



Zinc and cadmium halide compounds with the tridentate ligand 2-(methylsulfanyl)-N-(pyridin-2-ylmethylidene)aniline showing yellow luminescence



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ABSTRACT

Five mononuclear complexes, i.e. ZnCl₂ (**1**), [ZnLBr₂](CH₃CN) (**2**), ZnLBr₂ (**3**), CdCl₂ (**4**), and CdLBr₂ (**5**), with L = 2-(methylsulfanyl)-N-(pyridin-2-ylmethylidene)aniline, have been synthesized and characterized. For [ZnLBr₂](CH₃CN) only a few crystals were obtained from the main batch of ZnLBr₂. Their crystal structures and solid-state luminescence properties both at room temperature and 77 K have been investigated. All compounds contain 5-coordinated Zn(II) or Cd(II) ions in a square-pyramidal geometry, distorted towards trigonal bipyramidal. The phase purity of all compounds has been evaluated by Powder XRD and IR. All five compounds show photoluminescent properties both at room temperature and 77 K. In the solid state, the compounds exhibit yellow luminescence with the maximum of emission at around 540 nm. By cooling down to 77 K, the shape and position of the emission spectra of all these compounds remains more or less constant.

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1. Introduction

Luminescent materials based on transition metals and lanthanoids have found wide applications in lighting [1–3], luminescence sensing [4–6] and optical devices [7]. Among them, d¹⁰ metal complexes comprising zinc(II) and cadmium(II) with a variety of ligands have drawn extensive attention in the past decades due to their attractive luminescence properties [8–10]. Schiff bases have been widely employed in coordination chemistry due to their easy accessibility and structural varieties [11]. Transition metal Schiff-base complexes show great importance in catalysis [12], photochemistry [13], biochemistry [14] and materials science [15].

Selected zinc(II) and cadmium(II) Schiff-base complexes with excellent luminescence properties have been reported in the literature [16,17]. In this work, we have synthesized a series of mononuclear zinc(II) and cadmium(II) coordination compounds

using the tridentate NNS-donor Schiff-base ligand 2-(methylsulfanyl)-N-(pyridin-2-ylmethylidene)aniline (abbreviated as L). The characterization and structure determination of the compounds have been performed through NMR, IR, elemental analysis, X-ray crystallography and Powder XRD. The photophysical properties have been studied by solid-state absorption spectra and further by solid-state excitation and emission spectra. During the writing phase of the paper it was found that the zinc bromide compound was studied in 1972, but only its crystal structure was reported [18]. This structure appears to be isomorphous with our compound, ZnLBr₂, but determined at room T and reported with a higher R value.

2. Experimental

2.1. Materials and general methods

2-(Methylthio)aniline and pyridine-2-carboxaldehyde were purchased from Sigma–Aldrich. Pyridine-2-carboxaldehyde was distilled before use; the other chemicals and solvents were used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX300 spectrometer. Elemental analysis

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for C, H, N was performed at the Microanalytical laboratory Kolbe in Germany. FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device. X-ray powder diffraction patterns were obtained on a Philips PW 1050 diffractometer using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). The room-temperature excitation and emission spectra were measured on a Shimadzu RF-5301PC spectrofluorophotometer. Solid-state absorption spectra were recorded with the Avantes absorbance setup, using the Avantes AvaSpec-2048UA CCD spectrometer as detector, and the AvaLight-DH-S Deuterium-Halogen light source. The low-temperature emission spectra (77 K) were measured using a homemade sample holder with an irradiance calibrated CCD spectrometer (Avantes AvaSpec-2048UA) as a detector. A 1000 W xenon lamp (LOT) and a Spex monochromator were used as the excitation source. Photoluminescence quantum yields were measured using the absolute method [19]. An integrating sphere (Avantes AvaSphere 30REFL) and an CCD spectrometer (Avantes AvaSpec-2048UA) was used.

2.2. Ligand synthesis

The ligand 2-(methylsulfanyl)-N-(pyridin-2-ylmethylidene)aniline (L) was synthesized following a literature procedure [20]. A solution of 2-(methylthio)aniline (0.64 g, 4.6 mmol) and fresh distilled pyridine-2-carboxaldehyde (0.50 g, 4.6 mmol) in toluene (50 mL) was refluxed for 24 h. The reaction mixture was then filtered and the solvent was evaporated under reduced pressure. The crude product was recrystallized from toluene/hexane. Yellow crystals of pure ligand were obtained. Yield: 0.83 g (75%). $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 8.67$ (d, 1H), 8.57 (s, 1H), 8.33(d,1H), 7.80 (t, 1H), 7.36 (t, 1H), 7.27 (m, 3H), 7.06 (d, 1H), 2.47 (s, 3H) ppm. $^{13}\text{C NMR}$ (300 MHz, CDCl_3): $\delta = 160.3$, 154.7, 149.6, 147.9, 136.7, 134.8, 127.33, 125.3, 125.2, 124.6, 122.0, 117.5, 14.86 ppm. IR (ν): 1620 (m), 1469 (s), 1433 (s), 1346 (w), 1266 (w), 1194 (w), 1068 (w), 1040 (w), 992 (m), 879 (s), 778 (vs), 749 (vs), 739 (vs), 726 (vs), 691 (s), 648 (m), 613 (s), 549 (s), 481 (vs) cm^{-1} .

2.3. General procedure for synthesis of the compounds ZnLCl_2 (1), ZnLBr_2 (2) + (3), CdLCl_2 (4), and CdLBr_2 (5)

The ligand L (0.22 g, 1 mmol) was dissolved in 10 mL MeOH. To this solution, the metal salt (1 mmol; ZnCl_2 , ZnBr_2 , CdCl_2 and CdBr_2 , respectively) in MeOH (10 mL) was added dropwise; the mixture was then stirred at 80 °C for 2 h. The precipitate was filtered and washed with hot MeOH three times, then dried in air. The yellow compounds were finally recrystallized from acetonitrile. ZnLCl_2 (1), yield: 0.25 g (70%); ZnLBr_2 (2 + 3), yield: 0.25 g (54%); CdLCl_2 (4), yield: 0.24 g (58%); CdLBr_2 (5), yield: 0.27 mg (54%).

Basic spectroscopic data for each compound

ZnLCl_2 (1). $^1\text{H NMR}$ (300 MHz, DMSO): $\delta = 8.76$ (d, $J = 4.7$ Hz, 1H), 8.57 (s, 1H), 8.18 (d, $J = 7.9$ Hz, 1H), 8.02 (t, $J = 7.7$ Hz, 1H), 7.59 (m, 1H), 7.30 (m, 2H), 7.24 (m, 2H), 2.44 (s, 3H) ppm. $^{13}\text{C NMR}$ (300 MHz, DMSO): $\delta = 160.7$, 150.3, 137.8, 128.0, 126.5, 125.6, 124.9, 122.1, 118.1, 14.3 ppm. Elemental Anal. Calc. for $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_2\text{S}_2\text{Zn}$: C, 42.92 (42.83); H, 3.31 (3.32); N, 7.83 (7.68); S, 8.66 (8.79). IR (ν): 1627 (w), 1596 (s), 1563 (w), 1479 (w), 1441 (s), 1368 (m), 1298 (s), 1235 (m), 1203 (m), 1100 (m), 1044 (m), 1020 (s), 978 (s), 952 (m), 911 (m), 778 (vs), 744 (vs), 642 (s), 565 (s), 495 (s), 469 (s) cm^{-1} .

ZnLBr_2 (2 + 3). $^1\text{H NMR}$ (300 MHz, DMSO): $\delta = 8.76$ (d, $J = 4.8$ Hz, 1H), 8.56 (s, 1H), 8.19 (d, $J = 8.5$ Hz, 1H), 8.02 (t, $J = 7.7$ Hz, 1H), 7.59 (m, 1H), 7.31 (m, 2H), 7.24 (m, 2H), 2.45 (s, 3H) ppm. $^{13}\text{C NMR}$ (300 MHz, DMSO): $\delta = 160.7$, 150.3, 137.8, 127.9, 126.4, 125.6, 124.8, 122.0, 118.1, 14.3 ppm. Elemental Anal. Calc. for $\text{C}_{13}\text{H}_{12}\text{Br}_2\text{N}_2\text{S}_2\text{Zn}$: C, 34.91 (34.43); H, 2.79 (2.67); N, 6.30 (6.18);

S, 6.84 (7.07). IR (ν): 1618 (w), 1588 (s), 1559 (w), 1474 (m), 1428 (s), 1369 (s), 1301 (s), 1238 (m), 1198 (m), 1150 (m), 1094 (m), 1044 (m), 1016 (s), 980 (s), 912 (m), 796 (vs), 767 (s), 761 (s), 744 (vs), 722 (s), 640 (s), 575 (s), 497 (s), 465 (w) cm^{-1} . After recrystallization from MeCN the sample showed visually distinguishable two kinds of crystals (in an approximate ratio of 1:5); two different crystals (i.e. 2 and 3) were used for single-crystal XRD studies.

CdLCl_2 (4). $^1\text{H NMR}$ (300 MHz, DMSO): $\delta = 8.76$ (d, $J = 3.9$ Hz, 1H), 8.60 (s, 1H), 8.18 (d, $J = 7.8$ Hz, 1H), 8.04 (t, $J = 7.7$ Hz, 1H), 7.68 (m, 1H), 7.32 (m, 2H), 7.25 (m, 2H), 2.44 (s, 3H) ppm. $^{13}\text{C NMR}$ (300 MHz, DMSO): $\delta = 160.8$, 150.3, 138.0, 128.0, 126.6, 125.7, 125.1, 122.7, 118.4, 14.5 ppm. Elemental Anal. Calc. for $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_2\text{S}_2\text{Cd}$: C, 38.40 (37.93); H, 2.91 (2.94); N, 6.94 (6.81); S, 7.26 (7.79). IR (ν): 1624 (w), 1590 (s), 1563 (w), 1479 (w), 1438 (s), 1372 (m), 1304 (s), 1236 (m), 1199 (m), 1101 (m), 1014 (s), 979 (s), 965 (m), 910 (m), 776 (vs), 761 (vs), 741 (vs), 637 (s), 572 (s), 498 (s), 465 (s) cm^{-1} .

CdLBr_2 (5). $^1\text{H NMR}$ (300 MHz, DMSO): $\delta = 8.76$ (d, $J = 4.7$ Hz, 1H), 8.59 (s, 1H), 8.19 (d, $J = 7.9$ Hz, 1H), 8.05 (t, $J = 7.6$ Hz, 1H), 7.60 (m, 1H), 7.32 (m, 2H), 7.26 (m, 2H), 2.45 (s, 3H) ppm. $^{13}\text{C NMR}$ (300 MHz, DMSO): $\delta = 160.8$, 150.3, 138.0, 128.0, 126.7, 125.7, 125.1, 122.7, 118.4, 14.5 ppm. Elemental Anal. Calc. for $\text{C}_{13}\text{H}_{12}\text{Br}_2\text{N}_2\text{S}_2\text{Cd}$: C, 31.56 (31.20); H, 2.26 (2.42); N, 5.68 (5.60); S, 6.18 (6.41). IR (ν): 1628 (w), 1590 (s), 1567 (w), 1475 (m), 1435 (m), 1373 (s), 1304 (m), 1232 (m), 1198 (m), 1097 (m), 1044 (m), 1011 (m), 984 (s), 903 (s), 780 (vs), 758 (vs), 743 (s), 637 (s), 571 (s), 492 (s), 460 (m) cm^{-1} .

2.4. Single crystal structure determinations

A single crystal of compound 1 was mounted at the diffractometer and measured both at room temperature (293 K) and at 173 K by using a Nonius Kappa CCD area detector diffractometer. A graphite monochromated MoK α radiation source ($\lambda = 0.71073 \text{ \AA}$) was employed. Standard programs like SIR-92 [21], SHELXS-97 and SHELXL-97 [22] were used for data structure solution and structure refinement. The structure was solved by direct methods and refined with a full-matrix least-squares procedure based on F^2 . All of the non-hydrogen atoms were refined anisotropically. All other C–H hydrogen atoms (except C7–H7A) were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atom bonded to C7 was visible in the last stages of refinement and was refined freely (distance C7–H7A = 0.93(2) Å). See Table 1 for more details.

Crystals of 2, 3 and 4 were selected for the X-ray measurements and mounted to nylon loop using the oil-drop method [23] and data were collected using Bruker Kappa APEXII diffractometer (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$) at 123 K. A crystal of 5 was mounted on a MitGen loop in oil and data collected on Bruker APEX2 CCD diffractometer at beamline 11.3.1 of the Advanced Light Source (Synchrotron radiation, $\lambda = 0.7749 \text{ \AA}$) at 100 K. A total of 658 frames for CdLCl_2 , 1159 frames for $[\text{ZnLBr}_2](\text{CH}_3\text{CN})$, 718 frames for ZnLBr_2 and 2880 frames for CdLBr_2 were collected. The frames were integrated with the Bruker SAINT software package [24] using a narrow-frame algorithm and their intensities were corrected for Lorentz and polarization effects. An absorption correction was applied using the Multi-Scan method (SADABS) [24]. The programs SHELXS2014 [22], SHELXL2014 [25] were used for structure solution and structure refinement. The non-hydrogen atoms were refined anisotropically. The H atoms were situated at calculated positions and refined isotropically riding with the heavy atom connected. More details are in Tables 1 and 2.

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