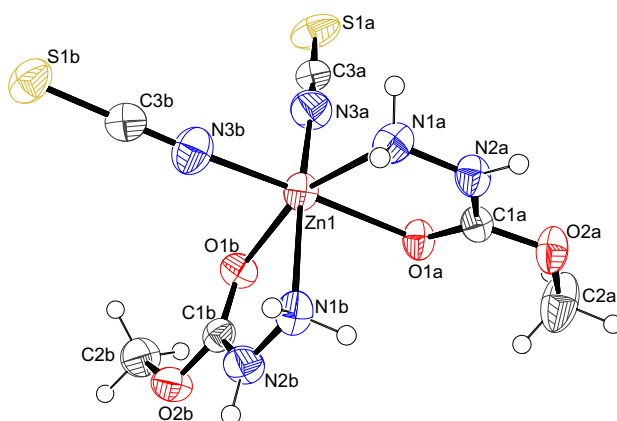
Figure 3:   The molecular structure of **3** showing 50% displacement ellipsoids.

deviation = 0.007 Å) and the N1b-containing ligand (rms deviation = 0.014 Å) by 0.121(3) Å and 0.252(3) Å, respectively. Corresponding data for Zn1 in **3** are 0.005 Å and 0.013 Å (rms deviation), and 0.150(3) and 0.286(3) Å (metal distance), respectively. The dihedral angles between the ligand mean planes in **2** and **3** are 88.38(8)° and 86.92(6)°; whereas in **1**, the inversion-related chelate planes of the Ec ligands are of course parallel.

The Co–N_{Ec} distance in **1** is 2.147(2) Å, whereas in **2** and **3**, the pairs of M–N_{Mc} distances are 2.166(2) and 2.176(2) Å, and 2.163(1) and 2.201(1) Å, respectively. These distances are greater than the M–N_t (t = thiocyanate) distance(s) of 2.071(2) Å in **1**, 2.038(2) and 2.040(2) Å in **2**, and 2.017(2) and 2.032(2) Å in **3**, which presumably reflects the stronger coordination of the anionic thiocyanate over the neutral carbazate ligands. In **1**, the thiocyanate is coordinated almost linearly with the cobalt [Co–N–C = 176.6(1)°], whereas in the Mc compounds, the thiocyanate shows distinct bending, with M–N–C bond angles of 167.9(2) and 168.3(2)° in **2** and 165.7(1) and 169.5(1)° in **3**. In all three complexes, the

Table 2.   Selected bond lengths (Å) and angles (°) for **1**.

Co1–N3	2.0705(15)		
Co1–O1	2.1356(11)		
Co1–N1	2.1492(14)		
N3–Co1–O1[i]	88.90(5)	N3–Co1–O1	91.10(5)
N3[i]–Co1–N1[i]	88.94(6)	O1[i]–Co1–N1[i]	77.94(5)
N3[i]–Co1–N1	91.06(6)	O1[i]–Co1–N1	102.06(5)

Note: Symmetry code: (i) $1-x$, $1-y$, $1-z$.

Table 3.   Selected bond lengths (Å) and angles (°) for **2**.

Co1–N3a	2.0387(17)	Co1–N3b	2.0398(18)
Co1–O1a	2.1657(13)	Co1–N1a	2.1674(16)
Co1–O1b	2.1691(13)	Co1–N1b	2.1778(17)
N3a–Co1–N3b	96.89(8)	N3a–Co1–O1a	87.42(7)
N3b–Co1–O1a	174.88(6)	N3a–Co1–N1a	97.76(7)
N3b–Co1–N1a	100.01(7)	O1a–Co1–N1a	76.61(5)
N3a–Co1–O1b	92.41(6)	N3b–Co1–O1b	90.41(7)
O1a–Co1–O1b	92.15(5)	N1a–Co1–O1b	164.41(6)
N3a–Co1–N1b	166.03(7)	N3b–Co1–N1b	90.99(7)
O1a–Co1–N1b	85.35(6)	N1a–Co1–N1b	92.18(6)
O1b–Co1–N1b	75.96(5)		

Table 4.   Selected bond lengths (Å) and angles (°) for **3**.

Zn1–N3a	2.0179(14)	Zn1–N3b	2.0324(15)
Zn1–N1a	2.1647(12)	Zn1–O1b	2.1857(10)
Zn1–N1b	2.2026(13)	Zn1–O1a	2.2426(10)
N3a–Zn1–N3b	98.63(6)	N3a–Zn1–N1a	99.77(6)
N3b–Zn1–N1a	100.41(5)	N3a–Zn1–O1b	91.42(5)
N3b–Zn1–O1b	92.63(5)	N1a–Zn1–O1b	161.26(4)
N3a–Zn1–N1b	163.24(6)	N3b–Zn1–N1b	91.99(6)
N1a–Zn1–N1b	90.94(5)	O1b–Zn1–N1b	75.09(4)
N3a–Zn1–O1a	86.77(5)	N3b–Zn1–O1a	173.82(5)
N1a–Zn1–O1a	75.59(4)	O1b–Zn1–O1a	90.21(4)
N1b–Zn1–O1a	83.44(4)		

thiocyanate is almost linear with N–C–S angles ranging from 178.3(2) to 179.5(1)°. The N–C [1.147(2)–1.154(2) Å] and C–S [1.626(2)–1.638(2) Å] bond lengths are as expected for N-coordination of the anion [17].

An overall comparison of the MN_4O_2 polyhedra in **1**, **2**, and **3** reveals that the octahedron in **1** has a volume of 12.39 Å^3, a quadratic elongation of 1.016, and an angular variance, ζ [18] of 53.7°^{2}. The corresponding data for **2** are 12.50 Å^3, 1.018, and 57.2°^{2}, respectively, and for **3**, 12.68 Å^3, 1.023, and 70.5°^{2}, respectively. Apart from the slightly larger value of ζ for **3**, these values are similar, indicating that the degrees of distortion of the octahedra are more or less equal.

3.5. *Crystal packing*

The crystal packing in **1**, **2**, and **3** is largely achieved through N–H⋯O and N–H⋯S hydrogen bonds (table 5). In **1**, the NH_2 group of each symmetry-equivalent Ec ligand forms one

Table 5.   Hydrogen-bond parameters (Å and °) for **1–3**.

D–H⋯A	D–H (Å)	H⋯A (Å)	D⋯A (Å)	D–H⋯A (°)
Compound 1				
N1–H1A⋯O1[i]	0.91	2.54	3.4173(19)	162
N1–H1B⋯S1[ii]	0.91	2.73	3.4727(15)	140
N2–H2⋯S1[iii]	0.87	2.62	3.3003(16)	136
Compound 2				
N1A–H1A⋯S1A[i]	0.90	2.56	3.3812(18)	152
N1A–H2A⋯O1B[ii]	0.90	2.29	3.1130(19)	152
N2A–H3A⋯O1B[ii]	0.86	2.09	2.8758(18)	152
N1B–H1B⋯S1A[ii]	0.90	2.49	3.3654(17)	166
N1B–H2B⋯S1B[iii]	0.90	2.53	3.3700(16)	156
N2B–H3B⋯S1B[iv]	0.86	2.52	3.3776(18)	174
Compound 3				
N1A–H1A⋯S1A[i]	0.90	2.58	3.3797(13)	149
N1A–H2A⋯O1A[ii]	0.90	2.26	3.0936(15)	153
N2A–H3A⋯O1B[ii]	0.86	2.08	2.8734(14)	154
N1B–H1B⋯S1A[ii]	0.90	2.50	3.3739(14)	163
N1B–H2B⋯S1B[iii]	0.90	2.53	3.3763(12)	156
N2B–H3B⋯S1B[iv]	0.86	2.53	3.3827(14)	174

Note: Symmetry codes: for **1** (i) $x - 1$, y, z; (ii) $-x$, $1 - y$, $1 - z$; (iii) x, $y - 1$, z; for **2** and **3** (i) $-x - \frac{1}{2}$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (ii) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (iii) $-x$, $-y$, $-z$; (iv) $x + 1$, y, z.

weak N–H⋯O and one N–H⋯S hydrogen bond to an adjacent complex; at the same time, the complex accepts the same hydrogen bonds from its neighbors on both sides of the chain. This leads to [1 0 0] infinite chains of molecules (figure 4) incorporating centrosymmetric $R_2^2(8)$ loops for the N–H⋯O bonds and $R_2^2(12)$ loops for the N–H⋯S bonds. The [1 0 0] chains are cross-linked through the N2–H⋯S hydrogen bonds to form supramolecular [0 0 1] sheets (figure 5), which only interact by van der Waals' forces.

In isostructural **2** and **3**, the Mc ligands show quite different hydrogen-bonding behavior. Both the N1a and N2a of Mc form N–H⋯O hydrogen bonds to both O atoms of the
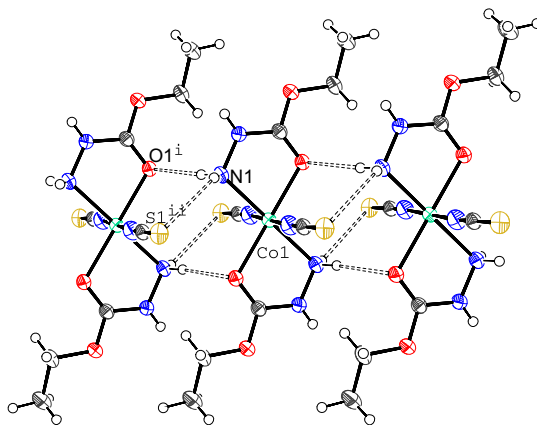

Figure 4:   Fragment of a [1 0 0] hydrogen-bonded chain in the crystal structure of **1** with hydrogen bonds shown as double-dashed lines. Symmetry codes: (i) $x - 1$, y, z; (ii) $-x$, $1 - y$, $1 - z$.
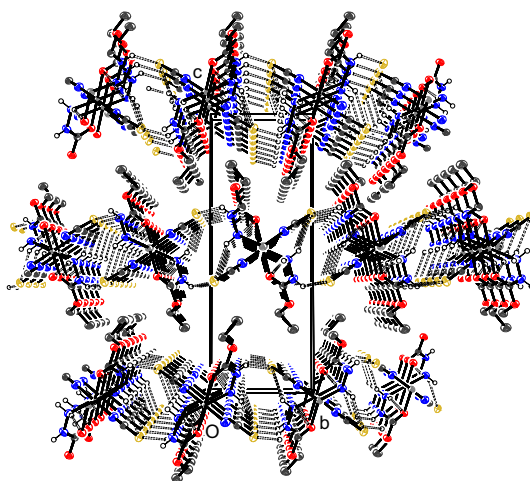
Figure 5: The unit-cell packing for **1** viewed approximately down [1 0 0] showing the [0 0 1] hydrogen-bonded sheets. The C-bonded hydrogens are omitted for clarity.

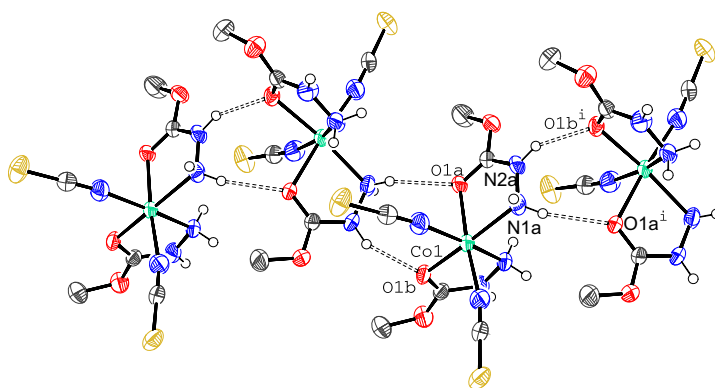Figure 6: Fragment of a [0 1 0] hydrogen-bonded chain in the crystal structure of **2** with hydrogen bonds shown as double-dashed lines. Symmetry code: (i) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$.

coordinated Mc ligands of the adjacent molecule. This results in [0 1 0] chains generated by a crystallographic 2_1 axis incorporating unusual $R_2^2(7)$ loops (figure 6). Compounds **2** and **3** also feature N–H⋯S hydrogen bonds, which lead to a 3-D network in the crystal.

4. Discussion

A Cambridge Structural Database [19] (version 5.34 of December 2012 with one update) survey of $[Co(NCS)_2L_2]$ (L = N,O-bidentate ligand) complexes revealed 10 structures with a *cis* conformation of the thiocyanate N atoms and three with a *trans* conformation. For example, $[Co(NCS)_2(C_9H_{11}NO_2)_2]$ ($C_9H_{11}NO_2$ = isopropyl pyridine-2-carboxylate) [20] and

[Co(NCS)$_2$(C$_7$H$_9$NO$_2$)$_2$] [C$_7$H$_9$NO$_2$ = 2,6-bis(hydroxymethyl)pyridine] [21] are *cis,* and [Co(NCS)$_2$(C$_{16}$H$_{24}$N$_2$OS)$_2$]   [C$_{16}$H$_{24}$N$_2$OS = 2-(3-(cyclohexylammonio)-propyliminomethyl)-phenolato] [22] is *trans*. However, none of the bidentate ligands in these complexes have close chemical similarity as Ec and Mc have in **1** and **2**. A similar survey for [Zn(NCS)$_2$L$_2$] structures revealed just two *cis* complexes, [Zn(NCS)$_2$(C$_7$H$_6$N$_2$O)$_2$] (C$_7$H$_6$N$_2$O = 2-pyridyl-amide) [23] and [Zn(NCS)$_2$(C$_{13}$H$_9$NOS)$_2$] [C$_{13}$H$_9$NOS = phenyl(pyridin-2-yl)methanone] [24], and one *trans* complex, [Zn(NCS)$_2$(C$_{13}$H$_{16}$CBrClN$_2$OS)$_2$] [C$_{13}$H$_{16}$CBrClN$_2$OS = 2-bromo-4-chloro-6-((2-isopropylammonioethylimino)methyl)phenolato] [25].

The previously reported crystal structures of Co^{2+} complexes with carbazate ligands are limited to simple molecular salts of [Co(Mc)$_3$]$^{2+}$ [26] or [Co(Ec)$_3$]$^{2+}$ *tris*-chelates [7(a)]. *Tris*-chelates of Zn^{2+} are known with both Mc [27] and Ec [28] ligands, as well as a coordination polymer with chelating Mc ligands and bridging formate ions [7(c)]. The M–N metal–carbazate bond distances reported for **1–3** are consistent with those in the literature [7(a)] and [26–28].

In [Co(Mc)$_3$]$^{2+}$ [26], the N–Co–O ligand bite angles lie between 77.60° and 78.72° (mean = 78.23°); two of the chelate rings are close to planar, and the other is twisted about the Co–N bond. There are four crystallographically distinct [Co(Ec)$_3$]$^{2+}$ cations in [Co(Ec)$_3$](NO$_3$)$_2$ [7(a)], and the mean ligand bite angle is 78.21° (range = 77.60°–78.96°). The 12 chelate rings adopt various conformations: Six are (near) planar and five are twisted about the Co–N bond; just one envelope conformation (with the NH$_2$ as the flap) is seen. In [Zn(Mc)$_3$]$^{2+}$ [27], the three chelate rings are close to planar, and the ligand bite angles are very similar (77.28°, 78.34°, and 78.36°; mean = 78.00°). For the two crystallographically distinct [Zn(Ec)$_3$]$^{2+}$ cations described in reference [28], the ligand bite angles are clustered in the narrow range 77.05°–78.17° (mean = 77.69°), but the chelate rings adopt a variety of conformations including near planar, an envelope with the NH$_2$ as the flap, and twisted about the Zn–N and C–O bonds. All these examples indicate that the carbazate chelate ring is relatively flexible and can adopt different conformations to presumably optimize crystal packing effects.

5. Conclusion

By varying the pendant alkyl group of the carbazate ligand (L) from methyl to ethyl, we were able to isolate *cis* and *trans* pseudo-isomers with equivalent M(NCS)$_2$L$_2$ formulas. These lead to completely different packing *motifs* in the crystals, although the same types of hydrogen bonds connect the molecules. Their physical properties are consistent with their crystal structures and corresponding data for related compounds reported previously.

Supplementary material

^{1}H and ^{13}C{^{1}H} NMR spectra for Mc and **3**; magnetic susceptibility plots for **1** and **2**, IR spectra of **1–3**, UV/visible spectra of **1** and **2**, and TGA/DTA traces for **1–3**. Full details of the crystal structures of **1** (CCDC 929867), **2** (CCDC 929868), and **3** (CCDC 929869) in cif format are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, or E-mail: deposit@ccdc.cam.ac.uk.

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Supplemental data

Supplemental data for this article can be accessed here. [http://dx.doi.org/10.1080/00958972.2014.965697]

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