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One dimensional coordination polymers generated from Cd(II) tri-*tert*-butoxysilanethiolates and flexible aliphatic diamines

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ABSTRACT

This work concerns the coordination chemistry of cadmium(II) tri-*tert*-butoxysilanethiolates in the presence of aliphatic diamines. Reactions of the binuclear $[Cd\{SSi(OtBu)_3\}_2]_2$ with the respective diamines yielded five new neutral one-dimensional coordination polymers, $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_4H_{12}N_2)(CH_3OH)]_n$ (**1**), $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_5H_{14}N_2)(CH_3OH)]_n$ (**2**), $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_6H_{16}N_2)(CH_3OH)]_n$ (**3**), $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_7H_{18}N_2)]_n$ (**4**) and $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_8H_{20}N_2)]_n$ (**5**), which adopt different spatial chain topologies. The new polymers were fully characterized by X-ray single-crystal diffraction, elemental analysis and IR spectroscopy. The thermal stabilities of complexes (**1**), (**3**) and (**4**) complexes were studied by thermogravimetry (TG, DTG).

1. Introduction

Complexes of d^{10} metal ions, for example cadmium, arouse considerable attention from researchers. The stereochemical flexibility and ability to coordinate various types of ligands lead to cadmium compounds that exhibit interesting structural features and potential applications, for instance in light emitting diodes (LEDs), biomedical analyses, fluorescence, cancer phototherapy, gas adsorbents or catalysts [1–12].

The design of artificial self-assembling systems requires a deep knowledge of many factors, such as the preference of metal ions for specific coordination environments, ligand geometry and relative orientation of donor groups as well as reaction conditions, *e.g.* temperature of the synthesis or solvent polarity [13–17]. In the synthesis of various organic–inorganic networks the most extensively explored are bipyridyl derivatives, which play the role of rigid linkers. Because of their abundant coordination modes to metal ions they allow diverse structural topologies with transition metals to be obtained as well as complicated supramolecular networks through aromatic interactions [18–20].

For many years we have been interested in the syntheses of metal complexes that contain silanethiolate residues. The most investigated silanethiol is the sterically hindered tri-*tert*-butoxysilanethiol $(tBuO)_3SiSH$, which is relatively stable under atmospheric conditions [21] and applied as an S-ligand in the syntheses of complexes enables numerous mono-, bi- and polynuclear metal tri-*tert*-butoxysilanethiolates to be obtained [22–31]. This particular silanethiol was used in synthesizing biomimetic complexes that imitate the structure and geometry of the active sites found in some metalloproteins [32–40], as well as in the design and construction of coordination polymers. We have carried out reactions of Co(II), Cd(II) and Zn(II) tri-*tert*-butoxysilanethiolates with bidentate 4,4′-bipy, pyrazine and quinoxaline ligands, and so far we have obtained only one coordination polymer, $[Co\{\mu\text{-}SSi(tBuO)_3\}\{SSi(tBuO)_3\}(\mu\text{-}4,4'\text{-bipy})]_n$, and several binuclear silanethiolates with metallic centers bridged by bidentate ligands [41–44]. Recently, we have considered non-rigid ligands, like aliphatic diamines, to be excellent candidates as building elements in multidimensional networks. Their conformational flexibility and ability to act as H-bond acceptors and donors may lead to the formation of supramolecular structures with unusual topological structures. For our experiments we chose bimetallic and neutral cadmium tri-*tert*-butoxysilanethiolate $[Cd\{SSi(OtBu)_3\}_2]_2$ [45] and a group of flexible aliphatic diamines, varying in the number of carbon atoms in the chain, for the purpose of checking whether there are some structural relationships between the length of the flexible chain of the N-donor ligands used in the syntheses and the topologies of the potentially obtained complexes.

Despite the wealth of experimental data on bipyridyl complexes, there is nothing about the use of aliphatic diamines for the construction of coordination polymers. Moreover, there is no information about compounds that contain thiolate residues and aliphatic diamines coordinated simultaneously to a metallic center. There is only *Saber's* work describing three 1D cadmium thiocyanato complexes with a SCN residue as a bridging element [46].

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As a result of our experiments we have obtained five novel and neutral heteroleptic cadmium tri-*tert*-butoxysilanethiolates with polymeric structures and bidentate aliphatic diamines as linkers. Herein we describe their syntheses, crystal structures, spectral and thermal analysis. All the obtained complexes are stable under atmospheric conditions and show various spatial arrangements of the polymeric chains.

2. Experimental

2.1. Materials

Tri-*tert*-butoxysilanethiol and $[Cd\{SSi(OtBu)_3\}_2]_2$ were synthesized as reported previously [21,45]. All other starting materials were obtained from commercial sources without further purification.

2.2. Synthesis

Complexes (**1**)–(**5**) were obtained using the same synthetic procedure. To a solution of $[Cd\{SSi(OtBu)_3\}_2]_2$ (1.34 g, 1 mmol) dissolved in 20 mL of methanol, the respective amine [(**1**) 1,4-diaminobutane (0.21 mL, 2 mmol), (**2**) 1.5-diaminopentane (0.24 mL, 2 mmol), (**3**) 1,6-diaminohexane (0.24 g, 2 mmol), (**4**) 1,7-diaminoheptane (0.24 g, 2 mmol) and (**5**) 1,8-diaminooctane (0.29 g, 2 mmol)] was added. The resultant mixtures were left at room temperature for a few days to yield colorless crystals of complexes (**1**)–(**5**), stable under atmospheric conditions.

2.2.1. $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_4H_{12}N_2)\cdot(CH_3OH)]_n$ (**1**)

Anal. Calc. for $C_{29}H_{68}S_2Si_2O_7N_2Cd$: C, 44.00; H, 8.91; S, 8.10; N, 3.54. Found: C, 44.02; H, 8.70; S, 8.40; N, 3.68%. M. p. 163–164 °C. IR (solid state) ν (cm^{-1}): 3321 (s), 3261 (s), 3170 (s), 2982 (vs), 2928 (vs), 2871 (s), 1591 (s), 1471 (s), 1386 (vs), 1362 (vs), 1239 (vs), 1177 (vs), 1042 (vs br), 1014 (vs), 965 (vs), 911 (m), 822 (s), 802 (s).

2.2.2. $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_5H_{14}N_2)(CH_3OH)]_n$ (**2**)

Anal. Calc. for $C_{30}H_{72}S_2Si_2O_7N_2Cd$: C, 44.73; H, 9.00; S, 7.96; N, 3.48. Found: C, 44.69; H, 8.98; S, 7.98; N, 3.47%. M. p. 175–176 °C. IR (solid state) ν (cm^{-1}): 3329 (s), 3261 (s), 3179 (w), 2975 (vs), 2935 (vs), 2898 (s), 1600 (s), 1471 (s), 1388 (vs), 1362 (vs), 1240 (vs), 1193 (vs), 1057 (vs), 1137 (vs), 997 (vs), 928 (w), 822 (s), 813 (m), 700(s).

2.2.3. $[Cd_2\{SSi(OtBu)_3\}_4(\mu\text{-}C_6H_{16}N_2)]_n$ (**3**)

Anal. Calc. for $C_{54}H_{124}S_4Si_4O_{12}N_2Cd_2$: C, 44.45; H, 8.57; S, 8.79; N, 1.92. Found: C, 45.74; H, 8.98; S, 8.15; N, 3.51%. M. p. 153–155 °C. IR (solid state) ν (cm^{-1}): 3497 (m), 3342 (s), 3267 (s), 3156 (w), 2969 (vs), 2928 (vs), 2863 (vs), 2704 (w), 1630 (s), 1590 (s), 1470 (s), 1387 (vs), 1363 (vs), 1238 (vs), 1186 (vs br), 1017 (vs br), 1014 (vs), 908 (m), 819 (s), 801 (s).

2.2.4. $[Cd\{SSi(OtBu)_3\}_2(\mu\text{-}C_7H_{18}N_2)]_n$ (**4**)

Anal. Calc. for $C_{31}H_{72}S_2Si_2O_6N_2Cd$: C, 46.45; H, 9.05; S, 8.00; N, 3.49. Found: C, 46.39; H, 8.98; S, 8.01; N, 3.50%. M. p. 152–154 °C. IR (solid state) ν (cm^{-1}): 3337 (s), 3302 (s), 3260 (s), 3237 (m), 3133 (w), 2972 (vs), 2927 (vs), 2870 (s), 2764 (w), 2699 (w), 1586 (s), 1471 (s), 1456 (s), 1386 (vs), 1361 (vs), 1239 (vs), 1187 (vs), 1056 (vs), 1042 (vs), 1022 (s), 1001 (vs), 987 (vs), 909 (m), 820 (s), 802 (s), 747 (w), 725 (w).

2.2.5. $[Cd_2\{SSi(OtBu)_3\}_4(\mu\text{-}C_8H_{20}N_2)]_n$ (**5**)

Anal. Calc. for $C_{56}H_{128}N_2O_{12}S_4Si_4Cd_2$: C, 45.23; H, 8.67; S, 8.62; N, 1.88. Found: C, 45.35; H, 8.68; S, 8.61; N, 1.91%. M. p. 139–140 °C. IR (solid state) ν (cm^{-1}): 3342 (m), 3278 (m), 2977 (vs), 2933 (vs), 2887 (s), 1727 (w), 1589 (s), 1474 (s), 1388 (vs), 1364 (vs), 1241 (vs), 1186 (vs), 1103 (w), 1043 (vs), 1019 (s), 933 (m), 825 (s), 824 (s).

Table 1
Crystallographic data and structure refinement for complexes (**1**)–(**5**).

	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
Empirical formula	$C_{29}H_{70}CdN_2O_7S_2Si_2$	$C_{30}H_{72}CdN_2O_7S_2Si_2$	$C_{108}H_{248}Cd_4N_4O_{24}S_8Si_8$	$C_{31}H_{72}CdN_2O_6S_2Si_2$	$C_{56}H_{128}Cd_2N_2O_{12}S_4Si_4$
M_r (g mol^{-1})	791.57	805.60	2917.90	801.561	1487.00
T (K)	298(2)	120(2)	120(2)	120(2)	120(2)
λ (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1$
a (Å)	9.0876(3)	10.0393(3)	48.1097(9)	10.2109(3)	14.0835(3)
b (Å)	16.8473(5)	14.6229(6)	14.4214(2)	13.5526(5)	19.4941(4)
c (Å)	29.8773(8)	16.8956(5)	25.2096(5)	15.4806(5)	15.3310(4)
α (°)	90	113.520(4)	90.0	89.220(3)	90.0
β (°)	106.875(3)	96.729(3)	117.382(2)	81.646(3)	109.126(3)
γ (°)	90	102.267(3)	90.0	83.857(3)	90.0
V (Å$^{3)}$	4377.3(2)	2165.15(13)	15531.0(5)	2107.37(12)	3976.71(16)
Z	4	2	4	2	2
D_{calc} (Mg m^{-3})	1.201	1.236	1.248	1.263	1.242
θ range (°)	2.34 to 25.50	2.46 to 25.50	2.23 to 25.50	2.26 to 25.50	2.52 to 25.50
Limiting indices	$-11 \leqslant h \leqslant 9$ $-20 \leqslant k \leqslant 20$ $-36 \leqslant l \leqslant 30$	$-12 \leqslant h \leqslant 11$ $-13 \leqslant k \leqslant 17$ $-20 \leqslant l \leqslant 20$	$-58 \leqslant h \leqslant 58$ $-11 \leqslant k \leqslant 17$ $-30 \leqslant l \leqslant 29$	$-9 \leqslant h \leqslant 12$ $-16 \leqslant k \leqslant 16$ $-18 \leqslant l \leqslant 18$	$-15 \leqslant h \leqslant 17$ $-20 \leqslant k \leqslant 23$ $-18 \leqslant l \leqslant 8$
Reflections collected/unique	16311/8132	13419/8048	54085/14477	12998/7839	15643/12953
R_{int}	0.0266	0.0275	0.0250	0.0244	0.0187
Completeness to θ_{max}/%	99.9	99.9	99.9	99.9	99.9
μ (mm^{-1})	0.686	0.695	0.765	0.712	0.748
Data/restraints/parameters	8132/19/412	8048/6/481	14477/8/833	7839/0/431	12953/1/757
Goodness-of-fit (GOF) on F^2	1.066	1.092	1.059	1.055	1.051
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0742$ $wR_2 = 0.2042$	$R_1 = 0.0592$ $wR_2 = 0.1540$	$R_1 = 0.0352$ $wR_2 = 0.0866$	$R_1 = 0.0386$ $wR_2 = 0.0950$	$R_1 = 0.0333$ $wR_2 = 0.0854$
R indices (all data)	$R_1 = 0.0823$ $wR_2 = 0.2115$	$R_1 = 0.0716$ $wR_2 = 0.1604$	$R_1 = 0.0441$ $wR_2 = 0.0913$	$R_1 = 0.0469$ $wR_2 = 0.0984$	$R_1 = 0.0361$ $wR_2 = 0.0867$
Largest difference in peak and hole (e Å^{-3})	3.277 and −1.048	2.171 and −0.774	1.189 and −0.832	0.840 and −0.423	1.353 and −0.623