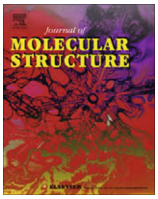
Journal of Molecular Structure 970 (2010) 19–26

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Synthesis and supramolecular structure of Zn, Cd, Hg complexes constructed by 2,3-naphtho-15-crown-5

Cheng-Juan Li, Ze-Jing Feng, Jian-Min Dou *, Da-Cheng Li, Da-Qi Wang

Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China

ARTICLE INFO

Article history:
Received 28 September 2009
Received in revised form 17 December 2009
Accepted 22 December 2009
Available online 4 January 2010

Keywords:
2,3-Naphtho-15-crown-5
Crystal structure
d^{10} metal complexes
Thiocyanato ligands
Weak interactions

ABSTRACT

Three novel crown ether complexes containing d^{10} metals and 2,3-naphtho-15-crown-5 (N15C5): $[Na(N15C5)H_2O]_2[Zn(NCS)_4]$ (**1**), $[Na(N15C5)]_2Cd_2(SCN)_6]$ (**2**) and $\{Na[Na(N15C5)]\}[Hg(SCN)_4]$ (**3**) have been prepared and characterized by elemental analysis, FT-IR spectra, UV–vis spectra and single-crystal X-ray diffraction. All the complexes are composed of complex cations of crown and anions of corresponding d^{10} metals bridged by SCN^- groups in different modes. Cooperative interactions of both coordinative bonds and weak interactions connect these ions to result into interesting supramolecular structures and these structures become more and more complicated with the central metals from Zn, Cd to Hg. In complex **1**, neighboring complex cations and complex anions interact with each other through O–H···S weak interactions, leading to three-dimensional supramolecular structures. In complex **2**, the μ_2 and μ_3-bridging SCN^- groups bridge Cd atoms into one-dimensional chains with crown cations attached above and below the chains, respectively. In complex **3**, tetrahedral $[Hg(SCN)_4]^{2-}$ hold both kinds of cations (crown cations and discrete alkali metal ions) together into a novel one-dimensional double-chain with large thickness of 10.32 Å, the section consisting of Na atoms are arranged with the sequence of Na1Na2Na2Na1 and interesting alternatively arranged sixteen- or eight-membered rings.

1. Introduction

Supramolecular coordination assemblies have been the subject of great interest in recent years owning to their potential application in catalysis, optical properties, clathration, etc. [1–3]. The crown ethers are promising for fabricating such supramolecular coordination assemblies due to their great unusual coordination numbers, especially those containing aromatic rings, which can act as building blocks to form 1D (one-dimensional) to 3D (three-dimensional) supramolecular structures by coordinative bonds, hydrogen bonds, π–π stacking, cation–π interactions and other weak interactions [4–8]. Previous papers from our laboratories have described the syntheses and supramolecular structures of the naphtho crown ether complexes, such as: $[Na(N15C5)]_2[Pd(SCN)_4]$, $[Na(N15C5)]_2[Pt(SCN)_4]$ [9], $[Na(N15C5)_2]_2[Pt(mnt)_2]$, $[Na(N15C5)]_2[Pt(i\text{-}mnt)_2]$ [10], $[Na(N15C5)]_2[Cu(mnt)_2]$ [11], $[Na_2(N15C5)_2(NO_3)][Cu(NO_3)_3(H_2O)]$ [12], $[Na(N15C5)_2]_2[Ni(mnt)_2]$ [13], $[Na(N15C5)]_2[Ni(mnt)_2]$ [13], which are assembled by the π–π stacking interactions between the naphthylene moieties.

In addition, thiocyanato ligand has been widely used to construct coordination polymers with the properties of a polarizable π system and two different donor atoms N and S, which can exhibit diverse coordination or bridging modes to hard or adjacent acid (such as Mn^{2+}, Co^{2+}, Ni^{2+}, etc.) through N atom and soft acid (such as Cd^{2+}, Cu^+, Hg^{2+}, etc.) through S atom or different bridging modes to construct novel topologies and various types of supramolecular structures with particular properties [14–17].

In the present paper we extended the work on the preparation and structures of naphtho crown ether complexes, and carried out the reactions of N15C5 with $ZnCl_2$, $CdCl_2·2.5H_2O$ and $HgCl_2$ with the presence of NaSCN. Three novel complexes $[Na(N15C5)H_2O]_2[Zn(NCS)_4]$ (**1**), $[Na(N15C5)][Cd(SCN)_3]$ (**2**) and $\{Na[Na(N15C5)]\}[Hg(SCN)_4]$ (**3**) were obtained and characterized. Structural analysis indicated they possess interesting 0D and 1D structures due to the diverse coordination mode of both thiocyanato groups and d^{10} metal centers.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were commercially purchased and used without further purification. N15C5 [18] was prepared as the literature. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 II Elemental Analyzer. FT-IR spectra were

---

* Corresponding author. Tel.: +86 0635 8239069; fax: +86 0635 8239121.
E-mail address: jmdou@lctu.edu.cn (J.-M. Dou).

0022-2860/$ - see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.molstruc.2009.12.036

recorded in the range 400–4000 cm^{-1} with a Nicolet-460 FT-IR spectrophotometer using KBr pellets. UV–vis spectra were performed on HP-8453 UV–vis spectrophotometer in DMSO.

Caution! Due to the high toxicity, carefulness should be needed when dealing with Cd and Hg salts.

2.2. Preparation of $[Na(N15C5)(H_2O)]_2[Zn(NCS)_4]$ (**1**)

Complex **1** was prepared by adding 10 mL aqueous mixture of $ZnCl_2$ (0.034 g, 0.25 mmol) and NaSCN (0.81 g, 10 mmol) to a solution of N15C5 (0.16 g, 0.5 mmol) in 10 mL dichloromethane. The reaction mixture was stirred for 2 h at room temperature and filtrated. The precipitate was dissolved in CH_3CN. The single crystal was obtained by slowly evaporating the solution after a week. Yield: 82% (based on Zn). m.p. > 300 °C. (Found: C, 47.16; H, 4.60; N, 5.66%. Calcd. for $C_{40}H_{48}N_4Na_2O_{12}S_4Zn$. C, 47.23; H, 4.72; N, 5.51%). Selected FT-IR: v/cm^{-1} 3466(m), 3036(w), 2918(m), 2878(m), 2079(vs), 1630(m), 1603(w), 1508(m), 1487(m), 1452(m), 1383(w), 1253(s), 1168(s), 1115(vs), 1095(m), 1052(m), 936(m), 862(m), 755(m), 618(m), 427(m). UV–vis (DMSO, λ_{max}, nm, ε, $M^{-1}cm^{-1}$): 226, 325.

2.3. Preparation of $[Na(N15C5)]_2[Cd_2(SCN)_6]$ (**2**)

The reaction of complex **2** is analogous to that of **1**, using $CdCl_2 \cdot 2.5H_2O$ instead of $ZnCl_2$. Yield: 79% (based on Cd). m.p. > 300 °C. (Found: C, 40.05; H, 3.59; N, 6.72%. Calcd. for $C_{42}H_{44}Cd_2N_6Na_2O_{10}S_6$. C, 40.13; H, 3.50; N, 6.69%). Selected FT-IR: v/cm^{-1} 3036(w), 2924(m), 2875(m), 2120(vs), 1631(m), 1603(w), 1507(m), 1478(m), 1454(m), 1384(m), 1255(s), 1160(m), 1116(s), 1088(m), 934(m), 828(m), 745(m), 619(m), 474(m). UV–vis (DMSO, λ_{max}, nm, ε, M^{-1} cm^{-1}): 226, 325.

2.4. Preparation of $[Na(N15C5)]Na\ [Hg(SCN)_4]$ (**3**)

The reaction of complex **3** is analogous to that of **1**, using $HgCl_2$ instead of $ZnCl_2$. Yield: 69% (based on Hg), m.p. > 300 °C. (Found: C, 33.01; H, 2.86; N, 7.10%. Calcd. for $C_{22}H_{22}HgN_4Na_2O_5S_4$, C, 33.11; H, 2.76; N, 7.02%). FT-IR (KBr, cm^{-1}): 3036(w), 2923(m), 2876(m), 2126(s), 2114(vs), 2074(s), 1629(m), 1603(w), 1510(m), 1483(m), 1457(m), 1384 (m), 1257(s), 1173(m), 1115(s), 1090(m), 943(m), 863(m), 750(m), 618(m), 476(m). UV–vis (DMSO, λ_{max}, nm, ε, M^{-1} cm^{-1}): 228, 325.

2.5. Determination of crystal structure

Suitable single crystals of **1**, **2** and **3** were glued to fine glass fibers, respectively, and were then mounted on Bruker Smart-1000 CCD diffractometer with Mo-K_α (radiation, 0.71073 Å). The intensity data were collected at 298 ± 2 K. The structures were solved by direct methods and expanded using Fourier techniques with SHELXL-97 program [19]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were added theoretically, riding on the concerned atoms and not refined. No information is given about the localization of the water molecule's hydrogen atoms. Detailed information about crystal data and structure determinations are summarized in Table 1.

3. Results and discussion

3.1. FT-IR and electronic spectra

The band at 3036 cm^{-1} is clearly due to the ν(Ar—H) vibrations of the naphthylene moiety in **1**, **2** and **3**. The bands due to δ(Ar—H) vibrations of naphthylene group appear at 745, 755 and 750 cm^{-1} for complexes **1**, **2** and **3**, respectively. The $\delta(CH_2CH_2)$ and $\nu(CH_2CH_2)$ vibrations of N15C5 in the three complexes take place at 1452, 1454, 1384 cm^{-1} and 2875, 2924 cm^{-1}, respectively. Bands in the region of 1088–1257 cm^{-1} are characteristic of C—O—C groups of N15C5 in three complexes. For the three complexes, the characteristic peaks at 1630, 1603, 1510 and 1487 cm^{-1} are assigned to the ν(CC) vibrations of the naphthylene group, which are comparable to the ν(CC) vibrations of the naphthylene group of N9C3 (1469–1625 cm^{-1}) [20]. The $\nu(C{\equiv}N)$ vibrations of SCN^- in complexes **1, 2** and **3** are observed at 2079, 2120 and 2114 cm^{-1}, respectively, which are similar to that of $[Na(N15C5)]_2[M(SCN)_4]$ (M = Pd, Pt) (2109, 2107 cm^{-1}, respectively) [9].

Table 1
Crystal data and structure refinement for complexes **1**, **2** and **3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{40}H_{48}N_4Na_2O_{12}S_4Zn$	$C_{42}H_{44}Cd_2N_6Na_2O_{10}S_6$	$C_{22}H_{22}HgN_4Na_2O_5S_4$
Formula weight	1016.41	1255.97	797.25
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	23.021(8)	10.540(2)	8.382(2)
b (Å)	13.200(4)	11.483 (2)	10.928(2)
c (Å)	17.499(6)	11.702(2)	16.550(3)
α (°)	90	90.877(2)	81.095(3)
β (°)	115.248(4)	107.684(2)	75.774(3)
γ (°)	90	108.050(2)	83.425(3)
V (Å^3)	4810(3)	4018(5)	1187.2(8)
Z	4	1	2
D_{cald} (g cm^{-3})	1.404	1.638	1.830
μ (mm^{-1})	0.763	1.157	5.676
$F(0\,0\,0)$	2112	632	776
Crystal size (mm)	0.50 × 0.48 × 0.41	0.49 × 0.45 × 0.43	0.45 × 0.37 × 0.19
θ range (°)	1.96–25.01	1.84–25.01	1.89–25.01
Limiting indices $h/k/l$ (min, max)	−27, 27/−15, 15/−20, 20	−12, 12/−13, 9/−13, 12	−9, 8/−11, 13/−18, 19
Reflections collected	12,406	6676	7595
Independent reflections (R_{int})	4229 (0.0401)	4433 (0.0213)	5018 (0.0381)
Data/restraints/parameters	4229/3/286	4433/0/307	5018/0/343
GoF	1.004	1.002	1.007
R_1, wR_2 [$I > 2\sigma(I)$]	0.0375, 0.0798	0.0284, 0.0691	0.0498, 0.1233
R_1, wR_2 (all data)	0.0680, 0.0964	0.0373, 0.0753	0.0617, 0.1322
Largest diff. peak and hole (e Å^{-3})	0.385 and −0.391	0.477 and −0.597	2.215 and −2.250