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. ZnLCl_2 (**1**), $[\text{ZnLBr}_2](\text{CH}_3\text{CN})$ (**2**), ZnLBr_2 (**3**), CdLCl_2 (**4**), and CdLBr_2 (**5**), with $\text{L} = 2\text{-(methylsulfanyl)-N-(pyridin-2-ylmethylidene)aniline}$, have been synthesized and characterized. For $[\text{ZnLBr}_2](\text{CH}_3\text{CN})$ only a few crystals were obtained from the main batch of ZnLBr_2 . 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.

Keywords:

Zinc(II); Cadmium(II); Schiff base; Chloride; Bromide; Luminescence

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, d^{10} 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, $ZnLBr_2$, but determined at room T and reported with a higher R value.

2. Experimental part**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 ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer. Elemental analysis 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 spectrofluorimeter. 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%). ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (300 MHz, CDCl₃): δ = 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 ZnLCl₂ (1), ZnLBr₂ (2) + (3), CdLCl₂ (4), and CdLBr₂ (5).*

The ligand L (0.22 g, 1 mmol) was dissolved in 10 mL MeOH. To this solution, the metal salt (1 mmol; ZnCl₂, ZnBr₂, CdCl₂ and CdBr₂, 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. ZnLCl₂ (**1**), yield: 0.25 g (70%); ZnLBr₂ (**2**+**3**), yield: 0.25 g (54%); CdLCl₂ (**4**), yield: 0.24 g (58%); CdLBr₂ (**5**), yield: 0.27 mg (54%).

Basic spectroscopic data for each compound:

ZnLCl₂ (**1**). ¹H NMR (300 MHz, DMSO): δ = 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. ¹³C NMR (300 MHz, DMSO): δ = 160.7, 150.3, 137.8, 128.0, 126.5, 125.6, 124.9, 122.1, 118.1, 14.3 ppm. Elemental analysis found (calc) for C₁₃H₁₂Cl₂N₂SZn: 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.

ZnLBr₂ (**2+3**). ¹H NMR (300 MHz, DMSO): δ = 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. ¹³C NMR (300 MHz, DMSO): δ = 160.7, 150.3, 137.8, 127.9, 126.4, 125.6, 124.8, 122.0, 118.1, 14.3 ppm. Elemental analysis found (calc) for C₁₃H₁₂Br₂N₂SZn: 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.

CdLCl₂ (**4**). ¹H NMR (300 MHz, DMSO): δ = 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. ¹³C NMR (300 MHz, DMSO): δ = 160.8, 150.3, 138.0, 128.0, 126.6, 125.7, 125.1, 122.7, 118.4, 14.5 ppm. Elemental analysis found (calc) for C₁₃H₁₂Cl₂N₂SCd: 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.

CdLBr₂ (**5**). ¹H NMR (300 MHz, DMSO): δ = 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. ¹³C NMR (300 MHz, DMSO): δ = 160.8, 150.3, 138.0, 128.0, 126.7, 125.7, 125.1, 122.7, 118.4, 14.5 ppm. Elemental analysis found (calc) for C₁₃H₁₂Br₂N₂SCd: 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 ($\lambda = 0.71073$ Å) 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 using and refined with a full-matrix least-squares procedure based on F^2 using. 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, $\lambda = 0.71073$ Å) 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, $\lambda = 0.7749$ Å) at 100 K. A total of 658 frames for CdLCl₂, 1159 frames for [ZnLBr₂](CH₃CN), 718 frames for ZnLBr₂ and 2880 frames for CdLBr₂ 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.

Table 1. Crystallographic data collection and refinement of (1), (2) and (3).

Compound	(1) Low T: ZnLCl ₂	(1) Room T: ZnLCl ₂	(2) ZnLBr ₂ (CH ₃ CN)	(3) ZnLBr ₂
CCDC	1445927	1446902	1443691	1446921
Chemical formula	C ₁₃ H ₁₂ Cl ₂ N ₂ SZn	C ₁₃ H ₁₂ Cl ₂ N ₂ SZn	C ₁₅ H ₁₅ Br ₂ N ₃ SZn	C ₁₃ H ₁₂ Br ₂ N ₂ SZn
Formula mass	364.59	364.59	494.50	453.50
Temperature (K)	173(2)	293(2)	123(2)	123(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /n	<i>P</i> -1
<i>a</i> /Å	8.1510(10)	8.2405(2)	8.1053(4)	8.0102(4)
<i>b</i> /Å	27.268(3)	27.6821(6)	24.6650(12)	9.3086(5)
<i>c</i> /Å	6.9880(10)	7.09100(10)	9.0573(4)	10.9516(6)
α /°	90	90	90	76.836(2)
β /°	113.640(10)	114.2888(1)	101.970(10)	72.701(2)
γ /°	90	90	90	76.094(2)
<i>V</i> (Å ³)	1422.8(3)	1474.38(5)	1771.34(15)	745.97(7)
<i>Z</i>	4	4	4	2
Radiation type	MoK α	MoK α	MoK α	MoK α
Density (calculated g/cm ⁻³)	1.702	1.642	1.854	2.019
Absorption coefficient (mm ⁻¹)	2.233	2.155	6.014	7.129
<i>F</i> (000)	736	736	968	440
Crystal size (mm ³)	0.30×0.30×0.15	0.2×0.08×0.08	0.40×0.35×0.35	0.30×0.12×0.12
Goodness of fit on <i>F</i> ²	1.110	1.049	1.151	1.109
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0272, 0.0562	0.0273, 0.0625	0.0200, 0.0441	0.0189, 0.0440
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0311, 0.0576	0.0446, 0.0678	0.0237, 0.0451	0.0230, 0.0452

Table 2. Crystallographic data collection and refinement of (4) CdLCl₂ (5).

Compound	(4) CdLCl ₂	(5) CdLBr ₂
CCDC	1443712	1445920
Chemical formula	C ₁₃ H ₁₂ Cl ₂ N ₂ SCd	C ₁₃ H ₁₂ Br ₂ N ₂ SCd
Formula mass	411.61	500.53
Temperature (K)	123(2)	100(2)
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	7.5791(3)	7.6731(4)
<i>b</i> /Å	8.6549(4)	8.9064(4)
<i>c</i> /Å	11.3533(5)	11.5492(6)
α /°	84.1060(10)	84.129(2)
β /°	81.7830(10)	80.050(2)
γ /°	82.8210(10)	81.189(2)
<i>V</i> (Å ³)	728.58(5)	765.89(7)
<i>Z</i>	2	2
Radiation type	MoK α	Synchrotron; 0.77490 Å
Density (calculated g/cm ⁻³)	1.876	2.170
Absorption coefficient (mm ⁻¹)	1.994	8.364
<i>F</i> (000)	404	476
Crystal size (mm ³)	0.30×0.28×0.08	0.06 × 0.04 × 0.03
Goodness of fit on <i>F</i> ²	1.117	1.041
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2σ(<i>I</i>)]	0.0161, 0.0404	0.0258, 0.0630
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0173, 0.0410	0.0300, 0.0648

3. Results and discussion

3.1 Synthesis and characterization

The compounds ZnLCl₂, CdLCl₂ and CdLBr₂ crystallized without any solvents and in good phase purity, as discussed in the section Powder XRD and IR. The crystal structure of the compound ZnLBr₂ has been reported previously [18]. In our synthesis of ZnLBr₂, two different crystals were found and were isolated from the same batch; these two types of crystals were impossible to obtain as separate batches. Very interestingly, it appeared that one type of crystals crystallized with an acetonitrile molecule, namely [ZnLBr₂](CH₃CN), the other one without any solvent, namely ZnLBr₂. The elemental analysis of the bulk sample of ZnLBr₂ is not fully in agreement with the calculated values for the solvent-free complex. The slight deviation can be fitted with partial inclusion of acetonitrile, suggesting that [ZnLBr₂](CH₃CN) is present for only about 15% molar fraction in the powdered sample. However, the amount of [ZnLBr₂](CH₃CN)

present in the crystalline material may have been higher, as the powder was vacuum dried before the elemental analysis was performed.

3.2 Crystal structure descriptions

ZnLCl₂ (**1**), ZnLBr₂ (**2+3**), CdLCl₂ (**4**) and CdLBr₂ (**5**) all appeared to have the same molecular structure, and some of them are even isostructural with the same space group (see Tables 1 and 2). For this paper only the structure of ZnLCl₂ (**1**) at 173 K is discussed in detail, as an example (see Figure 1a); the low-T and room-T structures differ only marginally due to lattice contraction. The asymmetric unit contains only one molecule of ZnLCl₂. The Zn(II) ion is five coordinated by two N atoms and one S atom from the ligand, and two Cl⁻ anions, with Zn-N distances of 2.135(1) and 2.119(2) Å, a Zn-S distance of 2.698(1) Å, and Zn-Cl distances of 2.220(1) and 2.250(1) Å. The ligand is bound in a meridional fashion and the halide ions occupy the remaining equatorial and the apical position of a square pyramid. The found bond lengths and angles can be considered as normal [18, 26, 27]. The coordination sphere of Zn(II) is best described as slightly distorted from square pyramidal towards trigonal bipyramidal, with τ (tau) values [28] varying from 0.13-0.26 (see Table 3). One Cl⁻ anion is relatively close to a hydrogen from a C atom of a neighboring molecule, i.e. C(7)-H(7A)-Cl(2), which has a contact distance C(7)-Cl(2) of 3.542(2) Å with a C(7)-H(7A)-Cl(2) angle of 159°(1). The structure is further stabilized by intermolecular π - π stacking interactions. The distance between adjacent aromatic rings are 3.8209(15) Å and 3.8166(13) Å (see Figure 1b).

Figure 1a. The molecular structure (asymmetric unit of the crystal structure) and used atomic labelling of ZnLCl₂ (**1**) at 173 K. Ellipsoids are plotted at 50% probability.

Figure 1b: An impression of the π -stacking interactions in $\text{ZnLCl}_2(\mathbf{1})$. Distances given are between ring centers.

The asymmetric unit of $[\text{ZnLBr}_2](\text{CH}_3\text{CN}) (\mathbf{2})$ contains one molecule of the complex and one lattice solvent molecule (Figure S1). The Zn(II) ion in this case is also five-coordinated by two N atoms and one S atom from the ligand and two Br^- ions, in a geometry that is very similar to that of the unsolvated molecule. The five-coordinate geometry is defined by a τ value [28] of 0.26. The π - π stacking interactions between adjacent aromatic rings have a centroid to centroid distance of 3.8595(10) Å (see Figure S2). No significant hydrogen bonds can be found in the structure. The acetonitrile molecule just fills void space in the lattice.

In $\text{CdLCl}_2 (\mathbf{4})$ and $\text{CdLBr}_2 (\mathbf{5})$ the distortion from square pyramidal towards trigonal bipyramidal is larger than that in the case of the Zn(II) complexes, as seen from the τ values, which are 0.36 and 0.37, respectively. These changes are ascribed to the larger ionic radius of Cd(II). Relevant bond lengths, angles and τ values are also given in Table 3. In all structures the methyl substituent at sulfur points in opposite direction of the apical halide.

Table 3. Selected bond lengths (Å) and bond angles (°) of ZnLCl₂ (**1**), [ZnLBr₂](CH₃CN) (**2**), ZnLBr₂ (**3**), CdLCl₂ (**4**) and CdLBr₂ (**5**).

Distances and angles	1 : Low T ZnLCl ₂	1 : Room T ZnLCl ₂	2 : [ZnLBr ₂]. (CH ₃ CN)	3 : Low TR ZnLBr ₂	Lit: Room T ZnLBr ₂ [18]	4 : CdLCl ₂	5 : CdLBr ₂
M-N1	2.1191(14)	2.1330(16)	2.132(2)	2.149(2)	2.1496	2.355(1)	2.351(2)
M-N8	2.1354(14)	2.1389(16)	2.143(2)	2.143(2)	2.1215	2.345(1)	2.3431(19)
M-S15	2.6975(6)	2.7406(6)	2.639(1)	2.6318(5)	2.6444	2.7355(3)	2.7269(7)
M-Cl1/Br1	2.2196(7)	2.2324(8)	2.3745(3)	2.3759(3)	2.3669	2.4509(4)	2.5686(3)
M-Cl2/Br2	2.2504(7)	2.2550(6)	2.4233(3)	2.4157(3)	2.3990	2.4611(4)	2.5829(3)
Cl1/Br1-M-Cl2/Br2	112.29(2)	113.01(3)	114.98(1)	116.49(1)	117.41	106.03(1)	107.53(1)
Cl1/Br1-M-S15	107.29(2)	107.37(2)	97.51(1)	97.75(1)	95.77	104.27(1)	102.04(2)
Cl1/Br1-M-N1	111.58(5)	111.75(5)	106.54(4)	107.80(4)	108.40	98.01(3)	98.36(5)
Cl1/Br1-M-N8	103.60(5)	103.46(5)	111.18(4)	110.15(4)	108.40	153.54(1)	152.63(5)
Cl2/Br2-M-S15	87.49(2)	87.33(2)	92.18(2)	91.87(1)	91.23	100.23(1)	100.02(1)
Cl2/Br2-M-N1	97.51(5)	97.45(5)	94.79(4)	95.46(4)	95.54	113.83(3)	115.80(6)
Cl2/Br2-M-N8	143.02(5)	142.32(5)	133.50(4)	132.76(4)	132.62	100.43(3)	99.74(5)
S15-M-N1	135.19(4)	134.71(5)	149.16(4)	148.80(4)	148.12	131.86(3)	130.63(6)
S15-M-N8	73.29(4)	72.64(4)	76.42(4)	76.09(4)	76.19	70.17(3)	70.33(6)
N1-M-N8	76.64(5)	76.83(6)	77.04(6)	76.72(6)	76.36	71.00(4)	71.02(7)
τ value [28]	0.131	0.127	0.26	0.25	0.26	0.36	0.37

3.3 Powder XRD and IR spectroscopy

The crystallographic phase purity of all compounds has been checked by powder XRD and IR spectra. The ZnLCl_2 (**1**), CdLCl_2 (**4**) and CdLBr_2 (**5**) samples show high purity and the experimental Powder XRD patterns are highly similar to the simulated X-ray diffraction patterns calculated from the single-crystal structures (Figure 2a, c, d). In agreement with the observation that the compound ZnLBr_2 (**2+3**) contains two types of crystals, the experimental pattern contains all the main peaks from the two simulated patterns (Figure 2b). The IR spectra of all compounds are highly similar, which further supports that all the compounds are isostructural and that ZnLBr_2 (**3**) is the main form present in the ZnLBr_2 (**2+3**) bulk sample (Figure S3).

Figure 2. Experimental powder XRD patterns and simulated patterns from single-crystal structures. a) ZnLCl_2 (**1**). b) ZnLBr_2 (**2+3**). c) CdLCl_2 (**4**). d) CdLBr_2 (**5**).

3.4 Photophysical properties.

The solid-state absorption spectra of the ligand and four complexes are shown in Figure S4. The ligand exhibits a strong broad absorption band from 250 nm to 450 nm. The ZnLCl₂ (**1**), ZnLBr₂ (**2+3**) and CdLCl₂ (**4**) absorption bands are slightly narrower than that of the ligand in the blue region, while the absorption spectrum of CdLBr₂ (**5**) is similar to that of the ligand.

Room temperature excitation and emission spectra of ZnLCl₂ (**1**), ZnLBr₂ (**2+3**), CdLCl₂ (**4**) and CdLBr₂ (**5**) were recorded in the solid state, and are depicted in Figure 3. The compounds ZnLCl₂ (**1**) and CdLCl₂ (**4**) show a relatively intense yellow color emission, while ZnLBr₂ (**2+3**), CdLBr₂ (**5**) exhibit a medium intense yellow color emission upon irradiation of 400 nm. The emission spectra of all four compounds contain only one peak with a maximum at around 540 nm (535 nm for the chloride compounds, 545 nm for the bromide compounds), which is assigned to the ligand π - π^* transition [29-34]. For ZnLCl₂ (**1**), CdLCl₂ (**4**) and CdLBr₂ (**5**); although the excitation spectra contain two peaks, varying the excitation wavelength did not make any influence of the shape and position of emission spectra. The room temperature quantum yields of ZnLCl₂ (**1**) and CdLCl₂ (**4**) are 8% and 22%, respectively. The quantum yield of ZnLBr₂ (**2+3**) and CdLBr₂ (**5**) cannot be determined by our setup and is estimated to be at most 5%.

Figure 3. Room temperature excitation (black) and emission (red and green) spectra of a) ZnLCl₂ (**1**); b) ZnLBr₂ (**2+3**); c) CdLCl₂ (**4**); d) CdLBr₂ (**5**).

The emission spectra of all four compounds have also been recorded at 77 K (see Figure S5). The emission color changes at 290 K and 77 K have been calculated and are presented in the so-called CIE (Commission International d'Elairage) chromaticity diagram (see Figure S6). The CIE coordinates are listed in Table S1; although the coordinates at different temperatures are significantly different, the color of emission remains largely the same. The emission spectra of all samples at 77 K are almost identical to their room temperature emission spectra. Interestingly, only the emission of the compound CdLBr_2 seems to shift to a slightly more red color at lower temperatures.

4. Concluding Remarks

In summary, a series of Zn(II) and Cd(II) halide complexes, all containing the 2-(methylsulfanyl)-N-(pyridin-2-ylmethylidene)aniline ligand (L), has been successfully synthesized and characterized. The compounds ZnLCl_2 (**1**), ZnLBr_2 (**2+3**), CdLCl_2 (**4**) and CdLBr_2 (**5**) have the same molecular structure based on IR and X-ray diffraction data. For all compounds the structures were solved by single-crystal X-ray diffraction. The compound ZnLBr_2 was obtained as a mixture of two types of crystals, the pure ZnLBr_2 (**3**) and the acetonitrile solvate $[\text{ZnLBr}_2](\text{CH}_3\text{CN})$ (**2**); the unsolvated compound ZnLBr_2 (**3**) appears to be the main component. All five compounds show a bright yellow luminescence emission. Temperature changes have negligible influence on the emission spectra.

Appendix A. Supplementary data

CCDC 1445927, 1446902, 1443691, 1446921, 1443712, and 1445920 contain the supplementary crystallographic data for ZnLCl_2 (**1**, 173 K), ZnLCl_2 (**1**, 293 K), $[\text{ZnLBr}_2](\text{CH}_3\text{CN})$ (**2**), ZnLBr_2 (**3**), CdLCl_2 (**4**) and CdLBr_2 (**5**), respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Spectroscopic details in the supplementary data include: Packing and stacking diagrams for compounds **1** and **2**. Infrared spectra and diffuse reflectance spectra of all new compounds. Also the CIE (Commission International d'Elairage) chromaticity diagrams are presented, in graphics and tabular form.

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References

- [1] P. Pust, V. Weiler, C. Hecht, A. Tücks, A.S. Wochnik, A.K. Henß, D. Wiechert, C. Scheu, P.J. Schmidt, W. Schnick, *Nat Mater*, 13 (2014) 891-896.
- [2] C.F. Zhu, S. Chaussedent, S.J. Liu, Y.F. Zhang, A. Monteil, N. Gaumer, Y.Z. Yue, *J. Alloy. Compd.*, 555 (2013) 232-236.
- [3] X. Liu, S. Akerboom, S.H.C. Askes, I. Mutikainen, E. Bouwman, *Inorg. Chem. Commun.*, 61 (2015) 60-63.
- [4] H. Kim, G.R. You, G.J. Park, J.Y. Choi, I. Noh, Y. Kim, S.J. Kim, C. Kim, R.G. Harrison, *Dyes and Pigments*, 113 (2015) 723-729.
- [5] X.H. Qian, Z.C. Xu, *Chem. Soc. Rev.*, 44 (2015) 4487-4493.
- [6] X. Liu, S. Akerboom, M.d. Jong, I. Mutikainen, S. Tanase, A. Meijerink, E. Bouwman, *Inorg. Chem.*, 54 (2015) 11323-11329.
- [7] M. de Torres, S. Semin, I. Rzdolski, J.L. Xu, J.A.A.W. Elemans, T. Rasing, A.E. Rowan, R.J.M. Nolte, *Chem. Commun.*, 51 (2015) 2855-2858.
- [8] R. Ghosh, S.H. Rahaman, C.N. Lin, T.H. Lu, B.K. Ghosh, *Polyhedron*, 25 (2006) 3104-3112.
- [9] P. Suvanvapee, J. Boonmak, S. Youngme, *Polyhedron*, 102 (2015) 693-698.
- [10] A.B. Pradhan, S.K. Mandal, S. Banerjee, A. Mukherjee, S. Das, A.R. Khuda Bukhsh, A. Saha, *Polyhedron*, 94 (2015) 75-82.
- [11] M. Shyamal, A. Panja, A. Saha, *Polyhedron*, 69 (2014) 141-148.
- [12] K.C. Gupta, A.K. Sutar, *Coord. Chem. Rev.*, 252 (2008) 1420-1450.
- [13] N.K. Al Rasbi, J. Husband, *J. Photochem. Photobiol.*, 314 (2016) 96-103.
- [14] N. Raman, A. Kulandaisamy, C. Thangaraja, K. Jeyasubramanian, *Transit. Metal Chem.*, 28 (2003) 29-36.
- [15] Z.L. Liu, J. Zhang, T.F. Li, Z.N. Yu, S.X. Zhang, *J. Fluor. Chem.*, 147 (2013) 36-39.
- [16] Z. Zhang, W.X. Feng, P.Y. Su, X.Q. Lü, J.R. Song, D.D. Fan, W.K. Wong, R.A. Jones, C.Y. Su, *Inorg. Chem.*, 53 (2014) 5950-5960.
- [17] M. Maiti, D. Sadhukhan, S. Thakurta, S. Roy, G. Pilet, R.J. Butcher, A. Nonat, L.J. Charbonnière, S. Mitra, *Inorg. Chem.*, 51 (2012) 12176-12187.
- [18] A. Mangia, M. Nardelli, C. Palmieri, G. Pelizzi, *J. Cryst. Mol. Struct.*, 2 (1972) 99-106.
- [19] J.C.de Mello, H.F. Wittmann, R. Friend, *Adv.Mater.*, 9 (1997) 230-232
- [20] J.S. Costa, A.G. Castro, R. Pievo, O. Roubeau, B. Modéc, B. Kozlevcar, S.J. Teat, P. Gamez, J. Reedijk, *CrystEngComm*, 12 (2010) 3057-3064.
- [21] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.*, 27 (1994) 1045-1050.

- [22] G.M. Sheldrick, *Acta Crystallogr. Sect. A*, 64 (2008) 112-122.
- [23] T. Kottke, D. Stalke, *J. Appl. Crystallogr.*, 26 (1993) 615-619.
- [24] Bruker, APEX2, SAINT and SADABS, 2007 and 2009. , in, Bruker AXS Inc. , Madison, Wisconsin, USA, 2009.
- [25] G.M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem* 71 (2015) 3-8.
- [26] H.L. Gao, S.X. Jiang, Y.M. Hu, F.F. Li, Q.Q. Zhang, X.Y. Shi, J.Z. Cui, *Inorg. Chem. Commun.*, 44 (2014) 58-62.
- [27] C. Bolm, K. Weickhardt, M. Zehnder, T. Ranff, *Chem. Ber.*, 124 (1991) 1173-1180.
- [28] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc., Dalton Trans.*, (1984) 1349-1356.
- [29] B. Dutta, P. Bag, U. Flörke, K. Nag, *Inorg. Chem.*, 44 (2005) 147-157.
- [30] S. Banthia, A. Samanta, *J. Phys. Chem. B*, 110 (2006) 6437-6440.
- [31] W. Chen, Q. Peng, Y.D. Li, *Cryst. Growth Des.*, 8 (2008) 564-567.
- [32] Z. Li, A. Dellali, J. Malik, M. Motevalli, R.M. Nix, T. Olukoya, Y. Peng, H.Q. Ye, W.P. Gillin, I. Hernández, P.B. Wyatt, *Inorg. Chem.*, 52 (2013) 1379-1387.
- [33] S. Majumder, L. Mandal, S. Mohanta, *Inorg. Chem.*, 51 (2012) 8739-8749.
- [34] P. Yang, X.X. Wu, J.Z. Huo, B. Ding, Y. Wang, X.G. Wang, *CrystEngComm*, 15 (2013) 8097-8109.

Graphical abstract

Five-coordinated zinc and cadmium complexes with the ligand 2-(methylsulfanyl)-N-(pyridin-2-yl-methylidene)aniline have been synthesized, and characterized by NMR, IR, elemental analysis, X-ray crystallography, Powder XRD and luminescence.