Fig. 2. Contents of the unit cell.

structure because the normal equations are nearly singular.

The structure is built up of [(C$_5$H$_5$)CoCB$_{10}$H$_{11}$]$^-$ anions and [N(CH$_3$)$_4$]$^+$ cations. The anion and cation exhibit crystallographic symmetry m and 2 respectively. The anion can be described as an icosahedron with one Co, one C, and ten B atoms at its vertices. Within one anion, atom pairs C(2) and C(5), C(3) and C(4), BC(1) and BC(7), B(4) and B(8), B(5) and B(12), and B(6) and B(11) are related by the mirror plane. Co(2), C(1), B(3), B(9) and B(10) are on the mirror plane. Fig. 1 shows the anion viewed down the vector [150] with the numbering of the borane skeleton following the IUPAC system (Adams, 1972). Bond

lengths and angles are given in Table 2. The Co atom is coordinated to the pentagonal face containing BC(1), B(3), BC(7), B(11) and B(6). The mean value for Co—B and Co—BC distances is 2·054 Å which is close to the average in cobaltamonocarbaborate [(C$_5$H$_5$)Co$_2$CB$_9$H$_{10}$]$^-$ (Šubrtová, Línek, Novák, Petříček & Ječný, 1977). The mean Co—C = 2·050 Å agrees with the average found for mixed cyclopentadienylcobaltacarborane complexes. The mean values for the cage distances are B—B = 1·773 and BC—B = 1·739 Å, close to the average found in the same monocarbaborane ligand (Carroll, Green, Stone & Welch, 1975). The mean value of N—C in the [N(CH$_3$)$_4$]$^+$ cation is 1·484 Å. For terminal H atoms the average B—H = 1·10 and C—H = 0·94 Å. The packing of the molecules within the unit cell is shown in Fig. 2.

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Structure of Tetrakis[1-methyl-2(3H)-imidazolinethione]zinc(II) Nitrate Monohydrate

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Abstract. [Zn(C$_4$H$_6$N$_2$S)$_4$](NO$_3$)$_2$.H$_2$O, C$_{16}$H$_{24}$N$_8$S$_4$Zn^{2+}.2NO$_3^-$.H$_2$O, M_r = 664·09, orthorhombic, Pbca, a = 20·756 (8), b = 12·410 (5), c = 22·059 (8) Å, U = 5682·0 Å^3, Mo $K\alpha$, λ = 0·71069 Å, Z = 8, D_m = 1·53 (2), D_c = 1·55 Mg m^{-3}, μ = 1·14 mm^{-1}, $F(000)$ = 2736; final R = 0·046 for 2941 counter reflections. All four ligands are S-bonded to the metal (mean Zn—S 2·339 Å) to give a distorted tetrahedral ZnS$_4$ unit with S—Zn—S angles varying from 103·3 (1) to 121·5 (1)°. The complex cations are linked together by H bonding involving the amido H atoms of the ligand and the nitrate O atoms.

Introduction. Reaction of 1-methyl-2(3H)-imidazolinethione (mimt) with hydrated Zn^{II} nitrate in anhydrous ethanol gives a colourless crystalline material analysing as [Zn(mimt)$_4$(NO$_3$)$_2$].H$_2$O. The presence of the water molecule has been demonstrated by means of thermal

$[Zn(C_4H_6N_2S)_4](NO_3)_2.H_2O$

analysis (Creighton & Raper, 1979). Although mimt is potentially ambidentate, infrared and NMR data indicate it to be monodentate in the present complex, with Zn—S rather than Zn—N contacts. While conductivity studies show the complex to be a non-electrolyte in nitrobenzene, infrared spectroscopy indicates that the nitrate ions are not coordinated to Zn and to establish the coordination geometry of the complex the present X-ray study has been undertaken.

A crystal $0.32 \times 0.40 \times 0.60$ mm was mounted with b coincident with the rotation (ω) axis of a Stoe STADI-2 two-circle diffractometer. With monochromated Mo $K\alpha$ radiation and the background–ω-scan–background technique, 4621 unique reflections were measured of which 2941 had $I > 3\sigma(I)$ and were considered observed. [The net intensity $I = T - B$, where T = scan count, B = mean background count over the scan width; $\sigma(I) = (T + Bc/2t)^{1/2}$, where c = scan time, t = time for background measurements at each end of the scan.] Corrections for Lorentz, polarization and absorption effects were made. The Zn atom was located from the Patterson function and the remaining atoms from successive electron-density maps. Methyl H atoms were included in positions calculated

from the geometry of the molecule (C—H = 1.08 Å) and the positional parameters of the H atoms attached to the heterocyclic atoms were not refined. Common isotropic temperature factors were applied to the methyl, amido, and ethylenic H atoms and refined to final values of $U = 0.177\,(24)$, $0.086\,(24)$ and $0.104\,(16)$ Å^2 respectively. Scattering factors were calculated from an analytical approximation (*International Tables for X-ray Crystallography*, 1974) and the weighting scheme was $w = 1.4035/[\sigma^2(F_o) + 0.0007(F_o)^2]$. Full-matrix refinement gave $R = 0.046$ and $R' = 0.048$. The O atom of the water molecule is poorly defined with a high isotropic temperature factor [final $U = 0.367\,(10)$ Å^2] and the associated H atoms could not be satisfactorily located. The final difference map showed no peaks >0.29 e Å^{-3}. The final atomic parameters are given in Table 1.*

Table 1. *Final fractional coordinates* ($\times 10^4$, for Zn $\times 10^5$)

E.s.d.'s for the non-hydrogen atoms are in parentheses.

	x	y	z		x	y	z
Zn	37902 (3)	51789 (5)	14149 (3)	C(13)	4893 (3)	3018 (7)	1965 (4)
S(1)	4294 (1)	4754 (1)	499 (1)	C(23)	4236 (3)	4174 (6)	2654 (3)
S(2)	3136 (1)	3683 (1)	1617 (1)	C(43)	3843 (4)	2899 (8)	3252 (4)
S(3)	4381 (1)	5389 (1)	2316 (1)	C(53)	4230 (3)	2423 (7)	2867 (4)
S(4)	3321 (1)	6846 (1)	1221 (1)	C(14)	2435 (3)	6147 (5)	2355 (3)
O(1)	4323 (10)	4679 (19)	4600 (9)	C(24)	3260 (2)	7399 (5)	1926 (2)
O(11)	450 (2)	4273 (5)	1408 (3)	C(44)	3360 (3)	8522 (6)	2701 (3)
O(21)	423 (4)	5701 (8)	885 (5)	C(54)	2941 (3)	7771 (6)	2862 (3)
O(31)	1060 (3)	5588 (6)	1593 (3)	H(111)	5233	7813	655
O(12)	2458 (3)	5922 (6)	−1009 (2)	H(112)	5424	6429	638
O(22)	3059 (3)	4554 (5)	−1084 (2)	H(113)	4809	6902	1121
O(32)	2040 (3)	4387 (5)	−1255 (2)	H(121)	2066	4424	16
N(1)	642 (3)	5188 (6)	1298 (3)	H(122)	2568	5075	547
N(2)	2516 (4)	4961 (7)	−1115 (2)	H(123)	1938	4234	798
N(11)	4565 (2)	6846 (5)	201 (2)	H(131)	5003	2169	1941
N(31)	3853 (2)	6122 (6)	−375 (2)	H(132)	5334	3471	2018
N(12)	2734 (2)	3433 (4)	444 (2)	H(133)	4653	3264	1554
N(32)	3420 (2)	2236 (4)	725 (2)	H(141)	2190	6059	2784
N(13)	4469 (2)	3220 (5)	2487 (2)	H(142)	2703	5422	2258
N(33)	3846 (3)	3992 (5)	3133 (2)	H(143)	2085	6285	2001
N(14)	2877 (2)	7063 (4)	2386 (2)	H(31)	3463	5655	−524
N(34)	3559 (2)	8287 (4)	2121 (2)	H(41)	3672	7719	−807
C(11)	5039 (3)	7008 (7)	686 (3)	H(51)	4715	8218	−177
C(21)	4235 (2)	5944 (5)	110 (2)	H(32)	3751	1818	1005
C(41)	3937 (5)	7134 (9)	−582 (4)	H(42)	3413	1291	−79
C(51)	4377 (4)	7615 (7)	−227 (4)	H(52)	2604	2954	−456
C(12)	2298 (3)	4350 (6)	452 (3)	H(33)	3627	4655	3319
C(22)	3097 (2)	3111 (5)	914 (2)	H(43)	3593	2718	3660
C(42)	3257 (4)	1999 (6)	140 (3)	H(53)	4345	1621	2754
C(52)	2826 (3)	2738 (6)	−32 (3)	H(34)	3902	8577	1859
				H(44)	3478	9275	2870
				H(54)	2728	7575	3190

Discussion. Bond lengths and angles are given in Table 2 and mean planes in Table 3. The mimt ligands are all S-bonded to the metal to give a distorted tetrahedral ZnS$_4$ unit (Fig. 1) in which the S–Zn–S angles vary from 103·3 (1)–121·5 (1)°. The Zn–S distances [2·327 (2)–2·349 (2) Å] are comparable to the sum of the Zn and S tetrahedral covalent radii, 2·35 Å (Pauling, 1960), and to the values found in other tetrahedral Zn compounds [e.g. 2·312 (6)–2·429 (6) Å, bis-(dimethyldithiocarbamato)zinc(II) (Klug, 1966); 2·309 (4)–2·332 (4) Å, tris(thiourea)zinc(II) sulphate (Andreetti, Cavalca & Musatti, 1968); 2·316 (3),

2·327 (2) Å, bis(trithioperoxycumato)zinc(II) (Fackler, Fetchin & Fries, 1972); 2·329 (3)–2·363 (3) Å, tetra-phenylphosphonium tetrakis(thiophenolate)zincate(II) (Swenson, Baenziger & Coucouvanis, 1978)]. The ZnS$_4$ geometry is similar to that reported for tetrakis-(thiourea)zinc(II) nitrate (Vega, López-Castro & Már-quez, 1978), where the Zn–S distances are 2·324 (3) and 2·361 (3) Å and the S–Zn–S angles range from 100·0 (1) to 121·5 (1)°.

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Symmetry code: superscript: none x,y,z; (i) $0·5 - x$, $0·5 + y$, z; (ii) $0·5 - x$, $-0·5 + y$, z; (iii) $0·5 - x$, $1·0 - y$, $0·5 + z$; (iv) $-0·5 + x$, y, $0·5 - z$; (v) $0·5 - x$, $1·0 - y$, $-0·5 + z$

The coordination sphere

Zn–S(1)	2·335 (2)	Zn–S(3)	2·349 (2)
Zn–S(2)	2·343 (2)	Zn–S(4)	2·327 (2)
S(1)–Zn–S(2)	104·2 (1)	Zn–S(1)–C(21)	101·9 (2)
S(1)–Zn–S(3)	121·5 (1)	Zn–S(2)–C(22)	100·6 (2)
S(1)–Zn–S(4)	103·3 (1)	Zn–S(3)–C(23)	100·3 (2)
S(2)–Zn–S(3)	103·3 (1)	Zn–S(4)–C(24)	102·8 (2)
S(2)–Zn–S(4)	119·8 (1)		
S(3)–Zn–S(4)	106·0 (1)		

Geometry of the four ligand molecules ($X = 1$–4)

	$X = 1$	$X = 2$	$X = 3$	$X = 4$
S(X)–C(2X)	1·711 (6)	1·707 (5)	1·710 (7)	1·703 (5)
C(2X)–N(1X)	1·326 (8)	1·342 (7)	1·331 (9)	1·356 (6)
C(2X)–N(3X)	1·350 (7)	1·343 (8)	1·351 (9)	1·336 (8)
N(1X)–C(1X)	1·468 (8)	1·453 (8)	1·470 (10)	1·462 (8)
N(1X)–C(5X)	1·397 (10)	1·373 (8)	1·388 (10)	1·376 (8)
N(3X)–C(4X)	1·348 (13)	1·365 (9)	1·381 (12)	1·374 (8)
C(4X)–C(5X)	1·342 (13)	1·336 (11)	1·311 (11)	1·323 (9)

N(3)–H(3)	1·030*	C(4)–H(4)	1·047*	C(5)–H(5)	1·011*

	$X = 1$	$X = 2$	$X = 3$	$X = 4$
S(X)–C(2X)–N(1X)	128·0 (4)	127·1 (4)	126·9 (5)	127·1 (4)
S(X)–C(2X)–N(3X)	125·5 (5)	126·5 (4)	126·5 (5)	126·4 (4)
N(1X)–C(2X)–N(3X)	106·5 (5)	106·3 (5)	106·6 (6)	106·5 (4)
C(1X)–N(1X)–C(2X)	124·8 (6)	125·0 (5)	125·8 (6)	124·9 (4)
C(1X)–N(1X)–C(5X)	125·8 (6)	126·0 (5)	124·4 (7)	126·4 (5)
C(2X)–N(1X)–C(5X)	109·3 (5)	108·9 (5)	109·7 (6)	108·6 (5)
C(2X)–N(3X)–C(4X)	110·2 (6)	110·1 (5)	108·4 (6)	109·7 (5)
N(3X)–C(4X)–C(5X)	107·7 (8)	106·6 (6)	108·5 (7)	107·3 (6)
N(1X)–C(5X)–C(4X)	106·2 (6)	107·9 (6)	106·8 (7)	107·9 (5)

C(2)–N(3)–H(3)	120·8*	C(5)–C(4)–H(4)	128·1*
C(4)–N(3)–H(3)	129·1*	N(1)–C(5)–H(5)	112·7*
N(3)–C(4)–H(4)	122·4*	C(4)–C(5)–H(5)	139·2*

Nitrate groups

N(1)–O(11)	1·227 (10)	O(11)–N(1)–O(21)	121·2 (8)
N(1)–O(21)	1·201 (12)	O(11)–N(1)–O(31)	120·8 (7)
N(1)–O(31)	1·194 (9)	O(21)–N(1)–O(31)	118·0 (9)
N(2)–O(12)	1·221 (11)	O(12)–N(2)–O(22)	118·5 (8)
N(2)–O(22)	1·237 (10)	O(12)–N(2)–O(32)	121·7 (8)
N(2)–O(32)	1·255 (10)	O(22)–N(2)–O(32)	119·8 (8)

Hydrogen bonding

O(11^i)···H(34)	1·88	O(32^{iii})···H(33)	2·05
O(21^{ii})···H(32)	2·22	O(1^{iv})···O(21)	2·82
O(31^{ii})···H(32)	2·04	O(1^v)···O(21)	2·92
O(22)···H(31)	2·02		

* Average value.

Table 3. *Equations of the least-squares planes referred to orthogonal axes with distances (Å) of relevant atoms from the planes in square brackets*

Plane A: Zn, S(1), C(21)
$$-0·8782X - 0·2926Y - 0·3783Z + 9·9698 = 0·0$$

Plane B: Zn, S(2), C(22)
$$-0·8128X + 0·5446Y - 0·2069Z + 3·5389 = 0·0$$

Plane C: Zn, S(3), C(23)
$$0·8077X - 0·3829Y - 0·4483Z - 2·4936 = 0·0$$

Plane D: Zn, S(4), C(24)
$$0·9080X + 0·4055Y - 0·1050Z - 9·4214 = 0·0$$

Plane E: ligand 1
$$0·7245X - 0·3143Y - 0·6134Z - 3·9179 = 0·0$$
[S(1), 0·010 (2); C(21), −0·017 (5); N(11), 0·005 (5); N(31), −0·004 (5); C(11), −0·002 (7); C(41), 0·007 (10); C(51), 0·001 (9)]

Plane F: ligand 2
$$0·7459X + 0·5844Y - 0·3195Z - 6·3990 = 0·0$$
[S(2), −0·013 (2); C(22), 0·008 (5); N(12), 0·025 (5); N(32), 0·007 (5); C(12), −0·005 (7); C(42), −0·005 (8); C(52), −0·016 (7)]

Plane G: ligand 3
$$-0·7838X - 0·1282Y - 0·6076Z + 11·0948 = 0·0$$
[S(3), 0·006 (2); C(23), −0·018 (6); N(13), −0·021 (4); N(33), 0·004 (6); C(13), 0·021 (7); C(43), 0·023 (9); C(53), −0·015 (7)]

Plane H: ligand 4
$$-0·7408X + 0·5748Y - 0·3477Z + 1·1822 = 0·0$$
[S(4), 0·023 (2); C(24), −0·030 (5); N(14), −0·034 (5); N(34), −0·006 (5); C(14), 0·016 (6); C(44), 0·023 (7); C(54), 0·008 (7)]

Plane I: NO$_3^-$ group
$$0·6889X - 0·3801Y - 0·6173Z + 3·2911 = 0·0$$
[N(1), −0·006 (7); O(11), 0·002 (6); O(21), 0·002 (10); O(31), 0·002 (7)]

Plane J: NO$_3^-$ group
$$0·1522X + 0·2060Y - 0·9666Z - 4·4419 = 0·0$$
[N(2), −0·001 (5); O(12), 0·000 (5); O(22), 0·000 (5); O(32), 0·000 (5)]

Angles between planes (°); e.s.d.'s 1·2–1·9°

Plane A/Plane E	71·8	Plane E/Plane F	56·5
Plane B/Plane F	77·2	Plane E/Plane G	98·9
Plane C/Plane G	71·8	Plane E/Plane H	120·3
Plane D/Plane H	66·2	Plane F/Plane G	117·7
		Plane F/Plane H	96·1
		Plane G/Plane H	44·1

$[Zn(C_4H_6N_2S)_4](NO_3)_2 . H_2O$
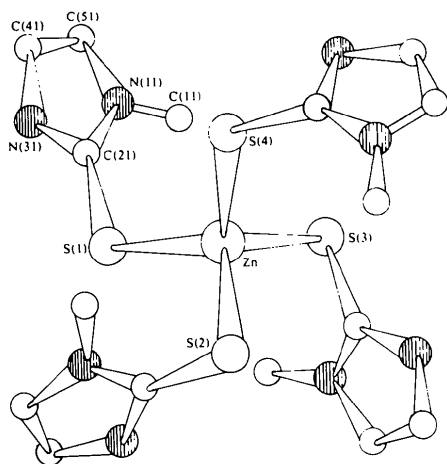
Fig. 1. The structure and atom-numbering scheme of the complex cation.

Fig. 2. Projection of the unit cell along **b**. The NO_3^- groups containing N(2) overlap in projection and are distinguished by the use of different shading for the N—O bonds. H bonding is represented by dashed lines.

The geometry of all four ligands is essentially the same, with only bond distances and angles involving H atoms varying significantly. The average bond distances and angles within the ligand are almost identical to those found in [Co(mimt)₄](ClO₄)₂ (Raper & Nowell, 1979), the C—S distance being relatively long and the C—N distances involving ethylenic C atoms being longer than those within the thioamido moiety. In both the Zn and Co complexes the C(4)—N(3) distances (Zn, mean 1·367; Co, 1·358 Å) are shorter than the C(5)—N(1) values (Zn, mean 1·384; Co, 1·387 Å) which may reflect the involvement of the N(3)—H atoms in H bonding and a subsequent increase in electron density at the associated N(3) atoms.

The ligands are essentially planar, the largest deviation from the least-squares planes being 0·034 Å for N(14). Each ligand is twisted out of the related Zn—S(X)—C(2X) plane, the resulting dihedral angles (66·2–77·2°) being similar to that found in the analogous Co cation (68·3°). This characteristically large value for the dihedral angle along with the small Zn—S(X)—C(2X) angles (mean 101·4°), suggest that the S atom in the present complex is largely sp^3 in character. The variation in the dihedral angles presumably reflects packing effects and the different nature of the H bonding for the four ligands.

The cations are linked together in the crystal by extensive H bonding involving the N(3)—H atoms and the two independent NO_3^- groups (Fig. 2). For three of the ligands (X = 1, 3, 4) the amido H interacts with just one O atom (O···H, 1·88–2·05 Å), while the fourth, H(32), is involved in a bifurcated H bond to two O
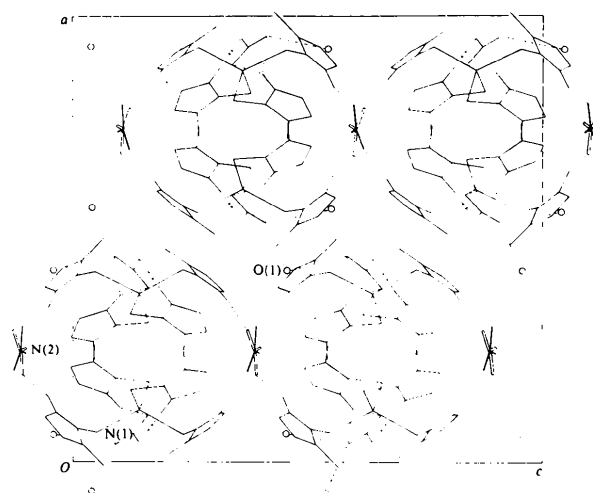
atoms of the same NO_3^- group. The water molecule is held within the lattice by H bonding to the N(1) nitrate groups. The nitrates are effectively planar with normal bond distances and angles (e.g. Vega, López-Castro & Márquez, 1978; Lebioda, 1977; Petrović & Ribár, 1975).

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