

are able to penetrate closest to the central metal ion as compared with the negatively charged isothiocyanate (Lumme *et al.*, 1983), chloride (Lumme, Lindell & Kivimäki, 1984) and bromide (Lumme & Lindell, 1985) ions. This penetration tendency does not follow the size order of the ligands and must depend more on their electrical properties.

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Structure of Bis(isothiocyanato)[*N,N,N*-tris(1-pyrazolylmethyl)amine]zinc(II)

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Abstract. $[\text{Zn}(\text{C}_{12}\text{H}_{15}\text{N}_7)(\text{NCS})_2]$, $M_r = 438.83$, monoclinic, $P2_1/c$, $a = 10.202$ (3), $b = 14.730$ (3), $c = 13.415$ (2) Å, $\beta = 112.11$ (2)°, $V = 1867.7$ (8) Å³, $Z = 4$, $D_x = 1.561$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 15.8$ cm⁻¹, $F(000) = 896$, $T = 295$ K, $R = 0.061$ for 1845 observed reflections with $I > 2.5\sigma(I)$. Zn is surrounded by two isothiocyanate N atoms at 1.928 (7) and 1.974 (9) Å and two azole N atoms at 2.004 (6) and 2.023 (6) Å in a distorted tetrahedral arrangement. The amine N atom is at 2.599 (7) Å which can be considered as semi-coordinated. This five-coordination is approximately trigonal bipyramidal. The coordination mode of the ligand is unusual in not utilizing one of its pyrazole groups.

Introduction. The tripodal ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine (amtd) coordinates to divalent transition-metal ions through its three pyrazole

N atoms and its amine N atom (van Driel, Driessen & Reedijk, 1985; Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985). The coordination mode of the ligand tris(1-pyrazolylmethyl)amine (amtp) is different from that of amtd, while amtp is only different from amtd by the lack of ring substituents. In several cases the ligand amtp loses one of its pyrazole groups upon coordination to transition-metal ions (Driessen, de Graaf & Wiesmeijer, 1987; Spek, Duisenberg, Driessen & Wiesmeijer, 1988), a behaviour which has not so far been encountered with amtd. Analytical data and infrared spectra of the $\text{Zn}(\text{amtp})(\text{NCS})_2$ compound show that the ligand amtp is intact, but its coordination mode seemed nevertheless different from that of amtd. To elucidate this enigma the crystal structure of this compound was determined and is presented in this paper.

Experimental. Crystals were grown from ethanol at room temperature. Data were collected (de Boer &

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Duisenberg, 1984) for a colourless transparent crystal (0.20 × 0.23 × 0.33 mm) mounted in a Lindemann-glass capillary with an Enraf-Nonius CAD-4F diffractometer using Zr-filtered Mo K α radiation. Lattice parameters and their e.s.d.'s were derived from the SET4 setting angles of 18 reflections with $16 < 2\theta < 26^\circ$. Intensity data for 4684 reflections (h 0:13, k 0:19, l -17:16; $\theta < 27.5^\circ$) were collected in the $\omega/2\theta$ scan mode with $\Delta\omega = 0.60 + 0.35 \tan\theta^\circ$. Two reference reflections (023, 202) measured every hour of X-ray exposure time indicated no decay over 64 h of X-ray exposure. The intensity data were corrected for Lp and for absorption with the Walker & Stuart (1983) procedure (corrections in the range 0.676–1.365), resulting in 1845 reflections with $I > 2.5\sigma(I)$. The space group was derived from the observed systematic absences. The structure was solved by direct methods (SHELXS86; Sheldrick, 1986) and refined on F by weighted full-matrix least squares on a MicroVaxII with SHELX76 (Sheldrick, 1976). H atoms were located from a difference map. Refinement with weights based on $w = 1/\sigma^2(F)$ converged at $R = 0.061$ [$wR = 0.035$; $S = 1.82$; 281 parameters; $(\Delta/\sigma)_{ave} = 0.07$; $(\Delta/\sigma)_{max} = 0.46$]. The refined parameter set included a scale factor, all coordinates, anisotropic thermal parameters for the non-H atoms and one common isotropic temperature factor for the H atoms. A final difference Fourier map did not show residual peaks outside -0.60 and $0.91 \text{ e } \text{\AA}^{-3}$. Scattering factors of Cromer & Mann (1968) and anomalous-dispersion terms from Cromer & Liberman (1970) were used. Final parameters are given in Table 1.* The program PLATON (Spek, 1982) was used for the calculation of the geometrical data and the thermal-motion ellipsoid plot.

Discussion. The monoclinic unit cell contains four molecules of the title compound with no abnormally short intermolecular contacts. Data on the geometry have been collected in Table 2. A thermal-motion ellipsoid plot along with the adopted numbering scheme is presented in Fig. 1. The Zn^{II} ion is surrounded by two azole N atoms of the amtp ligand and two N atoms of the isothiocyanate anions. The geometry around Zn is distorted tetrahedral with angles ranging from 97.8 (3) to 119.8 (3)°. Distances from Zn to the N atoms lie in the narrow range of 1.927 (7)–2.023 (7) Å. Zn is positioned 0.73 (1) Å outside the plane defined by N(12), N(22) and N(40), in the direction opposite to N(1). It cannot be excluded that some bonding also occurs from Zn to the amine N as the Zn–N(1) distance is 2.599 (7) Å. The resulting approximately trigonal pyramidal coordination geometry is rather

Table 1. Final coordinates and equivalent isotropic thermal parameters and their e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Zn	0.18575 (10)	0.13934 (6)	0.25302 (8)	0.0524 (3)
S(42)	0.5565 (2)	0.3296 (2)	0.4643 (2)	0.072 (1)
S(52)	-0.2183 (3)	0.2155 (2)	0.3084 (2)	0.079 (1)
N(1)	0.3918 (6)	0.0358 (4)	0.2526 (5)	0.035 (2)
N(11)	0.2677 (7)	0.0813 (4)	0.0717 (5)	0.048 (3)
N(12)	0.1686 (7)	0.1238 (4)	0.0988 (5)	0.053 (3)
N(21)	0.2519 (6)	-0.0525 (4)	0.3199 (5)	0.039 (2)
N(22)	0.1646 (6)	0.0201 (4)	0.3174 (5)	0.044 (3)
N(31)	0.6188 (7)	-0.0245 (4)	0.3688 (5)	0.044 (3)
N(32)	0.6128 (7)	-0.0954 (5)	0.4316 (5)	0.061 (3)
N(40)	0.3314 (7)	0.2230 (4)	0.3356 (5)	0.059 (3)
N(50)	-0.0001 (8)	0.1912 (5)	0.2355 (6)	0.077 (3)
C(10)	0.4085 (9)	0.0624 (6)	0.1539 (7)	0.048 (4)
C(13)	0.0571 (9)	0.1362 (6)	0.0071 (7)	0.062 (4)
C(14)	0.0883 (10)	0.1040 (7)	-0.0776 (7)	0.072 (4)
C(15)	0.2196 (11)	0.0696 (7)	-0.0346 (8)	0.069 (4)
C(20)	0.3264 (9)	-0.0519 (5)	0.2447 (7)	0.039 (3)
C(23)	0.1021 (8)	-0.0034 (6)	0.3854 (7)	0.050 (4)
C(24)	0.1486 (10)	-0.0892 (6)	0.4295 (7)	0.057 (4)
C(25)	0.2444 (8)	-0.1201 (5)	0.3874 (6)	0.047 (3)
C(30)	0.5163 (9)	0.0481 (6)	0.3500 (7)	0.043 (3)
C(33)	0.7140 (10)	-0.1544 (6)	0.4249 (8)	0.072 (4)
C(34)	0.7780 (9)	-0.1202 (7)	0.3593 (7)	0.062 (4)
C(35)	0.7160 (10)	-0.0390 (7)	0.3236 (7)	0.057 (4)
C(41)	0.4251 (9)	0.2672 (5)	0.3890 (6)	0.044 (3)
C(51)	-0.0850 (9)	0.1998 (6)	0.2647 (7)	0.052 (4)

Table 2. Bond distances (Å) and bond angles (°) for the non-H atoms

Zn–N(12)	2.023 (7)	N(21)–C(25)	1.367 (10)
Zn–N(22)	2.004 (6)	N(22)–C(23)	1.340 (11)
Zn–N(40)	1.927 (7)	N(31)–N(32)	1.358 (9)
Zn–N(50)	1.974 (9)	N(31)–C(30)	1.450 (11)
S(42)–C(41)	1.626 (9)	N(31)–C(35)	1.360 (13)
S(52)–C(51)	1.687 (10)	N(32)–C(33)	1.378 (13)
N(1)–C(10)	1.451 (11)	N(40)–C(41)	1.156 (11)
N(1)–C(20)	1.439 (10)	N(50)–C(51)	1.084 (13)
N(1)–C(30)	1.451 (11)	C(13)–C(14)	1.375 (13)
N(11)–N(12)	1.350 (10)	C(14)–C(15)	1.342 (15)
N(11)–C(10)	1.471 (12)	C(23)–C(24)	1.400 (13)
N(11)–C(15)	1.333 (12)	C(24)–C(25)	1.377 (13)
N(12)–C(13)	1.337 (11)	C(33)–C(34)	1.374 (14)
N(21)–N(22)	1.384 (9)	C(34)–C(35)	1.354 (14)
N(21)–C(20)	1.474 (11)	Zn...N(1)	2.599 (7)
N(12)–Zn–N(22)	111.1 (2)	N(21)–C(25)–C(24)	104.8 (7)
N(12)–Zn–N(40)	114.3 (3)	N(1)–C(30)–N(31)	113.2 (7)
N(12)–Zn–N(50)	102.3 (3)	N(32)–C(33)–C(34)	111.0 (8)
N(22)–Zn–N(40)	119.8 (3)	C(33)–C(34)–C(35)	106.2 (9)
N(22)–Zn–N(50)	97.8 (3)	N(31)–C(35)–C(34)	107.6 (8)
N(40)–Zn–N(50)	108.6 (3)	S(42)–C(41)–N(40)	179.8 (12)
C(10)–N(1)–C(20)	112.7 (6)	S(52)–C(51)–N(50)	178.6 (7)
C(10)–N(1)–C(30)	115.1 (7)	N(21)–N(22)–C(23)	104.5 (6)
C(20)–N(1)–C(30)	113.8 (6)	N(32)–N(31)–C(30)	118.5 (7)
N(12)–N(11)–C(10)	120.3 (6)	N(32)–N(31)–C(35)	111.5 (7)
N(12)–N(11)–C(15)	109.8 (7)	C(30)–N(31)–C(35)	129.6 (7)
C(10)–N(11)–C(15)	129.6 (8)	N(31)–N(32)–C(33)	103.6 (7)
Zn–N(12)–N(11)	122.9 (5)	Zn–N(40)–C(41)	174.6 (7)
Zn–N(12)–C(13)	129.9 (6)	Zn–N(50)–C(51)	149.8 (7)
N(11)–N(12)–C(13)	106.2 (6)	N(1)–C(10)–N(11)	108.6 (7)
N(22)–N(21)–C(20)	118.1 (6)	N(12)–C(13)–C(14)	109.5 (8)
N(22)–N(21)–C(25)	112.5 (6)	C(13)–C(14)–C(15)	106.2 (8)
C(20)–N(21)–C(25)	129.0 (6)	N(11)–C(15)–C(14)	108.2 (9)
Zn–N(22)–N(21)	121.0 (5)	N(1)–C(20)–N(21)	107.4 (6)
Zn–N(22)–C(23)	132.5 (6)	N(22)–C(23)–C(24)	110.2 (8)
C(23)–C(24)–C(25)	107.9 (8)	N(1)...Zn–N(50)	165.5 (3)

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and geometrical data concerning H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51047 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

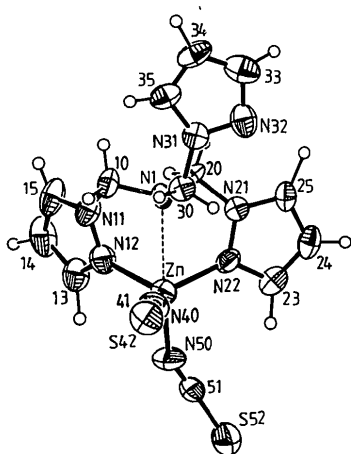


Fig. 1. Thermal-motion ellipsoid plot of $[\text{Zn}(\text{amp})(\text{NCS})_2]$. The surfaces have been drawn at the 50% probability level for non-hydrogen atoms and artificially small for H atoms.

unusual for Zn. In this respect it is of interest that the equatorial NCS ligand coordinates to Zn almost linearly [$\text{Zn}-\text{N}(40)-\text{C}(41) = 174.6(7)^\circ$] and the axial one with an angle of $149.8(7)^\circ$. Another remarkable feature of this compound is the third pyrazole group of the ligand amtp which does not coordinate to the Zn. In the compounds so far described with this type of poly(pyrazolyl)amine ligand, all pyrazole groups participate in the coordination of the central metal ion (Hulsbergen, Driessen, Reedijk & Verschoor, 1984; van Driel, Driessen & Reedijk, 1985; Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985; Paap, 1987). In other cases, when all the pyrazole groups of a particular poly(pyrazolyl)amine ligand seem not to fit, one of the pyrazole rings splits off

and the remaining groups coordinate (Driessen, de Graaff & Wiesmeijer, 1987; Spek, Duisenberg, Driessen & Wiesmeijer, 1988).

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Structure of Bis[1,3-bis(5-methyl-4-imidazolyl)-2-thiopropane-*N,N,S*]nickel(II) Hexafluorosilicate Pentahydrate

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Abstract. $[\text{Ni}(\text{C}_{10}\text{H}_{14}\text{N}_4\text{S}_2)_2]\text{SiF}_6 \cdot 5\text{H}_2\text{O}$, $M_r = 735.46$, monoclinic, $P2_1/c$, $a = 14.047(1)$, $b = 10.611(1)$, c

$= 20.782(2) \text{ \AA}$, $\beta = 103.65(1)^\circ$, $V = 3010.1(5) \text{ \AA}^3$, $Z = 4$, $D_x = 1.623 \text{ g cm}^{-3}$, $\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$, $\mu = 33.4 \text{ cm}^{-1}$, $F(000) = 1528$, $T = 295 \text{ K}$, $R = 0.059$ for 2922 observed reflections with $I > 2.5\sigma(I)$. The Ni^{II}

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