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

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(Received 26 March 2013; accepted 29 July 2014)

Three heteroleptic divalent-metal alkyl-carbazate-thiocyanate complexes, [M(NCS)2(NH2NHCO-OR)2] [M = Co and R = CH2CH3 (1); M = Co and R = CH3 (2); M = Zn and R = CH3 (3)], have been prepared and characterized, and their crystal structures determined. In 1, Co(II) adopts a fairly regular centrosymmetric trans-CoO2N4 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-MO2N4 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, CoC8H16N6O4S2, Mr = 383.32, P21/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) Å³, Z = 2, R(F) = 0.028, wR(F2) = 0.073; 2, CoC6H12N6O4S2, Mr = 355.27, P21/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) Å³, Z = 4, R(F) = 0.036, wR(F2) = 0.097; 3, ZnC6H12N6O4S2, Mr = 361.71, P21/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) Å³, Z = 4, R(F) = 0.031, wR(F2) = 0.084.

Keywords: Coordination isomerism; Thiocyanate anion; Bidentate ligand; Crystal structure

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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 (NH₂NHC(O)OH), are of interest. These molecules contain NH₂ 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 (NH₂NHC(O)CH₂CH₃, 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 KIO₃, 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 ¹³C{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$_8$H$_{16}$N$_6$O$_4$S$_2$Co: N$_2$H$_4$, 16.70; NCS$^-$, 30.80; Co, 15.33; C, 25.04; H, 4.17; N, 21.91%. Found: N$_2$H$_4$, 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$_6$H$_{12}$N$_6$O$_4$S$_2$Co: N$_2$H$_4$, 18.03; NCS$^-$, 32.65; Co, 16.60; C, 20.27; H, 3.38; N, 23.64%. Found: N$_2$H$_4$, 18.70 (18.03); NCS$^-$, 32.10; Co, 16.40; C, 20.60; H, 3.60; N, 23.30%.

**Compound 3:** colorless, 70% yield. Anal. Calcd for C$_6$H$_{12}$N$_6$O$_4$S$_2$Zn: N$_2$H$_4$, 17.71; NCS$^-$, 32.07; Zn, 18.09; C, 19.91; H, 3.32; N, 23.22%. Found: N$_2$H$_4$, 17.10; NCS$^-$, 31.50; Zn, 17.40; C, 20.20; H, 3.10; N, 23.40%. $^1$H NMR (400 MHz, D$_2$O, $\delta$ in ppm): 3.67 (s, 3H). $^{13}$C NMR (400 MHz, D$_2$O, $\delta$ 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 $U_{	ext{iso}}$(H) = 1.2$U_{	ext{eq}}$(N atom) or 1.5$U_{	ext{eq}}$(C atom). The methyl groups were allowed to rotate, but not to tip, to best fit the electron density.

| Empirical formula | Co$_8$H$_{16}$N$_6$O$_4$S$_2$ (1) | Co$_8$H$_{12}$N$_6$O$_4$S$_2$ (2) | ZnC$_6$H$_{12}$N$_6$O$_4$S$_2$ (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)                      |
| $\beta$ (°)      | 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                               |
| $\rho_{\text{calc}}$ (g cm$^{-3}$) | 1.619                          | 1.644                          | 1.673                          |
| $\mu$ (mm$^{-1}$) | 1.380                          | 2.018                          | 2.018                          |
| $F(000)$         | 394                             | 724                            | 736                            |
| $R_{\text{int}}$ | 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 \([\text{M(NCS)}_2(\text{L})_2]\). All the compounds are highly soluble in water. The following general scheme represents the synthesis of 1, 2, and 3:

\[
\text{MX}_2 \cdot n\text{H}_2\text{O} + 2\text{NH}_4\text{SCN} + 2\text{L} \rightarrow [\text{M(NCS)}_2(\text{L})_2] + 2\text{NH}_4\text{X} + n\text{H}_2\text{O}
\]

where \(X = \text{Cl}^-\) or \(\text{NO}_3^-\); \(M = \text{Co}^{2+}\), \(L = \text{Ec}(1)\); \(M = \text{Co}^{2+}\), \(L = \text{Mc}(2)\); \(M = \text{Zn}^{2+}\), \(L = \text{Mc}(3)\).

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 \(\nu_{\text{asym}}(\text{CN})\) 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 \(\lambda_{\text{max}} = 510\) 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 \(\lambda_{\text{max}}\) values arising from the different dispositions of the ligands in 1 and 2.

In the \(^1\text{H}\) NMR spectrum of the Mc ligand, the methoxy protons are a singlet at \(\delta = 3.72\) ppm, whereas the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum shows two peaks at \(\delta = 52.52\) and 159.45 ppm due to the methoxy and carbonyl carbon, respectively. In both the \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra of 3, the downfield shift of all these peaks indicates coordination of the carbonyl O of Mc to Zn. In addition, the \(^{13}\text{C}\{^1\text{H}\}\) 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 \(\mu_B\), respectively, which are higher than the spin-only value of 3.88 \(\mu_B\). 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) $1-x$, $1-y$, $1-z$. 
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–NEc distance in 1 is 2.147(2) Å, whereas in 2 and 3, the pairs of M–NMc 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–Nt (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
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 MN₄O₂ polyhedra in 1, 2, and 3 reveals that the octahedron in 1 has a volume of 12.39 Å³, a quadratic elongation of 1.016, and an angular variance, ζ [18] of 53.7°². The corresponding data for 2 are 12.50 Å³, 1.018, and 57.2°², respectively, and for 3, 12.68 Å³, 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 NH₂ group of each symmetry-equivalent Ec ligand forms one
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

| Compound 1 | D–H (Å) | H⋯A (Å) | D⋯A (Å) | D–H⋯A (°) |
|------------|---------|---------|---------|----------|
| N1–H1A⋯O1i | 0.91    | 2.54    | 3.417(19) | 162      |
| N1–H1B⋯S1ii | 0.91   | 2.73    | 3.472(15) | 140      |
| N2–H2⋯S1iii | 0.87  | 2.62    | 3.300(16) | 136      |

| Compound 2 | D–H (Å) | H⋯A (Å) | D⋯A (Å) | D–H⋯A (°) |
|------------|---------|---------|---------|----------|
| N1A–H1A⋯S1Aii | 0.90  | 2.56    | 3.381(18) | 152      |
| N1A–H2A⋯O1Aii | 0.90  | 2.29    | 3.113(19) | 152      |
| N2A–H3A⋯O1Bii | 0.86  | 2.09    | 2.8758 (18) | 152     |
| N1B–H1B⋯S1Aii | 0.90  | 2.49    | 3.3654(17) | 166      |
| N1B–H2B⋯S1Biii | 0.90  | 2.53    | 3.3700(16) | 156      |
| N2B–H3B⋯S1Biv | 0.86  | 2.52    | 3.3776(18) | 174      |

| Compound 3 | D–H (Å) | H⋯A (Å) | D⋯A (Å) | D–H⋯A (°) |
|------------|---------|---------|---------|----------|
| N1A–H1A⋯S1Aii | 0.90  | 2.58    | 3.3797(13) | 149      |
| N1A–H2A⋯O1Aii | 0.90  | 2.26    | 3.0936(15) | 153      |
| N2A–H3A⋯O1Bii | 0.86  | 2.08    | 2.8734(14) | 154      |
| N1B–H1B⋯S1Aii | 0.90  | 2.50    | 3.3739(14) | 163      |
| N1B–H2B⋯S1Biii | 0.90  | 2.53    | 3.3763(12) | 156      |
| N2B–H3B⋯S1Biv | 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) $x + 1, y, z$.  

Table 5. Hydrogen-bond parameters (Å and °) for 1–3.
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 \([\text{Co(NCS)}_2\text{L}_2]\) (\(\text{L} = \text{N,O-bidentate ligand}\)) complexes revealed 10 structures with a cis conformation of the thiocyanate N atoms and three with a trans conformation. For example, \([\text{Co(NCS)}_2(\text{C}_9\text{H}_{11}\text{NO}_2)_2]\) (\(\text{C}_9\text{H}_{11}\text{NO}_2 = \text{isopropyl pyridine-2-carboxylate}\)) [20] and
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)2L2 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

1H and 13C{1H} 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.
Supplemental data

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

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