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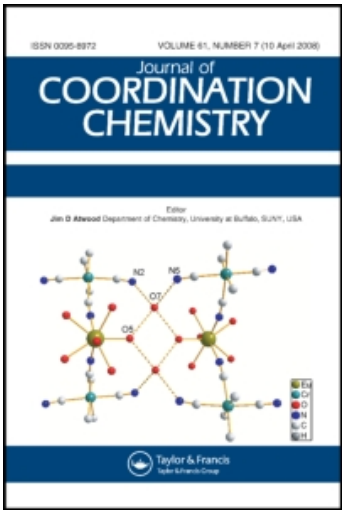

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Zinc halide complexes of imidazolidine-2-thione and its derivatives: X-ray structures, solid state, solution NMR and antimicrobial activity studies

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Zinc halide complexes of imidazolidine-2-thione and its derivatives: X-ray structures, solid state, solution NMR and antimicrobial activity studies

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The preparation and characterization of zinc complexes of formula ZnL_2X_2 (X = Cl and Br), with L = 1,3-diazinane-2-thione (Diaz), 1,3-diazipane-2-thione (Diap), imidazolidine-2-thione (Imt) and its methyl and *n*-propyl substituted derivatives, are described. The complexes dichlorobis(1-methylimidazolidine-2-thione-*S*)-zinc(II) (**1**) and dichlorobis(1-propylimidazolidine-2-thione-*S*)-zinc(II) (**2**) have been characterized by single-crystal X-ray methods. Both complexes adopt distorted tetrahedral geometry. Only intramolecular hydrogen bonding interactions are observed in **1** and **2**. Solution and solid state ^{13}C NMR show a significant shift of the C=S carbon resonance of the ligands, while other resonances are relatively unaffected, indicating that most likely the solid state structure is maintained in solution. Antimicrobial activity studies of the free ligands and their complexes show that ligands exhibit substantial antibacterial activities compared to the complexes.

Keywords: Zinc; Imidazolidine-2-thione; Crystal structure; MAS NMR; Antibacterial activity

1. Introduction

Thiol groups provide biological targets for metal ions, both essential (e.g. Zn in zinc fingers, Fe in iron–sulfur proteins) and toxic (e.g. Ni, Cd, Pb, exerting their deleterious effects in part through inhibition of thiol enzymes or substitution of essential metals in their thiolate binding sites) [1, 2]. It is therefore important to understand the nature of binding of these metal ions with thiols.

Complexes of heterocyclic ligands such as imidazolidine-2-thione (Imt) and its derivatives with metal ions are of special interest in bioinorganic chemistry because of the search for simple model compounds of metal-proteins [3–7]. In view of this, Cu(I), Au(I), Ag(I), Cd(II), Hg(II), Pd(II) complexes with these ligands have been widely investigated [8–11]. These ligands exist in the N=C–SH and N–C=S forms exhibiting thiol-thione equilibrium [12, 13]. However, it has been established that the thione form dominates in the solid state [14]. We have studied extensively the interaction

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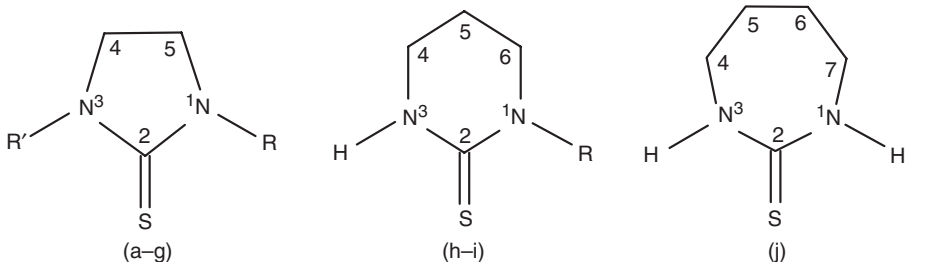

Scheme 1. Ligands (a): R = R′ = H, imidazolidine-2-thione (Imt); (b): R = CH_3, R′ = H, *N*-methylimidazolidine-2-thione (MeImt); (c): R = C_2H_5, R′ = H, *N*-ethylimidazolidine-2-thione (EtImt); (d): R = C_3H_7, R′ = H, *N*-propylimidazolidine-2-thione (PrImt); (e): R = *i*-C_3H_7, R′ = H, *N*-(*i*-propyl)imidazolidine-2-thione (*i*-PrImt); (f): R = CH_3, R′ = CH_3, *N*,*N*′-dimethylimidazolidine-2-thione (Me_2Imt); (g): R = C_2H_5, R′ = CH_3, *N*-ethyl-*N*′-methylimidazolidine-2-thione (EtMeImt); (h): R = H, 1,3-diazinane-2-thione (Diaz); (i): R = C_2H_5, *N*-ethyl-1,3-diazinane-2-thione (EtDiaz); (j): 1,3-diazipane-2-thione (Diap).

of metal ions with imidazolidine-2-thione (Imt) and its derivatives [15–17]. Here we report a series of $ZnCl_2$ and $ZnBr_2$ complexes with imidazolidine-2-thione and its derivatives. The complexes were studied in solution as well as in the solid state. The structures of the thiones used in this study are described in scheme 1. Antimicrobial activity was also studied for thione ligands and their corresponding complexes. These data will help to understand effects of these ligands along with other thiol containing ligands which are important from a biological point of view [3, 15].

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2. Experimental

2.1. *Materials*

$ZnCl_2$, $ZnBr_2$, CD_3OD and DMSO-d_6 were obtained from Fluka Chemical Co. All thiones were synthesized according to a procedure described in the literature by the addition of CS_2 to diamines in ether and then heating the resulting adduct at 100°C for 2–3 h, followed by crystallization from methanol [18–19].

2.2. *Synthesis of the complexes*

All [(>C=S)ZnX_2 (where X = Cl or Br)] complexes were prepared by dissolving the Zn^{2+} salt in a minimum amount of water and 2 mol equivalents of thiones in MeOH; the mixture was refluxed for 2 to 3 h. The solution was allowed to evaporate slowly and white crystalline products were isolated, for which satisfactory analyses were obtained.

2.3. *IR and NMR measurements*

Solid-state IR spectra of the ligands and their cyano(thione)silver(I) complexes were recorded on a Perkin Elmer FTIR 180 spectrophotometer using KBr pellets over the range 4000–400 cm^{-1}.

^{1}H NMR spectra were obtained on a Jeol JNM-LA 500 NMR spectrometer operating at 500.00 MHz. ^{13}C NMR spectra were obtained at 125.65 MHz with ^{1}H broadband decoupling at 298 K. Conditions were 32 k data points, 0.967 s acquisition time, 1.00 or 30.00 s pulse delay and 45° pulse angle. ^{13}C chemical shifts relative to TMS were assigned according to the literature [20].

Natural abundance ^{13}C solid state NMR spectra were obtained on the same spectrometer at 125.65 MHz (11.74 *T*), at an ambient temperature of 25°C. Samples were packed into 6 mm zirconium oxide rotors. Cross polarization and high power decoupling were employed. Pulse delays of 7.0 s and a contact time of 5.0 ms were used in the CPMAS experiments. Magic angle spinning rates were from 2000 Hz to 4000 Hz. Carbon chemical shifts were referenced to TMS by setting the high frequency isotropic peak of solid adamantine to 38.56 ppm. CPMAS spectra of thione carbons were analyzed using a published procedure [21].

2.4. *X-ray crystallography*

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Crystals were mounted on glass fibres. Diffraction data were recorded on a Bruker-AXS Smart Apex system equipped with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected using SMART [22]. Data integration was performed using SAINT [23]. An empirical absorption correction was carried out using SADABS [24]. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2 using SHELXTL [25] based on SHELX 97 [26]. An sp^2 hybridization was assumed for the nitrogen atoms of the NH groups. For compounds **1** and **2**, amine hydrogen atoms were located in a difference Fourier map and refined isotropically. Remaining H atoms were placed using a riding model. Crystallographic data are given in table 1. Selected bond lengths and angles are given in table 2. Complete bond lengths and bond angles, anisotropic thermal parameters and calculated hydrogen coordinates are deposited as supplementary material. ORTEP views of the complexes are given in figures 1 and 2, showing the atom labelling schemes.

Table 1. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_8H_{16}Cl_2N_4S_2Zn$	$C_{12}H_{24}Cl_2N_4S_2Zn$
Formula weight	368.64	424.74
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2/c$
Temperature (K)	298	298
Radiation	Mo-Kα ($\lambda = 0.71073$ Å)	
ρ_{Calcd} (g cm^{-3})	1.643	1.423
a (Å)	7.3675(10)	15.6576(15)
b (Å)	7.7183(10)	8.7668(9)
c (Å)	13.9644(18)	14.9260(14)
α (°)	94.545(2)	
β (°)	95.877(2)	104.654(2)
γ (°)	108.225(2)	
V (Å^3)	745.06(17)	1982.2(3)
Z	2	4
R_1	0.0308	0.0378
wR_2	0.0805	0.1013

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

Compound **1**			
Zn1–Cl1	2.2397(6)	S2–C5	1.714(2)
Zn1–Cl2	2.2710(6)	N3–C5	1.321(3)
Zn1–S1	2.3475(6)	N4–C5	1.324(3)
Zn1–S2	2.3690(7)	N1–C1	1.335(3)
S1–C1	1.701(2)	N2–C1	1.324(3)
Cl1–Zn1–Cl2	114.59(2)	Cl1–Zn1–S2	105.26(2)
Cl1–Zn1–S1	115.30(2)	Cl2–Zn1–S2	109.01(3)
Cl2–Zn1–S1	101.98(2)	S1–Zn1–S2	110.71(2)
Compound **2**			
Zn1–Cl1	2.2513(8)	S2–C7	1.714(3)
Zn1–Cl2	2.2483(8)	N1–C1	1.313(3)
Zn1–S1	2.3553(8)	N2–C1	1.315(4)
Zn1–S2	2.3645(8)	N3–C7	1.312(4)
S1–C1	1.715(3)	N4–C7	1.318(3)
Cl2–Zn1–Cl1	109.97(3)	Cl2–Zn1–S2	111.42(3)
Cl2–Zn1–S1	112.10(3)	Cl1–Zn1–S2	111.56(3)
Cl1–Zn1–S1	111.81(3)	S1–Zn1–S2	99.66(3)

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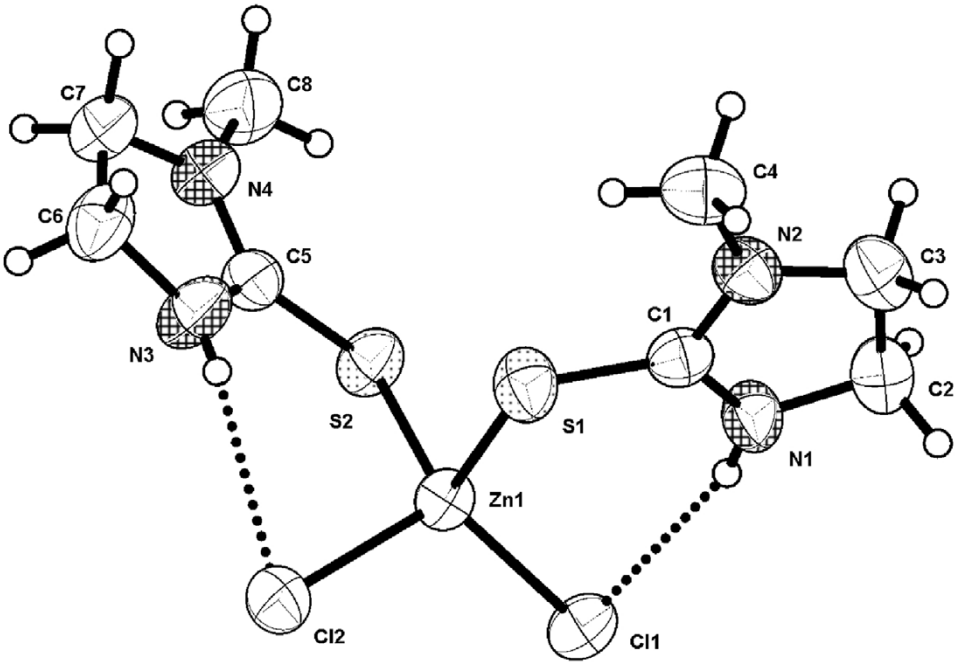

Figure 1. Molecular structure of (N-MeImt)$_2$ZnCl$_2$ (**1**) showing the atom labelling scheme.

2.5. *Bioactivity*

Antimicrobial activity was measured as described in the literature [27, 28]. It was evaluated by the minimum inhibitory concentration (MIC) on four microorganisms,

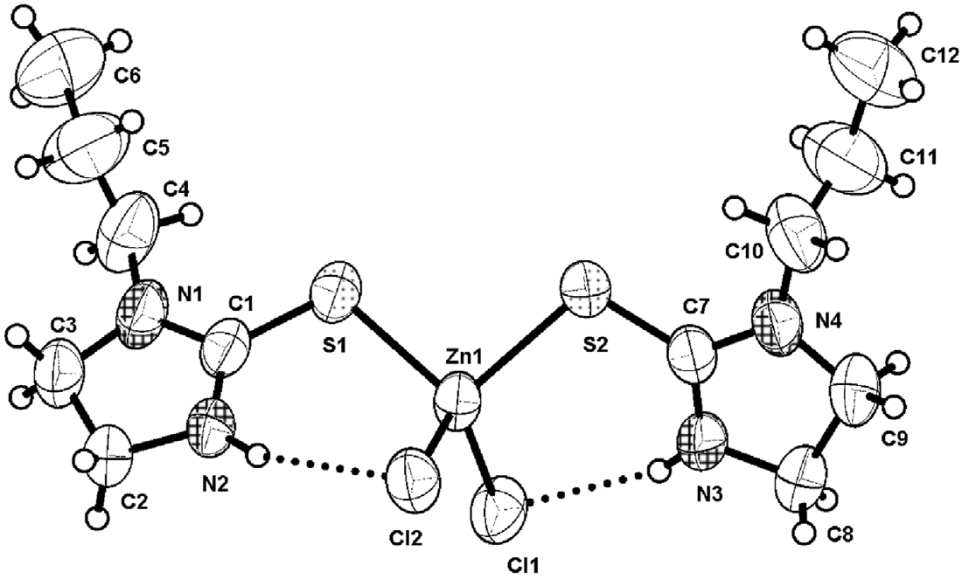

Figure 2. Molecular structure of $(N\text{-PrImt})_2ZnCl_2$ (**2**) showing the atom labelling scheme.

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namely Heterotropic Plate Counts (HPC), *Pseudomonas aeruginosa* (*P. aeruginosa*), Fecal Streptococcus (FS) and *Escherichia coli* (*E.coli*). Each analysis was carried out in duplicate to maintain maximum accuracy. Dosage of each chemical started from $10\,\mu g\,mL^{-1}$ and continued until MIC was reached. A maximum dose of $1000\,\mu g\,mL^{-1}$ was used as a stopping criterion. $Zn(Imt)_2X_2$ ($X = Cl^-$ or Br^-) and its derivatives are insoluble in water but bioactivities were measured in aqueous media.

3. Results and discussion

3.1. *Molecular structures of $(N\text{-MeImt})_2ZnCl_2$ (1) and $(N\text{-PrImt})_2ZnCl_2$ (2)*

Distorted tetrahedral geometry is observed in both compounds with bond angles in the range 101.98(2)–115.30(2)° and 99.66(3)–112.10(3)° for **1** and **2**, respectively. Variation of metal-ligand bond distances is more pronounced in **1**, primarily for Zn–Cl and relatively to a less extent for Zn–S. In **2** the two Zn–Cl distances are similar while Zn–S distances differ significantly. Observed values are in the same range as those found in $Zn(thiourea)_2Cl_2$ [29] and $Zn(4\text{-methoxybenzaldehydethiosemicarbazone})_2Cl_2$ [30]. Intramolecular hydrogen bonding interactions are present in both compounds between the *N*-bonded hydrogen chlorine atoms with an average $Cl\cdots H\text{–}N$ distance of 2.551 and 2.476 Å for **1** and **2**, respectively. While hydrogen bonding interactions are probably the main factor in the distortion of compound **1**, both the steric effect of the ligand and the relatively stronger hydrogen bonding interactions are effective in compound **2**.

3.2. *IR spectroscopy*

IR spectra of free ligands and their zinc(II) complexes show the ν(C=S) vibration, which occurs around 500 cm^{-1} for the free ligands, shifts towards lower frequency upon complexation, in accordance with data observed for other thione complexes [14–16]. Another important band observed in IR spectra of the thiones is ν(NH), which appears around 3200 cm^{-1}. Upon coordination to Zn(II) this band shifts to higher wave numbers (3270–3290 cm^{-1}). The presence of a band around 3200 cm^{-1} in the free ligands as well as the complexes indicates the existence of the thione form of the ligands in the solid state.

3.3. *NMR studies*

In ^{1}H NMR spectra of the complexes, the N–H signals of the thiones shifted downfield by 0.1 to 0.3 ppm from their positions in free ligands. Deshielding of the N–H proton is related to an increase of π electron density in the C–N bond upon complexation [15–17]. The appearance of the N–H signal shows that the ligands coordinate to Zn(II) via a thione group. The slight shift of NH indicates that the bonding of thione ligands with Zn(II) is very weak and DMSO may compete with the ligands, causing only minor shifts. We have observed in previous studies up to 0.7 to 1.0 ppm shifts for Ag(I) and Au(I) complexes with similar ligands [15–17, 31].

^{13}C NMR results for $ZnCl_2$ and $ZnBr_2$ complexes with imidazolidine-2-thione and its derivatives are given in table 3. Normally the C-2 resonance of the ligand is sensitive and shifts the most for d^{10} metal complexes. We have recently studied the complexation of Zn(II), Cd(II) and Hg(II) complexes with thiourea and selenourea where the ^{13}C NMR of >C=S and >C=Se showed 2–7 ppm and 3–10 ppm shifts, respectively, between the free and bound resonances [32]. However, in the present study, shifts of 1 ppm or less were observed for the C-2 resonances between free and bound >C=S

Table 3. ^{13}C chemical shifts of thiones and ZnX_2-thione complexes in DMSO-d_6.

Species	C-2	C-4	C-5	C-6	α-CH_2	β-CH_2	–CH_3
Imt	183.44	43.97	43.97				
$(Imt)_2ZnCl_2$	184.43	45.14	45.14				
$(Imt)_2ZnBr_2$	184.29	45.16	45.16				
MeImt	182.90	40.60	50.18				33.82
$(MeImt)_2ZnCl_2$	184.17	41.69	51.31				34.34
$(MeImt)_2ZnBr_2$	184.16	41.70	51.32				35.25
EtImt	183.70	41.76	48.15		41.54		12.46
$(EtImt)_2ZnCl_2$	183.32	41.83	48.17		41.54		12.65
$(EtImt)_2ZnBr_2$	183.46	41.82	48.17		41.56		12.54
PrImt	184.08	41.85	48.78		48.48	20.93	11.69
$(PrImt)_2ZnCl_2$	183.85	41.90	48.78		48.48	20.97	11.77
$(PrImt)_2ZnBr_2$	183.91	41.87	48.77		48.47	20.92	11.78
i-PrImt	183.17	41.94	43.02		46.68		19.54
$(i\ PrImt)_2ZnCl_2$	182.82	41.98	43.08		46.71		19.71
$(i\ PrImt)_2ZnBr_2$	182.77	42.01	43.12		46.74		19.68
Diaz	175.70	38.80	19.00	38.80			
$(Diaz)_2ZnCl_2$	175.10	40.83	20.01	40.83			
$(Diaz)_2ZnBr_2$	173.75	40.93	19.86	40.93			

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for both $ZnCl_2$ and $ZnBr_2$ in most of the complexes. This weak binding may also be due to DMSO solvent competing with the thione ligands.

Calculated solid state chemical shift tensors for the thiocarbonyl carbons of the zinc complexes are given in table 4 along with those of free ligands for comparison. As expected the isotropic shifts in the complexes show a shielding of 5–11 ppm relative to the free ligand. However, the shielding effect observed is solution is very small, presumably due to solvent effects. Some ligands and complexes show positive ^{13}C anisotropy, whereas other ligands and complexes show a negative anisotropy. This arises due to apparent swapping of the components σ_{11} and σ_{33}, and this should be taken into account when comparing shielding tensors between free ligand and complex. Studies of the chemical shift tensors of carbonyl carbon have shown that the principal axis of the σ_{33} tensor is perpendicular to the carbonyl sp^2 plane and the principal axes associated with σ_{22} and σ_{11} components are ca 10° and 80° off the C=O bond respectively [33]. Complexes **1** and **2** show that σ_{33} experiences large shielding from ligand to complex. The σ_{33} component can be assigned to the axis perpendicular to the sp^2 plane as in the carbonyl case. However, the parent ligand Imt behaves differently in the complex $(Imt)_2ZnBr_2$, where the largest shielding is observed for the σ_{22} component. This suggests that σ_{22} in complex **1** must be perpendicular to the sp^2 plane [34].

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3.4. *Bioactivity studies*

The results of the bioactivity studies are given in table 5. The free Imt ligand shows significant antimicrobial activity compared to Diaz and Diap. After complexation with Zn(II), antimicrobial activity is increased. Comparison between the activity of Imt and $Zn(Imt)_2Cl_2$, shows that HPC increased from 650 to 950, *P. aeruginosa* from 250 to 550, FS from 300 to 700, *E. coli* from 250 to 550 $\mu g\,mL^{-1}$. However, the bioactivity effect is significant for *N-i*PrImt itself. This ligand shows remarkable and superior activities

Table 4. ^{13}C chemical shift tensors[a] for the >C=S carbons.

Species	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η
Imt[b]	180.6	−270	−188	−84	145	0.85
$(Imt)_2ZnBr_2$	166.6	−88	−158	−261	−142	0.82
MeImt[b]	181.4	−106	−170	−266	−127	0.75
$(MeImt)_2ZnCl_2$	176.3	−246	−192	−91	128	0.64
$(MeImt)_2ZnBr_2$	177.0	−246	−190	−92	127	0.65
EtImt[b]	180.9	−101	−176	−266	−127	0.40
$(EtImt)_2ZnCl_2$	175.2	−242	−189	−93	123	0.66
$(EtImt)_2ZnBr_2$	176.3	−244	−189	−95	−122	0.68
PrImt[b]	180.1	−87	−173	−280	−150	0.85
$(PrImt)_2ZnCl_2$	175.0	−241	−195	−89	128	0.54
i-PrImt[b]	180.8	−83	−176	−281	−152	0.92
$(iPrImt)_2ZnCl_2$	174.4	−241	−190	−91	128	0.62
Diaz[b]	175.6	−246	−201	−79	145	0.47
$(Diaz)_2ZnCl_2$	169.5	−230	−209	−68	152	0.20
$(Diaz)_2ZnBr_2$	168.2	−235	−192	−78	137	0.47
EtDiaz[b]	176.2	−218	−185	−125	77	0.65
$(EtDiaz)_2ZnCl_2$	169.2	−225	−203	−81	133	0.24
$(EtDiaz)_2ZnBr_2$	169.3	−226	−201	−80	134	0.28

[a] $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$; $\eta = (\sigma_{22} - \sigma_{11})/2/3\Delta\sigma$.
[b] From reference [19].

Table 5. Antimicrobial activity ($\mu g\,mL^{-1}$) for Heterotropic Plate Counts (HPC), *Pseudomonas aeruginosa* (*P. aeruginosa*), Fecal Streptococcus (FS) *and Escherichia coli* (*E. coli*).

Test organism		Imt	Diaz	Diap
HPC		650	>1000	>1000
P. aeruginosa		250	550	>1000
FS		300	600	>1000
E. coli		250	525	>1000
	$ZnCl_2$	$Zn(Imt)_2Cl_2$	$(Diaz)_2ZnCl_2$	$(Diap)_2ZnCl_2$
HPC	>1000	950	950	>1000
P. aeruginosa	>1000	550	550	>1000
FS	>1000	700	625	950
E. coli	>1000	500	500	>1000
	N-*i*Pr-Imt	(*N*-*i*PrImt)$_2$-$ZnCl_2$	*N*-EtImt	(*N*-EtImt)$_2$$ZnCl_2$
HPC	525	>1000	600	>1000
P. aeruginosa	175	600	200	600
FS	250	500	250	425
E. coli	150	600	200	550

against gram negative *P. aeruginosa* and *E. coli*. Nevertheless, complexation with $ZnCl_2$ reduces the activities. These results are important because no bioactivities for any thione ligands are reported in the literature. Since thione and thiol are in equilibrium, the data can be related to thiol-containing complexes [27, 28].

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Supplementary material

Supplementary X-ray data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting deposition Nos 276052 and 276053 for compounds **1** and **2** respectively.

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