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Several coordination modes of the pentadentate ligand 2,6-diacetylpyridinebis(thiosemicarbazone)

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Abstract

The reaction between Zn(II) salts and the pentadentate ligand 2,6-diacetylpyridinebis(thiosemicarbazone) (H_2daptsc) produces various compounds, depending upon the H^+ ion concentration and the nature of the solvent from which the complex crystallizes. In the presence of nitric acid, the compound $[Zn(H_2daptsc)(H_2O)_2](NO_3)_2$ (**1**) is obtained. The mononuclear complex in **1** possesses a pentagonal bipyramidal geometry with an almost planar, fully protonated, H_2daptsc ligand and two axially bonded water ligands. Compound **2**, $[Zn_2(daptsc)_2]\cdot 2DMF$, was prepared and crystallized from dimethylformamide. The dinuclear complex in **2** contains two fully deprotonated ligands which arc coordinated to two Zn(II) ions with a distorted octahedral geometry. Compound **3**, $[Zn_2(daptsc)_2]\cdot MeOH\cdot H_2O$, was prepared and crystallized from methanol. The dinuclear unit in **3** is a structural isomer of complex **2**. The complex is asymmetric in which one zinc atom is six-coordinate and the other one is four-coordinate. Compound **1** is monoclinic, space group *Cc* with $a=21.930(3)$, $b=12.940(2)$, $c=7.345(1)$ Å, $\beta=104.22(3)°$, $V=2020(1)$ Å^3 and $Z=4$. Compound **2** is monoclinic, space group *C2/c* with $a=18.189(2)$, $b=15.716(2)$, $c=14.653(2)$ Å, $\beta=115.86(2)°$, $V=3769(1)$ Å^3 and $Z=4$. Compound **3** is triclinic, space group $P\bar{1}$ with $a=10.666(2)$, $b=16.282(2)$, $c=10.458(2)$ Å, $\alpha=90.79(2)$, $\beta=117.94(2)$, $\gamma=80.70(2)°$, $V=1579(1)$ Å^3 and $Z=2$.

Introduction

Mohan *et al.* reported the synthesis, physical properties and antitumor activity of several M(II) complexes with the quinquedentate ligand 2,6-diacetylpyridinebis(thiosemicarbazone) (H_2daptsc) (M = Mn, Fe, Co, Ni, Cu, Zn and Pt). Most of the complexes did not show any significant antitumor activity and were found to be toxic at doses used. However, the Zn(II) complex showed a significant activity [1].

To date, there is only one structural report of an H_2daptsc complex, $[Fe^{II}(H_2daptsc)(NCS)_2]$. This complex which possesses a pentagonal bipyramidal (PBP) geometry is obtained by reacting Fe(III) with the ligand [2].

The coordination chemistry of the oxygen analogue of H_2daptsc, 2,6-diacetylpyridinebis(semicarbazone) (H_2dapsc), has been studied extensively in several laboratories [3]. In most complexes of $[M(H_2dapsc)L_2]$ ($L=H_2O$, Cl, NCS) the geometry about the metal atom is pentagonal bipyramidal and the ligand is fully protonated. The structures of several compounds in which the ligand is deprotonated, $Hdapsc^-$, or doubly deprotonated $dapsc^{2-}$, have been reported [4]. Zn(II) forms with H_2dapsc PBP complexes such as $[Zn(H_2dapsc)L_2]$ ($L_2=$ Cl, Cl; Cl, H_2O) [3d]. A related PBP complex of Zn(II) with 2,6-diacetylpyridinebis(2-pyridylhydrazone) (H_2dapp) undergoes rearrangement upon deprotonation of the ligand and the dinuclear complex $[Zn_2(dapp)_2]$ is obtained. Each zinc atom in the complex is surrounded by six nitrogen atoms in a distorted octahedral configuration [5]. A similar dinuclear complex was obtained when a Zn(II) salt reacted with 6-diacetylpyridinebis(2-tenoylhydrazone) (H_2dapt) [6]. The ligand in $[Zn_2(dapt)_2]$ is doubly deprotonated and each zinc atom is surrounded by two oxygen and two nitrogen atoms from two different ligands. In addition, the two pyridine rings serve as bridges, linking the two zinc atoms, with Zn–N(Py) distances of about 2.6 Å. Similar bridging by pyridine groups occur in $[Zn_2(dapp)_2]$ [5].

We report here the preparation and structure of three complexes of Zn(II) with 2,6-diacetylpyridinebis(thiosemicarbazone), which dcmonstratc the various coordination modes of the ligand. $[Zn(H_2daptsc)(H_2O)_2](NO_3)_2$ (**1**) which is obtained from acidic solutions, possesses a regular PBP geometry with a planar H_2daptsc system and two axial water ligands.

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In $[Zn_2(daptsc)_2]\cdot 2DMF$ (**2**) each of the two fully deprotonated ligands, $daptsc^{2-}$, are coordinated to two zinc atoms with a distorted octahedral geometry. However, the interaction of Zn(II) with $H_2daptsc$ in methanol produces the asymmetric dinuclear complex $[Zn_2(daptsc)_2]\cdot MeOH\cdot H_2O$ (**3**) in which one zinc atom is six-coordinate and the other one is four-coordinate in an approximate octahedral and tetrahedral geometry, respectively.

Experimental

Preparation of $[Zn(H_2daptsc)(H_2O)_2](NO_3)_2$ *(1)*

$Zn(O_2CCH_3)_2\cdot 2H_2O$ (0.027 g) and $H_2daptsc$ (0.039 g), prepared by a literature method [1], were dissolved in a solution of 10 ml MeOH and 4 ml of 0.1 M HNO_3. The mixture was refluxed for 4 h, then cooled and kept in a vial. Yellow crystals of **1** were obtained after several days. *Anal.* Calc. for $C_{11}H_{19}N_9O_8S_2Zn$: C, 24.70; H, 3.58; N, 23.57. Found: C, 24.89; H, 3.44; N, 23.04%.

Preparation of $[Zn_2(daptsc)_2]\cdot 2DMF$ *(2)*

$ZnCl_2$ (0.017 g) and $H_2daptsc$ (0.039 g) were dissolved in 2 ml dimethylformamide and 10 ml of H_2O. The mixture was refluxed for 4 h and placed in a vial for slow evaporation. Yellow crystals of **2** were obtained after two weeks.

Preparation of $[Zn_2(daptsc)_2]\cdot MeOH\cdot H_2O$ *(3)*

$ZnCl_2$ (0.017 g) and $H_2daptsc$ (0.039 g) were dissolved in 10 ml of methanol. The solution was refluxed for 4 h and placed in a vial for slow evaporation. Yellow crystals of **3** were obtained after several days.

X-ray crystallography

Data were collected on a PW1100 Philips diffractometer. Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range of $12 < \theta < 16°$.

Data were measured by using an ω–2θ motion. Crystallographic data and other pertinent information are given in Table 1. For each crystal, Lorentz and polarization correction was applied. The heavy atom positions in **1**–**3** were obtained by using the results of SHELX-86 direct method analysis. In compound **1**, the systematic absences hkl, $h+k\neq 2n$ and $h0l$, $l\neq 2n$ indicated space group $C2/c$ or Cc. Refinement in the centrosymmetric space group $C2/c$ led to non-positive-definite thermal parameters for several atoms, a disordered NO_3^- group, several unrealistic bond distances and angles and discrepancy indices of $R = 12.54\%$ and $R_w = 18.58\%$. The choice of space group Cc is supported by the successful refinement and the lower values of the discrepancy indices, $R = 6.6\%$ and $R_w = 9.4\%$. All structures were refined to convergence using anisotropic thermal parameters for all Zn, S, O and N atoms in the coordination sphere in **1**, for all atoms except the DMF molecule of crystallization in **2** and for all Zn, S and N atoms in the coordination sphere in **3***. In structure **2**, the DMF molecule of crystallization is subjected to a two-fold disorder about an imaginary axis connecting the oxygen and the nitrogen atoms (O and N). Refinement of thc sitcs occupancics of thc three disordered carbon showed a 0.7–0.3 ratio among the two sites. The discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|2]^{1/2}$ are listed in Table 1.

Results and discussion

$[Zn(H_2daptsc)(H_2O)_2](NO_3)_2$ *(1)*

The atomic positional parameters are listed in Table 2. Table 3 presents the important bond lengths and angles and Fig. 1 shows the numbering scheme in **1**. The overall geometry of the complex is similar to that found in many H_2dapsc complexes having the general formula $[M(H_2dapsc)L_2]^{n+}$ ($L = H_2O$, Cl, NCS) [3] and that of $[Fe(H_2daptsc)(NCS)_2]$ [2]. The five donor atoms N(1), N(2), N(5), S(1) and S(2) form an approximately planar pentagon around the metal ion and the two water ligands are axially bonded, completing a coordination number of seven. The deviations from the pentagonal plane, defined by the five donor atoms, are relatively small with N(2) and N(5) showing the largest displacement of +0.166 and −0.205 Å, respectively. The average Zn–S distance in **1**, 2.580(3) Å, is slightly shorter than the corresponding one in the Fe(II) complex, 2.639(4) Å, on the other hand the average Zn–N(semicarbazone) distance, 2.346(3) Å, in **1** is slightly longer than the Fe–N distance of 2.297(10) Å [2].

$[Zn_2(daptsc)_2]\cdot MeOH\cdot 2DMF$ *(2)*

The atomic positional parameters are listed in Table 4. Table 5 presents the important bond lengths and angles and Fig. 2 shows the numbering scheme in **2**.

With four molecules in the cell of space group $C2/c$ there is only half a $[Zn_2(daptsc)_2]$ unit in the asymmetric unit with the other half related to it by a crystallographic two-fold axis. Each zinc atom in the dimeric complex is coordinated to two sulfur and two nitrogen atoms from two different, fully deprotonated,

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*All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE 1. Crystallographic data

Compound	1	2	3
Formula	$C_{11}H_{19}N_9O_8S_2Zn$	$C_{28}H_{40}N_{16}O_2S_4Zn_2$	$C_{23}H_{32}N_{14}O_2S_4Zn_2$
Formula weight	534.82	891.73	795.59
Space group	*Cc*	*C*2/*c*	*P*$\bar{1}$
a (Å)	21.930(3)	18.189(2)	10.666(2)
b (Å)	12.940(2)	15.716(2)	16.282(2)
c (Å)	7.345(1)	14.653(2)	10.458(2)
α (°)			90.79(2)
β (°)	104.22(3)	115.86(2)	117.94(2)
γ (°)			80.70(2)
V (Å)	2020(1)	3769(1)	1579(1)
Z	4	4	2
D_{calc} (g cm^{-3})	1.758	1.571	1.673
μ (cm^{-1})	14.04	14.71	17.48
Range of 2θ (°)	4–50	4–45	4–45
No. unique data	1913	2777	4021
Data with $F_o^2 > 3\sigma(F_o^2)$	1825	2288	2867
No. variables	183	263	281
R	0.066	0.048	0.070
R_w	0.094	0.058	0.085

TABLE 2. Positional parameters and e.s.d.s for **1**

Atom	*x*	*y*	*z*
Zn	0.20000(0)	0.69169(7)	0.40000(0)
S(1)	0.1260(1)	0.5406(2)	0.2679(5)
S(2)	0.2666(1)	0.5269(2)	0.4994(5)
O(1)	0.1643(4)	0.6937(5)	0.645(1)
O(2)	0.2329(4)	0.7005(6)	0.151(1)
N(1)	0.2059(4)	0.8623(5)	0.414(1)
N(2)	0.1071(5)	0.7634(7)	0.216(1)
N(3)	0.0584(6)	0.7067(8)	0.110(2)
N(4)	0.0140(5)	0.5461(7)	0.030(2)
N(5)	0.2972(5)	0.7430(7)	0.593(2)
N(6)	0.3422(5)	0.6760(7)	0.683(2)
N(7)	0.3811(5)	0.5111(8)	0.732(1)
C(1)	0.1572(5)	0.9189(8)	0.315(1)
C(2)	0.1588(5)	1.0285(8)	0.317(1)
C(3)	0.2143(4)	1.0772(8)	0.423(2)
C(4)	0.2634(5)	1.0155(9)	0.518(1)
C(5)	0.2591(4)	0.9083(8)	0.516(1)
C(6)	0.1012(5)	0.8629(9)	0.199(2)
C(7)	0.0459(6)	0.921(1)	0.088(2)
C(8)	0.0619(5)	0.5985(9)	0.128(2)
C(9)	0.3096(5)	0.8414(9)	0.619(2)
C(10)	0.3677(1)	0.884(1)	0.742(2)
C(11)	0.3330(5)	0.5723(8)	0.645(1)
N(8)	0.0094(4)	0.2276(7)	0.013(1)
O(3)	0.0582(5)	0.1880(8)	0.110(2)
O(4)	−0.0339(5)	0.170(1)	−0.079(2)
O(5)	0.0022(7)	0.3209(9)	0.014(2)
N(9)	0.3972(5)	0.7717(8)	0.267(2)
O(6)	0.3565(5)	0.7249(8)	0.156(1)
O(7)	0.3953(5)	0.8655(9)	0.293(2)
O(8)	0.4389(6)	0.719(1)	0.389(2)

e.s.d.s in the least significant digits are shown in parentheses.

TABLE 3. Important bond lengths (Å) and angles (°) for **1**

Zn–S(1)	2.573(3)		
Zn–S(2)	2.586(3)		
Zn–O(1)	2.128(9)		
Zn–O(2)	2.13(1)		
Zn–N(1)	2.213(7)		
Zn–N(2)	2.344(9)		
Zn–N(5)	2.348(9)		
S(1)–Zn–S(2)	74.9(1)	O(1)–Zn–O(2)	175.9(3)
S(1)–Zn–O(1)	89.9(2)	O(1)–Zn–N(1)	88.8(3)
S(1)–Zn–O(2)	91.8(3)	O(1)–Zn–N(2)	92.0(3)
S(1)–Zn–N(1)	143.1(3)	O(1)–Zn–N(5)	87.4(3)
S(1)–Zn–N(2)	72.8(3)	O(2)–Zn–N(1)	87.6(3)
S(1)–Zn–N(5)	146.9(3)	O(2)–Zn–N(2)	85.0(3)
S(2)–Zn–O(1)	94.1(2)	O(2)–Zn–N(5)	93.1(4)
S(2)–Zn–O(2)	90.0(3)	N(1)–Zn–N(2)	70.4(4)
S(2)–Zn–N(1)	141.9(3)	N(1)–Zn–N(5)	69.9(4)
S(2)–Zn–N(2)	147.1(3)	N(2)–Zn–N(5)	140.3(3)
S(2)–Zn–N(5)	72.3(2)		

ligand molecules. The distorted octahedral geometry about the metal atom is completed by two pyridine nitrogen atoms at distances of 2.571(4) and 2.705(5) Å. The Zn–N(Py)–Zn′ angle is 94.2(2)° and the Zn…Zn separation is 3.866(1) Å. The long Zn–N(Py) distances and the unfavorable geometry about the pyridine nitrogen imply that this contact may be regarded as a very weak interaction rather than a regular M–N bond. Most of the bond angles about the metal atoms depart substantially from the ideal 90 and 180° as can be seen from Table 5. Similar bridging pyridine systems were previously found in $[Zn_2(dapp)_2]\cdot 2CHCl_3\cdot 2H_2O$ [5] and $[Zn_2(dapt)_2]$ [6]. The Zn–N(Py) distances in these compounds are 2.59(1), 2.39(1) and 2.557(6), 2.599(8) Å, respectively.

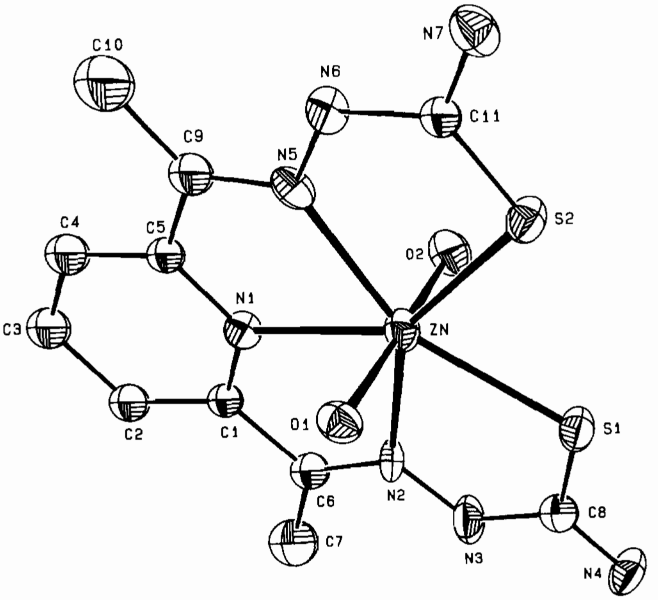

Fig. 1. The structure of $[Zn(H_2daptsc)(H_2O)_2]^{2+}$ in **1**.

TABLE 4. Positional parameters and e.s.d.s for **2**

Atom	x	y	z
Zn	0.41117(4)	0.16618(4)	0.2887(4)
S(1)	0.27968(9)	0.1049(1)	0.2009(1)
S(2)	0.5816(1)	0.24750(9)	0.0732(1)
N(1)	0.5676(3)	0.1532(3)	0.3822(3)
N(2)	0.4470(2)	0.0379(3)	0.3138(3)
N(3)	0.3915(3)	−0.248(3)	0.2600(3)
N(4)	0.2625(3)	−0.579(4)	0.1491(5)
N(5)	0.5956(2)	0.2850(3)	0.2790(3)
N(6)	0.5894(3)	0.3577(3)	0.2235(3)
N(7)	0.5741(3)	0.4154(3)	0.0743(4)
C(1)	0.5774(3)	0.0789(3)	0.4328(4)
C(2)	0.6379(4)	0.0675(4)	0.5315(4)
C(3)	0.6851(4)	0.1370(4)	0.5810(4)
C(4)	0.6734(3)	0.2125(4)	0.5322(4)
C(5)	0.6159(3)	0.2183(3)	0.4313(4)
C(6)	0.5171(3)	0.0123(3)	0.3790(4)
C(7)	0.5388(4)	−0.0794(4)	0.4033(5)
C(8)	0.3162(3)	0.0031(4)	0.2061(4)
C(9)	0.6083(3)	0.2965(3)	0.3720(4)
C(10)	0.6188(4)	0.3821(4)	0.4205(5)
C(11)	0.5812(3)	0.3439(3)	0.1310(4)
O	0.5362(3)	0.4189(3)	0.6435(4)
N	0.6201(3)	0.3461(3)	0.7834(4)
C(12)	0.5906(6)	0.4204(7)	0.7372(8)
C(13)	0.6840(7)	0.3514(8)	0.8940(9)
C(14)	0.5984(9)	0.266(1)	0.737(1)
C(12)′	0.558(1)	0.341(1)	0.677(2)
C(13)′	0.651(1)	0.419(2)	0.844(2)
C(14)′	0.657(2)	0.261(2)	0.822(2)

e.s.d.s in the least significant digits are shown in parentheses.

TABLE 5. Important bond lengths (Å) and angles (°) for **2**

Zn–S(1)	2.370(2)		
Zn–N(1)	2.571(4)		
Zn–N(1)′	2.705(5)		
Zn–N(2)	2.102(4)		
Zn–S(2)′	2.345(2)		
Zn–N(5)′	2.095(4)		
S(1)–Zn–S(2)′	110.75(7)	N(1)–Zn–N(1)′	85.1(2)
S(1)–Zn–N(1)	151.2(1)	N(1)–Zn–N(2)	69.1(2)
S(1)–Zn–N(1)′	89.0(1)	N(1)–Zn–N(5)′	98.4(2)
S(1)–Zn–N(2)	82.4(2)	N(1)–Zn–N(2)	85.9(1)
S(1)–Zn–N(5)′	105.5(2)	N(1)–Zn–N(5)′	68.3(1)
S(2)′–Zn–N(1)	87.2(1)	N(2)–Zn–N(5)′	152.5(1)
S(2)′–Zn–N(1)′	149.6(1)	Zn–N(1)–Zn′	94.2(2)
S(2)′–Zn–N(2)	118.5(1)		
S(2)′–Zn–N(5)′	83.9(1)		

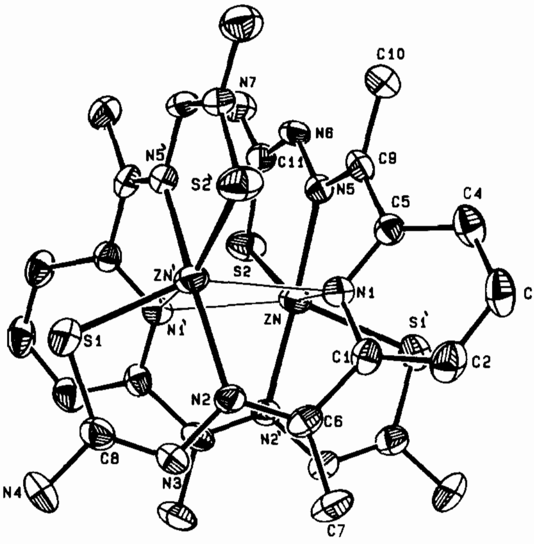

Fig. 2. The structure of $[Zn_2(daptsc)_2]$ in **2**.

$[Zn_2(daptsc)_2]\cdot CH_3OH\cdot H_2O$ (3)

The atomic positional parameters are listed in Table 6. Table 7 presents the important bond lengths and angles and Fig. 3 shows the numbering scheme in **3**.

The dinuclear complex **3** is a structural isomer of complex **2**. Its structure can be described as a distorted complex **2** which departs considerably from the C_2 symmetry. One of the zinc atoms, Zn(1) is coordinated to two sulfur and four nitrogen atoms in a distorted octahedron and Zn(2) is coordinated to two sulfur and two nitrogen atoms in a distorted tetrahedral geometry. From Table 7 it can be seen that most of the angles about Zn(1) and Zn(2) depart considerably from the ideal 90, 180 and 109.4°, respectively.

The two pyridine groups that serve as bridges between the two zinc atoms in **2** are much closer in **3** to Zn(1) with Zn–N(Py) distances of 2.46(1) and 2.366(9) Å. The Zn(2)...N(Py) separations, 2.737(9) and 2.909(9) Å, are considerably longer. The angles between the vector C(7)---N(4) which parallels the pyridine plane,

TABLE 6. Positional parameters and e.s.d.s for **3**

Atom	*x*	*y*	*z*
Zn(1)	0.2440(2)	0.2249(1)	0.2167(2)
Zn(2)	0.5944(2)	0.31179(9)	0.3454(2)
S(1)	0.2043(5)	0.0903(2)	0.1238(4)
S(2)	0.8069(4)	0.2629(3)	0.5543(4)
S(3)	0.5965(4)	0.4132(2)	0.1921(4)
S(4)	0.0108(4)	0.3010(3)	0.1763(4)
N(1)	0.137(2)	0.0604(8)	−0.149(1)
N(2)	0.178(1)	0.1930(7)	−0.096(1)
N(3)	0.212(1)	0.2523(6)	0.005(1)
N(4)	0.302(1)	0.3641(6)	0.2062(9)
N(5)	0.515(1)	0.3440(6)	0.489(1)
N(6)	0.599(1)	0.3136(6)	0.637(1)
N(7)	0.816(1)	0.2424(8)	0.807(1)
N(8)	0.569(1)	0.3793(7)	−0.066(1)
N(9)	0.558(1)	0.2673(7)	0.051(1)
N(10)	0.565(1)	0.2351(6)	0.178(1)
N(11)	0.487(1)	0.1621(6)	0.367(1)
N(12)	0.277(1)	0.2210(6)	0.431(1)
N(13)	0.177(1)	0.2624(8)	0.468(1)
N(14)	−0.038(1)	0.349(1)	0.393(2)
C(1)	0.173(2)	0.1204(9)	−0.048(2)
C(2)	0.209(1)	0.3271(8)	−0.041(1)
C(3)	0.171(2)	0.3495(9)	−0.198(2)
C(4)	0.231(1)	0.3908(7)	0.063(1)
C(5)	0.311(1)	0.4221(7)	0.304(1)
C(6)	0.250(1)	0.5069(8)	0.263(1)
C(7)	0.184(1)	0.5331(9)	0.116(1)
C(8)	0.178(1)	0.4751(8)	0.016(1)
C(9)	0.398(1)	0.3947(8)	0.456(1)
C(10)	0.349(2)	0.426(1)	0.565(2)
C(11)	0.730(1)	0.2750(8)	0.668(1)
C(12)	0.572(1)	0.3457(8)	0.053(1)
C(13)	0.566(1)	0.1555(8)	0.186(1)
C(14)	0.559(2)	0.0989(9)	0.068(2)
C(15)	0.575(1)	0.1221(8)	0.322(1)
C(16)	0.502(1)	0.1379(8)	0.497(1)
C(17)	0.612(2)	0.0729(9)	0.587(2)
C(18)	0.703(2)	0.0305(9)	0.535(2)
C(19)	0.685(2)	0.0552(9)	0.401(2)
C(20)	0.394(1)	0.1782(8)	0.536(1)
C(21)	0.415(2)	0.167(1)	0.690(2)
C(22)	0.057(2)	0.3026(9)	0.358(2)
Ol	0.059(2)	0.114(1)	0.537(2)
Ome	0.926(4)	0.107(2)	0.216(4)
Cme	0.857(5)	0.127(3)	0.078(5)

e.s.d.s in the least significant digits are shown in parentheses.

and the vectors N(4)---Zn(1) and N(4)---Zn(2) are 144.4 and 120.6°, respectively. The corresponding angles for the second pyridine ring are 153.6° [Zn(1)] and 113.6° [Zn(2)]. The very long Zn(2)---N(Py) distances and the relative positions of the pyridine rings in space rule out any kind of bonding to Zn(2). The Zn(1)...Zn(2) separation in **3**, 3.837(1) Å, is slightly shorter than in **2**.

Preparation and correlation of structures

The reaction, described by Mohan *et al.* [1], between Zn(II) and H_2daptsc, without the presence of a strong acid, yielded in our laboratory a dinuclear complex with deprotonated ligands. The production of a 2+ mononuclear species with a protonated H_2daptsc ligand, such as **1**, is achieved only when acid is added to the reaction mixture. The stability of the daptsc ligand towards hydrolysis of the C=S system, even in acidic aqueous solutions, is remarkable. The elemental analysis of **1**, the reasonable thermal parameters of all sulfur atoms and the Zn–S and C=S distances in **1**–**3** indicate that no hydrolysis which produced the C=O analog took place.

TABLE 7. Important bond lengths (Å) and angles (°) for **3**

Zn(1)–S(1)	2.405(4)	Zn(1)–N(12)	2.10(1)
Zn(1)–S(4)	2.436(4)	Zn(2)–S(2)	2.317(3)
Zn(1)–N(3)	2.12(1)	Zn(2)–S(3)	2.327(4)
Zn(1)–N(4)	2.46(1)	Zn(2)–N(5)	2.07(1)
Zn(1)–N(11)	2.266(9)	Zn(2)–N(10)	2.07(1)
S(1)–Zn(1)–S(4)	106.6(2)	N(3)–Zn(1)–N(12)	169.5(4)
S(1)–Zn(1)–N(3)	81.5(3)	N(4)–Zn(1)–N(11)	94.1(4)
S(1)–Zn(1)–N(4)	151.7(3)	N(4)–Zn(1)–N(12)	98.3(4)
S(1)–Zn(1)–N(11)	87.1(3)	N(11)–Zn(1)–N(12)	72.6(5)
S(1)–Zn(1)–N(12)	108.9(3)	S(2)–Zn(2)–S(3)	118.3(2)
S(4)–Zn(1)–N(3)	95.7(4)	S(2)–Zn(2)–N(5)	83.8(4)
S(4)–Zn(1)–N(4)	84.8(3)	S(2)–Zn(2)–N(10)	111.6(4)
S(4)–Zn(1)–N(11)	152.8(3)	S(3)–Zn(2)–N(5)	120.8(3)
S(4)–Zn(1)–N(12)	80.6(4)	S(3)–Zn(2)–N(10)	84.6(3)
N(3)–Zn(1)–N(4)	71.5(4)	N(5)–Zn(2)–N(10)	140.8(4)
N(3)–Zn(1)–N(11)	109.7(4)		

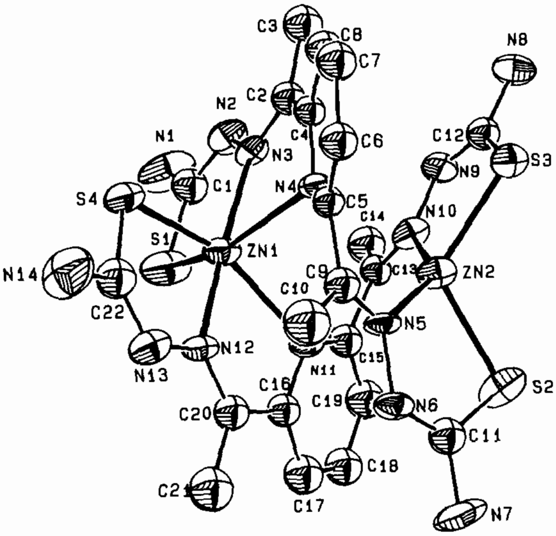

Fig. 3. The structure of $[Zn_2(daptsc)_2]$ in **3**.

The reported low conductivity and the disagreement between the formulation of the compound as '$[Zn(H_2daptsc)](OAc)_2$' and the found and calculated elemental analysis [1] led us to assume that the compound prepared and studied by Mohan *et al.* is in fact the dinuclear, uncharged $[Zn_2(daptsc)_2]$ complex. This may explain the differences observed in the far-IR spectrum and in the antitumor activity between the zinc and the other metal complexes [1].

The ability of related ligands to bind in various modes to metal atoms as a function of the H^+ ion concentration was previously demonstrated in several examples [4–6]. This work shows a new kind of coordination mode by the formation of structural isomers in which two metal atoms possess different coordination spheres as in **3**. It is reasonable to assume that the energy difference between the isomers in **2** and **3** is intrinsically small and that their structure is determined by the different packing forces in the crystals of **2** and **3**.

Supplementary material

Tables of structure factors, thermal parameters, non-essential bond distances and angles of **1–3** and positional parameters for hydrogen atoms in **2** (54 pages) are available from the authors.

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