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Coordination polymers of azido and thiocyanato Cd(II) and Zn(II) complexes based on 2,6-lutidine-*N*-oxide. Synthesis, characterization and luminescent properties

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ABSTRACT

The synthesis and structural characterization of the complexes *catena*-[Cd(2,6-lutidine-*N*-oxide)($\mu_{1,1}$-N_3)($\mu_{1,1,1}$-N_3)] (**1**), *catena*-[Cd(μ_2-2,6-lutidine-*N*-oxide)($\mu_{1,3}$-NCS)$_2$] (**2**), *catena*-[Zn(2,6-lutidine-*N*-oxide)($\mu_{1,1}$-N_3)$_2$] (**3**) and [Zn(2,6-lutidine-*N*-oxide)$_2$(NCS)$_2$] (**4**) where 2,6-lutidine = 2,6-dimethylpyridine-*N*-oxide, are reported. Single crystal X-ray crystallography revealed the polymeric nature of complexes **1**, **2**, and **3** as a 1D double chains "ladder of defective cubane", 2D with doubly μ(O,O) bridging of 2,6-lutidine-*N*-oxide and 1D, respective, and the monomeric nature of **4**. The emission spectral properties of the complexes were investigated and fluorescence enhancement was observed for complexes **2**–**4**.

1. Introduction

Small pseudo halide ions such as azide and thiocyanate have been the target over many years for the construction of coordination polymers (CPs) and polynuclear metal complexes due to their abilities to bind metal ions in a variety of coordination modes which led to the isolation of metal complexes with different topologies and frameworks [1–13]. In addition, these ligands have the ability to transmit the magnetic interaction when they are bridging paramagnetic centers and hence resulted in interesting magnetic properties [2–11]. The azide ion is a versatile ligand that can bridge metal ions in many different coordination bonding modes which include symmetric and asymmetric double bridges $\mu_{1,3}$-N_3^- (end-on-end, EE) [5–13] and $\mu_{1,1}$-N_3^- (end-on, EO) [5,9–11,14–23], $\mu_{1,1,3}$-N_3^-, $\mu_{1,1,1}$-N_3^-, $\mu_{1,1,1,1}$-N_3^-, $\mu_{1,1,2,2}$-N_3^-, and $\mu_{1,1,1,3,3,3}$-N_3^- [1–7], however, these modes are relatively limited in bridging thiocyanato complexes: $\mu_{1,3}$-NCS$^-$, $\mu_{1,1}$-NCS$^-$, $\mu_{3,3}$-NCS$^-$, $\mu_{1,1,3}$-NCS$^-$, $\mu_{1,3,3}$-NCS$^-$ and $\mu_{1,3,3,3}$-NCS$^-$ [7–10]. The observed different bonding modes for N_3^- and NCS$^-$ ligands were summarized recently [1,2,6,11]. The preference of a metal ion for adapting a specific coordination mode obviously depends mainly not only on the nature of metal ion but also on the skeletal nature of the coordinated ancillary coligand(s) as well as the steric environment imposed by these ligands [1–3,7].

The d^{10} metal ions Cd^{2+} and Zn^{2+} have different Lewis acidic properties. While Cd^{2+} behaves as hard acid, Zn^{2+} is on the border line between as a hard and soft Lewis acid. Therefore, a ligand such as NCS$^-$ with *N*-intermediate/*S*-soft Lewis base character would have a higher preference to bind Zn^{2+} from its N-terminal side, whereas Cd^{2+} has its highest preference to coordinate to the S-atom of the NCS$^-$ ion [12,13]. Due to the luminescent properties of this group of metal ions, a large number of Cd(II) and Zn(II) compounds have been synthesized with pseudohalide ligands [1,2,13–17], hoping to find some photochemical applications. In general, some Zn(II) and Cd(II) complexes, especially those derived from *N*-donor heterocyclic bases were shown to enhance or quench the fluorescence emission of the organic ligand [2,16,17]. The enhancement of fluorescence phenomenon through complexation attracts more attention because of the possible use of these complexes as photochemical devices [18].

In a continuous effort to explore the luminescent properties of azido and thiocyanato metal complexes of 3d^{10} and 4d^{10} of group 12 with pyridine-*N*-oxide compounds our intention is to combine the diverse coordination modes of the pseudohalide ligands (N_3^- and SCN$^-$) and to use pyridine-*N*-oxides as coligands which can

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coordinate metal ions through the oxygen atom of the N-oxide group to produce the common coordination mode of bonding as mono-dentate ligand or may act as a bridging ligand to simultaneously bind two metals, M–O(N)–M to afford the less common coordination mode. Therefore, herein we report the synthesis and structural characterization of a new series of Cd(II) and Zn(II) coordination polymers (**1**–**3**) and a mononuclear Zn(II) complex (**4**) based on 2,6-dimethylpyridine-*N*-oxide. The luminescent properties of the complexes were investigated at room temperature.

2. Experimental

2.1. Materials and physical measurements

2,6-Dimethylpyridine-*N*-oxide (2,6-lutidine-*N*-oxide, 2,6-lut-*N*-oxide) was purchased from TCI and the other chemicals were of analytical grade quality. Infrared spectra of solid complexes were recorded on a Bruker Alpha P (platinum-ATR-cap). UV–Vis–NIR spectra were performed with a LS950 Perkin–Elmer Lambda-spectrometer in the range from 4000 to 45 000 cm^{-1} (pulsed D_2O lamp). Emission Spectra were recorded with a Perkin–Elmer LS55 spectrofluorometer. Powder X-ray diffraction measurements were done with a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å) to check for purity of the phases of the title complexes (see Supplementary section). Elemental microanalyses were carried out with an Elementar Vario EN3 analyser.

Caution: Salts of azides and their metal complexes are potentially explosive and should be handled with great care and in small quantities. "Especially dry, crystalline Zn(N_3)$_2$ is extremely sensitive to shock and friction and can explode violently upon the slightest provocation" [19].

2.2. Synthesis of the complexes

2.2.1. Synthesis of catena-[Cd(2,6-lutidine-N-oxide)($\mu_{1,1}$-N_3)($\mu_{1,1,1}$-N_3)] (1)

A mixture of cadmium(II) sulfate hydrate (0.52 g, 1.96 mmol), 2,6-dimethylpyridine-*N*-oxide (0.31 g, 2.21 mmol) and NaN_3 (0.27 g, 4.15 mmol) was dissolved in 25 mL distilled water at room temperature. The solution was allowed to stand at 4 °C in the refrigerator. After two weeks, the yellow crystals which separated were collected by filtration and dried in air (yield: 0.32 g, 50%). *Anal.* Calc. for $C_7H_9CdN_7O$ (319.52 g/mol): C, 26.3; H, 2.8; N, 30.7. Found: C, 26.1; H, 2.8; N, 30.8%. Selected IR bands (ATR-IR, cm^{-1}): 2086 (vs), 1618 (w), 1574 (w), 1491 (m), 1457 (m), 1419 (m), 1376 (w), 1331 (w) 1304 (m), 1280 (w), 1220 (s) ν(O–N); 1162 (w), 1097 (w), 1029 (w), 993 (w), 906 (w), 835 (s), 778 (s), 689 (w), 650 (w), 626 (m), 599 (w), 571 (w), 524 (m).

2.2.2. Synthesis of catena-[Cd(μ_2-2,6-lutidine-N-oxide)($\mu_{1,3}$-NCS)$_2$] (2)

This complex was synthesized essentially as described for complex **1** except KSCN (0.39 g, 4.11 mmol) was used instead of NaN_3. The solution was allowed to stand at room temperature, where yellow crystals were separated by filtration (yield: 0.53 g, 76%). *Anal.* Calc. for $C_9H_9CdN_3OS_2$ (351.72 g/mol): C, 30.7; H, 2.6; N, 11.9. Found: C, 30.9; H, 2.9; N, 11.3%. Selected IR bands (ATR-IR, cm^{-1}): 2105 (vs), 1618 (w), 1581 (m), 1492 (m), 1387 (w), 1186 (s), 1102 (m), 1033 (w), 993 (w), 938 (w), 912 (w), 824 (s), 786 (s), 680 (m), 567 (w), 541 (w), 520 (m), 493 (w), 465 (m).

2.2.3. Synthesis of catena-[Zn(2,6-lutidine-N-oxide)($\mu_{1,1}$-N_3)$_2$] (3)

A mixture of $ZnSO_4 \cdot 7H_2O$ (2.59 g, 9.01 mmol), 2,6-dimethylpyridine-*N*-oxide (0.37 g, 3.00 mmol) and NaN_3 (1.22 g, 18.77 mmol) were dissolved in 20 mL distilled water. Colorless crystals were separated upon standing at room temperature for one day (yield: 0.47 g, 57%). These were collected by filtration and air dried. *Anal.* Calc. for $C_7H_9N_7OZn$ (272.58 g/mol): C, 30.8; H, 3.3; N, 36.0. Found: C, 30.7; H, 3.2; N, 36.1%. Selected IR bands (ATR-IR, cm^{-1}): 3351 (w), 3065 (w), 2639 (w), 2088 (vs), 2055 (vs), 1619 (w), 1581 (w), 1496 (m), 1454 (m), 1427 (w), 1384 (w), 1355 (m), 1294 (s), 1202 (s) ν(O–N); 1102 (m), 1029 (m), 990 (m), 926 (w), 834 (s), 784 (s), 718 (w), 668 (m), 600 (m), 573 (w), 532 (s).

2.2.4. Synthesis of [Zn(2,6-lutidine-N-oxide)$_2$(NCS)$_2$] (4)

A mixture of $ZnSO_4 \cdot 7H_2O$ (2.59 g, 9.00 mmol), 2,6-dimethylpyridine-*N*-oxide (0.41 g, 3.32 mmol) and KSCN (1.75 g, 18.00 mmol) were dissolved in 28 mL of distilled water. The resulting solution was then allowed to stand at room temperature. After 11 days, the colorless crystals which separated were collected by filtration (yield: 1.414 g, 55%). *Anal.* Calc. for $C_{16}H_{18}N_4O_2S_2Zn$ (427.85 g/mol): C, 44.9; H, 4.2; N, 13.1. Found: C, 45.3; H, 4.1; N, 12.8%. Selected IR bands (ATR-IR, cm^{-1}): 3383 (m, br), 2362 (w), 2073 (s), 2044 (vs), 1617 (m), 1577 (m), 1519 (w), 1492 (s), 1455 (s), 1420 (m), 1377 (m), 1277 (w), 1197 (s), 1163 (m), 1091 (m), 1034 (m), 992 (m), 963 (w), 922 (w), 829 (s), 785 (s), 683 (m), 616 (w), 571 (w), 548 (m), 524 (s), 482 (m).

2.3. X-ray crystal structure analysis

The X-ray single-crystal data of compounds **1**–**4** were collected on a Bruker-AXS APEX CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. The intensities were collected with Mo Kα radiation (λ = 0.71073 Å). Data processing, Lorentz-polarization and absorption corrections were performed using APEX, and the SADABS computer programs [20]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2, using the SHELXTL [21] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. For **1**, the Flack absolute structure parameter was refined to 0.02(4). Molecular plots were performed with the Mercury program [22].

3. Results and discussion

3.1. Synthesis of the complexes

Synthesis of the azido and thiocyanato Cd(II) or Zn(II) complexes **1**–**4** was very straight forward where an aqueous solution containing Cd(II) or Zn(II) sulfate, 2,6-dimethylpyridine-*N*-oxide and NaN_3 or KSCN were allowed to react at room temperature. The crystalline complexes, which were obtained in moderate yields (50–75%), were characterized by the elemental microanalyses, IR and by X-ray crystallography. The two six-coordinate Cd(II) complexes: *catena*-[Cd(2,6-lut-*N*-oxide)($\mu_{1,1}$-N_3)($\mu_{1,1,1}$-N_3)] (**1**) and *catena*-[Cd(μ_2-2,6-lut-*N*-oxide)($\mu_{1,3}$-NCS)$_2$] (**2**) with the general composition M(L)(X)$_2$ were synthesized by mixing $CdSO_4$, 2,6-lutidine-*N*-oxide and NaN_3 or KSCN in the molar ratio of 1:1:2. The low composition ratio of the lutidine was used to suppress the possible formation of the monomeric species Cd(L)$_n$(X)$_2$ (n = 2 or 4, pyridyl ligand, X = NCS^- or N_3^-) and to ensure the formation of polynuclear and/or coordination polymer through the azido or thiocyanato groups. Another factor that promotes the isolation of such M(L)(X)$_2$ species is the steric hindrance imposed by the two methyl groups in the lutidine skeleton. In case of Zn(II) complex (**4**), a composition ratio close to 3:1:2 was used for the same reason indicated