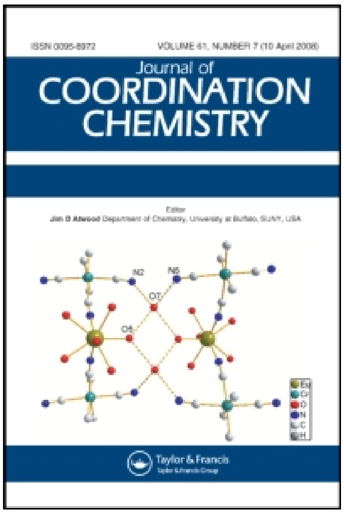

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FAR IR SPECTRA AND STRUCTURES OF Zn(II) COMPLEXES OF 2-AMINOTHIAZOLES

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FAR IR SPECTRA AND STRUCTURES OF Zn(II) COMPLEXES OF 2-AMINOTHIAZOLES

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IR spectra and molecular structures of ZnL_2X_2 (L = 2-NH_2-4-*R*-thiazole, *R* = H (at), CH_3; 2-NH_2-6-R_I-benzothiazole, R_I = H (abt), CH_3, OCH_3, OC_2H_5 or 2-NH_2-tetrahydrobenzothiazole; X = Cl, Br, I) have been studied. It was found that the complex character of the far IR spectra and difficulties in ν(NH_2) interpretation make conclusions regarding structure based only on IR data ambiguous, and in some cases discrepant. Single crystal X-ray data for the complexes with L = at, X = Br, I and L = abt, X = Br show that structures are built up of discrete tetrahedral ZnL_2X_2 molecules with monodentate ligands coordinated *via endo*-N atoms. It was found that in the coordination tetrahedra MN_2Cl_2 (M = Co^{2+}, Zn^{2+}) the central atom redistributes electron density between the thiazole ligands and the terminal Cl atoms.

KEYWORDS: thiazole, complexes, zinc, IR spectra, X-Ray structure.

INTRODUCTION

Recently, thiazole and aminothiazole complexes have been extensively studied.[1–6] The presence of at least three heteroatoms (endocyclic S and N (N_c) and NH_2 group (N_a)) without one of them to be favoured *a priori* as a coordinating centre, makes interpretation of far IR spectra rather complicated. On the basis of IR data N_c was usually found to be a coordination centre (ν(M-N_c) = 200–290cm^{-1});[1–3,5–7] more rarely N_a (ν(M-N_a) = 350–450cm^{-1});[8–10] for M-S coordination there is little evidence.[11–15] By X-ray analysis, only M-N_c bonds have been reported.[16–22]

Because of this uncertainty, interpretation of the IR spectra of such complexes can be done only on the basis of crystallographic investigation and from the analysis

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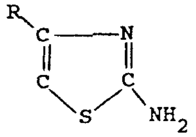
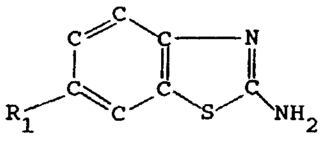
of spectroscopic data for large series of similar complexes. In the series of ZnL_2X_2 (X = Cl, Br or I) complexes with the following aminothiazole ligands



R = H (at)

CH_3 (amt)

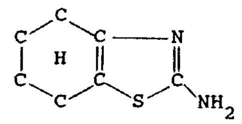


R_1 = H (abt)

CH_3 (ambt)

OCH_3 (amobt)

OC_2H_5 (aeobt)



(athbt)

only $Zn(abt)_2X_2$ has been studied so far.[3] The present work is devoted to study of IR spectra and molecular structures of some of the abovementioned complexes.

EXPERIMENTAL

Synthesis

The complexes were obtained by mixing ethanolic solutions of ZnX_2 and ligand in mol ratio 1:2 (the metallic salt was added to the ligand). The crystalline product which precipitated immediately was filtered off and washed with ethanol. Chemical analyses were performed by standard methods and correspond to the stoichiometry ZnL_2X_2.

IR Spectroscopy

IR spectra were recorded on Hitachi FIS-3 (150–400 cm^{-1}) and Carl Zeiss IR-20 (400–4000 cm^{-1}) spectrophotometers. The positions of IR bands are given in Table I.

X-Ray Structure Analysis

Single crystals of the complexes $Zn(at)_2Br_2$ (**1**), $Zn(at)_2I_2$ (**2**) and $Zn(abt)_2Br_2$ (**3**), suitable for X-ray analysis, were prepared by slow evaporation of ethanolic solutions at ambient temperatures. Crystal data and intensities were collected with an Enraf-Nonius CAD-4 single-crystal diffractometer.[23] The crystals mounted on glass fibres were found to be stable in air and during irradiation by X-rays. Relevant crystallographic information for (1)–(3) is summarized in Table II. All calculations were carried out on a PDP-11/44 computer at the Institute of Applied Mineralogy in Sofia. Locally modified SPD/PDP V3.0 crystallographic packages[24] were employed. Scattering factors for neutral atoms as coded in the SDP package were used. The positional and thermal parameters for the atoms in these structures are given in Table III; selected bond lengths and angles are outlined in Table IV. Lists of anisotropic thermal parameters and the F_o/F_c lists are available from the authors. Atom numbering and ORTEP plots of $Zn(at)_2Br_2$ and $Zn(abt)_2Br_2$ are shown in Figures 1 and 2, respectively. The conformations of the two structures are compared in Figure 3.

RESULTS AND DISCUSSION

The far IR bands of the complexes as well as of $Zn(bt)_2X_2$ (bt = benzothiazole) are reported in Table I. The operating range was chosen in agreement with the data for frequencies ν(Zn-X), ν(Zn-N_c) and ν(Zn-N_a).[25,26] Frequencies in brackets are

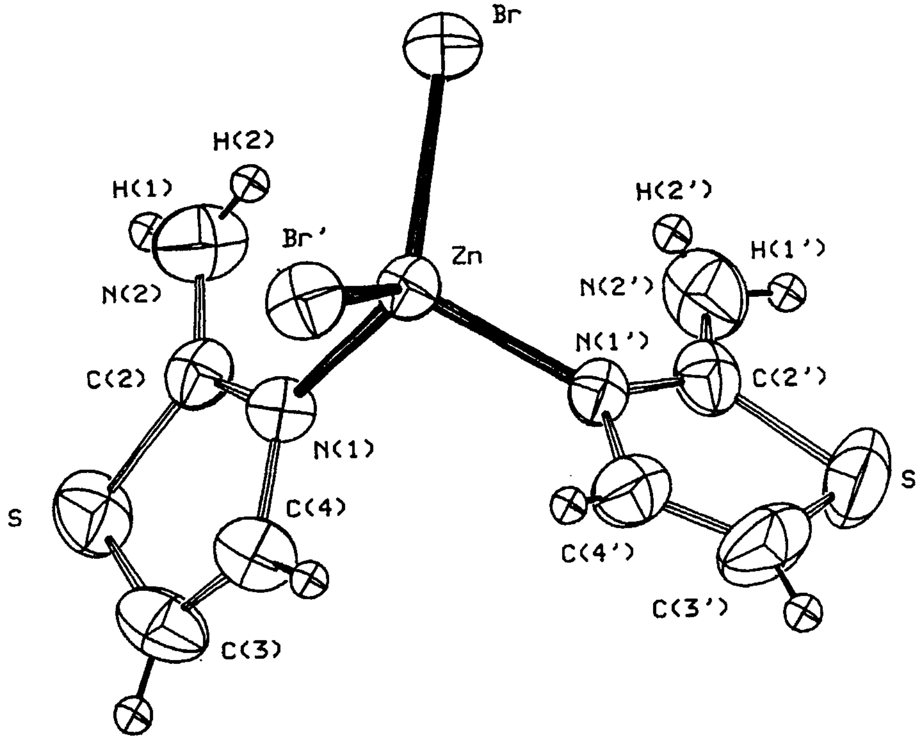


Figure 1 ORTEP II* plot of $Zn(at)_2Br_2$ with atom numbering. Non-hydrogen atoms denoted by 50% probability ellipsoids and H atoms are arbitrarily reduced.

* C.K. Johnson, "ORTEP II," Report ORNL-5138, (Oak Ridge National Laboratory, Tennessee, USA).

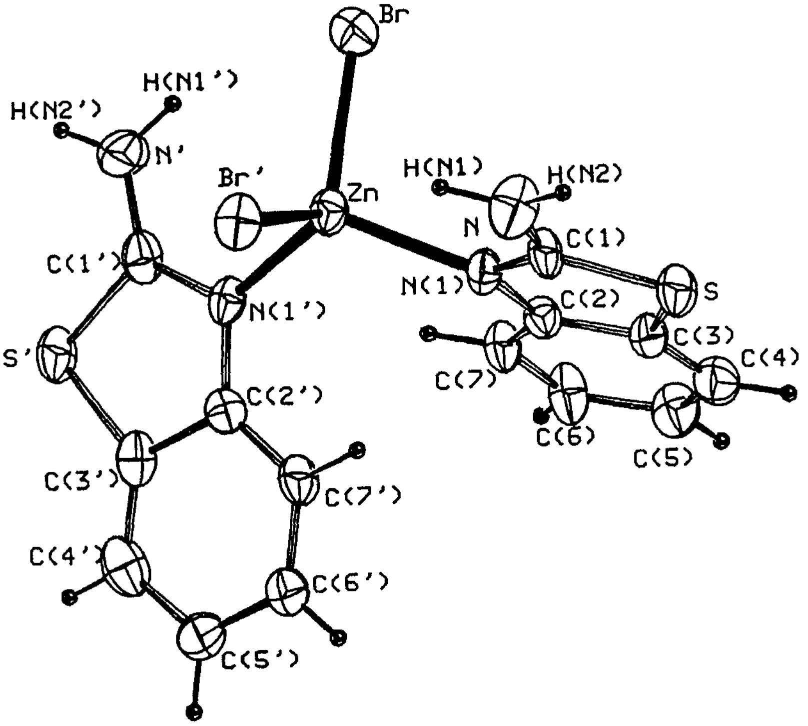


Figure 2 ORTEP II plot of Zn(abt)$_2$Br$_2$ showing numbering scheme, 50% probability ellipsoids for non-hydrogen atoms and arbitrarily reduced H-atoms.

overlapping bands. The ν(Zn-X) bands were identified using the observed changes upon replacing one halogen atom by another. These bands, although with changed shape, retain the high intensity typical of M-X vibrations.

Ratios of frequencies ν(Zn-X) (Table V) show that while ν(Zn-Br)/ν(Zn-Cl) is almost equal to the ratios obtained for other N-donors,[26] in the case of ν(Zn-I)/ν(Zn-Cl), and especially for ν(Zn-I)/ν(Zn-Br), the increase is considerable. This is in agreement with results of other thiazole complexes,[3,8,27] and indicates that in those compounds there is strong mixing of vibrations of neighbouring bonds in the coordination polyhedron. IR spectra of the chloride complexes are typical for tetrahedral ZnL$_2$Cl$_2$.[25,26] We suppose that the bromide and iodide have similar structures.

Because of the complex character of the IR spectra, the identification of the ligating atom is more complicated. For this purpose we use ν(Zn-N$_c$), ν(Zn-N$_a$), ν(NH$_2$) and β(NH$_2$) (Table I). The most important peculiarities of the spectra are as follows.

1. In more than half the complexes, the bands for ν(Zn-X) and ν(Zn-N$_c$) are in the same region and identification is difficult. In other cases, the number, position and intensity of the bands in the region 183–256 cm^{-1} are typical for ν(Zn-N$_c$) in tetrahedral ZnL$_2$X$_2$.

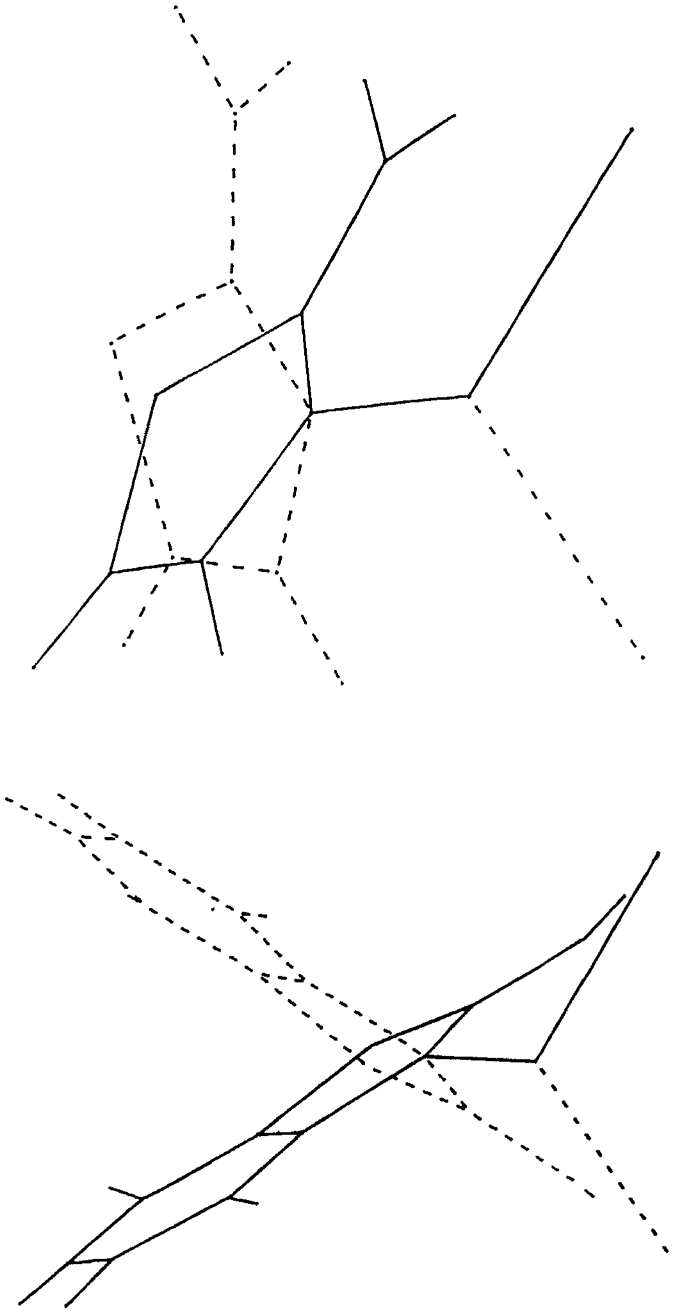


Figure 3 Conformation of Zn(at)$_2$Br$_2$ (a) and Zn(abt)$_2$Br$_2$ (b) viewed in projection down the N(3)-N(3′) axis as stick models. Solid [dashed] lines denote bonds to unprimed [primed] atoms.

Table I Selected far IR bands (400–150cm^{-1}) for the 2-aminothiazole complexes.

Complex	Far IR bands (400–150 cm^{-1})					
	ν(Zn-X)	ν(Zn-N$_c$)	$\beta(NH_2)$	Other bands	$\Delta\nu_{asNH_2}$	$\Delta\nu_{sNH_2}$
$Zn(at)_2Cl_2$	300s,290s[a]	225s,185s	400s	173m,168w	-131	-113
$Zn(at)_2Br_2$	(223s,215s)[b]	(223s)	398s	269m,177w,168m	-91	-83
$Zn(at)_2I_2$	(213s,204s)	(213s,204s)	402s 390s	287s	-78	-84
$Zn(amt)_2Cl_2$	(329s),284s,br	232s,220m	(329s)	165m	-98	-93
$Zn(amt)_2Br_2$	(232s),214s	(232s)	328s	152m	-105	-98
$Zn(amt)_2I_2$	201s,175s	234s	320s	167m	+8	+1
$Zn(abt)_2Cl_2$	326s,293s	228m,213s	318s	198w,164s,150s	-140	-88 -108
$Zn(abt)_2Br_2$	(220s,208s)	(220s,208s)	318s	169m,151m	-131	-95
$Zn(abt)_2I_2$	203s,(190m)	215m,(190m)	306s	332s,167w,157w	-143	-98
$Zn(ambt)_2Cl_2$	327s,295s	228m,212s	319s	212s,164s,152s	-72	-139
$Zn(ambt)_2Br_2$	(221s,206s)	(221s,206s)	317s	330w,171w,155m	-96	-128
$Zn(ambt)_2I_2$	204s,(192s)	212s,(192s)	305s	332w,197w,156w	-94	-93
$Zn(amobt)_2Cl_2$	296s,281s	206s,br,190m	322s		-58	-107
$Zn(amobt)_2Br_2$	(228s,210s)	262w,188m (210,br)	320s	164w	-63	-103
$Zn(amobt)_2I_2$	(214s,192s)	(214s,192s) 262s	318s		-58	-96
$Zn(aeobt)_2Cl_2$	297s,br, 285s	256w	324s	205m,184w,154m	-44	-22
$Zn(aeobt)_2Br_2$	228s,(210s)	253m,(210s)	323s	295s,200s,175w	-59	-20
$Zn(acobt)_2I_2$	205s,(190s)	225s,(190s)	323s	295s,165w,153w	-67	-24
$Zn(athbt)_2Cl_2$	316s,286s	242s,213s	395s	325w,160w	-109	-107
$Zn(athbt)_2Br_2$	(217s),205s	245s,(217)s	394s	338w,301s,295s, 245m,170w160w	-113	-106
$Zn(athbt)_2I_2$	(210s),186s	248s,(210s)	295s	351s,320m,295s, 243m,153w	-113	-107
$Zn(bt)_2Cl_2$	317s,304s	220s,187s		363m		
$Zn(bt)_2Br_2$	(228s,br)	(228s,br), 189s		364m		
$Zn(bt)_2I_2$	206s,(183s)	220s,(183s)		362m		

[a] S = strong, m = medium, br = broad. [b] The frequencies in brackets are overlapping bands or those of mixed vibrations.

Table II Crystal data and experimental details for (**1**)–(**3**).

	$Zn(at)_2Br_2$	$Zn(at)_2I_2$	$Zn(abt)_2Br_2$
Formula	$C_6H_8Br_2N_4S_2Zn$	$C_6H_8I_2N_4S_2Zn$	$C_{14}H_{12}Br_2N_4S_2Zn$
M	425.47	519.46	525.59
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	Pc
a, Å	8.741(1)	8.996(1)	8.659(1)
b, Å	11.468(2)	11.855(2)	12.447(3)
c, Å	13.348(3)	13.623(2)	8.239(1)
b, deg	106.52(1)	107.67(1)	102.94(1)
V, Å^3	1283(1)	1384(1)	865(1)
Z	4	4	2
Dx, g cm^{-3}	2.203	2.492	2.017
μ, mm^{-1}	8.42	6.50	6.26
$F(000)$	816	960	512
temperature, K	293	298	293
crystal size, mm	0.25 x 0.16 x 0.35	0.2 x 0.3 x 0.5	0.3 x 0.3 x 0.4
colour	pale brown	brown	colourless
monochromator	graphite crystal,	incident beam	
radiation, λ		MoK$_\alpha$,0.71073Å	
scan type	$\omega/2\tau$	$\omega/2\tau$	ω
scan speed, deg min^{-1}	3–10	1–10	3–10
scan width, deg	1.02 + 0.35tan(τ)	0.75 + 0.35tan(τ)	0.55 + 0.35tan(τ)
cell constants from	$20<\theta<22$	$18<\theta<20$	$20<\theta<22$
max sin(τ)/λ	0.638	0.638	0.703
hkl limits	0/11,0/14,–17/17	0/11,0/15,–17/17	0/11,0/17,–12/12
standard reflections		3 per 2 hours	
intensity variation, %	<1.0	<1.0	<2.0
reflections measured	2966	3029	2794
transmission factors, %	52.1–99.9	66.3–99.9	76.8–99.9
solution	Patterson, Br	Patterson, I	MULTAN 11/82*
H-atoms	refined	added	refined
refinement	full-matrix least-squares on F		
minimization function	$\Sigma w(F_o - F_c)^2$		
weighting scheme	$w = 4F_o^{\ 2}/\sigma^2(F_o^{\ 2})$		
reflections used	1616	2254	1420
number of variables	160	136	108
R	0.028	0.026	0.040
R_w	0.034	0.034	0.047
max Δ/σ	0.01	0.01	0.01
$\pm\Delta\rho$, e^{-3}	0.66,0.59	0.69,0.68	0.91,0.96

* P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.-P. De Clerq and M.M. Woolfson, MULTAN 11/82, A system of computer programs for the automatic solution of crystal structures from X-Ray diffraction data, (Universities of York, England and Louvain, Belgium, 1982).

Table III Positional and thermal parameters for (**1**) – (**3**).

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}(Å^2)
	$Zn(at)_2Br_2$			
Zn	0.02882(7)	0.24069(5)	0.32029(4)	0.0358(1)
Br	0.05182(7)	0.27119(6)	0.14900(4)	0.0515(2)
Br′	0.14483(7)	0.06279(5)	0.40024(4)	0.0473(1)
S(1)	0.2918(2)	0.5377(1)	0.5232(1)	0.0621(5)
S(1’)	- 0.5052(2)	0.2618(2)	0.2711(2)	0.0771(6)
N	0.2478(6)	0.4882(4)	0.3206(3)	0.059(1)
N’	- 0.3032(6)	0.3754(5)	0.1879(4)	0.064(2)
N(3)	0.1265(5)	0.3703(4)	0.4198(3)	0.037(1)
N(3’)	- 0.2047(5)	0.2344(4)	0.3171(3)	0.038(1)
C(2)	0.2171(6)	0.4586(4)	0.4096(4)	0.040(1)
C(2’)	- 0.3214(7)	0.2943(4)	0.2554(4)	0.045(2)
C(4)	0.1159(7)	0.3640(5)	0.5220(4)	0.048(2)
C(4’)	- 0.2598(6)	0.1603(5)	0.3819(4)	0.053(2)
C(5)	0.1930(8)	0.4453(5)	0.5865(4)	0.058(2)
C(5’)	- 0.4165(7)	0.1642(6)	0.3662(5)	0.074(2)
H(N1)	0.198(6)	0.447(4)	0.259(4)	0.0633*
H(N1’)	- 0.268(6)	0.381(5)	0.157(4)	0.0633*
H(N2)	0.299(6)	0.559(4)	0.310(4)	0.0633*
H(N2’)	- 0.398(6)	0.419(4)	0.135(4)	0.0633*
H(4)	0.049(6)	0.283(4)	0.533(4)	0.0633*
H(4’)	- 0.169(6)	0.107(5)	0.433(4)	0.0633*
H(5)	0.207(6)	0.456(5)	0.662(4)	0.0633*
H(5’)	- 0.477(6)	0.128(5)	0.404(4)	0.0633*
	$Zn(at)_2I_2$			
Zn	0.03007(6)	0.24421(4)	0.31963(4)	0.0324(1)
I	0.05200(4)	0.27299(3)	0.13726(2)	0.04407(8)
I’	0.15860(3)	0.05806(3)	0.40256(2)	0.03940(8)
S(1)	0.2852(2)	0.5277(1)	0.5303(1)	0.0598(4)
S(1’)	- 0.4935(2)	0.2652(1)	0.2681(1)	0.0658(5)
N	0.2529(6)	0.4832(4)	0.3333(3)	0.067(1)
N’	- 0.2967(5)	0.3810(4)	0.1920(3)	0.057(1)
N(3)	0.1248(4)	0.3688(3)	0.4225(3)	0.0359(9)
N(3’)	- 0.1987(4)	0.2389(3)	0.3147(3)	0.035(1)
C(2)	0.2156(5)	0.4535(4)	0.4172(4)	0.041(1)
C(2’)	- 0.3149(5)	0.2981(4)	0.2555(4)	0.040(1)
C(4)	0.1081(6)	0.3620(4)	0.5211(3)	0.047(1)
C(4’)	- 0.2537(6)	0.1644(5)	0.3741(3)	0.049(1)
C(5)	0.1833(7)	0.4392(5)	0.5866(4)	0.059(2)
C(5’)	- 0.4058(6)	0.1657(5)	0.3582(4)	0.065(2)
H(N1)	0.243(6)	0.455(4)	0.294(4)	0.0633*
H(N1’)	- 0.236(6)	0.378(5)	0.167(4)	0.0633*
H(N2)	0.291(6)	0.558(5)	0.336(4)	0.0633*
H(N2’)	- 0.382(6)	0.424(5)	0.158(4)	0.0633*
H(4)	0.043(6)	0.314(5)	0.526(4)	0.0633*
H(4’)	- 0.179(6)	0.123(5)	0.422(4)	0.0633*
H(5)	0.183(6)	0.460(4)	0.656(4)	0.0633*
H(5’)	- 0.446(6)	0.152(5)	0.394(4)	0.0633*

Table III (*Continued*)

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}(Å^2)
	Zn(abt)$_2$Br$_2$			
Zn	0	0.25172(9)	0	0.0292(2)
Br	-0.1420(1)	0.26013(7)	-0.2852(2)	0.0371(2)
Br'	-0.1654(2)	0.24700(8)	0.1968(2)	0.0480(3)
S(1)	0.1966(4)	0.5908(2)	0.1043(4)	0.0372(7)
S(1')	0.1859(4)	-0.0901(2)	-0.0191(4)	0.0386(7)
N	-0.051(1)	0.5053(6)	-0.107(1)	0.046(3)
N'	-0.056(1)	-0.0000(8)	0.077(1)	0.053(3)
N(3)	0.130(1)	0.3882(6)	0.056(1)	0.030(2)
N(3')	0.125(1)	0.1128(6)	-0.004(1)	0.029(2)
C(2)	0.079(1)	0.4866(7)	0.003(1)	0.032(3)
C(2')	0.072(1)	0.0159(7)	0.027(1)	0.033(3)
C(4)	0.270(1)	0.3948(8)	0.182(1)	0.028(3)
C(4')	0.261(1)	0.1064(8)	-0.061(1)	0.029(3)
C(5)	0.325(1)	0.4993(7)	0.222(1)	0.029(3)
C(5')	0.318(1)	0.0010(7)	-0.079(1)	0.032(3)
C(6)	0.461(1)	0.5191(8)	0.339(1)	0.040(3)
C(6')	0.452(2)	-0.0188(7)	-0.130(2)	0.044(3)
C(7)	0.546(1)	0.4315(9)	0.420(1)	0.043(3)
C(7')	0.537(1)	0.0686(9)	-0.175(2)	0.047(3)
C(8)	0.491(1)	0.3267(8)	0.378(1)	0.040(3)
C(8')	0.484(1)	0.1716(8)	-0.161(1)	0.040(3)
C(9)	0.355(1)	0.3078(7)	0.264(1)	0.032(3)
C(9')	0.346(1)	0.1909(7)	-0.105(1)	0.033(3)
H(N1)	-0.10(1)	0.477(8)	-0.18(2)	0.0633*
H(N2)	-0.07(2)	0.556(7)	-0.15(2)	0.0633*
H(N1')	-0.11(1)	0.040(8)	0.13(1)	0.0633*
H(N2')	-0.08(1)	-0.032(6)	0.09(1)	0.0633*
H(6)	0.50(1)	0.593(8)	0.35(2)	0.0633*
H(6')	0.48(1)	-0.085(8)	-0.16(2)	0.0633*
H(7)	0.60(1)	0.445(9)	0.49(1)	0.0633*
H(7')	0.62(1)	0.056(9)	-0.20(1)	0.0633*
H(8)	0.54(1)	0.274(8)	0.44(2)	0.0633*
H(8')	0.57(1)	0.227(8)	-0.19(2)	0.0633*
H(9)	0.32(2)	0.244(7)	0.25(2)	0.0633*
H(9')	0.31(2)	0.262(7)	-0.09(2)	0.0633*

* Starred atoms were refined with fixed U_{iso}.

Table IV Selected bond distances (Å) and angles (°) for (**1**) – (**3**).

	Zn(at)$_2$Br$_2$	Zn(at)$_2$I$_2$	Zn(abt)$_2$Br$_2$
Zn-X	2.377(1)	2.574(1)	2.398(1)
Zn-X'	2.390(1)	2.586(1)	2.393(2)
Zn-N(3)	2.014(4)	2.036(4)	2.035(8)
Zn-N(3')	2.031(4)	2.039(4)	2.044(8)
S(1)-C(2)	1.728(6)	1.720(5)	1.743(10)
S(1)-C(5)	1.732(7)	1.719(6)	1.733(9)
S(1')-C(2')	1.719(6)	1.712(5)	1.74(1)
S(1')-C(5')	1.705(8)	1.713(7)	1.76(1)
N-C(2)	1.334(7)	1.332(6)	1.30(1)
N'-C(2')	1.336(8)	1.352(6)	1.29(2)
N(3)-C(2)	1.317(6)	1.311(6)	1.34(1)
N(3)-C(4)	1.395(6)	1.398(6)	1.40(1)
N(3')-C(2')	1.309(7)	1.313(6)	1.34(1)
N(3')-C(4')	1.393(7)	1.387(6)	1.36(1)
C(4)-C(5)	1.317(8)	1.313(7)	1.40(1)
C(4')-C(5')	1.326(9)	1.319(7)	1.42(1)
X-Zn-X'	114.4(1)	112.3(1)	114.3(1)
X-Zn-N(3)	112.9(1)	115.4(1)	108.9(2)
X-Zn-N(3')	110.1(1)	110.2(1)	100.3(2)
X'-Zn-N(3)	106.8(1)	106.3(1)	104.6(3)
X'-Zn-N(3')	106.0(1)	107.5(1)	112.9(3)
N(3)-Zn-N(3')	106.0(2)	104.6(1)	116.1(3)
C(2)-S(1)-C(5)	89.5(3)	89.4(2)	90.8(4)
C(2')-S(1')-C(5')	89.4(3)	89.2(2)	90.5(5)
Zn-N(3)-C(2)	130.9(3)	130.9(3)	124.0(7)
Zn-N(3)-C(4)	118.2(4)	118.4(3)	123.9(6)
C(2)-N(3)-C(4)	110.5(5)	110.3(4)	110.8(8)
Zn-N(3')-C(2')	126.4(4)	127.7(3)	123.6(8)
Zn-N(3')-C(4')	122.1(4)	122.4(3)	123.8(6)
C(2')-N(3')-C(4')	111.4(5)	109.9(4)	112.0(9)
S(1)-C(2)-N	121.8(4)	121.1(4)	121.5(7)
S(1)-C(2)-N(3)	113.7(4)	113.9(4)	114.0(7)
N-C(2)-N(3)	124.5(5)	125.0(4)	124.4(9)
S(1')-C(2')-N'	121.9(5)	122.0(4)	121.9(8)
S(1')-C(2')-N(3')	113.5(5)	114.4(4)	113.9(9)
N'-C(2')-N(3')	124.7(6)	123.6(4)	124.2(10)
N(3)-C(4)-C(5)	116.1(6)	115.4(5)	115.0(8)
N(3')-C(4')-C(5')	113.9(7)	115.7(5)	115.9(9)
S(1)-C(5)-C(4)	110.3(5)	110.9(4)	109.3(7)
S(1')-C(5')-C(4')	111.7(6)	110.8(4)	107.7(9)

Table V Ratio of ν(Zn-X) frequencies in the IR spectra of the 2-aminothiazole complexes, ZnL$_2$X$_2$.

	Br/Cl	I/Cl	I/Br		Br/Cl	I/Cl	I/Br
at	0,74	0,71	0,96	ambt	0,68	0,62	0,92
amt	0,71	0,61	0,87	amobt	0,77	0,72	0,94
bt	0,72	0,65	0,90	aeobt	0,77	0,69	0,90
abt	0,67	0,62	0,92	athbt	0,69	0,66	0,97

2. The $\nu(NH_2)$ bands show negative shifts in comparison with the free ligands. In some cases the shifts are significant. This may indicate participation of the amino group in coordination. This ambiguity, and in some cases ever discrepancy, of the data could be resolved by X-ray analysis of (**1**)–(**3**). The structures are built up of discrete ZnL_2X_2 molecules. The compounds (**1**) and (**2**) are isomorphous and have a structure similar to the chloride complex[28] which, however, crystallizes in a different lattice. Monodentate thiazole ligands are coordinated to Zn *via* the *endo*-N atom. The tetrahedral ZnN_2X_2 surrounding has a distorted geometry with Zn-N distances in the range 2.014–2.044, Zn-X within 2.377–2.398 (Br) and 2.574–2.568Å(I).

Bonding angles about the central atom vary from 100.3 to 115.4°. In $Zn(at)_2Cl_2$ as in the cases of the corresponding $CoCl_2$ complexes with benzothiazole,[19] **at**[18] and **abt,**[29] elongation of the M-N bonds in the coordination tetrahedra $[MN_2Cl_2]$ leads to a shortening of M-Cl bonds and *vice versa*. This shows that the central atom redistributes electron density between the ligands and the terminal chlorine atoms. This was not observed in the cases of $Zn(at)_2X_2$ (X = Br, I) and $Zn(abt)_2Br_2$ where the Zn-N and Zn-X lengths change in a similar way. The **at** and **abt** ligands are planar to within 0.017(5)Å for **at** and 0.022(9)Å for **abt**. Zn is displaced from the least-squares planes of the ligands by max. 0.195(1), 0.201(1) and 0.327(1)Å for (**1**)–(**3**) respectively. The dihedral angle between the planes of the ligands in discrete $Zn(at)_2X_2$ (X = Br,I) molecules is 107.9(1), 106.2(1) and in $Zn(abt)_2Br_2$, 64.8(2)°.

The C(2)-S(1)-C(5) angle (89.5(3)-90.8(4)°) is typical for S-containing five-membered heterocycles.[30,31] In **at**, the average S(1)-C(2) bond length is 1.724(5) Å and S(1)-C(5) is 1.725(7)Å. For uncoordinated **at** they are 1.744(5) and 1.721(5)Å. This shows that complex formation leads to significant π-electron density in the C(5)-S(1)-C(2) fragment of **at**. The π-character of the S(1)-C(2) and S(1)-C(5) bonds[32] is 39% and 45%, respectively.

At the same time there is a lengthening of both C(2)-N(3) and C(4)-N(3) bonds by 0.01–0.02Å. As in the case with $Co(abt)_2Cl_2$, this can be explained by assuming a transfer of d_π-electrons of the metal atom to a p_π^* antibonding orbital of N(3).

Crystallographic evidence together with NMR[33] and DSC data[34] shows that complex formation with thiazole ligands results not only in σ-donation but also π-interaction involving metal and endocyclic nitrogen. Since the Zn-N(3) distances (2.014(4)–2.044(8)Å) are normal for σ bonds,[35] this suggests that the π-interaction between Zn and aminothiazole ligands is relatively weak.

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