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Dipicolylamino-methoxy-1,2,4,5-tetrazine ligand and its metal complexes: structural and photophysical studies[†]

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[†]*Dedicated to Prof. Miguel Julve on the occasion of his 65th anniversary*

Abstract

The ligand 6-methoxy-N,N-bis(pyridin-2-ylmethyl)-1,2,4,5-tetrazin-3-amine (**L**) has been prepared by nucleophilic substitution from 3-chloro-6-dipicolylamino-1,2,4,5-tetrazine (**1**). The ligand **L**, together with two neutral zinc(II) and cadmium(II) metal complexes, respectively formulated as [ZnLCl₂] (**2**) and [CdLCl₂]₂ (**3**), have been crystallized and analyzed by single crystal X-ray diffraction analysis. The two metal complexes are isostructural and crystallize in the monoclinic system, space group *P2₁/c*. The structure analysis indicates that the amino nitrogen atom is involved in semi-coordination with the metal centers, thus leading to distorted coordination geometries. Photophysical studies of the ligand and its corresponding metal complexes **2** and **3** show a switch-on of the luminescence upon chelation with the diamagnetic Zn(II) and Cd(II) metal ions.

Keywords

Tetrazine ligand; Dipicolylamine; Crystal structures; Zinc complex; Cadmium complex; Luminescent complexes

1. Introduction

The nitrogen heterocycle 1,2,4,5-tetrazine (TTZ) [1] and its very numerous derivatives are remarkable due to their low lying π^* type LUMO orbital [1b], which is responsible for their facile reversible reduction to stable radical anions [2] as well as for the occurrence of anion- π interactions in the solid state [3]. They have been widely used as dienophiles in Diels-Alder cycloaddition reactions with inverse demand [4] and have also found a general use as high-energy materials with pure TTZ organic compounds [5] or, more recently, with TTZ based metal complexes [6] for “safer” explosives. Also, halogen and oxygen substituted TTZ derivatives exhibit emission properties arising from a symmetry forbidden $n-\pi^*$ excitation [7]. In coordination chemistry the TTZ unit, thanks to its strong electron withdrawing character, constitutes an interesting platform for the construction of electroactive ligands and metal complexes [8]. Accordingly, symmetric ditopic ligands, such as 3,6-dipyridyl-TTZ and analogues [9], 3,6-dipyrimidyl-TTZ [3f,10], 3,6-dibenzocarboxylate-TTZ [11], 3,6-dicarboxymethyl ester [12], 3,6-bis(hydrazine)-TTZ [13], or, more recently, 3,6-bis(picolylamino)-TTZ [14] as well as their corresponding bimetallic complexes or coordination polymers have been prepared. While these ditopic ligands are usually prepared either through a modified Pinner type synthesis or by nucleophilic substitution of the chloro substituent in 3,6-dichloro-TTZ [1b], the nucleophilic monosubstitution of the 3,6-dichloro-TTZ allowed obtaining monotopic ligands. Thus, dipicolylamine-TTZ [15] and pyrazolyl-TTZ [6] ligands and complexes have been reported. As mentioned above, halogen and oxygen substituted derivatives exhibit emission properties. We have therefore recently described the synthesis of a Cl-TTZ-dipicolylamine ligand, that is, 3-chloro-6-dipicolylamino-1,2,4,5-tetrazine (**1**), and have demonstrated the modulation of the TTZ fluorescence in the case of its Zn(II) and Cd(II) homo-bimetallic transition metal complexes [15b]. Note that that such d^{10} metal cations are often used to prepare different coordination compounds that exhibit fascinating structures and photoluminescence properties [16]. As a continuation of this work, we describe herein the synthesis, structural characterization and the photophysical properties of the CH_3O -TTZ-dipicolylamine ligand, namely 6-methoxy-N,N-bis(pyridin-2-ylmethyl)-1,2,4,5-tetrazin-3-amine (**L**) and its corresponding Zn(II) (**2**) and Cd(II) (**3**) complexes.

2. Experimental

2.1 General considerations

Reactions were carried out under air and using HPLC grade solvents. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 300 spectrometer operating at 300 MHz for ^1H and 76 MHz for ^{13}C . Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet; d, doublet; t, triplet. The IR spectra were recorded on ATR Bruker Vertex 70 spectrophotometer in the 4000–400 cm^{-1} range. MALDI-TOF MS spectra were recorded on Bruker Biflex-IIIITM apparatus, equipped with a 337 nm N_2 laser. ESI-MS spectra were achieved on a Bruker MicrO-Tof-Q 2 spectrometer. Elemental analyses were recorded using Flash 2000 Fisher Scientific Thermo Electron analyzer.

UV-Vis absorption spectra of the three compounds in acetonitrile were measured on a Cary 5000 (Agilent) spectrophotometer. Steady-state emission and excitation spectra likewise in acetonitrile at concentrations of around 5×10^{-1} M were recorded on a Fluorolog 3 (Horiba-Jobin-Yvon) spectrophotometer and corrected for the spectral response of the apparatus.

2.2. Crystal structure determinations

For the ligand **L** and the complex **2** X-ray single crystal diffraction data were collected on an Agilent Technologies SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K α radiation ($\lambda=1.54184\text{\AA}$). For the Cd-complex **3** X-ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer, operating with a Mo-K α ($\lambda = 0.71073\text{\AA}$) X-ray tube with a graphite monochromator. The structures were solved by direct methods SHELXS-97 [17] and refined on F^2 by full matrix least-squares techniques using the SHELX97 program [18] within WINGX [19]. All non-H atoms were refined anisotropically and multiscan empirical absorption was applied using the CrysAlisPro program (CrysAlisPro, AgilentTechnologies, V1.171.38.41r, 2015). The H atoms were included in the calculation without refinement.

Table 1. Crystallographic data, details of data collection and structure refinement parameters

	L	2	3
Formula	$\text{C}_{15}\text{H}_{15}\text{N}_7\text{O}$	$\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{N}_7\text{OZn}$	$\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{N}_7\text{OCd}$
M [$\text{g}\cdot\text{mol}^{-1}$]	309.34	445.61	492.64
T [K]	130.01(10)	292.1(2)	293(2)
Wavelength (\AA)	1.54184	1.54184	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [\AA]	8.5113(3)	7.2476(3)	7.3610(11)
b [\AA]	16.7775(6)	15.8089(5)	15.9190(7)
c [\AA]	10.5811(3)	16.5296(7)	16.7050(18)
β [$^\circ$]	103.054(3)	97.800(4)	93.700(9)

V [Å ³]	1471.92(8)	1876.38(13)	1953.4(4)
Z	4	4	4
ρ_{calcd} [g·cm ⁻³]	1.396	1.577	1.675
μ [mm ⁻¹]	0.781	4.614	1.410
Goodness-of-fit on F ²	1.070	1.027	1.046
Final R_1/wR_2 [$I > 2\sigma(I)$]	0.0387/0.0951	0.0388/0.1049	0.0572/0.1430
R_1/wR_2 (all data)	0.0475/0.1033	0.0534/0.1279	0.1043/0.1746

2.3. Synthesis of the ligand 6-methoxy-N,N-bis(pyridin-2-ylmethyl)-1,2,4,5-tetrazin-3-amine (**L**)

3-Chloro-6-di(2-picolyl)amine-1,2,4,5-tetrazine (**1**) was synthesized according to a procedure previously described by us [15]. To a solution of **1** (100 mg, 0.32 mmol) in 40 mL of methanol was added a freshly prepared solution of sodium methoxide 3.2 mL (0.1 M) in methanol. The mixture was stirred at room temperature for 1 hour. The resulting solution was evaporated under reduced pressure. The product was purified by silica gel column chromatography (ethyl acetate/dichloromethane (3/1, v/v)) to give the ligand **L** as a red precipitate (75 mg, 76 %). Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent after column chromatography. ¹H NMR (300 MHz, CDCl₃) δ 8.54 (m, 2H), 7.54 (td, ³J = 7.7 Hz, ⁴J = 1.7 Hz, 2H), 7.22 (d, ³J = 7.8 Hz, 2H), 7.10 (m, 2H), 5.11 (s, 4H), 4.06 (s, 3H). IR (ATR, cm⁻¹): 3035 (w), 2948 (w), 1574 (s), 1475 (m), 1421 (s), 1282 (s), 1190 (s), 1038 (m), 993 (s). MALDI-TOF MS: $m/z = 310.0$ [**L** – H]⁺. Elemental analysis for C₁₅H₁₅N₇O; Calculated: C 58.24%, H 4.89%, N 31.70%; Found: C 58.22%, H 4.78%, N 31.65%.

2.4. Synthesis of the zinc complex [ZnLCl₂] (**2**)

To a solution of ligand **L** (25 mg, 0.08 mmol) in 10 mL of dichloromethane was added a solution of anhydrous zinc chloride ZnCl₂ (11 mg, 0.08 mmol) in 15 mL of methanol and the mixture was stirred for 1 hour. The resulting solution was left undisturbed for 1 day at room temperature. Orange crystals (25 mg, 71%) suitable for X-ray were obtained. ¹H NMR (300 MHz, DMSO-d₆) δ 8.54 (m, 2H), 7.78 (t, ³J = 7.7 Hz, 2H), 7.43 (d, ³J = 7.9 Hz, 2H), 7.32 (t, ³J = 8.4 Hz, 2H), 5.11 (s, 4H), 4.07 (s, 3H). IR (ATR, cm⁻¹): 2971 (w), 1610 (m), 1572 (w), 1488 (s), 1358 (s), 1156 (m), 1020 (s), 975 (s), 801 (m). MALDI-TOF MS: $m/z = 308.5$ [**L** – H]⁺, 408.5 [Zn(**L**)Cl]⁺; ESI-MS: $m/z = 309.5$ [**L** – H]⁺, 407.9 [Zn(**L**)Cl]⁺. Elemental analysis for C₁₅H₁₅Cl₂N₇OZn; Calculated: C 40.43%, H 3.39%, N 22.00%; Found: C 40.08%, H 3.26%, N 21.81%.

2.5. Synthesis of the cadmium complex [CdLCl₂] (**3**)

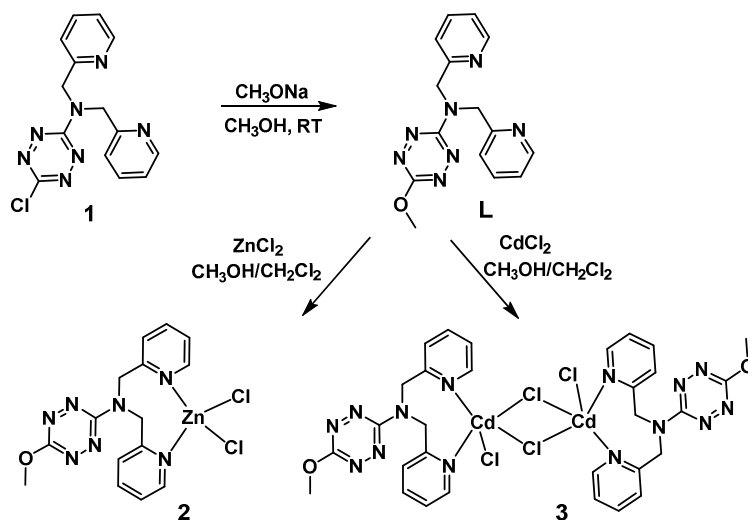
To a solution of ligand **L** (25 mg, 0.08 mmol) in 10 mL of dichloromethane, was added a solution of cadmium chloride CdCl₂ (15 mg, 0.08 mmol) in 15 mL of methanol and the mixture was

stirred for 1 hour. The resulting solution was left undisturbed for 1 day at room temperature. Red crystals (29 mg, 74%) suitable for X-ray were obtained. ^1H NMR (300 MHz, DMSO- d_6) δ 8.53 (m, 2H), 7.78 (t, $^3J = 8.6$ Hz, 2H), 7.42 (d, $^3J = 7.9$ Hz, 2H), 7.33 (t, 8.3, 2H), 5.12 (s, 4H), 4.07 (s, 3H). IR (ATR, cm^{-1}): 2970 (w), 1605 (m), 1575 (w), 1484 (s), 1357 (s), 1152 (w), 1016 (s), 972 (s), 806 (m). MALDI-TOF MS: $m/z = 308.5$ [$\text{L} - \text{H}$] $^+$, 458.5 [$\text{Cd}(\text{L})\text{Cl}$] $^+$; ESI-MS: $m/z = 309.5$ [$\text{L} - \text{H}$] $^+$, 457.9 [$\text{Cd}(\text{L})\text{Cl}$] $^+$. Elemental analysis for $\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{N}_7\text{OCd}$; Calculated: C 36.57%, H 3.07%, N 19.90%; Found: C 36.32%, H 2.94%, N 19.95%.

3. Results and discussion

3.1. General synthetic strategy

The nucleophilic substitution of the chlorine atom in Cl-TTZ-dipica (**1**) was performed by the reaction of **1** with sodium methoxide in methanol (Scheme 1). The resulting CH_3O -TTZ-dipica ligand **L** was obtained in good yield as a red precipitate. We have previously demonstrated the switch on of the luminescence of Cl-TTZ-dipica **1** upon chelation with Zn(II) and Cd(II) metal centers [15b]. Now we have reacted the CH_3O -TTZ-dipica ligand **L** with MCl_2 ($\text{M} = \text{Zn}(\text{II}), \text{Cd}(\text{II})$) in 1:1 ratios (Scheme 1) in a mixture of dichloromethane/methanol. The resulting [ZnLCl_2] (**2**) and [CdLCl_2] $_2$ (**3**) complexes were obtained in good yields as orange crystals.



Scheme 1. Synthesis of the ligand **L** and the metal complexes **2** and **3**.

3.2. Crystal structures description

Suitable single crystals for X-ray analysis have been obtained for ligand **L** upon slow evaporation of an ethylacetate/dichloromethane solution. Ligand **L** crystallizes in the monoclinic system $P2_1/n$ with an entire molecule as an independent fragment in the unit cell (Fig. 1). The N–N bonds in the tetrazine ring (1.32–1.33 Å, Table S1) have typical values for tetrazine based molecules.

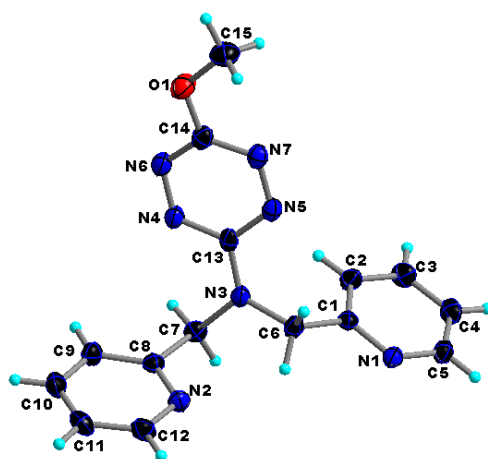


Fig. 1. Molecular structure of **L**. Displacement ellipsoids for non-H atoms are drawn at 50% probability level.

In the crystal packing, numerous π - π interactions between the tetrazine ring and pyridyl units of two adjacent molecules are observed (Fig. 2). Interestingly the presence of electron donating methoxy group may, in principle, saturate the π -acidity of the tetrazine ring making it not favourable for any additional interactions. However, in the present case, we observe a completely opposite feature: the molecules of **L** form 2D-network due to the short inter-planar distances (3.53, 3.70 Å), while the Cl-TTZ-dipica ligand is slightly dimerized possessing longer distances for the π - π interactions (3.85 Å) [15b] between pyridyl moieties despite the presence of the electron withdrawing chlorine substituent. The values 3.53 and 3.70 Å are longer than the common established for π - π interactions (3.60 Å), however they cannot be ignored. W.-Y. Su *et al* described a series of Zn complexes possessing the longer values of π - π interactions (3.84 Å) [20]. The crystal structure of **L** is also further sustained by intermolecular hydrogen bonds between a nitrogen atom of the tetrazine ring and a hydrogen atom from the pyridine unit (Fig. S1, Table S2).

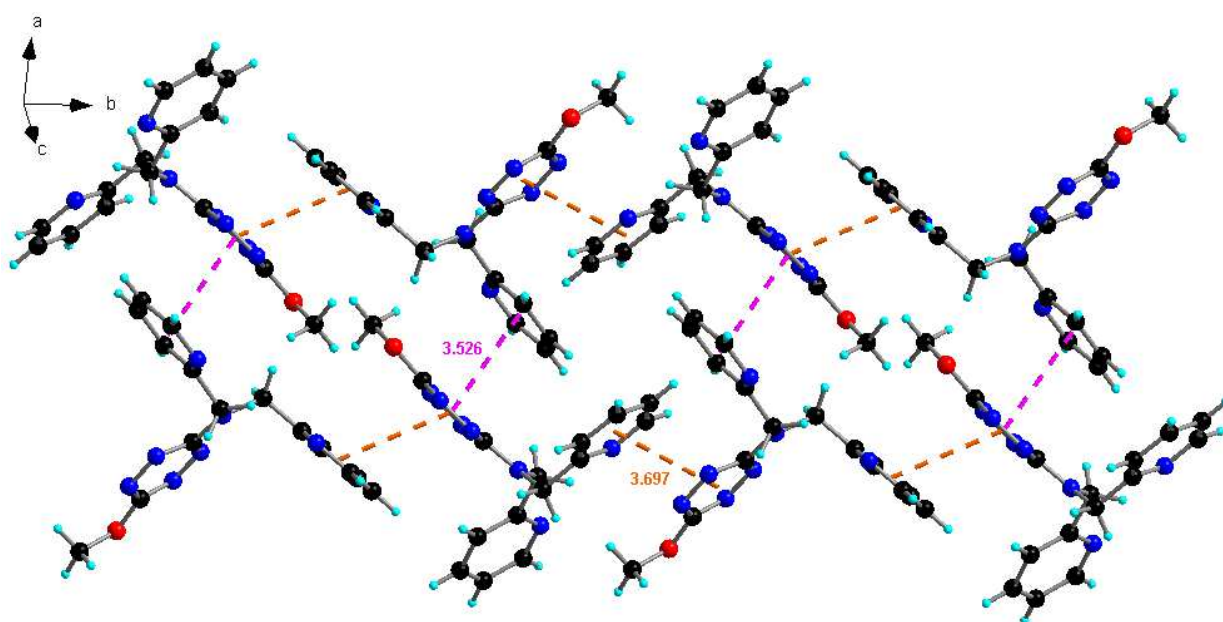
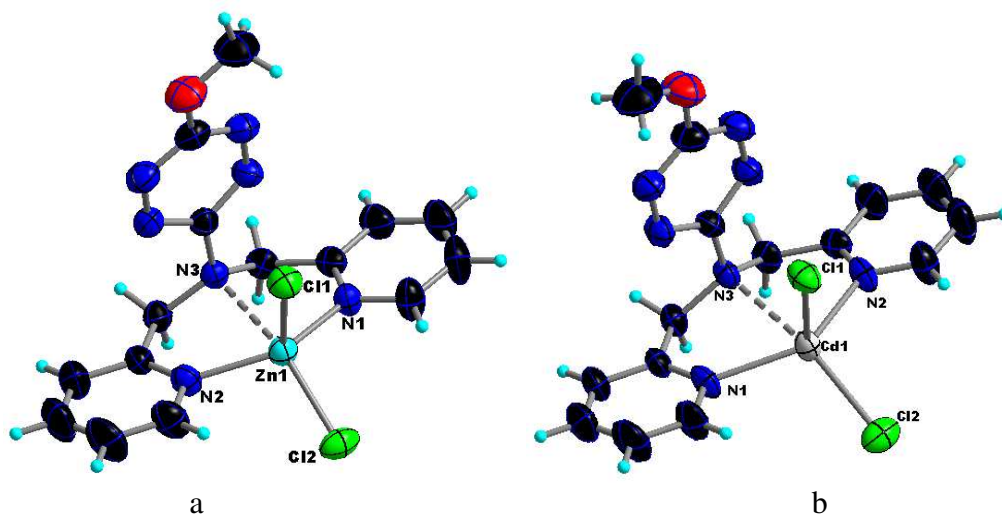


Fig. 2. Interaction between tetrazine and pyridine rings in **L**.

The X-Ray analyses of both metal complexes **2** and **3** revealed that they crystallize in the monoclinic system $P2_1/c$. The presence of the methoxy group in the ligand breaks the symmetry of both compounds, thus making the entire complex an independent fragment (Fig. 3).

The structure of the zinc complex **2** can be regarded as mononuclear, as the value of the Zn – Cl1' bond is too long (3.2343(10) Å, Table 2, see also Table S3) to consider it as a chemical bond. However, the cadmium complex **3** is binuclear, possessing a much shorter Cd – Cl2' distance (2.8950(17) Å, Table 2, see also Table S5). Thus, the coordination geometry of the zinc cation can be considered as a highly distorted tetrahedral, rather than a trigonal pyramid (Fig. 4a), formed by the Cl anion and the N atoms of the pyridine units. The bond angles of the Zn ion are in the range of 98.15(7) – 141.54(11)°, which are in the normal range for other reported Zn complexes with N, Cl-donor atoms [15]. The coordination environment of Cd in complex **3** can be described as a distorted trigonal bipyramid, where the axial sites are formed by chlorine atoms (Fig. 4b). The angles in equatorial plane of the Cd ion range from 107.26(11) – 139.15(17)°, while the value of the axial Cl1–Cd1–Cl2' angle is 175.08(4)°. Both metal complexes form semi-coordination bonds with the amine N atom (N3): for complex **2** the contribution of this bond to the total valence of the Zn(II) cation is negligible (0.095, 4.7%). In contrast, for Cd(II), the same bond has higher valence bond contribution (0.14, 7%).



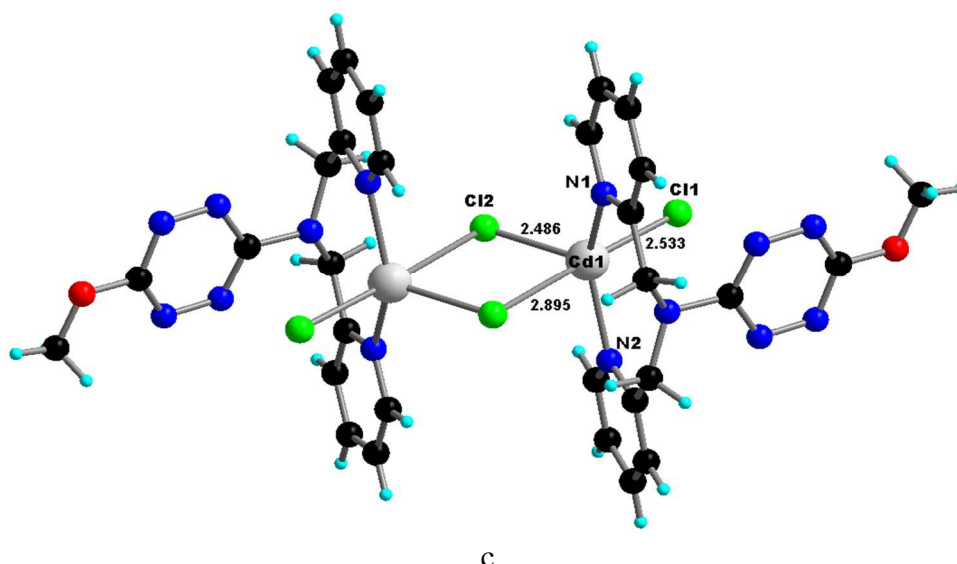


Fig. 3. Molecular structure of complex **2** (a), independent motif in the unit cell of complex **3** (b) and dimeric structure of complex **3** (c). Displacement ellipsoids for non-H atoms are drawn at 50% probability level.

Table 2. Selected lengths (Å) and angles (°) for complexes **2** and **3**.

[Zn(L)Cl ₂] (2)		[Cd(L)Cl ₂] ₂ (3)	
Zn1—Cl1	2.3271(9)	Cd1—N1	2.267(4)
Zn1—Cl2	2.2772(8)	Cd1—N2	2.278(4)
Zn1—N1	2.055(2)	Cd1...N3	2.684(4)
Zn1—N2	2.063(2)	Cd1—Cl1	2.5331(15)
Zn1...N3	2.6438(28)	Cd1—Cl2	2.4854(16)
		Cd1'...Cl2	2.8947(15)
Cl2—Zn1—Cl1	107.47(3)	Cl1—Cd1—Cl2'	175.08(4)
N1—Zn1—Cl1	98.15(7)	Cl2—Cd1—Cl1	103.85(5)
N1—Zn1—Cl2	103.42(7)	Cl2—Cd1—Cl2'	80.83(5)
N1—Zn1—N2	141.54(11)	N1—Cd1—Cl1	94.05(11)
N2—Zn1—Cl1	99.34(7)	N1—Cd1—Cl2	107.26(11)
N2—Zn1—Cl2	103.53(7)	N1—Cd1—Cl2'	83.01(11)
		N1—Cd1—N2	139.15(17)
		N2—Cd1—Cl1	95.87(11)
		N2—Cd1—Cl2	108.56(11)
		N2—Cd1—Cl2'	83.92(11)

(') = 2 - x; - y; 1 - z.

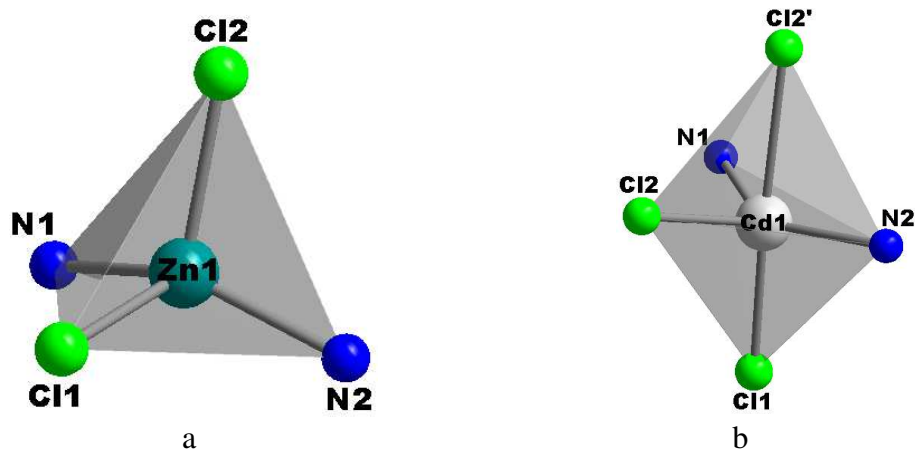


Fig. 4. Distorted tetrahedral and trigonal bipyramid geometries for complexes **2** (a) and **3** (b).

The crystalline packing of both complexes is sustained by numerous intermolecular hydrogen bonds (Tables S4 and S6) between chlorine atoms and H from the MeO group and aromatic ones. These additional interactions form a 2D network in the *ac* plane (Fig. 5, Figs S2-S6).

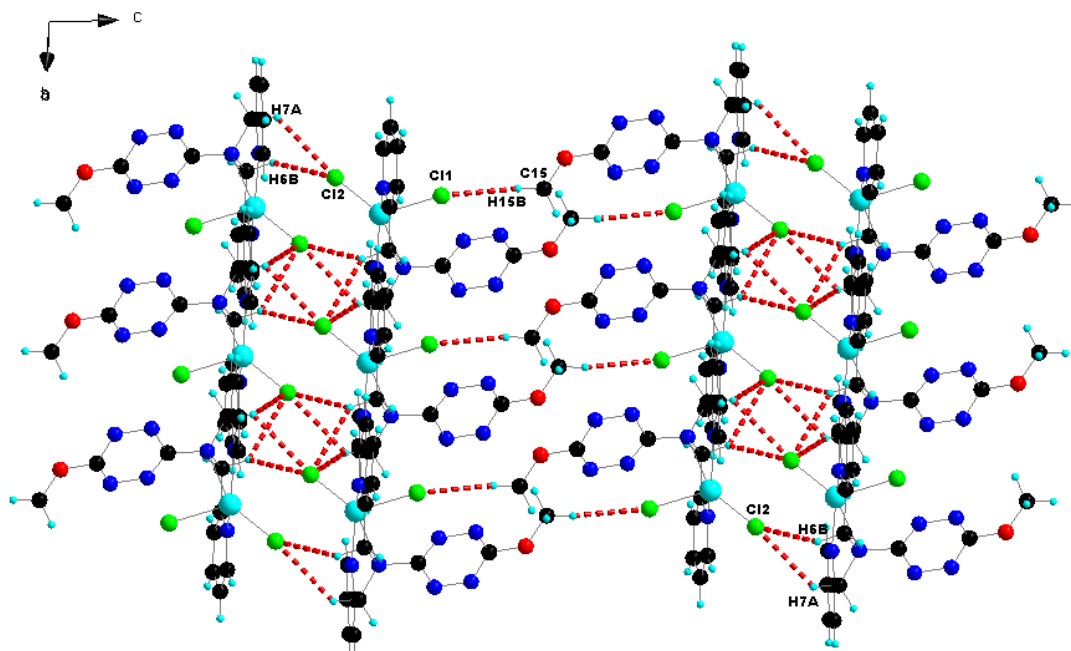


Fig. 5. The formation of 2D network due to the intermolecular hydrogen bonds in complex **2**.

3.3. Photophysical properties of ligand **L** and complexes **2** and **3**

Since the lone pair of the amino N atom is involved in semi-coordination with the metal centers, a modulation of the fluorescence is expected to occur as in the case of the corresponding chloro-tetrazine-dipica ligand [15]. The absorption spectrum of ligand **L** measured in acetonitrile exhibits two absorption bands in the UV-visible region located at around 426 and 527 nm (Fig 6). As compared to Cl-TTZ-dipica **1**, we notice a small red shift of both absorption bands which might be due to the mesomeric effect of the methoxy group. The high-energy absorption band corresponds to a π - π^* transition of the tetrazine unit with a strong contribution due to the conjugation by the amine nitrogen of the dipica unit [15]. The low-energy absorption band located at 527 nm is due to an n - π^* transition of the tetrazine unit [15].

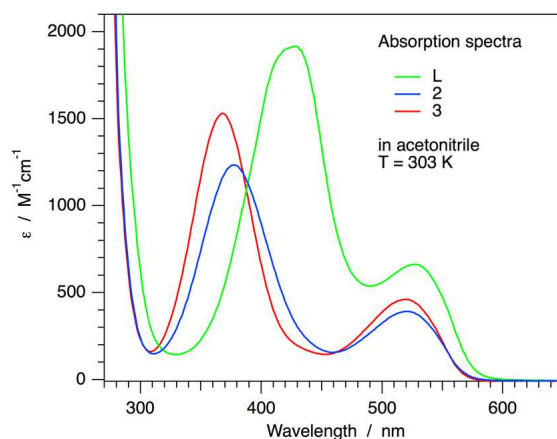


Fig. 6. Absorption spectra shown with molar extinction coefficients for ligand **L** and complexes **2** and **3** in acetonitrile at room temperature.

The absorption spectra of complexes **2** and **3** (Fig. 6) measured in acetonitrile show the same behavior as the free ligand **L** (two absorption bands in the UV-visible region) but with a rather strong blue shift (> 50 nm) for the $\pi-\pi^*$ transition now centered at 375 and 368 nm for complexes **2** and **3** (Table 3), respectively. The low-energy absorption band that corresponds to the $n-\pi^*$ transition of the tetrazine ring is however only slightly blue shifted (< 10 nm) and is located at around 521 and 520 nm (Table 3), respectively. This behavior is similar to the one observed for Cl-TTZ-dipica **1** and its corresponding Zn(II) and Cd(II) metal complexes; the strong blue shift of the $\pi-\pi^*$ transition has been attributed to the semi-coordination of the metal cation to the amine nitrogen of dipica which reduces the conjugation with the tetrazine ring [15].

Table 3. Comparison of absorption and emission properties of the ligand **L** and Zn(II) and Cd(II) complexes **2** and **3** at room temperature in acetonitrile.

Sample	Absorption/nm	Emission/nm
Ligand L	426/527	-
Zn complex 2	375/521	575
Cd complex 3	368/520	574

While the previously reported Cl-TTZ-dipica ligand **1** exhibited a very weak luminescence [15], the present ligand **L** is not luminescent at all in acetonitrile solution at room temperature. In both cases, this behavior is attributed to the quenching of the TTZ based luminescence by the presence of the electron donating amine group, which is conjugated with the TTZ ring. Upon coordination with diamagnetic metal centers such as Zn(II) and Cd(II) we can expect the rigidifying of the ligand and the participation of the amino nitrogen lone pair in semi-coordination with the metal cations and thus the switch-on of the luminescence of the TTZ unit.

Indeed, the two complexes emit weakly but clearly at room temperature in the visible region around 575 nm showing that the chelation with the metal cation provokes the switch-on of the luminescence of the free ligand. The corresponding emission and excitation spectra of the complexes **2** and **3** are shown in Fig. 7. Note that the excitation spectra perfectly match the absorption spectra, thus proving that the observed luminescence is intrinsic to the complexes. The emission behavior of the present complexes can be compared to that of the corresponding Zn(II) and Cd(II) complexes of Cl-TTZ-dipica complexes, yet with a small shift (~ 5 nm) to lower energies [15b]. As mentioned above, the switch-on of the luminescence of the free ligand upon chelation is very likely due to a less flexible structure of the ligand in the complexes and, especially, to the absence of electronic conjugation between TTZ and the amino nitrogen lone pair which is now involved in semi-coordination with the metal centers.

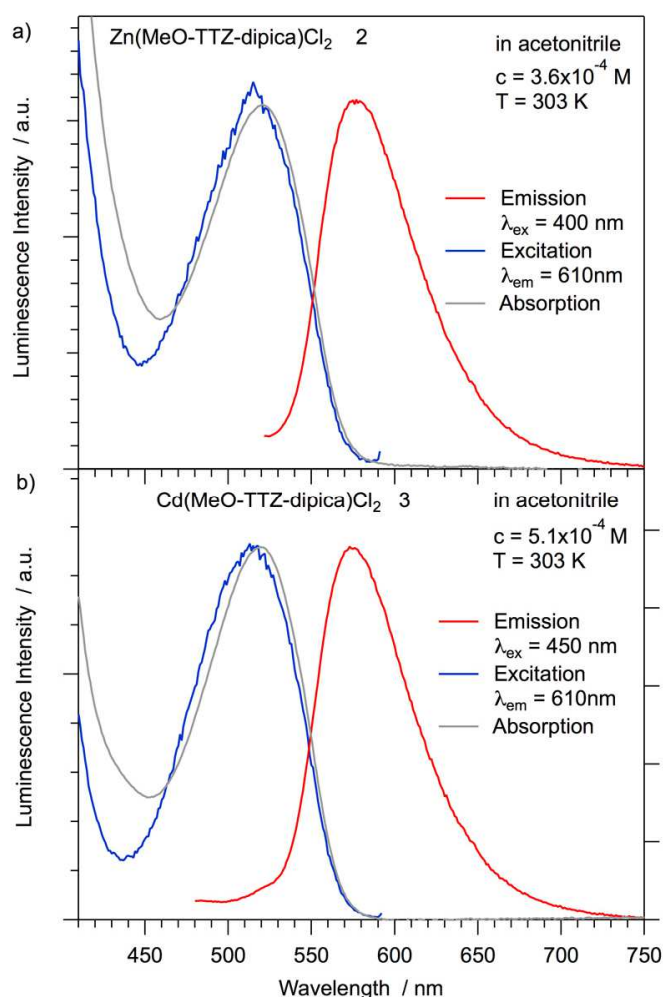


Fig. 7. Emission and excitation spectra of complexes **2** (a) and **3** (b) in acetonitrile at room temperature. For direct comparison with the excitation spectra the absorption spectra are included.

4. Conclusions

The ligand 6-methoxy-3-dipicolylamino-1,2,4,5-tetrazine (CH₃O-TTZ-dipica) **L** has been synthesized and structurally characterized. Its stoichiometric reaction with diamagnetic transition metal centers Zn(II) and Cd(II) afforded two neutral metal complexes [Zn**L**Cl₂] (**2**) and [Cd**L**Cl₂]₂ (**3**) that were structurally characterized. The crystal structure analyses indicated that the zinc(II) complex is mononuclear and presenting a highly distorted tetrahedral geometry while the cadmium(II) complex is dinuclear and showing a distorted trigonal bipyramid. In addition, we have shown that the nitrogen from the amino group of the ligand is involved in semi-coordination with the metal ions. The absorption spectra exhibit mainly two absorption bands in the UV-visible region for the free ligand and for the two complexes. The performed luminescence studies showed that the ligand **L** is not luminescent, very likely because of the participation of the lone pair of the nitrogen atom in the conjugation with TTZ unit. The semi-coordination of this nitrogen atom to the metal ions allows the resulting Zn(II) and Cd(II) metal complexes to be luminescent. These examples of complexes based on this new functional ligand (CH₃O-TTZ-dipica) **L** demonstrate that the combination of the tetrazine unit with a coordination moiety is a valuable strategy to prepare new metal complexes with original tunable photophysical properties. The complexation ability of ligand **L** towards metal cations such as Mn(II), Co(II),... should afford metal complexes with tunable magnetic properties. From a different perspective, 3,6-substituted *s*-tetrazine derivatives have shown interesting antitumor activity [21], therefore this constitutes as well a possible direction of investigation for the new tetrazine ligands and complexes.

Appendix A. Supplementary data

CCDC 1909348 – 1909350 contain the supplementary crystallographic data for Ligand **L**, complexes **2** and **3**. 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.

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