Interaction of Zinc and Cadmium Bis(benzothiazole-2-thiolates) with Nitrogen Bases

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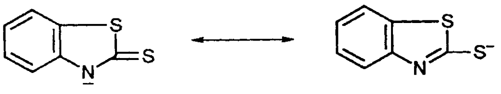
The reactions of polymeric $[Zn(C_7H_4NS_2)_2]$ and $[Cd(C_7H_4NS_2)_2]$ with pyridine (py), 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) lead to the formation of mononuclear adducts which have been characterized by elemental analysis and infrared spectroscopy. The complexes $[Zn(C_7H_4NS_2)_2(py)_2]$ **1**, $[Zn(C_7H_4NS_2)_2(bipy)]$ **2** and $[Cd(C_7H_4NS_2)_2(py)_2]$ **3** were structurally characterized by X-ray crystallography. Adducts **1** and **2** have distorted-tetrahedral ZnN_2S_2 cores. The zinc ions are co-ordinated to the two exocyclic S atoms of the benzothiazole-2-thiolates and to two nitrogen atoms from the py or bipy base. The Zn–S and Zn–N bond distances are 2.324(1) and 2.063(4) Å in **1** and 2.310(13) and 2.096(4) Å in **2**. The complex $[Zn(C_7H_4NS_2)_2(phen)]$ was found to be isomorphous to **2**. Adduct **3** shows a distorted-octahedral CdN_4S_2 unit formed by two bidentate S,N benzothiazole-2-thiolates and two *cis* pyridine nitrogen atoms. The two exocyclic S atoms are located at the axial positions. The mean Cd–S and Cd–N bonds of the bidentate ligands in **3** are 2.706(10) and 2.422(30) Å and the corresponding mean Cd–N(py) is 2.334(4) Å. The infrared spectra of the adducts in the range 650–200 cm^{-1} are discussed in the light of the known structures. The thermal degradation of complexes **1**–**3** affords ZnS or CdS.

Investigation of the role that zinc and cadmium thiolate complexes play in biological chemistry has stimulated numerous studies on zinc(II) and cadmium(II) co-ordination compounds with sulfur ligation.[1–13] In particular, zinc and cadmium complexes with N_2S_2 ligand cores are of increasing interest as structural and spectroscopic models for metal binding sites in a number of metallothioneins and metalloregulatory proteins.[14–19] Alkane- and aromatic thiolates with mono- and bi-dentate nitrogen bases have been the ligands more frequently used in these model compound studies. Heterocyclic thiolates usually have more than one donor atom potentially available for co-ordination, and no straightforward prediction of their co-ordination to the metal centre can be made. Among these ligands, the benzothiazole-2-thiolate anion ($C_7H_4NS_2^-$) is of interest in view of its biological activity and important practical applications as an anticorrosion agent and as an accelerator in the rubber vulcanization process.[20] Although extensively studied by spectroscopic methods, crystal structures on metal complexes of this ligand are scarce.



Previous studies on anionic zinc(II) and cadmium(II) adducts containing the $C_7H_4NS_2^-$ ligand showed uni- (N or exocyclic S) and bi-dentate (N and exocyclic S) bonding modes in the former, whereas the bidentate (N, exocyclic S) mode only has been found in the latter.[22,23] Recently, a crystalline sample of polymeric $[\{Cd(C_7H_4NS_2)_2\}_n]$ was isolated from dimethylformamide and shown to contain linear chains of octahedrally co-ordinated cadmium atoms (CdN_2S_4) with extended networks of Cd_2S_2 four-membered rings involving the exocyclic-S atoms as bridges.[24] The synthesis of the pyridine adduct $[Cd(C_7H_4NS_2)_2]\cdot 2py$ has been previously reported[23] but no structural information is available. Herein, we report our studies of the reactions of polymeric $[\{Zn(C_7H_4NS_2)_2\}_n]$ and $[\{Cd(C_7H_4NS_2)_2\}_n]$ with the N-donor bases pyridine, 2,2′-bipyridine and 1,10-phenanthroline leading to the complexes $[M(C_7H_4NS_2)_2(py)_2]$, $[M(C_7H_4NS_2)_2(bipy)]$ and $[M(C_7H_4NS_2)_2(phen)]$ (M = Zn or Cd). X-Ray analyses of $[Zn(C_7H_4NS_2)_2(py)_2]$, $[Zn(C_7H_4NS_2)_2(bipy)]$ and $[Cd(C_7H_4NS_2)_2(py)_2]$ were also performed.

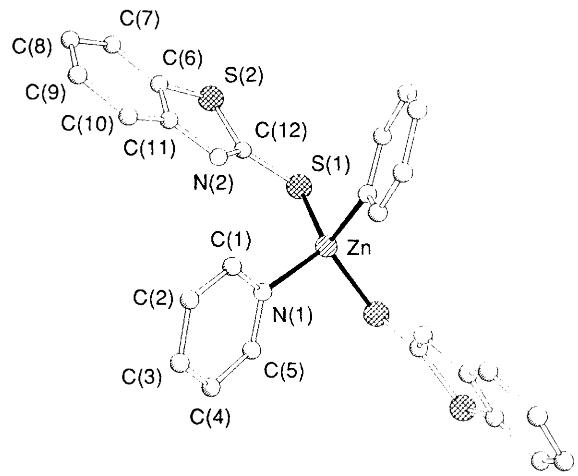


Fig. 1 Structure of $[Zn(C_7H_4NS_2)_2(py)_2]$ and numbering scheme

Results and Discussion

The zinc and cadmium adducts $[M(C_7H_4NS_2)_2(py)_2]$,

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Crystal data and details of data collection and refinement

Empirical formula	$C_{24}H_{18}N_4S_4Zn$	$C_{24}H_{16}N_4S_4Zn$	$C_{24}H_{18}CdN_4S_4$
M_r	556.0	554.0	603.1
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)	*Pccn* (no. 56)
a/Å	23.985(7)	8.641(1)	16.318(2)
b/Å	7.191(2)	11.253(1)	16.515(2)
c/Å	16.114(4)	14.203(1)	18.936(2)
α/°		102.40(1)	
β/°	119.72(1)	105.71(1)	
γ/°		106.50(1)	
U/Å^3	2413.7(11)	1209.4(2)	5103.1(10)
Z	4	2	8
D_c/g cm^{-3}	1.530	1.521	1.570
F(000)	1136	564	2416
Crystal size/mm	0.20 × 0.20 × 0.25	0.15 × 0.20 × 0.25	0.15 × 0.15 × 0.35
Range for *h*, *k*, *l*	0–16, 0–7, −17 to 14	0–9, −12 to 11, −15 to 14	0–17, 0–17, 0–20
No. of reflections collected	1354	3469	3358
No. of observed reflections	1031 [$I > 2\sigma(I)$]	2534 [$I > 3\sigma(I)$]	1706 [$I > 2\sigma(I)$]
μ/mm^{-1}	1.38	1.38	1.20
Absorption correction (maximum, minimum)	1.077, 0.943	1.059, 0.931	1.031, 0.946
g^a	0.0002	0.0009	0.0003
No. of refined parameters	150	298	299
R, R'^b	3.09, 3.10	3.12, 3.56	3.03, 2.98
Goodness of fit	1.34	1.12	0.91
Data to parameter ratio	7.0:1	9.3:1	5.9:1
Final Δ*F* ripple/e Å^{-3}	0.34, −0.58	0.34, −0.66	0.22, −0.24

[a] Weighting scheme, $w = 1/[\sigma^2(F) + gF^2]$. [b] $R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$, $R' = (\Sigma||F_o| - |F_c||w^{\frac{1}{2}}/(\Sigma|F_o|w^{\frac{1}{2}})$.

Table 2 Atomic coordinates (× 10^4) for $[Zn(C_7H_4NS_2)_2(py)_2]$ **1**

Atom	*x*	*y*	*z*
Zn	0	1241(1)	2500
S(1)	575(1)	−804(2)	3759(1)
S(2)	1731(1)	−209(2)	5685(1)
N(1)	443(2)	3093(4)	2034(2)
N(2)	1259(2)	2383(5)	4402(2)
C(1)	677(2)	4716(6)	2480(3)
C(2)	916(2)	6056(6)	2135(3)
C(3)	925(3)	5723(7)	1306(4)
C(4)	708(3)	4054(8)	860(3)
C(5)	465(2)	2777(6)	1230(3)
C(6)	2128(2)	1904(5)	5953(3)
C(7)	2673(2)	2473(7)	6775(3)
C(8)	2903(2)	4231(7)	6809(3)
C(9)	2583(2)	5424(7)	6044(3)
C(10)	2041(2)	4893(6)	5232(3)
C(11)	1808(2)	3115(6)	5179(3)
C(12)	1169(2)	664(5)	4550(3)

Table 3 Atomic coordinates (× 10^4) for $[Zn(C_7H_4NS_2)_2(bipy)]$ **2**

Atom	*x*	*y*	*z*
Zn	4 413(1)	5 537(1)	2 353(1)
S(1)	6 797(1)	6 851(1)	3 786(1)
S(2)	9 949(1)	8 872(1)	3 820(1)
S(3)	4 724(1)	4 038(1)	1 080(1)
S(4)	5 456(1)	1 681(1)	1 488(1)
N(1)	2 285(3)	4 934(2)	2 815(2)
N(2)	2 758(3)	6 314(2)	1 545(2)
N(3)	7 117(3)	7 846(2)	2 253(2)
N(4)	5 115(3)	3 431(2)	2 840(2)
C(1)	2 162(4)	4 273(3)	3 487(3)
C(2)	808(5)	4 063(4)	3 849(3)
C(3)	−442(4)	4 547(4)	3 505(3)
C(4)	−355(4)	5 205(3)	2 796(3)
C(5)	1 028(3)	5 383(3)	2 457(2)
C(6)	1 231(4)	6 066(3)	1 685(2)
C(7)	−49(4)	6 415(3)	1 127(3)
C(8)	240(5)	7 005(4)	418(3)
C(9)	1 793(5)	7 243(4)	259(3)
C(10)	3 027(4)	6 888(3)	842(3)
C(11)	8 257(4)	8 783(3)	2 017(3)
C(12)	7 883(5)	9 117(3)	1 126(3)
C(13)	9 109(6)	10 096(4)	1 007(4)
C(14)	10 689(7)	10 722(5)	1 741(4)
C(15)	11 106(6)	10 432(5)	2 632(4)
C(16)	9 872(4)	9 438(4)	2 778(3)
C(17)	7 801(4)	7 811(3)	3 173(2)
C(18)	5 462(4)	2 535(3)	3 310(2)
C(19)	5 638(4)	2 612(3)	4 327(3)
C(20)	5 993(5)	1 651(4)	4 699(3)
C(21)	6 149(5)	606(5)	4 065(4)
C(22)	5 996(5)	498(4)	3 065(3)
C(23)	5 669(4)	1 486(3)	2 689(3)
C(24)	5 083(4)	3 122(3)	1 896(3)

$[M(C_7H_4NS_2)_2(bipy)]$ and $[M(C_7H_4NS_2)_2(phen)]$ (M = Zn or Cd) were prepared in good yield by the reaction of $[\{Zn(C_7H_4NS_2)_2\}_n]$ and $[\{Cd(C_7H_4NS_2)_2\}_n]$ with the corresponding N-donor ligands. The solid compounds are stable when kept in a dry atmosphere. Crystal data for the complexes $[Zn(C_7H_4NS_2)_2(py)_2]$ **1**, $[Zn(C_7H_4NS_2)_2(bipy)]$ **2** and $[Cd(C_7H_4NS_2)_2(py)_2]$ **3** are given in Table 1 and the final atomic coordinates in Tables 2–4 respectively. Figs. 1–3 show the structural diagrams and the atomic numbering schemes. Bond distances and angles are given in Table 5. The zinc complexes **1** and **2** are mononuclear with the basic tetrahedral ZnN_2S_2 co-ordination units determined by two exocyclic S atoms from two benzothiazole-2-thiolate ligands, and by two N atoms from the py or bipy donor ligands. The S and N atoms of the heterocyclic ring of the benzothiazole-2-thiolate ligands do not participate in the co-ordination. Complex **1** has a crystallographically imposed C_2 symmetry with the metal atom lying on the crystallographic two-fold rotational axis. The Zn–S distance [2.324(1) Å] in **1** and the two [2.298(1) and 2.323(1) Å] in **2** are significantly longer than such distances reported for the mononuclear arenethiolates $[Zn(SC_6H_2Pr^i_3\text{-}2,4,6)_2(bipy)]$[15] [average Zn–S 2.256(3) Å] and $[Zn(SC_6H_4Me\text{-}p)_2(phen)]$[25] [average Zn–S 2.261(5) Å] and are closer to those reported for the mononuclear alkanethiolate bis(2-amino-1,1-dimethylethanethiolato)zinc(II)[16] [average Zn–S 2.297(4) Å]. The weaker Zn–S bindings in **1** and **2** may be related to some degree of conjugation between the exocyclic C–S bond and the heterocyclic ring of the benzothiazole-2-thiolate ligands. The

Table 4 Atomic coordinates (× 10^4) for $[Cd(C_7H_4NS_2)_2(py)_2]$ **3**

	Molecule A			B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cd	−2500	7500	−2630(1)	2500	7500	301(1)
S(1)	−3745(1)	8567(1)	−2430(1)	1376(1)	6331(1)	76(1)
S(2)	−3296(1)	9537(1)	−1124(1)	489(1)	6749(1)	−1286(1)
N(1)	−1773(4)	8231(4)	−3476(3)	1740(4)	8248(3)	1118(3)
N(2)	−2345(3)	8497(3)	−1723(3)	1526(3)	7690(3)	−670(3)
C(1)	−1404(5)	7892(5)	−4005(4)	2082(4)	8600(4)	1665(4)
C(2)	−909(6)	8304(7)	−4480(5)	1668(7)	9110(5)	2101(4)
C(3)	−831(6)	9112(6)	−4391(5)	863(6)	9268(5)	1980(5)
C(4)	−1201(6)	9462(5)	−3851(5)	500(6)	8906(6)	1428(4)
C(5)	−1667(6)	9010(5)	−3409(4)	953(5)	8389(5)	1011(4)
C(6)	−2335(4)	9373(4)	−750(3)	720(4)	7666(4)	−1688(3)
C(7)	−1971(5)	9731(5)	−165(4)	433(4)	7986(4)	−2317(4)
C(8)	−1191(6)	9504(5)	12(4)	694(5)	8752(5)	−2521(4)
C(9)	−778(5)	8939(5)	−378(4)	1235(5)	9168(4)	−2113(4)
C(10)	−1132(5)	8574(4)	−959(4)	1549(4)	8850(4)	−1487(3)
C(11)	−1925(4)	8796(4)	−1146(4)	1285(4)	8092(4)	−1283(3)
C(12)	−3080(4)	8824(4)	−1775(3)	1177(4)	6974(4)	−606(3)

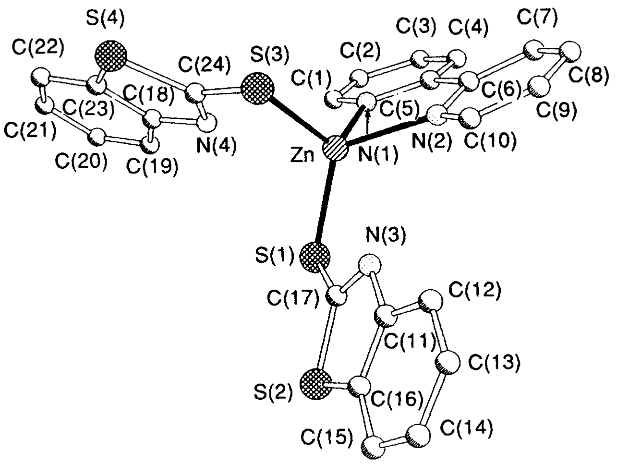

Fig. 2 Structure of $[Zn(C_7H_4NS_2)_2(bipy)]$ and numbering scheme

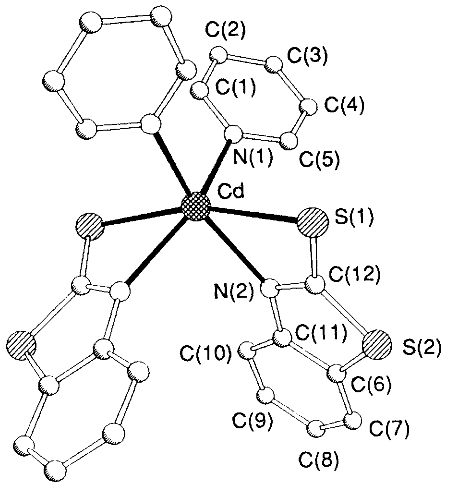

Fig. 3 Structure of $[Cd(C_7H_4NS_2)_2(py)_2]$ and numbering scheme

Table 5 Selected bond lengths (Å) and angles (°)

(*a*) $[Zn(C_7H_4NS_2)_2(py)_2]$ **1**

Zn–S(1)	2.324(1)	Zn–N(1)	2.063(4)
S(1)–Zn–N(1)	122.4(1)	S(1)–Zn–S(1A)	101.5(1)
N(1)–Zn–S(1A)	106.3(1)	N(1)–Zn–N(1A)	99.6(2)

(*b*) $[Zn(C_7H_4NS_2)_2(bipy)]$ **2**

Zn–S(1)	2.298(1)	Zn–S(3)	2.323(1)
Zn–N(1)	2.100(3)	Zn–N(2)	2.092(3)
S(1)–Zn–S(3)	118.9(1)	S(1)–Zn–N(1)	108.7(1)
S(3)–Zn–N(1)	118.7(1)	S(1)–Zn–N(2)	121.2(1)
S(3)–Zn–N(2)	104.6(1)	N(1)–Zn–N(2)	78.8(1)

(*c*) $[Cd(C_7H_4NS_2)_2(py)_2]$ **3**

	A	B
Cd–S(1)	2.715(2)	2.696(2)
Cd–N(2)	2.392(5)	2.451(5)
Cd–N(1A)	2.330(6)	2.337(6)
Cd–N(1)	2.330(6)	2.337(6)
Cd–S(1A)	2.715(2)	2.696(2)
Cd–N(2A)	2.392(5)	2.451(5)
S(1)–Cd–N(1)	98.1(2)	97.0(2)
N(1)–Cd–N(2)	94.8(2)	94.9(2)
N(1)–Cd–S(1A)	92.9(2)	95.0(1)
S(1)–Cd–N(1A)	92.9(2)	95.0(1)
N(2)–Cd–N(1A)	154.7(2)	155.4(2)
S(1)–Cd–N(2A)	105.5(1)	103.4(1)
N(2)–Cd–N(2A)	88.2(2)	82.8(2)
N(1A)–Cd–N(2A)	94.8(2)	94.9(2)
S(1)–Cd–N(2)	62.1(1)	62.1(1)
S(1)–Cd–S(1A)	163.9(1)	161.8(1)
N(2)–Cd–S(1A)	105.5(1)	103.4(1)
N(1)–Cd–N(1A)	93.1(3)	97.1(3)
S(1A)–Cd–N(1A)	98.1(2)	97.0(2)
N(1)–Cd–N(2A)	154.7(2)	155.4(2)
S(1A)–Cd–N(2A)	62.1(1)	62.1(1)

average C–S and C–N bond distances in the RN–C–S groups in **1** and **2** of *ca.* 1.72 and 1.30 Å are shorter than the single C–S (1.77 Å) and C–N (1.35 Å) bonds in 2-methylthiobenzothiazole[26] and benzothiazole-2-thione,[27] respectively. This tendency to electron delocalization on the RN–C–S group of the heterocyclic anionic ligand has been reported previously for related complexes.[20–28] The mean Zn–N(py) and Zn–N(bipy) distances of 2.063(4) Å in **1** and 2.096(4) Å in **2** are in good agreement with the values of 2.064 and 2.088 Å for these bonds in tetrahedral complexes.[29] The departures from tetrahedral symmetry are shown in **1** by the angles S–Zn–S 101.5(1) and N–Zn–N 99.6(2)° and the corresponding values in complex **2** are 118.9(1) and 78.8(1)° respectively. The larger distortion in **2** may be ascribed to the constraints imposed by the chelate ring involving the 2,2′-bipyridine ligand.

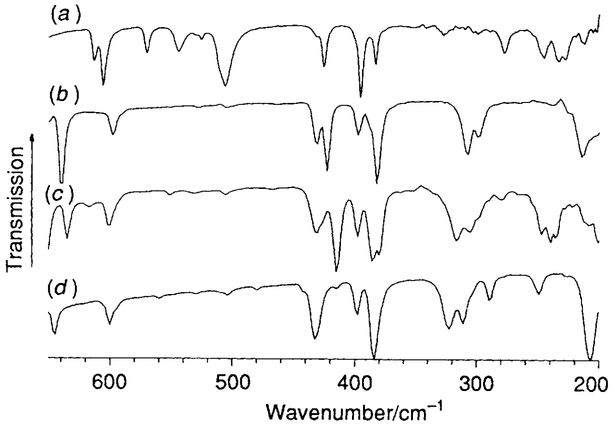

Fig. 4 Far-infrared spectra of [{Zn($C_7H_4NS_2$)$_2$}$_n$] (*a*), [Zn($C_7H_4NS_2$)$_2$(py)$_2$] (*b*), [Zn($C_7H_4NS_2$)$_2$(bipy)] (*c*) and [Zn($C_7H_4NS_2$)$_2$(phen)] (*d*)

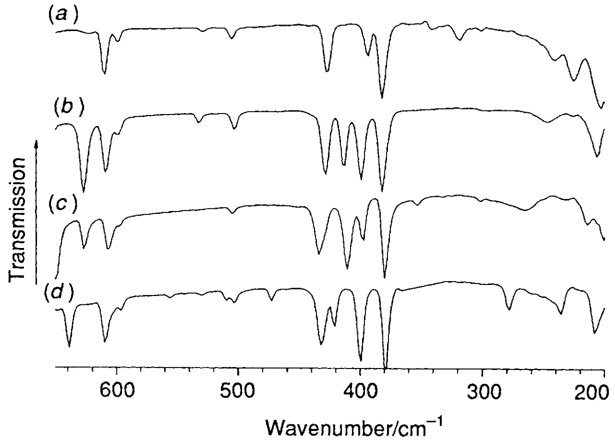

Fig. 5 Far-infrared spectra of [{Cd($C_7H_4NS_2$)$_2$}$_n$] (*a*), [Cd($C_7H_4NS_2$)$_2$(py)$_2$] (*b*), [Cd($C_7H_4NS_2$)$_2$(bipy)] (*c*) and [Cd($C_7H_4NS_2$)$_2$(phen)] (*d*)

Complex **3** crystallizes in the orthorhombic space group *Pccn* and contains two crystallographically independent molecules. The X-ray analysis shows that the two molecules denoted as A and B in Table 5 differ only slightly in bond distances and angles. The cadmium atom in each molecule is co-ordinated to two *trans* exocyclic S atoms and to two *cis* thiazole N atoms from two bidentate benzothiazole-2-thiolates and by two *cis* pyridine N atoms, Fig. 3. The departure of the CdN_4S_2 co-ordination polyhedron from octahedral geometry is shown by the deviation of the axial Cd–S bonds by 15.6 (molecule A) and 16.8° (molecule B) from the normal to the equatorial plane. The four N atoms of the co-ordination sphere define an equatorial belt of *ca.* 1 Å where the Cd atom is to be found. The average Cd–S [2.706(10) Å] and Cd–N [2.422(30) Å] bonds of the chelate $C_7H_4NS_2^-$ ligands are similar to those given[23] for anionic [Cd($C_7H_4NS_2$)$_3$]$^-$ [2.667(6) and 2.474(11) Å], the closest analogue to structure **3**. The average Cd–N(py) bond of 2.334(4) Å is similar to values reported for related six- and seven-co-ordinated complexes.[29] It appears that the excess of electron density on the cadmium atom due to the four nitrogen donor atoms is just compensated by the lengthening of the axial Cd–S bonds. It is interesting that under similar conditions the zinc ion in complex **1** becomes four-co-ordinated with the nitrogen atoms of the benzothiazole-2-thiolate ligands in non-interactive positions. Complex **3** is crystallographically isostructural with the previously reported[30] [Co($C_7H_4NS_2$)$_2$(py)$_2$] and [Ni($C_7H_4NS_2$)$_2$(py)$_2$]. Comparison of structure **3** with that of the cobalt complex [Co–S 2.595(5), Co–N 2.158(4) and Co–N(py) 2.120(4) Å] shows that the bonding of the ligands in the present structure is considerably weaker. Structures **1** and **3** illustrate the structural diversity that can result in zinc(II) and cadmium(II) thiolates. This is of particular interest since in most previous studies on zinc, cadmium and cobalt complexes with simple thiolate and nitrogen ligands four-co-ordination was found to be predominant.[7,15,31] Recently, a number of reports have dealt with the differences in the co-ordination chemistry of these thiolates which may have relevance to their different biological activity.[15,17,32]

Vibrational Spectra.—The infrared spectra of the adducts reported here show the characteristic vibrational features associated with benzothiazole-2-thiolate[33] and with the corresponding nitrogen-donor ligands (pyridine, 2,2′-bipyridine or 1,10-phenanthroline). Our attention has been focused on the low-frequency region 600–200 cm^{-1} where the metal-to-ligand sensitive modes are expected. These modes are difficult to assign empirically and may be broadly described as metal-to-ligand vibrations coupled with angular motions. However, regardless of the detailed assignments of these bands, comparison of the spectra of the reactants with those of the adducts may provide an effective criterion for metal–ligand bonding. Polymeric [{Zn($C_7H_4NS_2$)$_2$}$_n$] shows a number of bands at low frequency (< 280 cm^{-1}), Fig. 4(*a*). Upon pyridine addition a new set of strong bands appears in the range 320–290 cm^{-1}, which may be associated with the prevailing contribution of Zn–S terminal modes, Fig. 4(*b*). The Zn–N(py) mode at *ca.* 200 cm^{-1} occurs within the range reported for this mode in [ZnX_2(py)$_2$] complexes[34] (X = halide). These results are consistent with the formation of tetrahedral complexes, as shown above by X-ray crystallography. The spectra of the isomorphous [Zn($C_7H_4NS_2$)$_2$(bipy)] and [Zn($C_7H_4NS_2$)$_2$(phen)] [Figs. 4(*c*) and 4(*d*)] are similar to that of the py adduct, with a number of additional vibrational modes from the bidentate ligands. The spectra of the cadmium adducts show weak features in the low-frequency region with small changes from that for polymeric [{Cd($C_7H_4NS_2$)$_2$}$_n$], Fig. 5. These results are consistent with the formation of mononuclear adducts by depolymerization with no change in the metal co-ordination number, as shown above for [Cd($C_7H_4NS_2$)$_2$(py)$_2$] by X-ray analysis.

Thermolysis.—Thermogravimetric analyses have been made for complexes **1**–**3**. The complexes are non-volatile and decompose in air to give the corresponding metal sulfides as shown by elemental analysis for the metal and sulfur. Thermogravimetric analysis of **1** and **3** show decreases in weight of 28.8 and 26.2% in the temperature ranges 134–226 and 128–185 °C respectively. The mass losses correspond exactly to two pyridine molecules. Adduct **1** continues losing mass up to *ca.* 700 °C, leaving a solid residue of 14% (calc. for ZnS: 17%), whereas **3** loses mass smoothly up to 580 °C leaving a residue of 20% (calc. for CdS: 23.9%). Adduct **2** starts to decompose at 204 °C and proceeds smoothly up to 700 °C, leaving a residue of 15% (calc. for ZnS: 17.5%).

Experimental

All commercially available reagents and chemicals were of analytical or reagent-grade purity and used as received. Microanalyses were performed at UMYMFOR (Unidad de Microanálisis y Métodos Físicos Orgánicos). Zinc and cadmium were analysed by atomic absorption spectroscopy at the Analytical Laboratory of the Inorganic Chemistry Department. Infrared spectra were recorded in the range 4800–200 cm^{-1} on a Nicolet 510P FT-IR spectrophotometer. The samples were Nujol and halogenocarbon mulls supported between CsI disks; CsI pellets were also run and no significant differences were observed. Thermogravimetry (TG) diagrams were recorded on a Mettler TG-50 thermal analyser in a dynamic atmosphere of pure air at a heating rate of 5° min^{-1}.

Preparation of Compounds.—The compounds $[\{Zn(C_7H_4NS_2)_2\}_n]$ and $[\{Cd(C_7H_4NS_2)_2\}_n]$ were prepared by slight modifications of the literature methods.[22,23]

To a solution of benzothiazole-2-thione (3.35 g, 0.02 mol) in hot ethanol (100 cm^3) was added $[Zn(O_2CMe)_2\cdot 2H_2O]$ (2.20 g, 0.01 mol) with stirring, $[\{Zn(C_7H_4NS_2)_2\}_n]$ precipitated as a pale yellow solid which was filtered off, washed with ethanol and dried under vacuum at 80 °C. Yield: 3.40 g, 85%. The compound $[\{Cd(C_7H_4NS_2)_2\}_n]$ was similarly obtained by reaction of benzothiazole-2-thione (3.35 g, 0.02 mol) with $[Cd(O_2CMe)_2\cdot 2H_2O]$ (2.70 g, 0.01 mol). Yield: 3.55 g, 80%.

$[Zn(C_7H_4NS_2)_2(py)_2]$ **1**. To dry pyridine (10 cm^3) at room temperature was slowly added powdered solid $[\{Zn(C_7H_4NS_2)_2\}_n]$ (1.99 g, 0.005 mol) in small portions with stirring. The yellow solution was filtered to remove traces of solids and allowed to stand for 1 week at room temperature, during which time colourless crystals of the product were isolated by filtration and dried under a nitrogen stream. Yield: 2.22 g, 80% (Found: C, 51.25; H, 3.00; N, 10.30; Zn, 11.25. $C_{24}H_{18}N_4S_4Zn$ requires C, 51.85; H, 3.35; N, 10.10; Zn, 11.75%).

$[Zn(C_7H_4NS_2)_2(bipy)]$ **2**. To a suspension of polymeric $[\{Zn(C_7H_4NS_2)_2\}_n]$ (1.99 g, 0.005 mol) in chloroform (10 cm^3) at room temperature was added 2,2′-bipyridine (3.12 g, 0.02 mol) in chloroform–dimethylformamide (1 : 1, 20 cm^3). After stirring for 2 h a yellow solution formed. It was filtered to remove traces of solids and allowed to stand at room temperature. After 5 d yellow-green crystals were collected by vacuum filtration and washed with acetone. Yield: 2.22 g, 85% (Found: C, 51.80; H, 3.05; N, 9.95; Zn, 10.75. $C_{24}H_{16}N_4S_4Zn$ requires C, 52.05; H, 2.90; N, 10.10; Zn, 11.80%).

$[Zn(C_7H_4NS_2)_2(phen)]$. To a suspension of polymeric $[\{Zn(C_7H_4NS_2)_2\}_n]$ (1.99 g, 0.005 mol) in chloroform (10 cm^3) at room temperature was added 1,10-phenanthroline (1.80 g, 0.01 mol) in chloroform–dimethylformamide (1 : 1, 20 cm^3). After stirring at 60 °C for 12 h an orange solution formed. It was filtered to remove traces of solids and allowed to stand at room temperature. After 2 weeks yellow-green crystals were collected by vacuum filtration. Yield: 2.02 g, 70% (Found: C, 54.10; H, 2.85; N, 9.50; Zn, 10.85. $C_{26}H_{16}N_4S_4Zn$ requires C, 54.00; H, 2.80; N, 9.70; Zn, 11.30%).

$[Cd(C_7H_4NS_2)_2(py)_2]$ **3**. This complex was prepared in a similar manner to its zinc analogue using powdered $[\{Cd(C_7H_4NS_2)_2\}_n]$ (2.20 g, 0.005 mol). A yellow precipitate was formed which was filtered off and recrystallized from toluene–pyridine (1 : 1). Yield: 2.70 g, 90% (Found: C, 48.05; H, 3.20; Cd, 17.80; N, 9.40. $C_{24}H_{18}CdN_4S_4$ requires C, 47.80; H, 3.00; Cd, 18.65; N, 9.30%).

$[Cd(C_7H_4NS_2)_2(bipy)]$. This adduct was obtained in a similar manner to its zinc analogue from $[\{Cd(C_7H_4NS_2)_2\}_n]$ (2.22 g, 0.005 mol) and bipy (3.12 g, 0.02 mol). Green-yellow crystals separated after 3 d. Yield: 1.95 g, 65% (Found: C, 47.25; H, 2.50; Cd, 19.20; N, 9.50. $C_{24}H_{16}CdN_4S_4$ requires C, 47.95; H, 2.65; Cd, 18.70; N, 9.30%).

$[Cd(C_7H_4NS_2)_2(phen)]$. This adduct was made in a similar manner to its zinc analogue from $[\{Cd(C_7H_4NS_2)_2\}_n]$ (2.22 g, 0.005 mol) and 1,10-phenanthroline (1.80 g, 0.01 mol). Bright yellow crystals were obtained after 1 week. Yield: 1.80 g, 65% (Found: C, 50.10; H, 2.70; Cd, 18.75; N, 8.75. $C_{26}H_{16}CdN_4S_4$ requires C, 49.95; H, 2.60; Cd, 18.00; N, 8.95%).

Crystal Structure Determinations.—Crystals of adducts **1**–**3** suitable for X-ray analysis were grown slowly on standing for a few days or weeks. Recrystallization was carried out when necessary from benzene or toluene in the presence of an excess of the N donor to avoid decomposition to the starting materials. The crystal data and details of data collection and refinement are summarized for the three crystal structures in Table 1. Diffraction intensities were collected at 298 K on a Siemens R3m diffractometer, using the ω–2θ scan mode, with monochromatized, Mo-Kα radiation (λ = 0.710 69 Å), scan speed 4.18–29.30° min^{-1} and $3 < 2\theta < 45°$. Two standard reflections checked every 48 showed no significant crystal decay. Intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods, using the program package SHELXTL PLUS[35] (personal computer version), and refined by full-matrix least squares. At isotropic convergence H atoms were included in their idealized positions, with isotropic thermal parameters fixed at 0.08 $Å^2$, and corrections for absorption were applied using DIFABS.[36] In the final least-squares refinements all non-H atoms were treated anisotropically.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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