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The Structure of Zinc(II) *N*,*N*-Diisopropyldithiocarbamate {Bis[μ-(*N*,*N*-diisopropyldithiocarbamato-μ-*S*,*S'*]-bis(*N*,*N*-diisopropyldithiocarbamato)-dizinc(II)}

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Abstract. $\{Zn[S_2CN(i\text{-}C_3H_7)_2]_2\}_2$, $C_{28}H_{56}N_4S_8Zn_2$, $M_r = 1672{\cdot}0$, monoclinic, $P2_1/a$, $a = 16{\cdot}857$ (3), $b = 11{\cdot}168$ (3), $c = 11{\cdot}408$ (3) Å, $\beta = 111{\cdot}8$ (2)°, $U = 1994{\cdot}3$ Å^3, $D_m = 1{\cdot}385$ (flotation, chloroform/monochlorobenzene), $D_x = 1{\cdot}393$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·64 mm^{-1}, $Z = 2$. The structure was refined to $R = 0{\cdot}029$ for 3609 independent reflexions by the block-diagonal least-squares method. The molecules are dimeric, and each Zn atom is coordinated by five S atoms at distances of 2·335 (1), 2·342 (1), 2·377 (1), 2·454 (1) and 2·815 (1) Å. The crystal is isostructural with the ethyl analogue $\{Zn[S_2CN(C_2H_5)_2]_2\}_2$ [Bonamico, Mazzone, Vaciago & Zambonelli (1965). *Acta Cryst.* **19**, 898–909].

Introduction. As part of a series of investigations on metal complexes with sulphur as a ligating atom, the crystal structure of the title compound was determined. Powder of the complex was obtained by mixing aqueous solutions of sodium diisopropyldithiocarbamate and zinc acetate, and colourless crystals were grown from acetone.

Intensity data were collected on a Rigaku automatic four-circle diffractometer with a specimen shaped into an approximate sphere of diameter 0·3 mm. The reflexions within the range $2\theta < 55°$ were measured by the ω–2θ scan technique using graphite-monochromated Mo $K\alpha$ radiation. In total 4788 reflexions were measured and significant counts were recorded for 3609 independent reflexions [$|F| > 3\sigma(F)$]. The intensities were corrected for Lorentz and polarization factors but not for absorption.

All the non-hydrogen atoms were located by routine application of the heavy-atom method followed by Fourier syntheses. Difference Fourier syntheses gave the positions of all the H atoms. The structure was refined by the block-diagonal least-squares method, with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for H atoms, to an R of 0·029 for 3609 reflexions. A final difference Fourier map showed no peak greater than 0·25 e Å^{-3}. The atomic scattering factors as well as the correction factors for anomalous scattering were taken from *International*

Table 1. *Atomic parameters* (*for non-hydrogen atoms* $\times 10^4$; *for* H $\times 10^3$) *with estimated standard deviations in parentheses*

	x	*y*	*z*
Zn	497 (1)	780 (1)	1441 (1)
S(1)	368 (1)	−1591 (1)	551 (1)
S(2)	−458 (1)	−329 (1)	2054 (1)
S(3)	1975 (1)	804 (1)	1938 (1)
S(4)	1038 (1)	2389 (1)	3002 (1)
N(1)	−798 (1)	−2605 (2)	1329 (2)
N(2)	2740 (1)	2441 (2)	3741 (2)
C(1)	−367 (2)	−1622 (2)	1308 (2)
C(2)	−1395 (2)	−2720 (3)	2024 (3)
C(3)	−698 (2)	−3722 (3)	678 (3)
C(4)	−951 (2)	−2538 (3)	3445 (3)
C(5)	−2192 (2)	−1965 (4)	1423 (3)
C(6)	−177 (3)	−4626 (4)	1650 (4)
C(7)	−1548 (3)	−4198 (4)	−216 (4)
C(11)	2013 (2)	1944 (2)	2988 (2)
C(12)	3600 (2)	2100 (3)	3762 (3)
C(13)	2744 (2)	3398 (3)	4653 (3)
C(14)	3706 (2)	2377 (4)	2517 (4)
C(15)	3857 (2)	846 (3)	4237 (3)
C(16)	3227 (3)	2999 (4)	6004 (3)
C(17)	3070 (3)	4567 (4)	4347 (4)
H(21)	−157 (2)	−358 (3)	189 (3)
H(31)	−43 (2)	−351 (3)	21 (3)
H(41)	−42 (2)	−309 (3)	381 (3)
H(42)	−128 (2)	−284 (3)	386 (3)
H(43)	−78 (2)	−175 (3)	373 (3)
H(51)	−259 (2)	−225 (3)	163 (3)
H(52)	−213 (2)	−118 (3)	158 (3)
H(53)	−244 (3)	−204 (4)	48 (4)
H(61)	−16 (2)	−532 (4)	123 (4)
H(62)	32 (2)	−439 (3)	215 (3)
H(63)	−54 (3)	−489 (5)	227 (5)
H(71)	−144 (2)	−483 (3)	−65 (3)
H(72)	−195 (2)	−458 (4)	16 (4)
H(73)	−196 (3)	−359 (4)	−74 (4)
H(121)	399 (2)	263 (3)	440 (3)
H(131)	217 (2)	350 (3)	453 (3)
H(141)	430 (3)	228 (4)	272 (4)
H(142)	354 (2)	315 (3)	227 (3)
H(143)	344 (2)	181 (3)	185 (3)
H(151)	355 (2)	26 (3)	371 (3)
H(152)	383 (2)	70 (3)	499 (3)
H(153)	450 (2)	66 (4)	438 (4)
H(161)	310 (3)	362 (4)	660 (4)
H(162)	305 (2)	222 (4)	618 (4)
H(163)	390 (3)	286 (4)	614 (4)
H(171)	368 (2)	451 (4)	440 (4)
H(172)	271 (3)	480 (4)	347 (4)
H(173)	310 (3)	518 (5)	493 (5)

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Tables for X-ray Crystallography (1974). Final atomic coordinates are listed in Table 1.*

Discussion. The title compound, $\{Zn[S_2CN(i\text{-}Pr)_2]_2\}_2$, is isostructural with the ethyl analogue $[Zn(S_2CNEt_2)_2]_2$ (Bonamico, Mazzone, Vaciago & Zambonelli, 1965). A perspective view of the molecule is presented in Fig. 1 with the atom-numbering scheme. The bond distances and angles are given in Tables 2 and 3. The compound forms a centrosymmetric binuclear complex in the crystal. One of the two crystallographically independent dithiocarbamate ions (*A*) acts as a bridging group linking two Zn atoms to form the dimer. This ligand *A* forms simultaneously a four-membered chelate ring with a longer Zn—S(1) bond. The other dithiocarbamate ion (*B*) coordinates to the Zn atom through two S atoms approximately in the molecular plane, also forming a four-membered chelate ring. Three of the five Zn—S bond lengths, Zn—S(2), Zn—S(3) and Zn—S(1′), are normal, but the fourth, Zn—S(4), is slightly longer and the fifth, Zn—S(1), is much longer. These features are essentially identical to those found in the ethyl analogue, though all the values obtained in the present work are much more accurate. The molecular structure of the methyl analogue is quite different: the Zn atom is tetrahedrally surrounded by four S atoms and the molecular symmetry is C_2 (Klug, 1966). The Zn environments in $\{Zn[S_2CN(i\text{-}Pr)_2]_2\}_2$, $[Zn(S_2CNEt_2)_2]_2$ and $[Zn(S_2CNMe_2)_2]_2$ are compared in Table 2.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *involving the* Zn *atom*

A prime denotes the atom related by the centre of symmetry.

	$\{Zn[S_2CN(i\text{-}Pr)_2]_2\}_2$	$[Zn(S_2CNEt_2)_2]_2$*	$[Zn(S_2CNMe_2)_2]_2$†
Zn—S(1)	2·815 (1)	2·815 (2)	3·036 (6)
—S(2)	2·335 (1)	2·331 (3)	2·312 (6)
—S(3)	2·342 (1)	2·355 (3)	2·333 (6)
—S(4)	2·454 (1)	2·443 (3)	2·429 (6)
—S(1′)	2·377 (1)	2·383 (3)	2·373 (6)
Zn···Zn′	3·545 (1)	3·545 (4)	3·973 (6)
S(1)—Zn—S(2)	68·89 (3)	69·6	–
—S(3)	91·78 (3)	93·6	–
—S(4)	155·31 (2)	160·0	–
—S(1′)	94·33 (2)	94·4	–
S(2)—Zn—S(3)	136·40 (3)	137·7	136·5 (2)
—S(4)	106·41 (3)	106·9	108·4 (2)
—S(1′)	103·98 (3)	107·8	110·7 (2)
S(3)—Zn—S(4)	75·00 (3)	75·8 (2)	76·4 (2)
—S(1′)	116·55 (3)	112·1	113·7 (2)
S(4)—Zn—S(1′)	110·18 (3)	105·2	105·8 (2)
Zn—S(1)—C(1)	79·4 (1)	78·3	–
Zn′—S(1)—C(1)	100·6 (1)	102·3 (3)	96·5 (7)
Zn—S(2)—C(1)	95·8 (1)	93·9 (6)	96·5 (6)
Zn—S(3)—C(11)	86·4 (1)	84·5 (6)	84·0 (6)
Zn—S(4)—C(11)	83·2 (1)	81·9 (6)	82·0 (7)
Zn—S(1)—Zn′	85·70 (1)	85·6	–

* Bonamico *et al.* (1965).
† Klug (1966).

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *within the dithiocarbamate ligands*

S(1)—C(1)	1·756 (3)	S(1)—C(1)—S(2)	115·9 (2)
S(2)—C(1)	1·712 (3)	S(3)—C(11)—S(4)	115·4 (1)
S(3)—C(11)	1·733 (3)	S(1)—C(1)—N(1)	121·3 (2)
S(4)—C(11)	1·723 (3)	S(2)—C(1)—N(1)	122·8 (2)
		S(3)—C(11)—N(2)	122·8 (2)
C(1)—N(1)	1·321 (4)	S(4)—C(11)—N(2)	121·9 (2)
C(11)—N(2)	1·329 (3)	C(1)—N(1)—C(2)	124·2 (3)
		C(1)—N(1)—C(3)	121·4 (3)
N(1)—C(2)	1·501 (5)	C(11)—N(2)—C(12)	124·2 (3)
N(1)—C(3)	1·492 (4)	C(11)—N(2)—C(13)	121·0 (2)
N(2)—C(12)	1·491 (4)	C(2)—N(1)—C(3)	114·4 (2)
N(2)—C(13)	1·491 (4)	C(12)—N(2)—C(13)	114·8 (2)
		N(1)—C(2)—C(4)	112·9 (2)
C(2)—C(4)	1·527 (4)	N(1)—C(2)—C(5)	111·7 (3)
C(2)—C(5)	1·517 (5)	N(1)—C(3)—C(6)	109·5 (3)
C(3)—C(6)	1·516 (5)	N(1)—C(3)—C(7)	112·7 (3)
C(3)—C(7)	1·513 (5)	N(2)—C(12)—C(14)	112·5 (2)
C(12)—C(14)	1·528 (6)	N(2)—C(12)—C(15)	113·1 (3)
C(12)—C(15)	1·506 (5)	N(2)—C(13)—C(16)	111·1 (3)
C(13)—C(16)	1·518 (4)	N(2)—C(13)—C(17)	111·5 (3)
C(13)—C(17)	1·507 (6)	C(4)—C(2)—C(5)	114·1 (3)
		C(6)—C(3)—C(7)	113·9 (3)
		C(14)—C(12)—C(15)	113·9 (3)
		C(16)—C(13)—C(17)	112·6 (3)

The geometry around the Zn atom is intermediate between a tetragonal pyramid and a trigonal bipyramid. The metal atom is displaced by 0·69 (1) Å from the mean basal plane of the tetragonal pyramid, S(2)S(3)S(4)S(1′), or by 0·15 (1) Å from the equatorial plane of the trigonal bipyramid, S(2)S(3)S(1′).

The Zn atom is almost coplanar with each of the dithiocarbamate ions, the displacements from the planes of the *A* and *B* ions being 0·07 (1) and 0·11 (1)

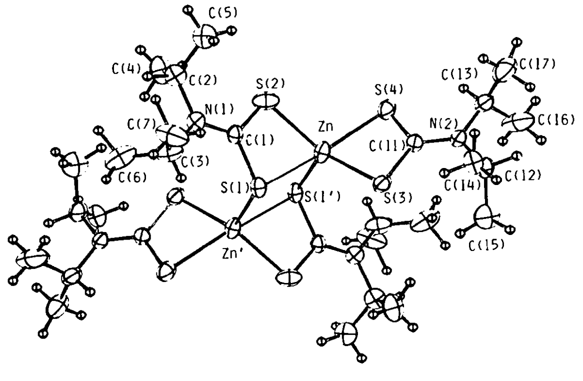

Fig. 1. A perspective view of the molecule showing thermal ellipsoids at 50% probability. Hydrogen atoms are represented by 0·1 Å radius spheres.

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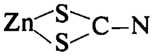
* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34330 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Å respectively. In the *B* ion the two S—C bond lengths are nearly equal, and the two Zn—S bonds lie approximately in the ligand plane. Thus the  $Zn\langle{}^{S}_{S}\rangle C{-}N$ group makes a conjugate system. Within the *A* ion, however, the S(1)—C(1) bond is significantly longer than S(2)—C(1). This is consistent with the fact that the S(1) atom is bonded to two Zn atoms with a shorter S(1)—Zn′ bond out of the ligand plane and a longer S(1)—Zn bond lying in the plane. Thus the π-bond character seems to be localized on the S(2)—C(1) bond.

The calculations were made on a FACOM 230-75 computer of this Institute using the *UNICS* II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). Part of this work was supported by a Grant-in-Aid for Scientific Research No. 354161 from the Ministry of Education, Science and Culture.

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α-L-Xylopyranose: A Neutron Diffraction Refinement*

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Abstract. The crystal structure of α-L-xylopyranose, $C_5H_{10}O_5$, has been refined with neutron diffraction data collected at two different wavelengths. The anisotropic extinction corrections derived for the two wavelengths agreed within 1σ. The heavy-atom coordinates are in good agreement with those from a previous X-ray study [Hordvik (1971). *Acta Chem. Scand.* **25**, 2175–2182]. The more accurate unit-cell data (298 K) are $a = 9{\cdot}213$ (1), $b = 12{\cdot}639$ (1), $c = 5{\cdot}618$ (1) Å ($\lambda = 1{\cdot}54051$ Å), $V = 654{\cdot}18$ Å^3, $M_r = 150{\cdot}13$, space group $P2_12_12_1$, $Z = 4$, $D_c = 1{\cdot}524$ Mg m^{-3}. The hydrogen bonding consists of a finite chain which originates at the anomeric hydroxyl and terminates at the ring oxygen, with H$\cdots$O distances ranging from 1·731 to 1·843 Å. The conformation of the pyranose ring is unusual in that it is a perfect $^1C_4$ (L) chair.

Introduction. This refinement forms part of a neutron-diffraction study of carbohydrates aimed at providing the accurate data relating to the hydrogen-atom positions which are necessary to understand the rules which govern the stereochemistry of the hydrogen bonding in the crystal structures of polyhydric molecules (*cf.* Jeffrey & Takagi, 1978).

α-L-Xylopyranose was obtained from Sigma Chemical Company. Transparent crystals suitable for single-crystal neutron diffraction were grown by slow evaporation of a 95% ethanol–water solution at room temperature. The crystal and experimental data and the structure refinement parameters are given in Table 1.

Cell constants and three-dimensional neutron diffraction data were collected with wavelengths 1·0541 [data set (I)] and 1·1604 Å [data set (II)] at room temperature on the Brookhaven High-Flux Beam Reactor single-crystal diffractometer as described by Takagi & Jeffrey (1977*a*).

The atomic coordinates from the X-ray determination (Hordvik, 1971) were used as the initial values for separate refinement of (I) and (II) by full-matrix least squares, minimizing $\sum w|F_o^2 - k^2F_c^2|^2$ (Busing, Martin & Levy, 1962). A difference Fourier map revealed the positions of all hydrogen atoms. The refinement parameters and neutron scattering lengths used are defined in Takagi & Jeffrey (1977*a*). The final anisotropic extinction parameters for (I) and (II) agree within the σ's for one of the sets, indicating that these parameters are indeed a property of the crystal rather than of the experiment. The final positional parameters are listed in Table 2. The two sets of refined parameters agree within 2·5σ, those of (I) being the more

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