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#### The Influence of the Metal Cation and the N-Donor Ligand on the

#### Reactivity and Structures of Cd and Zn Coordination Compounds with 3-

#### **Bromopyridine and 3-Chloropyridine**

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#### Abstract

Reaction of cadmium thiocyanate and zinc thiocyanate with an excess of 3-bromopyridine and 3-chloropyridine leads to single crystals of four coordination compounds of composition  $M(NCS)_2(3$ -bromopyridine)<sub>4</sub> (M = Cd (Cd1-Br), Zn (Zn1-Br)) and  $M(NCS)_2(3$ chloropyridine)<sub>4</sub> (M = Cd (Cd1-Cl), Zn (Zn1-Cl)). These compounds forms pairs of isotypic compounds (Cd1-Br and Zn1-Br in space group P-1 and Cd1-Cl and Zn1-Cl in space group C2/c) in which the metal cation are octahedral coordinated by two terminal thiocyanato anions and four neutral N-donor ligands into discrete complexes. If less N-donor ligands are used in the synthesis, compounds of composition  $M(NCS)_2(3-bromopyridine)_2$  (M = Cd (Cd2-Br), Zn (Zn2-Br)) and M(NCS)<sub>2</sub>(3-chloropyridine)<sub>2</sub> (M = Cd (Cd2-Cl), Zn (Zn2-Cl)) are obtained. In the crystal structure of the isotypic compounds Cd2-Br and Cd2-Cl (monoclinic space group  $P2_1/c$ ) the metal cations are octahedral coordinated by two N-donor ligands and four thiocyanato anions and are linked into chains by the anionic ligands. In contrast, the Zn compounds **Zn2-Br** and **Zn2-Cl** are not isotypic but form similar discrete complexes in which the metal cations are tetrahedral coordinated by two terminal N-bonded thiocyanato anions

and two neutral N-donor ligands. On heating compounds **1** half of the ligands are removed and a transformation into compounds **2** is observed. The structures and reactivity of these compounds are discussed and compared with those of related compounds.

**Keywords:** Crystal Structures / Coordination Compounds / 3-Bromopyridine / 3-Chloropyridine / Thermal Properties

#### Introduction

Recently, the synthesis and characterization of coordination polymers have been intensively studied, in order to prepare new compounds with interesting physical or chemical properties.<sup>[1-14]</sup> To reach this goal strategies for a more rational design of structures must be developed and structure-property relationships must be investigated in detail.<sup>[15-27]</sup> This approach, called "Crystal Engineering" includes investigations for a better understanding of intermolecular interactions in the context of crystal packing.<sup>[28-31]</sup>

In our own research we are interested in the synthesis, structures and magnetic properties of transition metal thio- and selenocyanates based on Mn(II), Fe(II), Co(II) and Ni(II) in which the metal cations are linked by  $\mu$ -1,3-bridging anions into chains because such compounds frequently show interesting magnetic properties including metamagnetism and single chain magnetic behavior.<sup>[32-38]</sup> Unfortunately these compounds are less chalcophilic and therefore, the formation of compounds in which the anionic ligands are only terminal *N*-bonded are energetically favored. However, the desired compounds with a bridging coordination can selectively be prepared by thermal decomposition of precursors in which the anionic ligands are only terminal *N*-bonded but using this procedure usually only microcrystalline powders are obtained that cannot be characterized by single crystal X-ray diffraction.<sup>[39-43]</sup> To

overcome this problem compounds using the more chalcophilic cadmium can be prepared, which in contrast to the paramagnetic counterpart prefer a bridging coordination whereas the compounds with only terminal *N*-bonded cations are sometimes more difficult to prepare and some representative examples for both coordination modes are given in the reference list.<sup>[44-52]</sup> Some of the Cd compounds are isotypic to their paramagnetic analogs and thus, the structures of the latter can be determined by Rietveld refinement.<sup>[53-57]</sup> In this context it is mentioned that also the corresponding Zn compounds can be used to retrieve structural information on their paramagnetic counterparts if they are tetrahedrally coordinated, which is sometimes observed for e.g. cobalt(II).<sup>[58-60]</sup> This is the reason why we are interested in the chemistry of Cd and Zn thio- and selenocyanato coordination compounds especially based on different pyridine derivatives. In this context it is of interest in which cases Zn and Cd forms isotypic compounds and which N-donor ligands can be exchanged without changing the overall structure.

In recent work we investigated e.g. Co(II) and Zn(II) thiocyanates with 2-methyl-, 2-chloroand 2-bromopyridine as co-ligand.<sup>[60]</sup> We have observed eight compounds of composition  $M(NCS)_2(L)_2$  (M = Co, Zn and L = 2-methyl-, 2-chloro- and 2-bromopyridine). The Co and Zn compound with 2-chloropyridine crystallizes in two different modifications of which the thermodynamic stable forms at room-temperature are isotypic to the 2-methylpyridine compounds whereas the metastable forms are isotypic to the 2-bromopyridine compounds, which means that they adopts the structure of that ligand, which obviously needs more space in the crystal. The exchange of a methyl group by a chloro atom without changing the structure is not very surprising and this is known as the chloro-methyl exchange rule but obviously even a chloro atom might sometimes be exchanged by a bromo atom and the structure remains constant.<sup>[28, 29, 60, 61]</sup> Surprisingly, with these ligand no octahedrally coordinated complexes of composition M(NCS)<sub>2</sub>(L)<sub>4</sub> can be prepared and this might have steric reasons because of the bulky substituent in 2-position. To investigate this in more detail

we decided to prepare Cd and Zn thiocyanato coordination compounds with the N-donor ligands mentioned above where the methyl group, the chloro and the bromo substituent is in 3-position. However, two compounds with 3-methylpyridine were already reported in literature. The Zn compound of composition Zn(NCS)<sub>2</sub>(3-methylpyridine)<sub>2</sub> crystallizing orthorhombic in space group Pnma and the Cd compound  $Cd(NCS)_2(3-methylpyridine)_2$ crystallizing in space group P-1.<sup>[62, 63]</sup> Therefore, our investigations focus on the corresponding compounds with 3-chloro- and 3-bromopyridine. Here we report on these investigations. JUS

#### Results

#### Synthetic investigations

To investigate which compounds based on Cd(NCS)<sub>2</sub>, Zn(NCS)<sub>2</sub> and 3-bromopyridine as well as 3-chloropyridine can be synthesized at room-temperature different molar ratios of these reactants were reacted in water. Afterwards all residues were investigated by X-ray powder diffraction, elemental analysis and IR spectroscopy, which lead to the formation of eight new compounds (Table 1). If an excess of the N-donor ligands is used, the composition of the residues is in only rough agreement with that calculated for  $M(NCS)_2(3-chloropyridine)_4$  (M = Cd (Cd1-Cl), Zn (Zn1-Cl)) and for  $M(NCS)_2(3$ -bromopyridine)<sub>4</sub> (M = Cd (Cd1-Br), Zn (Zn1-Br)) (Table 1). The asymmetric CN-stretching vibration is found between 2057 and 2069 cm<sup>-1</sup> for these compounds, which indicates that only terminal N-bonded anions are present (Table 2 and Fig. S1-S4 in the supplementary material).<sup>[64-66]</sup>

In contrast, if the ratio between metal thiocyanato and the N-donor ligands is reduced, compounds were obtained for which the results of the elemental analysis is in very good agreement with that calculated for compounds of composition  $M(NCS)_2(3-chloropyridine)_2$ (M = Cd (Cd2-Cl), Zn (Zn2-Cl)) and of  $M(NCS)_2(3$ -bromopyridine)\_2 (M = Cd (Cd2-Br), Zn (**Zn2-Br**)) (Table 1 and experimental section).

Table 1.	Compounds	that are ob	otained if C	$d(NCS)_2$ or	$Zn(NCS)_2$	were reacted	with	different
amounts	of 3-bromop	vridine and	3-chloropy	ridine in w	ater at roon	n-temperature	•	

Molar ratio	Cd(	NCS) <sub>2</sub>	Zn(NCS) <sub>2</sub>		
	3-bromopyridine	3-chloropyridine	3-bromopyridine	3-chloropyridine	
1:8	Cd1-Br/Cd2-Br	Cd1-Cl/Cd2/Cl	Zn1-Br/Zn2-Br	Zn1-Cl/Zn2-Cl	
1:6	Cd1-Br/Cd2-Br	Cd1-Cl/Cd2/Cl	Zn1-Br/Zn2-Br	Zn1-Cl/ Zn2-Cl	
1:4	Cd1-Br/Cd2-Br	Cd1-Cl/Cd2/Cl	Zn1-Br/Zn2-Br	Zn1-Cl/ Zn2-Cl	
1:2	Cd1-Br/Cd2-Br	Cd2-Cl	Zn2-Br	Zn2-Cl	
1:1	Cd2-Br	Cd2-Cl	Zn2-Br	Zn2-Cl	
2:1	Cd2-Br	Cd2-Cl	Zn2-Br	Zn(NCS) <sub>2</sub>	
4:1	Cd(NCS) <sub>2</sub>	Cd(NCS) <sub>2</sub>	Zn(NCS) <sub>2</sub>	Zn(NCS) <sub>2</sub>	

**Table 2.** Values of the asymmetric stretching vibration  $v_{as}(CN)$  in compounds 1 and 2.

compound	$v_{\rm as}(\rm CN) / \rm cm^{-1}$	Coordination mode		
Cd(NCS) <sub>2</sub> (3-bromopyridine) <sub>4</sub> (Cd1-Br)	2057	terminal		
Zn(NCS) <sub>2</sub> (3-bromopyridine) <sub>4</sub> ( <b>Zn1-Br</b> )	2102, 2069	terminal		
Cd(NCS) <sub>2</sub> (3-chloropyridine) <sub>4</sub> (Cd1-Cl)	2057	terminal		
Zn(NCS) <sub>2</sub> (3-chloropyridine) <sub>4</sub> (Zn1-Cl)	2098, 2068	terminal		
$[Cd(NCS)_2(3-bromopyridine)_2]_n (Cd2-Br)$	2105	µ-1,3-bridging		
Zn(NCS) <sub>2</sub> (3-bromopyridine) <sub>2</sub> (Zn2-Br)	2102, 2071	terminal		
$[Cd(NCS)_2(3-chloropyridine)_2]_n$ (Cd2-Cl)	2108	µ-1,3-bridging		
Zn(NCS) <sub>2</sub> (3-chloropyridine) <sub>2</sub> (Zn2-Cl)	2098, 2065	terminal		

The asymmetric stretching vibration is observed at 2105cm<sup>-1</sup> for **Cd2-Br** and at 2108 cm<sup>-1</sup> for **Cd2-Cl**, strongly indicating that the metal cations are linked by  $\mu$ -1,3-bridging anionic ligands (Table 2 and Fig. S5-S6 in the supplementary material). For **Zn2-Br** and **Zn2-Cl** these values amount to 2071 and 2065 cm<sup>-1</sup> indicating that still terminal *N*-bonded thiocyanato anions are present (Table 2 and Fig. S7-S8 in the supplementary material).

To verify the nature of all these residues crystallization experiments were performed, leading to single crystals for all compounds that were investigated by single crystal X-ray diffraction

(see below). Based on these results X-ray powder pattern were calculated and compared with the experimental pattern (Figure 1 and Fig. S9 in the supplementary material).



Figure 1. Experimental powder pattern of Cd2-Br (top: A) and Cd2-Cl (top: C), Zn2-Br (bottom: A) and Zn2-Cl (bottom: C) together with the calculated pattern for Cd2-Br (top: B) and Cd2-Cl (top: D), Zn2-Br (bottom: B) and Zn2-Cl (bottom: D).

This clearly shows that all compounds of composition  $M(NCS)_2(L)_4$  (M = Cd, Zn, L = 3chloro- and 3-bromopyridine) (1) are contaminated with different amounts of the compounds of composition  $M(NCS)_2(L)_2$  (2) (Fig. S9 in the supplementary material). This is a bit surprising because there were no indication for a contamination of the Cd compounds from

IR-spectroscopy. In contrast, compounds 2 are obtained as single crystalline phases (Figure 1).

#### Crystal structures of the compounds of composition $M(NCS)_2(L)_4$

 $Cd(NCS)_2(3$ -bromopyridine)\_4 (**Cd1-Br**) and  $Zn(NCS)_2(3$ -bromopyridine)\_4 (**Zn1-Br**) are isotypic and crystallize in the triclinic space group *P*-1 with two formula units in the unit cell (Table 3). The asymmetric unit consists of two crystallographic independent metal(II) cations located on centers of inversion as well as two crystallographically independent thiocyanato anions and four N-donor ligands (Figure 2). Each metal cation is coordinated by two terminal *N*-bonded thiocyanato anions and four 3-bromopyridine ligands within a slightly distorted octahedral geometry (Figure 2: left and Table 2).



**Figure 2.** View of the coordination sphere of the metal cation (left) and overlay plot of both crystallographically independent metal complexes (right) in the crystal structure of **Zn1-Br** as a representative (black = metal(II), dark-grey = bromine / sulfur, grey = nitrogen, light-grey = carbon, white = hydrogen). ORTEP plots of **Cd1-Br** and **Zn1-Br** can be found in Figures S10-S11 in the supplementary material.

The MN<sub>6</sub> octahedra are slightly distorted with distances in range of 2.236(7) Å to 2.440(9) Å in **Cd1-Br** and of 2.088(4) Å to 2.298(4) Å in **Zn1-Br** and angles ranging from 78.4(3) ° to 101.6(3) ° and 180 ° in **Cd1-Br** and of 81.42(14) ° to 93.32(14) ° and 180 ° in **Zn1-Br** (Table S1-S2 in the supplementary material). The structural parameters in both crystallographically independent complexes are comparable but significant differences are found in the torsion of the 6-membered rings and the orientations of the anionic ligands (Figure 2: right).

The 3-chloropyridine compounds **Cd1-Cl** and **Zn1-Cl** are also isotypic but crystallize in the monoclinic space group *C*2/c with four formula units in the unit cell (Table 3). The asymmetric unit consists of one metal(II) cation located on a center of inversion as well as one thiocyanato anion and two 3-chloropyridine ligands in general positions and therefore, in contrast to the 3-bromopyridine compounds only one crystallographically independent complex is present. As in the 3-bromopyridine compounds the metal cations are 6-fold coordinated within slightly distorted octahedral with distances with distances ranging from 2.260(3) Å to 2.391(2) Å in **Cd1-Cl** and of 2.0725(15) Å to 2.2713(18) Å in **Zn1-Cl** and angles ranging from 88.02(9) ° to 91.98(9) ° and 180 ° in **Cd1-Cl** and of 88.55(7) ° to 91.45(7) ° and 180 ° in **Zn1-Cl** (Table S3-S4 in the supplementary material).

In the crystal structure of the 3-chloropyridine compounds the anionic ligands are arranged in corrugated layers that elongate along the crystallographic *a*-axis (Figure 3: bottom). The 3-chloropyridine ligands are stacked in the direction of the crystallographic *c*-axis but are slightly shifted along the *a*-axis (Figure 3: bottom). In this arrangement no  $\pi$ - $\pi$  interactions are present but the halide substituent of one complexe is oriented directly below the plane of the 6-membered ring of a neighbored complex and these C-Br… $\pi$  interactions might contribute to the stabilization of this structure. As mentioned above the 3-bromopyridine compounds are not isotypic to the 3-chloropyridine compounds but both structures are strongly related (Figure 3). In the 3-bromopyridine compounds a very similar arrangement is

observed and differences are predominantly found in the torsion of the N-donor ligands. Therefore, the complexes that are equivalent in the monoclinic *c*-centered 3-chloropyridine structure are different in the triclinic 3-bromopyridine structures and this might be traced back to packing effects because of the bulky bromine substituent (Figure 3).



**Figure 3.** Crystal structure of the 3-bromopyridine compounds (top) and the 3-chloropyridine compounds (bottom) along the crystallographic *c*-axis (black = metal(II), dark-grey = bromine / chlorine / sulfur, grey = nitrogen, light-grey = carbon, white = hydrogen). ORTEP plots of **Cd1-Cl** and **Zn1-Cl** can be found in Fig. S12- S13 in the supplementary material.

#### Crystal structures of the compounds of composition $M(NCS)_2(L)_2$

Cd(NCS)<sub>2</sub>(3-bromopyridine)<sub>2</sub> (Cd2-Br) and Cd(NCS)<sub>2</sub>(3-chloropyridine)<sub>2</sub> (Cd2-Cl) are isotypic and crystallize in the centrosymmetric monoclinic space group  $P2_1/n$  with two formula units in the unit cell (Table 3). The asymmetric unit consists of one cadmium(II) cation located on a center of inversion, one thiocyanato anion as well as one N-donor ligand in general position. In the crystal structure each cadmium(II) cation is coordinated by two *N*and two *S*-bonded thiocyanato anions and two *trans*-oriented neutral co-ligands within slightly distorted octahedra. The CdN<sub>6</sub> distances ranging from 2.278(2) Å to 2.7323(7) Å (angles from 87.60(6) ° to 92.40(6) ° and 180 °) for Cd2-Br and from 2.283(2) Å to 2.7223(8) Å (angles from 87.09(6) ° to 92.91(6) ° and 180 °) for Cd2-Cl (Table S5-S6 in the supplementary material). The cadmium(II) cations are connected by  $\mu$ -1,3-bridging thiocyanato anions into chains, which elongate in the direction of the crystallographic *b*-axis (Figure 4).



**Figure 4.** View of the thiocyanato chains in the crystal structure of **Cd2-Br** as a representative (black = metal(II), dark-grey = bromine / sulfur, grey = nitrogen, light-grey = carbon, white = hydrogen). ORTEP plots of **Cd2-Br** and **Cd2-Cl** can be found in Fig. S14-S15 in the supplementary material.

The interchain cadmium...cadmium separation within the thiocyanato chains amount to 5.8630(2) Å for Cd2-Br and to 5.8596(12) Å for Cd2-Cl and the shortest interchain distances between the metal cations are 9.7056(5) Å in Cd2-Br and 8.5123(25) Å in Cd2-Cl.

In contrast to the Cd compounds, the Zn compounds with 3-bromopyridine (**Zn2-Br**) as well as 3-chloropyridine (Zn2-Cl) exhibits a completely different structure even if their composition is identical.  $Zn(NCS)_2(3$ -bromopyridine)<sub>2</sub> crystallizes orthorhombic in space group  $P2_12_12$  with two formula units in the unit cell, whereas  $Zn(NCS)_2(3-chloropyridine)_2$ crystallizes in the monoclinic space group  $P2_1/c$  with four formula units in the unit cell (Table 3). In **Zn2-Br** the Zn atoms are located on a crystallographic 2-fold rotation axis, whereas in Zn2-Cl all atoms are located in general positions. In the crystal structure of both compounds each zinc(II) cation is coordinated by two terminal N-bonded thiocyanato anions and two 3bromopyridine respectively two 3-chloropyridine ligands within slightly distorted tetrahedra (Figure 5). The Zn-N distances ranges from 1.929(4) Å to 2.041(4) Å (angles between 104.42(15) ° to 115.09(19) °) in Zn2-Br and from 1.923(3) Å to 2.045(2) Å (angles 103.74(11) ° to 122.48(13) °) in Zn2-Cl (Table S7-S8 in the supplementary material). In both crystal structures the discrete complexes are stacked in the direction of the crystallographic baxis (Fig. S18 in the supplementary material). In Zn2-Br the discrete complexes are arranged in columns along the *c*-axis with the 3-chloropyridine ligands perfectly stacked onto each other maximizing  $\pi$ - $\pi$  interactions within the complexes of the same column (Figure 5: top). Moreover, weak Br...S intermolecular interactions are found between the bromo substituents and the S atoms of the anionic ligands. In **Zn2-Cl** the discrete complexes are also stacked along the *c*-axis, but in this case neighboring columns interact via intermolecular  $\pi$ - $\pi$ interactions (Figure 5: bottom). Moreover, in this structure the anionic ligands are also stacked along the c-axis but points in opposite directions in order that these polar anions can

interacted *via* dipole-dipole interactions (Figure 5). Finally, a more dense packing is observed than for **Zn2-Br**.



**Figure 5.** Crystal structure of **Zn2-Br** (top) and **Zn2-Cl** (bottom) with view along the crystallographic *c*-axis (black = metal(II), dark-grey = bromine / chlorine / sulfur, grey = nitrogen, light-grey = carbon, white = hydrogen). ORTEP plots of **Zn2-Br** and **Zn2-Cl** can be found in figures S16- S17 in the supplementary material.

#### Thermoanalytical investigations

Even if compounds Cd1-Br, Zn1-Br, Cd1-Cl and Zn1-Cl are contaminated with different amounts of Cd2-Br, Zn2-Br, Cd2-Cl and Zn2-Cl they were investigated for their thermal properties using simultaneously differential thermoanalysis and thermogravimetry. In this context the question raises if e.g. compounds of composition M(NCS)<sub>2</sub>(L)<sub>2</sub> are obtained as intermediates and if they corresponds to the compounds obtained from the liquid phase or if they will represent a polymorphic modifications as reported previously.<sup>[54]</sup> On heating these compounds in a thermobalance to 400 °C, several mass steps are observed in the TG curve, which are accompanied with endothermic events in the DTA curve (Figure 6 and Fig. S19 in the supplementary material). The DTG curve shows that most of these steps are well separated (Figure 6).



Figure 6. DTG, TG and DTA curves for Cd1-Br (left) and Cd1-Cl (right). Heating rate =  $4^{\circ}$ C/min; given are the peak temperatures  $T_{\rm P}$  in °C and the mass loss in %.

For **Cd1-Br** the experimental mass loss in the first and second TG step is a bit lower than that calculated for the removal of two and one 3-bromopyridine ligand respectively ( $\Delta m_{calc}$  -3-

bromopyridine = 18.4%), because of the contamination with a small amount of Cd2-Br but indicates that a compound of composition Cd(NCS)<sub>2</sub>(3-bromopyridine)<sub>2</sub> has formed in the first step, that transforms into Cd(NCS)<sub>2</sub>(3-bromopyridine) on further heating (Figure 6). Error! Reference source not found.For the 3-chloropyridine compound Cd1-Cl very large deviations from the values calculated for the removal of half of the N-donor ligands are found ( $\Delta m_{calc}$  -3-chloropyridine = 16.6%), which can be traced back to the strong contamination of this compound with Cd2-Cl (see above). Similar investigations for the Zn compound Zn1-Br and Zn2-Cl shows also larger deviations from the calculated values because as shown above even this compound was contaminated with Zn2-Br respectively Zn2-Cl (Fig. S19 in the supplementary material). In contrast to the Cd compounds there is no hint for the formation of a further compound of composition Zn(NCS)<sub>2</sub>(L).

To identify the nature of the intermediates formed in the first and second TG step additional TG experiments were performed, stopped after the first TG and second TG step and the residues obtained were investigated by X-ray powder diffraction (Figure 7 and Fig. S20 in the supplementary material).

These experiments clearly show that compounds Cd2-Br, Cd2-Cl, Zn2-Br and Zn2-Cl has formed in the first TG step as phase pure materials. However, if the residues formed after the second step are isolated and investigated by XRPD measurements it is found that they are amorphous to X-rays.



**Figure 7.** Experimental X-ray powder pattern of the residues obtained in the TG heating step of **Cd1-Br** (A) and **Cd1-Cl** (C) together with the calculated XRPD pattern of **Cd2-Br** (B) and **Cd2-Cl** (D).

#### Investigations on the stability of compounds 1

As mentioned above our synthetic investigations have shown that the compounds of composition  $M(NCS)_2(L)_4$  are always contaminated with different amounts of those of composition  $M(NCS)_2(L)_2$  indicating that the latter are more stable. To investigate this question into more detail Cd(NCS)<sub>2</sub> and Zn(NCS)<sub>2</sub> were reacted with 3-bromopyridine as well as 3-chloropyridine in ratio 1:6 and the residues that have formed were investigated by X-ray powder diffraction as function of time. It is obvious that the reaction of Cd(NCS)<sub>2</sub> and 3-bromopyridine in water leads to the formation of Cd1-Br in the beginning but after 3 d a mixture of Cd1-Br and Cd2-Br is obtained, which completely transforms into Cd2-Br after 4 d (Figure 8: top). Similar investigations on the 2-chloropyridine compounds with Cd also show that in the beginning Cd1-Cl forms, that transforms into Cd2-Cl *via* a mixture of both compounds as intermediate (Figure 8: bottom). Similar observations were made if Zn(NCS)<sub>2</sub>

is reacted with these ligands, which finally always lead to the formation of **Zn2-Cl** and **Zn2-Br** (Figure S21 and S22 in the supplementary material). These experiments clearly proves that independent of the metal cation and the neutral N-donor ligand compounds **2** are more stable than compounds **1**, even if a large excess of the N-donor ligand is used in the synthesis.



**Figure 8.** Calculated powder pattern of the **Cd1** (A) and **Cd2** (E) compounds together with the pattern powder pattern obtained after reacting  $Cd(NCS)_2$  with 3-bromopyridine (top) and 3-chloropyridine (bottom) in ration 1:6 for 1 d (B), 3 d (C) and 4 d (D).

#### Discussion on the influence of the metal cation and the N-donor ligand

The present work originates from previous investigations on corresponding thiocyanato compounds, especially with 2-methyl, 2-chloro- and 2-bromopyridine as N-donor ligand. In this context we investigated how many compounds are available and if the metal cations or the neutral N-donor ligands can be exchanged without changing the overall crystal structure. First of all in the present work compounds of composition  $M(NCS)_2(L)_4$  could be prepared even with Zn in which the metal cations are octahedrally coordinated. Such compounds cannot be prepared with the N-donor ligands that are substituted in 2-position which support the assumption that this can be traced back to the sterical demand of the bulky substituents neighbored to the coordinating nitrogen atom.<sup>[60]</sup> However, as we have shown the preparation of the octahedral complexes with the 3-substituted ligands is also difficult to achieve and independent of the molar ratio of the reactants they are always contaminated with the compounds of composition  $M(NCS)_2(L)_2$ . Consequently it must be assumed that the latter are more stable which is also be supported by our experiments on the stability of these compounds. In the case of Cd this originates from the fact that this metal cation is more chalcophilic and thus, the  $\mu$ -1,3-bridging coordination is energetically favored. This is exactly the reason why such compounds can be used as structural analogs for the paramagnetic compounds where this situation is reversed.<sup>[54-56]</sup> In the case of Zn which is less chalcophilic and which exhibits a much lower ionic radii the situation is different because in contrast to Cd, Zn compounds always prefer a tetrahedral coordination and thus, the tetrahedral complexes are more stable than the octahedral and structures similar to that of Cd2-Br and Cd2-Cl are unknown.

Surprisingly, independent of the metal cation none of the 3-methylpyridine compounds reported recently are isotypic to those with 3-chloropyridine reported in this contribution and this one exception from the so-called chloro-methyl exchange rule. <sup>[28, 29, 61]</sup> Moreover, the Zn and Cd 3-bromopyridine compounds **Cd1-Br** and **Zn1-Br** are isotypic, which shows that in

this case the metal cation plays only a minor role. This is the same for the 3-chloropyridine compounds **Zn1-Cl** and **Cd1-Cl** but which are not isotypic to those with 3-bromopyridine. However, carefully inspection of the crystal structures clearly shows that the packing of the complexes is very similar and only small structural differences in the torsion of the substituted pyridine rings are found.

Interestingly, for the compounds of composition  $M(NCS)_2(L)_2$  the situation is reversed in order that **Cd2-Br** and **Cd2-Cl** are isotypic. This strongly indicates that the exchange of a bromo substituent by a chloro substituent in several cases does not have dramatically influence on the overall structure and that both substituents behave isotropic in such structures. The fact that this is not valid for the Zn compounds **Zn2-Br** and **Zn2-Cl** indicates that the bromine and the chlorine substituent does not behave isotropic in these structures and that specific more directional intermolecular interactions might be of importance.

#### Conclusion

In this work it was shown that the position of the substituent in pyridine N-donor ligands dramatically influence the stability of octahedral complexes of composition  $M(NCS)_2(L)_4$ . Moreover, it was observed that for Cd as metal cation compounds with a  $\mu$ -1,3-bridging coordination are more stable than those in which the anionic ligand is only terminal bonded and this might also be responsible for the former observation. In the case of Zn the chalcophility play only a minor role because the tetrahedral coordination is always preferred over the octahedral and this might predominantly traced back to its small cation radii. It was also demonstrated that in most cases the bromo substituent can be exchanged by a chloro substituent without large changes in the overall crystal structure. Finally, the compounds of composition  $M(NCS)_2(L)_2$  can easily be prepared and exhibits crystal structures that are

expected and that are similar to those of the corresponding paramagnetic compounds. Consequently they can be used to retrieve structural information for their paramagnetic analogs, which are sometimes more difficult to prepare in this stoichiometry.

#### **Materials and Methods**

#### Experimental

 $CdSO_4 \cdot 8/3H_2O$ , ZnSO<sub>4</sub>, Ba(NCS)<sub>2</sub>·3H<sub>2</sub>O, 3-bromopyridine and 3-chloropyridine were obtained from Alfa Aesar and Sigma Aldrich, respectively. All chemicals were used without further purification.  $Cd(NCS)_2$  and  $Zn(NCS)_2$  were prepared by a reaction of equimolar amounts of  $CdSO_4 \cdot 8/3H_2O$  and  $ZnSO_4$  with  $Ba(NCS)_2 \cdot 3H2O$  in water. The resulting precipitate of BaSO<sub>4</sub> were filtered off and the filtrate were concentrated to complete dryness resulting in white residues of  $Cd(NCS)_2$  and  $Zn(NCS)_2$ . The purity was checked by XRPD and CHNS analysis. All crystalline powders were prepared by stirring the reactants in solution at room-temperature. Afterwards all residues were filtered off, washed with water and diethyl ether and dried in air.

**Preparation of**  $Cd(NCS)_2(3$ **-bromopyridine**)<sub>4</sub> (*Cd1-Br*): Single crystal suitable for X-ray structure determination were obtained by the reaction of Cd(NCS)<sub>2</sub> (34.2 mg, 0.15 mmol) and 3-bromopyridine (58.6 µL, 0.6 mmol) in 2 mL water a closed snap cap vial. Colorless block-shaped single-crystals were obtained after two days in a mixture with **Cd2-Br**.

**Preparation of**  $Zn(NCS)_2(3$ -bromopyridine)\_4 (Zn1-Br): Single crystal suitable for X-ray structure determination were obtained by the reaction of  $Zn(NCS)_2$  (27 mg, 0.15 mmol) and 3-bromopyridine (58.6 µL, 0.6 mmol) in 2 mL water a closed snap cap vial. Colorless block-shaped single-crystals were obtained after four days in a mixture with **Zn2-Br**.

**Preparation of**  $Cd(NCS)_2(3$ -chloropyridine)\_4 (Cd1-Cl): Single crystal suitable for X-ray structure determination were obtained by the reaction of Cd(NCS)\_2 (34.2 mg, 0.15 mmol) and 3-chloropyridine (56.5 µL, 0.6 mmol) in 2 mL water a closed snap cap vial. Colorless block-shaped single-crystals were obtained after one day in a mixture with Cd2-Cl.

**Preparation of**  $Zn(NCS)_2(3$ -chloropyridine)\_4 (Zn1-Cl): Single crystal suitable for X-ray structure determination were obtained by the reaction of  $Zn(NCS)_2$  (27 mg, 0.15 mmol) and 3-chloropyridine (56.5 µL, 0.6 mmol) in 2 mL water a closed snap cap vial. Colorless block-shaped single-crystals were obtained after two days in a mixture with **Zn2-Cl**.

*Preparation of Cd*(*NCS*)<sub>2</sub>(*3-bromopyridine*)<sub>2</sub> (*Cd2-Br*): Colorless block-shaped single crystal were obtained by reaction of Cd(NCS)<sub>2</sub> (34.2 mg, 0.15 mmol) and 3-bromopyridine (29.3  $\mu$ L, 0.3 mmol) in 2 mL water a snap cap vial. A white crystalline powder was obtained with a 4-fold excess of all reactants. Yield based on Cd(NCS)<sub>2</sub>: 323.41 mg (98.8 %). Elemental analysis for C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub>CdN<sub>4</sub>S<sub>2</sub> (544.56): calcd. C 26.47, H 1.48, N 10.29, S 12.18; found C 26.41, H 1.41, N 10.25, S 12.22. IR (ATR):  $v_{max} = 2105$  (s), 1583 (m), 1556 (m), 1506 (w), 1467 (m), 1416 (m), 1321 (m), 1229 (m), 1195 (m), 1100 (m), 1041 (m), 1023 (m), 982 (w), 941 (w), 917 (w), 796 (m), 769 (m), 711 (m), 688 (s), 630 (m), 466 (m), 456 (m), 406 (m) cm<sup>-1</sup>.

*Preparation of*  $Zn(NCS)_2(3$ -*bromopyridine*)\_2 (Zn2-Br): Colorless block-shaped single crystal were obtained by reaction of  $Zn(NCS)_2$  (27 mg, 0.15 mmol) and 3-bromopyridine (29.3 µL, 0.3 mmol) in 2 mL water a snap cap vial. A white crystalline powder was obtained with a 5-fold excess of all reactants. Yield based on  $Zn(NCS)_2$ : 359 mg (96.3 %). Elemental analysis for  $C_{12}H_8Br_2ZnN_4S_2$  (497.54): calcd. C 28.97, H 1.62, N 11.26, S 12.89; found C 29.02, H 1.59, N 11.22, S 12.91. IR (ATR):  $v_{max} = 2071$  (s), 1596 (m), 1558 (m), 1470 (w), 1420 (m), 1397 (m), 1322 (m), 1234 (m), 1195 (m), 1101 (m), 1041 (m), 992 (m), 964 (w), 928 (w), 854 (w), 803 (m), 721 (m), 693 (m), 649 (m), 479 (m), 411 (m) cm<sup>-1</sup>.

*Preparation of Cd*(*NCS*)<sub>2</sub>(*3-chloropyridine*)<sub>2</sub> (*Cd2-Cl*): Colorless block-shaped single crystal were obtained by reaction of Cd(NCS)<sub>2</sub> (34.2 mg, 0.15 mmol) and 3-chloropyridine (28.3 µL, 0.3 mmol) in 2 mL water a snap cap vial. A white crystalline powder was obtained with a 5-fold excess of all reactants. Yield based on Cd(NCS)<sub>2</sub>: 334.56 mg (97.9 %). Elemental analysis for C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>CdN<sub>4</sub>S<sub>2</sub> (455.66): calcd. C 31.63, H 1.77, N 12.30, S 14.07; found C 31.61, H 1.72, N 12.28, S 14.04. IR (ATR):  $v_{max} = 2108$  (s), 1584 (m), 1563 (m), 1471 (w), 1453 (m), 1419 (m), 1321 (m), 1233 (m), 1195 (m), 1168 (m), 1112 (m), 1094 (m), 1030 (w), 982 (w), 941 (w), 915 (m), 798 (s), 769 (w), 738 (m), 690 (s), 632 (m), 462 (m), 456 (m), 411 (m) cm<sup>-1</sup>.

*Preparation of*  $Zn(NCS)_2(3$ -*chloropyridine*)\_2 (Zn2-Cl): Colorless block-shaped single crystal were obtained by reaction of  $Zn(NCS)_2$  (27.2 mg, 0.15 mmol) and 3-chloropyridine (28.3 µL, 0.3 mmol) in 2 mL water a snap cap vial. A white crystalline powder was obtained with a 2-fold excess of all reactants. Yield based on  $Zn(NCS)_2$ : 122 mg (99.4 %). Elemental analysis for  $C_{12}H_8Cl_2ZnN_4S_2$  (408.64): calcd. C 35.27, H 1.97, N 13.71, S 15.69; found C 35.18, H 1.96, N 13.69, S 15.68. IR (ATR):  $v_{max} = 2098$  (s), 2065 (s), 1597 (m), 1566 (m), 1478 (w), 1427 (m), 1331 (m), 1244 (m), 1202 (m), 1124 (m), 1097 (m), 1054 (m), 955 (m), 921 (w), 849 (w), 803 (w), 752 (m), 688 (s), 649 (m), 480 (m), 433 (m), 411 (m) cm<sup>-1</sup>.

*Elemental Analysis:* CHNS analysis was performed using an EURO EA elemental analyzer, fabricates by EURO VECTOR Instruments and Software.

*Spectroscopy:* All IR data were obtained using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Mattson.

*X-Ray Powder Diffraction (XRPD):* The measurements were performed using 1) a PANalytical X'Pert Pro MPD Reflection Powder Diffraction System with CuK $\alpha$  radiation ( $\lambda$  = 154.0598 pm) equipped with a PIXcel semiconductor detector from PANanlytical and 2) a

Stoe Transmission Powder Diffraction System (STADI-P) with CuK $\alpha$  radiation ( $\lambda$  = 154.0598 pm) that was equipped with a linear position-sensitive detector from STOE & CIE.

*Differential Thermal Analysis and Thermogravimetry (DTA-TG):* The heating-rate dependent DTA-TG measurements were performed in a nitrogen atmosphere (purity: 5.0) in  $Al_2O_3$  crucibles using a STA-409CD instrument from Netzsch. All measurements were performed with a flow rate of 75 mL·min<sup>-1</sup>. The instrument was calibrated using standard reference materials.

Single-crystal structure analyses: Single-crystal data collections were carried out on an imaging plate diffraction system: Stoe IPDS-1 for Zn1-Br and Zn2-Cl and Stoe IPDS-2 for Cd1-Br, Cd1-Cl, Zn1-Cl, Cd2-Br, Zn2-Br and Cd2-Cl with MoK $\alpha$  radiation. The structures were solved with direct methods using SHELXS-97 and structure refinements were performed against F2 using SHELXL-97.<sup>[67]</sup> Numerical absorption correction was applied using programs X-RED and X-SHAPE of the program package X-Area.<sup>[68-70]</sup> All non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined isotropic with  $U_{iso}(H) = -1.2 U_{eq}(C)$  using a riding model with C-H = 0.95 Å for Cd1-Br, Zn1-Br, Cd1-Cl, Zn1-Cl, Zn2-Br and Zn2-Cl and C-H = 0.93 Å for Cd2-Br and Cd2-Cl. The crystals of compound Cd1-Br are non-merohedrally twinned. Both individuals were indexed separately and from the orientation matrices the twin matrix was calculated. Afterwards symmetry related reflections were merged and a data file in HKLF5 format was generated and used in the refinement (BASF parameter: 0.36428). Details of the structure determination are given in Table 3.

CCDC-949655 (Cd1-Br), CCDC-949659 (Zn1-Br), CCDC-949656 (Cd1-Cl), CCDC-949560 (Zn1-Cl) and CCDC-949657 (Cd2-Br), CCDC-949661 (Zn2-Br), CCDC-949658 (Cd2-Cl) and CCDC-949662 (Zn2-Cl) contain the supplementary crystallographic data for

this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif.

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	Cd1-Br	Zn1-Br	Cd1-Cl	Zn1-Cl	Cd2-Br	Cd2-Cl	Zn2-Br	Zn2-Cl
Formula	$C_{22}H_{16}Br_4N_6S_2Cd$	$C_{22}H_{16}Br_4N_6S_2Zn$	$C_{22}H_{16}Cl_4N_6S_2Cd$	$C_{22}H_{16}Cl_4N_6S_2Zn$	$C_{12}H_8Br_2N_4S_2Cd$	$C_{12}H_8Cl_2N_4S_2Cd$	$C_{12}H_8Br_2N_4S_2Zn$	$C_{12}H_8Cl_2N_4S_2Zn$
MW / g⋅mol <sup>-1</sup>	860.5572	813.54	682.73	635.70	544.56	455.64	497.53	408.61
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	C2/c	<i>C</i> 2/c	$P2_1/n$	<i>P</i> 2 <sub>1</sub> /n	P21212	$P2_1/c$
a /Å	8.7166(4)	8.8179(7)	14.1878(7)	13.9572(8)	9.7056(5)	9.5616(19)	12.2702(6)	14.1336(7)
<i>b</i> / Å	9.4960(5)	9.2362(9)	12.6689(4)	12.4252(8)	5.8630(2)	5.8596(12)	15.1966(8)	14.4289(8)
<i>c</i> / Å	17.5878(9)	17.3570(17)	16.4032(8)	16.2901(8)	15.0251(8)	14.883(3)	4.7040(2)	7.9149(4)
α/°	101.923(4)	100.418(11)	90	90	90	90	90	90
β/°	94.335(4)	93.207(11)	110.358(4)	109.116(4)	102.804(4)	101.64(3)	90	93.913(6)
γ/°	91.995(4)	91.950(11)	90	90	90	90	90	90
$V/Å^3$	1418.41(12)	1386.7(2)	2764.2(2)	2669.3(3)	833.73(7)	816.7(3)	877.13(7)	1610.34(14)
<i>T /</i> K	200	200	200	200	298	298	200	200
Ζ	2	2	4	4	2	2	2	4
$D_{\text{calc}} / \text{mg} \cdot \text{m}^3$	2.015	1.948	1.641	1.582	2.169	1.853	1.884	1.685
$\mu$ / mm <sup>-1</sup>	6.574	6.822	1.351	1.501	6.3949	1.915	6.190	2.112
$ heta_{ m max}$ / $^{\circ}$	26.05	27.00	27.00	27.50	27.98	28.00	27.50	27.50
Refl. collected	5576	11670	12238	8835	13475	9868	13206	11096
Unique reflections	5576	5931	3011	3014	1989	1969	2007	3688
R <sub>int</sub>	9.44	5.18	3.51	3.59	2.79	2.85	7.45	6.27
Refl. $[F_0 > 4\sigma(F_0)]$	3960	4201	2528	2380	1893	1712	1760	2824
Parameters	320	320	160	160	98	97	96	191
$R_1 [F_0 > 4\sigma(F_0)]$	5.66	4.00	3.61	3.27	2.73	2.73	3.70	4.17
$wR_2$	18.58	11.95	6.77	6.64	5.36	5.18	8.65	9.73
GOF	1.021	0.786	1.141	1.048	1.256	1.141	1.076	1.025
$\Delta  ho_{ m max/min}$ / e·Å <sup>-3</sup>	1.065 / -1.081	0.783 / -0.736	0.393 / -0.406	0.347 / -0.348	0.459 / -0.552	0.261 / -0.322	0.661 / -0.658	0.595 / -0.509

**Table 3.** Selected crystal data and details on the structure determination from single crystal data for all compounds.

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C

Eight new coordination compounds based on  $Cd(NCS)_2$  and  $Zn(NCS)_2$  with 3-chloro- and 3bromopyridine were prepared, structurally characterized and investigated for their stability.

- New coordination compounds based on Cd(II) and Zn(II) thiocyanate with 3bromopyridine and 3-chloropyridine were prepared.
- The influence of the substituent in pyridine N-donor ligands on the stability of the complexes were studied.
- The Cd(II) compounds prefer a  $\mu$ -1,3-bridging coordination of the anions, whereas Zn(II) prefer terminal N-bonding.
- The Zn and Cd compounds of composition M(NCS)<sub>2</sub>(L)<sub>4</sub> are isotypic, whereas those of composition  $M(NCS)_2(L)_2$  are not.