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Interaction of Metal Ions with Pyrimidine Derivatives: X-ray Crystal Structure of Tetrakis(1-methylpyrimidine-2-thione)zinc(II) Perchlorate–Bisacetone

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Abstract

The structure of $[Zn(C_5H_6N_2S)_4](ClO_4)_2.2(CH_3)_2CO$, $C_{20}H_{24}Cl_2N_8O_8S_4Zn.C_6H_{12}O_2$, has been refined to $R = 0{\cdot}035$ for 1850 counter reflexions. Crystals are orthorhombic with $a = 46{\cdot}744$ (1), $b = 20{\cdot}347$ (1), $c = 8{\cdot}015$ (1) Å, space group $Fdd2$, $Z = 8$. The Zn atom lies on a twofold axis and is tetrahedrally coordinated by N atoms of four 1-methylpyrimidine-2-thione ligands. Independent Zn—N distances are 2·058 and 2·060 Å, and the N—Zn—N angles are in the range 107·3–113·3°. The complex cation has approximate $\bar{4}$ (S_4) point symmetry. Perchlorate ions and the acetone molecules are not coordinated, and there is no hydrogen bonding. Corresponding Mn and Co derivatives are isomorphous with the Zn complex.

Introduction

There is considerable interest in the interaction of metal ions with nucleic acid constituents (*e.g.* Hodgson, 1977; Marzilli, 1977; Hunt, Griffith & Amma, 1976). As part of the studies on the formation and structure of metal complexes of S-containing derivatives, the title compound was prepared by Goodgame & Leach (1978) together with the analogous Co and Mn complexes, and X-ray powder photographs showed these to be isomorphous. A single-crystal X-ray study of the Zn complex (which provided the most suitable crystals) was undertaken to determine whether these were tetrahedral N-bonded systems, or whether the S atoms were also involved in bonding to the metal as in tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III) (Cartwright, Goodgame, Jeeves, Langguth & Skapski, 1977; Cartwright, Langguth & Skapski, 1979).

Experimental

Tetrakis(1-methylpyrimidine-2-thione)zinc(II) perchlorate was obtained as yellow needles (after *ca* 4 d) by the reaction in acetone of zinc perchlorate hexahydrate and 1-methylpyrimidine-2-thione (in a 1:4 molar ratio). Chemical analysis indicated that the crystals contained acetone of solvation in a Zn:acetone ratio of 1:2 (Goodgame & Leach, 1978).

Photographs showed the crystals to be orthorhombic with systematic conditions hkl: $h + k, k + l = 2n$, $h0l$: $h + l = 4n$, and $0kl$: $k + l = 4n$, which uniquely determine the space group as $Fdd2$. Measurements (at 284 K) of high-angle α_1 and α_2 reflexions on a diffractometer gave $a = 46{\cdot}744$ (1), $b = 20{\cdot}347$ (1), $c = 8{\cdot}015$ (1) Å, $U = 7623{\cdot}1$ Å^3, $D_c = 1{\cdot}54$ Mg m^{-3} for $Z = 8$ formula units of $C_{26}H_{36}Cl_2N_8O_{10}S_4Zn$, $M_r = 885{\cdot}2$, $F(000) = 3648$, and $\mu(\text{Cu } K\alpha) = 4{\cdot}80$ mm^{-1}.

Intensities were measured on a Siemens off-line automatic four-circle diffractometer. A crystal 0·41 × 0·10 × 0·03 mm was mounted with **c** parallel to the φ axis of the diffractometer. Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) at a take-off angle of 3·0°, a Ni β-filter and a Na(Tl)I scintillation counter were used. The θ–2θ scan technique was employed with a five-value measuring procedure (Allen, Rogers & Troughton, 1971). 1856 independent reflexions were measured (to $\theta = 71°$), of which 134 were judged to be unobserved with $I < 2{\cdot}58\sigma(I)$. The 28,8,0 reflexion was monitored as a reference every 50 reflexions, and its net count did not alter significantly. The intensities were scaled with the reference reflexion, and Lorentz and polarization corrections were applied.

Solution and refinement of the structure

A sharpened Patterson synthesis showed the Zn atom to be on a twofold axis, and its position was fixed at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$. The positions of the two independent S atoms were also obtained from the Patterson synthesis, and least-squares refinement gave $R = 0{\cdot}365$. All the remaining non-hydrogen atoms were located from a difference synthesis, and refinement with Zn, Cl and S atoms anisotropic and the rest isotropic reduced R to 0·092. Fully anisotropic refinement gave $R = 0{\cdot}058$. All 18 H atoms were located from a difference synthesis, and were included as a fixed-atom contribution with the isotropic temperature factors of their parent C atoms. Anomalous-dispersion corrections were applied to Zn, S and Cl, and a weighting scheme was introduced to give $R = 0{\cdot}049$.

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Table 1. *Fractional coordinates with e.s.d.'s in parentheses*

The 1-methylpyrimidine-2-thione ligands are numbered (*mn*), where *m* is the ring number and *n* the atom number.

	x	*y*	*z*
(*a*) Complex cation			
Zn(1)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
N(11)	0·19478 (8)	0·3410 (2)	0·8562 (5)
C(11)	0·19573 (15)	0·3971 (3)	0·9676 (8)
C(12)	0·21868 (9)	0·3247 (2)	0·7625 (6)
S(12)	0·24962 (2)	0·36462 (6)	0·7832 (2)
N(13)	0·21581 (7)	0·2742 (2)	0·6497 (5)
C(14)	0·19179 (10)	0·2397 (2)	0·6416 (6)
C(15)	0·16791 (10)	0·2543 (3)	0·7377 (7)
C(16)	0·17020 (10)	0·3059 (3)	0·8438 (7)
N(21)	0·28919 (8)	0·3836 (2)	0·1631 (5)
C(21)	0·31338 (13)	0·3816 (3)	0·0456 (8)
C(22)	0·28192 (9)	0·3269 (2)	0·2473 (6)
S(22)	0·29883 (3)	0·25650 (6)	0·2196 (2)
N(23)	0·25965 (7)	0·3316 (2)	0·3587 (5)
C(24)	0·24475 (11)	0·3870 (2)	0·3746 (7)
C(25)	0·25156 (13)	0·4435 (2)	0·2850 (8)
C(26)	0·27418 (13)	0·4403 (2)	0·1825 (7)
(*b*) Perchlorate anion			
Cl(1)	0·16313 (3)	0·05831 (6)	0·5983 (2)
O(1)	0·14772 (14)	0·1007 (3)	0·7057 (10)
O(2)	0·14701 (12)	0·0026 (4)	0·5623 (17)
O(3)	0·18878 (16)	0·0384 (6)	0·6735 (14)
O(4)	0·16692 (37)	0·0844 (7)	0·4469 (13)
(*c*) Acetone molecule			
O(31)	0·06552 (9)	0·1846 (2)	0·2970 (7)
C(31)	0·09052 (12)	0·1777 (3)	0·2616 (8)
C(32)	0·09990 (17)	0·1281 (4)	0·1376 (11)
C(33)	0·11315 (18)	0·2161 (5)	0·3420 (15)

Table 2. *Fractional coordinates of the hydrogen atoms*

The H atom positions are unrefined and the atoms are numbered such that the first two digits correspond to the number of the parent C atom.

	x	*y*	*z*
H(111)	0·177	0·404	1·024
H(112)	0·211	0·390	1·053
H(113)	0·201	0·439	0·902
H(14)	0·191	0·201	0·562
H(15)	0·149	0·229	0·730
H(16)	0·191	0·318	0·788
H(211)	0·316	0·427	−0·006
H(212)	0·331	0·370	0·105
H(213)	0·309	0·350	−0·046
H(24)	0·227	0·389	0·453
H(25)	0·245	0·403	0·343
H(26)	0·285	0·476	0·103
H(321)	0·082	0·104	0·093
H(322)	0·110	0·149	0·040
H(323)	0·113	0·095	0·189
H(331)	0·106	0·249	0·416
H(332)	0·128	0·186	0·393
H(333)	0·125	0·241	0·244

The intensities were now corrected for absorption (Busing & Levy, 1957), with a 12 × 12 × 12 grid and with crystal path lengths determined by the vector-analysis procedure of Coppens, Leiserowitz & Rabinovich (1965). Refinement as previously reduced R to 0·038. Six strong low-angle reflexions judged to be suffering from extinction were excluded from refinement and the weighting scheme was adjusted to give a final R of 0·035. The final difference synthesis was featureless, with a maximum electron density of 0·2 e Å^{-3}.

In the later stages of refinement the weighting scheme used was that suggested by Hughes (1941), where $w = 1$ for $F < F^*$, $w^{1/2} = F^*/F$ for $F \geq F^*$, with $F^* = 60$ as the optimum value. Scattering factors were from Doyle & Turner (1968) except for H (Stewart, Davidson & Simpson, 1965); the anomalous-dispersion corrections for Zn, Cl, and S were from Cromer & Liberman (1970). The atomic coordinates are listed in Table 1, and the unrefined coordinates of the H atoms in Table 2.†

An updated version of April 1974 of the crystal structure calculations system XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the solution and refinement of the structure. The calculations were carried out on the University of London CDC 7600 computer, with *CRYLSQ* used for refinement. Steering-tape generation, data processing and structural illustrations were performed with the Imperial College CDC 6500 computer.

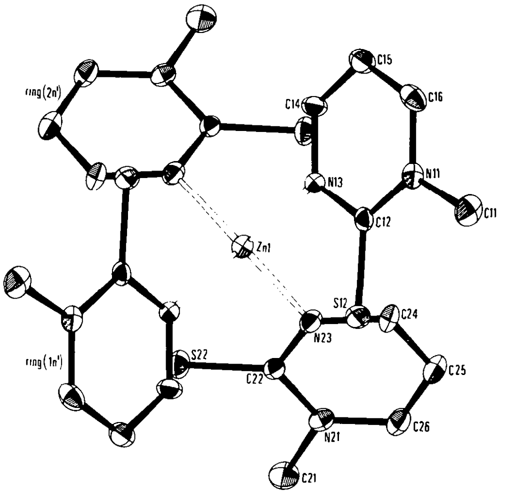

Fig. 1. A view down the diad axis of the $[Zn(1\text{-methylpyrimidine-2-thione})_4]^{2+}$ cation, showing its approximate $\bar{4}$ point symmetry. Thermal-vibration ellipsoids are scaled to enclose 20% probability.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33879 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Description of the structure and discussion

The crystal structure consists of three discrete components: tetrakis(1-methylpyrimidine-2-thione)zinc(II) cations, perchlorate anions, and acetone molecules. Only the first of these are of interest in this structure, and Figs. 1 and 2 show two views of the cation. Fig. 1 also shows the thermal-vibration ellipsoids of the non-hydrogen atoms (Johnson, 1965). The more important interatomic distances and bond angles are given in Table 3.

The Zn atom lies on a crystallographic twofold axis, although the cation has, in fact, approximate $\bar{4}$ (S_4) point symmetry. Four N(*m*3) atoms of 1-methylpyrimidine-2-thione ligands coordinate tetrahedrally to the Zn atom, with the six N—Zn—N angles in the range 107·3–113·3°. The two crystallographically independent Zn—N lengths are 2·058 and 2·060 Å, and are similar to those found in other tetrahedral Zn complexes, *e.g.* 2·040 and 2·068 Å in *catena*-dichloro-*μ*-(9-methyladenine)-zinc(II) (McCall & Taylor, 1976) or 2·05 Å in trichloro(9-methyladenine)zinc(II) (McCall & Taylor, 1975), although there are examples of Zn—N distances < 2 Å, such as 1·999 Å in the outer complex [Zn(imidazole)$_4$](ClO$_4$)$_2$ (Bear, Duggan & Freeman, 1975).

Unlike in tris(4,6-dimethylpyrimidine-2-thionato)-cobalt(III) (Cartwright *et al.*, 1977, 1979) where both N and S are donors, the S atoms in the title complex are not coordinated to the metal, with Zn···S separations of 3·206 and 3·255 Å. The relatively undistorted tetrahedral angles about Zn, and the near equality of the Zn—N(*m*3)—C(*m*2) and Zn—N(*m*3)—C(*m*4) angles, suggest that any Zn—S interactions are of little importance in this cation. A mean C—S length of 1·659 Å is similar to those found in compounds where the S atom is not coordinated to a metal, such as 1·673 Å in sodium 5,6-dihydro-2-thiouracil-6-sulphonate monohydrate (Jain, Lee, Martes & Pitman, 1978) and 1·659 Å in 2-thiocytosine picrate (De Lucas, Hearn & Brigg, 1977). In compounds where the S atom binds to a metal the C—S bond has less double-bond character and is significantly longer, *e.g.* a mean of 1·729 Å in tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III) (Cartwright *et al.*, 1977, 1979) or 1·740 Å in Ru(PPh$_3$)$_2$-(pyS)$_2$ (Fletcher & Skapski, 1972).

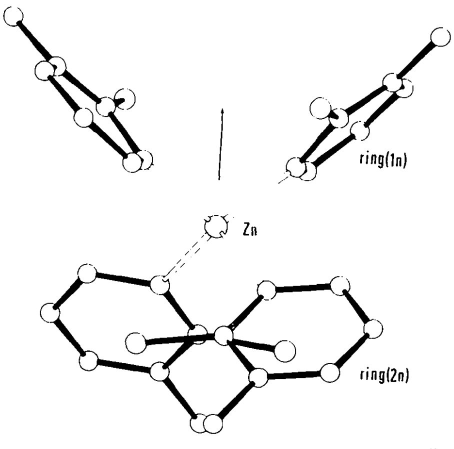

Fig. 2. The complex cation viewed normal to the crystallographic diad axis.

There are no significant differences between the two independent rings, and the bond lengths and angles within the pyrimidine rings are unexceptional.

Results of least-squares calculations (Table 4) show that there is probably a slight flexing of the pyrimidine rings. The pattern of deviations is very similar for both rings, and the maximum deviation in each case is 0·024 Å for C(12) and C(22) respectively. The exocyclic

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

The superscript (I) refers to atoms in the following position: $\frac{1}{2}-x, \frac{1}{2}-y, z$.

(*a*) Complex cation			
Zn(1)—N(13)	2·058 (4)	Zn(1)—N(23)	2·060 (4)
Mean Zn—N	2·059		
Zn(1)···S(12)	3·255 (1)	Zn(1)···S(22)	3·206 (1)
N(13)—Zn(1)—N(23)	107·3 (1)	N(13)—Zn(1)—N(13$^{\rm I}$)	108·7 (1)
N(13)—Zn(1)—N(23$^{\rm I}$)	110·1 (1)	N(23)—Zn(1)—N(23$^{\rm I}$)	113·3 (2)
N(11)—C(12)	1·386 (6)	N(21)—C(22)	1·379 (6)
C(12)—N(13)	1·376 (6)	C(22)—N(23)	1·375 (6)
N(13)—C(14)	1·326 (6)	N(23)—C(24)	1·331 (6)
C(14)—C(15)	1·389 (7)	C(24)—C(25)	1·392 (7)
C(15)—C(16)	1·355 (8)	C(25)—C(26)	1·341 (9)
C(16)—N(11)	1·357 (6)	C(26)—N(21)	1·360 (6)
N(11)—C(11)	1·450 (7)	N(21)—C(21)	1·472 (7)
C(12)—S(12)	1·667 (5)	C(22)—S(22)	1·651 (4)
Zn(1)—N(13)—C(12)	119·1 (3)	Zn(1)—N(23)—C(22)	117·8 (3)
Zn(1)—N(13)—C(14)	120·2 (3)	Zn(1)—N(23)—C(24)	121·0 (3)
C(12)—N(13)—C(14)	120·7 (4)	C(22)—N(23)—C(24)	121·2 (4)
N(13)—C(14)—C(15)	122·7 (5)	N(23)—C(24)—C(25)	122·0 (5)
C(14)—C(15)—C(16)	116·8 (5)	C(24)—C(25)—C(26)	117·2 (5)
C(15)—C(16)—N(11)	121·4 (5)	C(25)—C(26)—N(21)	121·2 (5)
C(16)—N(11)—C(12)	121·1 (4)	C(26)—N(21)—C(22)	121·8 (4)
C(16)—N(11)—C(11)	119·0 (5)	C(26)—N(21)—C(21)	119·5 (5)
C(12)—N(11)—C(11)	119·8 (4)	C(22)—N(21)—C(21)	118·7 (4)
N(11)—C(12)—N(13)	117·2 (4)	N(21)—C(22)—N(23)	116·5 (4)
N(11)—C(12)—S(12)	121·9 (3)	N(21)—C(22)—S(22)	122·8 (3)
N(13)—C(12)—S(12)	120·9 (3)	N(23)—C(22)—S(22)	120·7 (3)
(*b*) Perchlorate anion			
Cl(1)—O(1)	1·416 (7)	Cl(1)—O(2)	1·391 (8)
Cl(1)—O(3)	1·402 (9)	Cl(1)—O(4)	1·336 (11)
O(1)—Cl(1)—O(2)	110·3 (5)	O(2)—Cl(1)—O(3)	108·5 (6)
O(1)—Cl(1)—O(3)	110·5 (6)	O(2)—Cl(1)—O(4)	102·0 (8)
O(1)—Cl(1)—O(4)	112·2 (7)	O(3)—Cl(1)—O(4)	113·1 (8)
(*c*) Acetone molecule			
O(31)—C(31)	1·211 (7)	C(31)—C(32)	1·483 (10)
		C(31)—C(33)	1·465 (11)
O(13)—C(31)—C(32)	121·5 (6)	C(32)—C(31)—C(33)	116·4 (6)
O(31)—C(31)—C(33)	122·1 (6)		

atoms are in general slightly, but significantly, out of the ring planes, by as much as 0·116 Å in the case of Zn(1) and ring (2*n*). Each ring is approximately normal to its symmetry-related equivalent. Thus ring (1*n*) makes an angle of 89·2° with ring $(1n^{\mathrm{I}})$, while for rings (2*n*) and $(2n^{\mathrm{I}})$ the angle is 85·0°. The inclination between the two independent rings (1*n*) and (2*n*) is 56·6° and similar to that (60·0°) between (2*n*) and $(1n^{\mathrm{I}})$, where the superscript I has the same meaning as in Table 3.

Fig. 3 shows a stereoscopic view (Johnson, 1965) of the packing. As the non-donor N atoms in the ligands are methylated there is no opportunity to form hydrogen bonds between the cation and perchlorate anions or acetone. Thus the acetone molecules simply fill gaps in the structure and are held by van der Waals forces. The tetrahedral perchlorate anions show the commonly observed tendency to slight disorder/high thermal vibration.

Table 4. *Planarity of the* 1-*methylpyrimidine*-2-*thione ligands*

Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space, and distances of atoms from the least-squares planes are in Å. Atoms not defining planes are marked by asterisks.

Plane 1: $15{\cdot}11x - 12{\cdot}69y + 5{\cdot}71z = 3{\cdot}51$

N(11)	−0·010	C(12)	0·024	N(13)	−0·022
C(14)	0·007	C(15)	0·008	C(16)	−0·006
Zn(1)*	−0·053	S(12)*	0·103	C(11)*	−0·072

Plane 2: $28{\cdot}77x + 5{\cdot}66y + 5{\cdot}91z = 11{\cdot}45$

N(21)	0·008	C(22)	−0·024	N(23)	0·020
C(24)	−0·001	C(25)	−0·015	C(26)	0·012
Zn(1)*	0·116	S(22)*	−0·100	C(21)*	−0·001

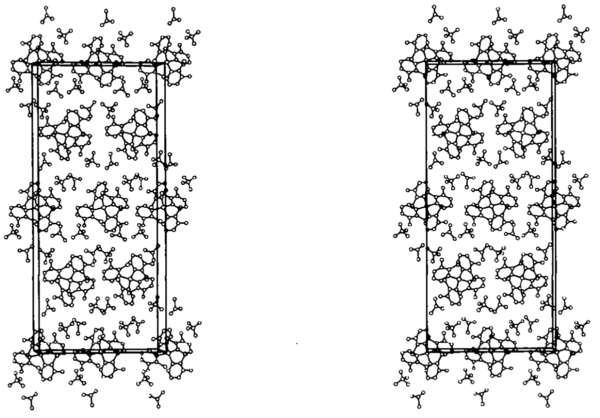

Fig. 3. A stereoscopic view of the packing. The *a* axis is vertical, *b* is to the left and *c* is out of the paper from an origin in the bottom right-hand corner.

This structure determination has shown that the title complex is a tetrahedral N_4 system, and hence the analogous Co and Mn derivatives will have very similar structures. There seems to be no structural evidence for the existence of tetrahedral N_4 systems for Mn, and only one example (Bear, Duggan & Freeman, 1975) for outer-complex Zn compounds.

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