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Coordination chemistry of substituted [1,2,4]triazolo[1,5-*a*]pyrimidines with first-row transition-metal ions: Synthesis, spectroscopy and single-crystal structure analysis

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Dedicated to Professor Bernhard Lippert to celebrate his contribution to chemistry.

Abstract

A number of new coordination compounds with transition-metal salts and triazole-based heterocyclic ligands is described. The ligands used are disubstituted [1,2,4]triazolo[1,5-a]pyrimidines, with as substituents: ethyl, methyl and phenyl, and in addition a 2-methylthio-dimethyl ligand was used (sdmtp). To determine the structures of the coordination compounds in a number of cases 3D crystal structure determinations have been carried out, i.e. for $[Fe(NCS)_2(detp)_3(H_2O)]$, $[Co(NCS)_2(sdmtp)_2(H_2O)]$, $[ZnBr_2(fmtp)_2]$, $[Ni(NCS)_2(detp)_3(CH_3OH)]$ and $[Fe(NCS)_2(fmtp)_2(H_2O)_2](fmtp)$. The latter compound is quite unusual as it contains an uncoordinated fmtp ligand in the crystal lattice with special packing features. The ligands and the coordination compounds have been further characterized by NMR, IR and LF spectra, as well as by C, H, N element analyses. The coordination around the metal varies from 4 (Zn), via 5 (Co) to 6 (for Ni and Fe).

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1. Introduction

Triazolopyrimidines (traditional IUPAC name: [1,2, 4]triazolo[1,5-*a*]pyrimidines) are versatile ligands as they have several nitrogen atoms with accessible lone pairs to bind to Lewis acids like metal ions (see the structure in Scheme 1, with the current IUPAC ring numbering).

These ligands contain 6–5 condensed rings and therefore resemble the nucleobases adenine and guanine, of the natural DNA. A variety of complexes of metals salts with this ligand and other triazoles is already known and reviewed

* Corresponding author. *E-mail address:* reedijk@chem.leidenuniv.nl (J. Reedijk). [1,2]. Previous work from this laboratory has mainly been focusing on symmetric, and methyl substituted tp-based ligands [2–13] Also other groups have been studying this type of ligands [14–19]. In general triazoles and pyrimidines can act as bridges between metals, but also coordinate monodentately [20–22]. The steric effects of substituents in these ligands are interesting and have not been explored in great detail, especially substituents at position 2 are hardly known, and also 2 different substituents at positions 5 and 7 are not known. So we have set up a systematic study towards the steric effects of substituents by studying a variety of reactions with transition-metal(II) salts. The results of this work are described below, for the following 3 ligands (Scheme 2). In the case of the ligand fmtp it is



Scheme 1. The unsubstituted ligand tp and its IUPAC ring-numbering system.



Scheme 2. The ligands fmtp, sdmtp and detp as used in this study.

not known a priori how the substituents are distributed over the 5 and 7 positions, just like in e.g. 3(5)-methyl pyrazole [23] and an X-ray structure of a metal coordination compound would help to discriminate. Therefore, a selection of 5 different compounds was made for which suitable single crystals were isolated and this study has been supplemented with some other compounds for which structures will be proposed based on spectral analogies with the known compounds.

2. Experimental

2.1. Starting materials

Hydrated metal salts, solvents, diketones and 5-amino-1,2,4-triazole were used as commercially available, without further purification. The intermediate 3-methylthio-5amino-1,2,4-triazole was obtained from Aldrich.

2.2. Synthesis of the ligands

The synthesis of the ligands was carried out by a longknown condensation procedure [2,24] at 160 °C, from a diketone and an amino-triazole schematically given below in Scheme 3, followed by recrystallization from ethanol. Yields were between 30% and 70% depending on the ligand. Characterization was done by IR and NMR spectroscopy.

2.3. Synthesis of the coordination compounds

The coordination compounds were prepared by the following general recipes:



Scheme 3. Synthesis scheme of substituted triazolopyrimidines; R, R' = Me, Ph, R'' = H, Me.

A solution of the metal salt in (0.01 mol) water was added to a warm aqueous solution of the ligand (0.01-0.04 mmol). Upon cooling to room temperature crystals of the desired compound appeared, which were collected by filtration. In some cases acetonitrile/water or pure acetonitrile were used as solvent. To prepare the thiocyanate compounds a metathesis reaction was used, starting from the metal nitrate and ammonium thiocyanate (1:2). Yields were found to be between 30% and 60%.

2.4. Physical and analytical methods

Infrared spectra of all compounds were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique ($4000-300 \text{ cm}^{-1}$, res. 4 cm⁻¹). NMR spectra were recorded on a Bruker instrument at 300 MHz, with the use of dmso as a solvent.

C, H, N determinations were performed on a Perkin– Elmer 2400 Series II analyzer. Ligand field spectra in the 300–2000 nm range were obtained on a Perkin–Elmer Lambda900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference.

2.5. X-ray diffraction studies

A suitable crystal for a coordination compound was selected from the mother liquid and mounted to a glass fibre using the oil-drop method. Diffraction data were collected on a Nonius KappaCCD diffractometer (graphitemonochromated Mo K α radiation). The structures were solved by direct methods. The programs COLLECT [25], SHELXS-97 [26], SHELXL-97 [27] were used for data reduction, structure solution and structure refinement, respectively. Refinement of F^2 was done against all reflections. All non-hydrogen atoms were refined anisotropically. The water H atoms in compounds 1, 3 and 4 and the methanol H atom in compound 2 were picked from a difference Fourier map and refined isotropically. All other H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Crystallographic data of the compounds are summarized in Table 1.

3. Results and discussion

3.1. General observations and spectral analyses

With many metal salts when applied in solution with one of the ligand solid products were formed often crystalline, and reproducible, irrespective of the used metal to ligand ratio. The so-obtained unique products are listed

Table 1 Crystal and refinement data for 5 new compounds (number and working code)

Compound	1	2	3	4	5
Molecular formula	C ₂₉ H ₃₈ FeN ₁₄ OS ₂	C ₃₀ H ₄₀ N ₁₄ NiOS ₂	C18H22CoN10OS4	C ₅₀ H ₄₄ FeN ₁₈ O ₂ S ₂	C24H20Br2N8Zn
Molecular weight	718.7	735.59	581.63	1049.0	645.67
$T(\mathbf{K})$	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	P21/c	Pbca	C2/c	Fdd2	P21
a (Å)	8.874(1)	18.251(3)	13.237(2)	22.909(5)	9.747.(2)
b (Å)	20.126(3)	17.341(3)	22.048(4)	57.095(11)	18.735(4)
c (Å)	19.973(3)	22.515(4)	9.241(2)	7.4460(15)	14.223(3)
α (°)	90.0	90.0	90.0	90.0	90.0
β (°)	101.44(3)	90.0	107.34(3)	90.0	97.56(3)
γ (°)	90.0	90.0	90.0	90.0	90.0
$V(\text{\AA}^3)$	3496.3(9)	7126(2)	2574.4(9)	9739(3)	2574.7(9)
Z	4	8	4	8	4
<i>F</i> (000)	1504	3088	1196	4352	1280
$D_{\rm calc}$ (Mg m ⁻³)	1.365	1.371	1.501	1.431	1.666
$\mu (\mathrm{mm}^{-1})$	0.597	0.709	1.023	0.458	4.087
Crystal size (mm)	$0.20\times0.20\times0.10$	$0.10 \times 0.06 \times 0.06$	$0.25\times0.25\times0.15$	$0.30 \times 0.20 \times 0.10$	$0.35 \times 0.15 \times 0.15$
Colour, shape	yellow, plate	blue, needle	purple, prism	yellow, prism	colourless, prism
θ Range (°)	2.31-27.51	3.10-27.53	3.21-27.53	3.36-25.90	2.89-27.52
Number of reflections collected	44 521	84051	16815	30534	33174
Number of independent reflections (R_{int})	7778 (0.0662)	8161 (0.1065)	2919 (0.0510)	4650 (0.0525)	11201 (0.0486)
Number of reflections parameters	436	444	162	335	633
S^{c} (Goodness of fit)	1.059	1.028	1.028	1.036	1.040
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0483,$	$R_1 = 0.0495,$	$R_1 = 0.0357,$	$R_1 = 0.0295,$	$R_1 = 0.0386,$
	$wR_2 = 0.0771$	$wR_2 = 0.0804$	$wR_2 = 0.0677$	$wR_2 = 0.0603$	$wR_2 = 0.0531$
R indices (all data)	$R_1 = 0.1297,$	$R_1 = 0.1411,$	$R_1 = 0.0716,$	$R_1 = 0.0439,$	$R_1 = 0.0883,$
	$wR_2 = 0.0988$	$wR_2 = 0.1039$	$wR_2 = 0.0787$	$wR_2 = 0.0652$	$wR_2 = 0.0631$
Largest difference in minimum and maximum $\left(\begin{array}{c} 1 \\ 1 \\ 1 \end{array} \right)^{\frac{1}{2}}$	-0.447 and 0.395	-0.406 and 0.404	-0.293 and 0.340	-0.269 and 0.190	-0.553 and 0.498

 $\overline{R = \sum_{o} ||F_{o}| - |F_{c}|| / \sum_{o} |F_{o}||, R_{w} = \left[\sum_{w} w \{|F_{o}||F_{c}|\}^{2} / w |F_{o}|^{2}\right]^{1/2}}.$ ^c Goodness-of-fit $S = \left[\sum_{w} w (F_{o}^{2} - F_{c}^{2})^{2} / (n-p)\right]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

in Table 2, with their composition and some spectral characteristics. They were all characterized by C, H, N analysis, which were found sufficient to prove the composition. All compounds have been characterized by common physical methods, i.e. infrared spectroscopy, ligand field spectroscopy, and for the Zn and Cd compounds by NMR. In five cases an X-ray structure determination was carried out to obtain molecular structure details (vide infra). These compounds will be numbered 1-5. The Table is complemented by 4 other, related compounds, for which a structure is proposed based on spectroscopy.

Some comments on their spectral data are given below. NMR spectra of the Zn and Cd complexes were recorded in dmso and compared with the respective free ligands. The effect of coordination on the ring vibrations is rather small, as deduced from the small shifts in the proton signals of the ligand. Also in the IR spectra of these and the other compounds the changes in the ring structure are small, as deduced from the small shifts in vibrations. The IR absorption bands for the anions in the complexes illustrate their presence and indicate coordination for the nitrate and for the thiocyanate-N.

Table 2

New coordination compound obtained with the ligation	nds detp, fmtp, sdmtp and some selected properties
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Compound	Colour	IR, NCS stretch and other data	Number of the compound	LF spectral maxima in 10^3cm^{-1}
[Fe(NCS) ₂ (detp) ₃ (H ₂ O)]	yellow	2082 and 2057	1	9.8 (d-d) octahedral
[Ni(NCS) ₂ (detp) ₃ (CH ₃ OH)]	blue	2101, 2073	2	9.4, 16.0, 26.1 (d-d) octahedral
$[Co(NCS)_2(detp)_2](H_2O)$	deep blue	2062	6	7.7 (br), 16.1, 20.2 sh (d-d): tetrahedral
[Co(NCS)2(sdmtp)2(H2O)]	purple	2069	3	5.5, 11.0, 17.3 (d-d, 5 coord)
[Fe(NCS) ₂ (fmtp) ₂ (H ₂ O)](fmtp)	orange-	2081	4	9.8 (d-d) octahedral
	yellow			
$[Co(NO_3)_2(fmtp)(H_2O)_4]$	orange	nitrate visible: 1423, 1299 cm^{-1}	7	8.5, 18.0 (sh), 21.0 (d-d) octahedral
$[ZnBr_2(fmtp)_2]$	white	a	5	colourless
$[CdI_2(fmtp)_2]$	white	a	8	colourless
[CdBr ₂ (fmtp)]	white		9	colourless

^a These 2 compounds display identical IR above 300 cm⁻¹.

The ligand field spectra of the Fe, Co and Ni compounds are illustrative for their structure; also a few spectra of compounds are listed for which no crystal structure determinations have been carried out. The crystal field parameters for the octahedral Fe, Co and Ni compounds, as deduced from the LF maxima given in Table 2, are as expected for such chromophores [28-30] and will not be discussed in detail. For the five-coordinate Co(II) compound, 3, the maxima at are indeed characteristic for such trigonal bipyramidal-based compounds [31]. In the two cases of Co compound for which no 3D structure is available, an octahedrally coordinated Co(II) is clearly visible for the fmtp complex, although the LF maximum cannot discriminate between a water and a nitrate oxygen donor. The IR spectrum suggests that the two nitrates are both monodentate coordinated. The LF spectrum of [Co(N- $CS_{2}(detp)_{2}(H_{2}O)$ strongly resembles a tetrahedral Co(II)with 4 relatively strong N-donor ligand, this would imply that the water is non-coordinated. In fact the water band in the IR spectrum is rather broad, suggesting the presence of lattice water.

From the two Cd compounds, the compound 9 is isomorphous with the zinc bromide compound 5. The monoadduct of the cadmium bromide has an unknown structure, but the IR spectra suggest a bonding of the ligand via the N3, just as in the other compounds.

3.2. Description of the X-ray structures

3.2.1. $[Fe(NCS)_2(detp)_3(H_2O)]$ (1)

Compound 1 crystallizes in the $P2_1/c$ monoclinic space group. An ORTEP perspective view of 1 is shown in Fig. 1. Selected bond lengths and angles are given in



Fig. 1. ORTEP drawing (30% probability level) of [Fe(NCS)2(detp)3 (H2O)](1). Hydrogen atoms are omitted for clarity.

Table 3. The iron(II) centre is in a octahedral coordination environment formed by three detp ligands, two Ncoordinated thiocvanate anions and one water molecule. The basal plane of the [FeN₅O] octahedron includes two cis NCS⁻ anions exhibiting normal Fe–N_{NCS} bond lengths for HS Fe^{II} species [32,33]. The other basal positions are occupied by the nitrogen N21 of a detp ligand and a water molecule at typical distances for this type of

Table 3

Sel	lected	bond	lengths	(A)	and	Angle	s (°)	in	compounds	1–5	
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0	1
Com	bound

Compound 1 Bond distance			
Fe1-N1	2.141(2)	Fe1-N4	2.116(3)
Fel-Ol	2.203(2)	Fe1-N21	2.218(2)
Fe1-N31	2.220(2)	Fe1-11	2.219(2)
Bond angle			
N1–Fe1–N4	93.02(10)	N4–Fe1–O1	89.61(9)
O1-Fe1-N21	87.45(8)	N21-Fe1-N1	89.89(10)
N11-Fe1-N31	176.67(9)		
Compound 2			
Bond distance			
Ni1-N1	2.070(3)	Ni1-N4	2.060(3)
Nil-N11	2.121(2)	Nil-O7	2.113(2)
Nil-N21	2.138(2)	Ni1–N31	2.135(2)
Bond angle			
N1-Ni1-N4	91.22(10)	N4-Ni1-O7	89.07(10)
07-Ni1-N11	87.38(9)	N11-Ni1-N1	90.64(10)
N21-Ni1-N31	178.78(9)		~ /
Compound 3			
Rond distance			
Col N1	1.082(2)	Col. 01	1 072(3)
Col N11	1.982(2)	01-01	1.972(3)
	2.234(2)		
Bona angle	110 (1(0)	$N_{12} C_{21} O_{1}$	120 20(7)
NI-Col-Nia	119.01(9)	NIa-Col-Ol	120.20(7)
OI-CoI-NI	120.20(7)	NII-Col-Nila	1/0.35(7)
Compound 4			
Bond distance			
Fel-N1	2.126(2)	Fel-N11	2.233(2)
Fe1–O1	2.151(2)		
Bond angle			
N1–Fe1–N11	87.57(6)	N1–Fe1–O1	88.11(8)
N1–Fe1–N1a	94.11(8)	N1–Fe1–N11a	95.37(6)
N1–Fe1–O1a	173.45(7)	O1–Fe–O1a	90.35(8)
N11–Fe1–N11a	175.70(6)		
Compound 5			
Bond distance			
Zn1–Br1	2.375(1)	Zn1–Br2	2.396(1)
Zn1–N11	2.040(3)	Zn1-N31	2.039(4)
Zn2–Br3	2.389(1)	Zn2–Br4	2.389(1)
Zn2-N51	2.047(3)	Zn2-N71	2.068(4)
Bond angle			
Br1-Zn1-Br2	118.01(4)	Br1–Zn1–N11	111.32(10)
Br1-Zn1-N31	102.29(9)	Br2-Zn1-N11	112.67(9)
Br2-Zn1-N31	100.25(9)	N11-Zn1-N31	111.04(15)
Br3–Zn2–Br4	115.59(4)	Br3-Zn2-N51	108.42(12)
Br3-Zn2-N71	102.83(9)	Br4–Zn2–N51	114.38(12)
Br4–Zn2–N71	102.49(10)	N51-Zn2-N71	112.48(15)

coordination geometry (Table 3) [34]. The basal angles vary between 87.45(8)° and 93.02(10)° (Table 3), reflecting an almost perfect octahedral geometry. The coordinated water molecule is hydrogen bonded to the nitrogen atoms N18 and N28 of two detp ligands (intramolecular H bonds: $N18 \cdots O1 = 2.916(3)$ Å and $N18 \cdots$ $H1-O1 = 152(3)^{\circ}$; $N28 \cdots O1 = 2.834(3)$ Å and $N28 \cdots$ H2–O1 = $146(3)^{\circ}$). The crystal packing of 1 reveals that two iron(II) units self-assemble through C-H··· π contacts and π - π interactions (Fig. S1). The face-to-face π - π stacks are separated by a distance of about 3.7 Å (Fig. S1A). The hydrogen atom H11G (from an ethyl substituent of a coordinated detp ligand) is in close contact (C–H···ring centroid = 2.74 Å) with the triazole ring of a detp ligand belonging to an adjacent iron(II) complex (Fig. S1B). The supramolecular dimer is generated by two C-H··· π and one π - π bonding interactions.

3.2.2. $[Ni(NCS)_2(detp)_3(CH_3OH)]$ (2)

Compound 2 crystallizes in the orthorhombic *P*bca space group. An ORTEP perspective view of 2 is shown in Fig. 2. The mononuclear unit consists of a Ni^{II} ion coordinated by two thiocyanate nitrogen atoms (N1 and N4), three monodentate detp ligands (N11, N21 and N31) and one methanol molecule (O7) in an octahedral environment comparable to the one of 1. Actually, the main difference between 1 and 2 is that 1 has a water molecule coordinated to the metal centre while 2 exhibits a methanol molecule at this position (see Figs. 1 and 2). The Ni–N_{NCS}, Ni–N_{detp}

C210

AC211

and Ni-O_{MeOH} bond lengths are in normal ranges for this type of NiN₅O chromophore [35]. The basal angles deviate by a maximum of 2.62° from the ideal angle of 90° for a perfect octahedron (see Table 3). The methanol hydrogen atom H7A forms a strong hydrogen bond with the detp nitrogen atom N18 (intramolecular H bonds: N18... O7 = 2.722(3) Å and $N18 \cdots H7A - O7 = 152(3)^{\circ}$). The crystal packing of 2 (Fig. S2) displays similarities with that of 1. Molecules of **2** are associated by means of C-H··· π bonding interactions (C–H···ring centroid = 2.83 Å; Fig. S2A). However, in this case, the detp ligands are not $\pi - \pi$ stacked (Fig. S2B), most likely owing to steric constraints induced by the methanolic methyl groups. Indeed, the rings that are π - π stacked in 1 (Fig. S1A) are now apart from each other as is evidenced in Fig. S2C. As a result, an infinite supramolecular 1D chain is generated by the self-assembly of complexes 2 through C–H/ π contacts (Fig. S2D), instead of dimers like in 1 (Fig. S1B).

3.2.3. $[Co(NCS)_2(sdmtp)_2(H_2O)]$ (3)

Compound 3 crystallizes in the monoclinic C_2/c space group. An ORTEP perspective view of complex 3 is depicted in Fig. 3. Selected bond lengths and angles are given in Table 3. The Co^{II} ion is in a distorted trigonal bipyramidal coordination environment ($\tau_5 = 0.84$; $\tau_5 = 0$ for a square pyramidal geometry and $\tau_5 = 1$ for a trigonal bipyramidal geometry) [36], formed by two crystallographically equivalent thiocyanate anions (nitrogen atoms N1 and N1a) and one water molecule (oxygen atom O1) in the trigonal plane, and by two symmetry-related sdmtp ligands (nitrogen atoms N11 and N11a) at the apical positions. The



Fig. 2. ORTEP drawing (30% probability level) of $[Ni(NCS)_2(detp)_3(CH_3OH)]$ (2). Hydrogen atoms are omitted for clarity.



Fig. 3. ORTEP drawing (30% probability level) of $[Co(NCS)_{2}-(sdmtp)_{2}(H_{2}O)]$ (3). Hydrogen atoms are omitted for clarity. Symmetry operation: (a) 1 - x, y, -1/2 - z.

Co–N_{NCS}, Co–N_{sdmtp} and Co–O_{water} are in the expected ranges [37]. The basal angles range between 119.61(9)° and 120.20(7)°, very close to the ideal value of 120°. The small distortion of the trigonal bipyramid is reflected by the axial angle N11–Co–N11a of 170.35(7)°. This distortion is obviously related to the very strong hydrogen bonding interactions between the sdmtp ligands and the coordinated water molecule (N18···O1 = 2.664(2) Å and N18···H1a–O1 = 152(3)°). Consequently, the angle N11– Co–N11a, involving the H bonded sdmtp ligands deviates from the ideal value by as much as 9.65° (see Fig. S3). The crystal packing of **3** reveals the presence of 1D supramolecular infinite chains assembled via π – π interactions between sdmtp ligands belonging to neighbouring cobalt complexes (π – π contacts of 3.381 Å; Fig. S3).

3.2.4. $[Fe(NCS)_2(fmtp)_2(H_2O)_2](fmtp)$ (4)

Compound 4 crystallizes in the Fdd2 orthorhombic space group. An ORTEP perspective view of 4 is shown in Fig. 4. Selected bond lengths and angles are given in Table 3. The iron(II) centre is in an almost perfect octahedral coordination environment. The basal plane of the octahedron is formed by two crystallographically related N-coordinating thiocyanates anions (N1 and N1a) and two water molecules (O1 and O1a). The axial positions of the [FeN₄O₂] octahedron are occupied by nitrogen atoms (N11 and N11a) of two crystallographically equivalent fmtp ligands. The Fe-N_{NCS} distances are within the normal range for HS Fe^{II} species (Fe–N1 = 2.126(2) Å) [38,39]. The Fe-N_{fmtp} and Fe-O bond lengths are typical for this type of coordination geometry [40]. The basal angles are close to the ideal value of 90°, varying from 88.11(8)° to 94.11(8)° (Table 3). Interestingly, each coordinated fmtp ligand is interacting with two non-coordinated fmtp ligands through π - π contacts (Fig. S4) with centroid · · · centroid distances of 3.549(1) Å (Cg1...Cg2; Fig. S4A) and 3.706(2) Å (Cg3···Cg4; Fig. S4A). The assembly between

bisligand complexes and free fmtp ligands generates a 1D supramolecular chain which is further stabilized by $S_{NCS} \cdots O_{water}$ contacts (Fig. S5B; S3 \cdots O1 = 3.272(2) Å).

3.2.5. $[ZnBr_2(fmtp)_2]$ (5)

Compound 5 crystallizes in the monoclinic P21 space group. An ORTEP perspective view of 5 is shown in Fig. 5. Selected bond lengths and angles are given in Table 3. The crystal lattice of 5 is constituted of two slightly different zinc(II) coordination compounds. Both Zn1 and Zn2 are in almost perfect tetrahedral environments ($\tau_4 = 0.92$ for Zn1 and $\tau_4 = 0.92$ for Zn2; $\tau_4 = 0$ for a square planar



Fig. 5. ORTEP drawing (30% probability level) of $[\text{ZnBr}_2(\text{fmtp})_2]$ (5). Hydrogen atoms are omitted for clarity.



Fig. 4. ORTEP drawing (30% probability level) of $[Fe(NCS)_2(fmtp)_2(H_2O)_2](fmtp)$ (4). Hydrogen atoms are omitted for clarity. Symmetry operation: (a) -x, -y, z.

geometry and $\tau_4 = 1$ for a tetrahedral geometry) [41], formed by two bromide anions and to monodentate fmtp ligands. The Cu–N and Cu–Br bond distances are in typical ranges for this type of [ZnN₂Br₂] tetrahedron [42,43]. The angles vary from 100.25(9)° to 118.01(4)° for Zn1 and from 102.49(10)° to 115.59(4)° for Zn2. The crystal packing of **5** shows the presence of π - π interactions between the heteroaromatic rings of the fmtp ligands with the phenyl substituents of two adjacent Zn units (Cg1···Cg2 = 3.483(3) Å and Cg3···Cg4 = 3.481(2) Å Fig. S6).

4. Concluding remarks

The study described above on the coordination behaviour of the triazolopyrimidines has shown that the ligands coordinate in all cases via N3. The ligands are versatile in their behaviour towards different metals and anions, resulting in interesting steric properties, and interference with hydrogen bonding from the solvent and to the anions. Which compounds are formed as described above is difficult to predict beforehand, and appears to depend strongly on the used metal and the selected anion.

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Appendix A. Supplementary material

CCDC 669962, 669963, 669964, 669965 and 669966 contain the supplementary crystallographic data for 1, 3, 4, 2 and 5. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figures with packing diagrams for the 5 compounds are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.02.020.

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