

Structure of Bis(4-*tert*-butyl-1,2,4-triazole-*N*¹)bis(isothiocyanato)zinc(II)*

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(Received 18 December 1981; accepted 15 March 1982)

Abstract. $\text{Zn}(\text{C}_6\text{H}_{11}\text{N}_3)_2(\text{NCS})_2$, $\text{C}_{14}\text{H}_{22}\text{N}_8\text{S}_2\text{Zn}$, monoclinic, space group $C2/c$, $a = 16.829$ (2), $b = 6.391$ (3), $c = 19.878$ (3) Å, $\beta = 103.873$ (3)°, $Z = 4$, $D_o = 1.37$ (1), $D_c = 1.38$ Mg m⁻³, $\mu = 1.42$ mm⁻¹. $R = 0.0356$, $R_w = 0.0353$ for 1306 independent reflections. The compound consists of monomeric units in which the Zn^{II} ion is tetrahedrally surrounded by two N-donating NCS^- ions and two *tert*-butyltriazole groups coordinating by only one N atom each.

Introduction. Coordination compounds with 1,2,4-triazole (abbreviated trz) as a ligand have interesting features because of the different modes of coordination. The possibility of its existence in two tautomeric forms gives rise to complexes with 1,2- and 2,4-bridging trz units. 1,2-Bridging trz occurs in $\text{Cu}(\text{trz})\text{Cl}_2$ (Jarvis, 1962) and in $\text{Ni}_3(\text{trz})_6(\text{NO}_3)_6(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$ (Reimann & Zocchi, 1971). 2,4-Bridging trz groups are found in the layered structures of $\beta\text{-Ni}(\text{trz})_2(\text{NCS})_2$ and related compounds with Mn^{II} (Engelfriet, 1980), Fe^{II} (Engelfriet & Verschoor 1981), Co^{II} , Cu^{II} and Zn^{II} (Engelfriet, den Brinker, Verschoor & Gorter, 1979). Compounds with only monodentately coordinating triazoles are found in the mononuclear complexes $\text{Mn}(\text{trz})(\text{H}_2\text{O})_4 \cdot \text{SO}_4$ (Gorter & Engelfriet, 1981) and $\text{Cr}(\text{CO})_5(4\text{-Metrz})$ (Vos, Haasnoot, Verschoor, Long & Vos, 1982). A substituent on the 4-position of the triazole ring leaves only monodentate and 1,2-bicoordination as possibilities. This was found with the thiocyanate compounds of 4-*R*-trz ligands [$R = \text{Me}$ (Engelfriet, Verschoor & Vermin, 1979), $R = \text{Et}$ (Vos, Haasnoot & Groeneveld, 1981; Vos, de Kok & Verschoor, 1981) and $R = \text{Ph}$ (Engelfriet, Verschoor & den Brinker, 1980)]. These 4-substituted triazoles form predominantly binuclear species, with three bridging triazoles. The ability of triazoles to form a bridge between transition-metal ions makes these complexes particularly interesting from a magnetochemistry point of view (Engelfriet, 1980; Vos, Haasnoot & Groeneveld, 1981).

The coordination behaviour of 4-*tert*-butyl-1,2,4-triazole, abbreviated *t*-Butrz, towards a number of

transition-metal thiocyanates shows remarkable differences compared to the previously described 4-*R*-trz complexes (Groeneveld, Haasnoot, Vos & Reedijk, 1982). Elemental analysis of $\text{Zn}(t\text{-Butrz})_2(\text{NCS})_2$ suggested the existence of a mononuclear compound, but the possibility of a polynuclear structure could not be excluded.

Since the *tert*-butyl group mainly determines the symmetry of the triazole ring it was not possible to decide from IR data with certainty whether the triazole ligand is coordinated mono- or bidentately. To gain more insight about the complicated IR spectra, a crystal structure determination of the title compound was undertaken.

t-Butrz was prepared as described elsewhere (US Patent, 1974; Groeneveld, Haasnoot, Vos & Reedijk, 1982). Commercially available chemicals were used without further purification. Single crystals were grown from an aqueous solution containing stoichiometric amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, *t*-Butrz and NH_4NCS .

A single crystal $0.55 \times 0.08 \times 0.13$ mm was mounted on an Enraf-Nonius CAD-4 diffractometer. Mo $K\alpha$ radiation, monochromatized by graphite, was applied to determine the precise unit-cell parameters, and to record the intensities at room temperature, using the θ - 2θ scan method for all reflections with $2 < \theta < 25^\circ$.

The data were corrected for Lorentz and polarization effects. Because the azimuth scans of the reflections 020 and 040 showed rather high intensity variations, ranging from 91 to 105%, an absorption correction (de Graaff, 1973) was also applied at a later stage. The experimental density was determined in a mixture of dibromoethane and cyclohexane.

The structure was solved by conventional heavy-atom techniques and refined by least squares, minimizing $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/\sigma_F^2$. Discrepancy factors are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Systematic extinctions for hkl , $h + k$ odd, and $h0l$, l odd, indicated space group Cc or $C2/c$; $C2/c$ is justified by the results.

* 1,2,4-Triazole Complexes. XVIII.

Table 1. Fractional coordinates ($\times 10^4$) and isotropic temperature factors (\AA^2) of the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Zn	0*	2444 (2)	2500*	3.64 (1)
N(1)	687 (2)	4205 (5)	3199 (1)	5.3 (1)
C(1)	1028 (2)	5447 (6)	3576 (2)	4.1 (1)
S(1)	1494 (1)	7177 (2)	4119 (1)	6.41 (4)
N(1,1)	745 (1)	652 (5)	2098 (1)	3.47 (8)
N(1,2)	1582 (2)	771 (5)	2338 (1)	5.4 (1)
C(1,3)	1876 (2)	-483 (6)	1938 (2)	5.3 (1)
N(1,4)	1286 (1)	-1400 (5)	1453 (1)	3.16 (7)
C(1,5)	497 (2)	-632 (5)	1577 (1)	3.7 (1)
C(1,6)	1373 (2)	-2921 (5)	900 (1)	3.42 (9)
C(1,7)	2256 (2)	-3006 (8)	872 (3)	6.2 (2)
C(1,8)	1116 (5)	-5044 (6)	1104 (4)	8.8 (2)
C(1,9)	849 (4)	2158 (9)	226 (2)	8.4 (2)

* Special position.

The three-dimensional Patterson synthesis revealed the position of the zinc atom on the twofold axis (0, y , $\frac{1}{2}$). The non-hydrogen atoms were found with the aid of the program *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, van den Hark & Prick, 1980). A difference synthesis phased by the heavy atoms revealed positions of the H atoms.

The temperature factors of some of the H and C atoms of the *tert*-butyl group tended to attain relatively high values. Therefore these positions were constrained (Waser, 1963). The H atoms were placed on calculated positions at a distance of 0.95 Å from the corresponding C atom, assuming a regular tetrahedral arrangement. The C—C distances in the *tert*-butyl group were held at 1.50 Å, being their mean value at this point of refinement. A further anisotropic refinement of the heavy atoms and isotropic refinement of the H atoms in six cycles, after absorption correction, finally led to $R = 0.036$ ($R_w = 0.035$) (significant reflections only). No extinction corrections were made.

Positional parameters of the non-hydrogen atoms are listed in Table 1. The isotropic temperature factors in Table 1 are calculated from the anisotropic temperature factors according to $B_{eq} = \frac{1}{3}\pi^2 \text{trace } \bar{U}$.

Discussion. Intramolecular distances and bond angles with their estimated standard deviations are listed in Tables 2 and 3. The structure is built up by monomeric units in which the Zn^{II} ions are positioned on a twofold axis. Each Zn is coordinated by two N-donating NCS⁻ groups and two non-bridging *t*-Butrz ligands. One

complete unit of Zn(*t*-Butrz)₂(NCS)₂ is depicted in Fig. 1, together with the atomic labelling as used in Table 1.

The positions of the mononuclear units in the unit cell are depicted in Fig. 2. As can be seen from Table 2, the ZnN₄ tetrahedron is slightly distorted. There is a good agreement between the geometry of the triazole ring in this compound and the rings in other 4-substituted triazoles (see Table 3). The differences with unsubstituted 1,2,4-triazoles are more substantial. From Table 3 it can be derived that the (de)localization of the π -electron density in the trz ring is mainly governed by the substituent on the 4-position and not

Table 2. Intramolecular distances (Å) and angles (°) in Zn(*t*-Butrz)₂(NCS)₂, except *t*-Butrz ring, but including the ring H atoms

Zn—N(1)	1.941 (3)	C(1,6)—C(1,7)	1.501 (4)
Zn—N(1,1)	2.000 (2)	C(1,6)—C(1,8)	1.508 (5)
N(1)—C(1)	1.146 (4)	C(1,6)—C(1,9)	1.499 (4)
C(1)—S(1)	1.611 (4)	C(1,3)—H(1,3)	0.95 (1)
N(1,4)—C(1,6)	1.500 (4)	C(1,5)—H(1,5)	0.93 (1)
N(1)—Zn—N(1,1)	107.2 (1)	N(1,1)—C(1,5)—H(1,5)	124 (2)
N(1)—Zn—N(2)*	109.1 (2)	N(1,4)—C(1,5)—H(1,5)	124 (2)
N(1,1)—Zn—N(2,1)†	110.2 (1)	C(1,3)—N(1,4)—C(1,6)	128.6 (3)
N(1,1)—Zn—N(2)	111.6 (1)	C(1,5)—N(1,4)—C(1,6)	128.0 (2)
Zn—N(1)—C(1)	171.3 (3)	N(1,4)—C(1,6)—C(1,7)	108.8 (3)
Zn—N(1,1)—C(1,5)	131.5 (2)	N(1,4)—C(1,6)—C(1,8)	107.6 (3)
Zn—N(1,1)—N(1,2)	121.1 (2)	N(1,4)—C(1,6)—C(1,9)	107.7 (3)
N(1)—C(1)—S(1)	178.7 (3)	C(1,7)—C(1,6)—C(1,8)	109.1 (4)
N(1,2)—C(1,3)—H(1,3)	123 (2)	C(1,7)—C(1,6)—C(1,9)	110.7 (4)
N(1,4)—C(1,3)—H(1,3)	124 (2)	C(1,8)—C(1,6)—C(1,9)	112.8 (5)

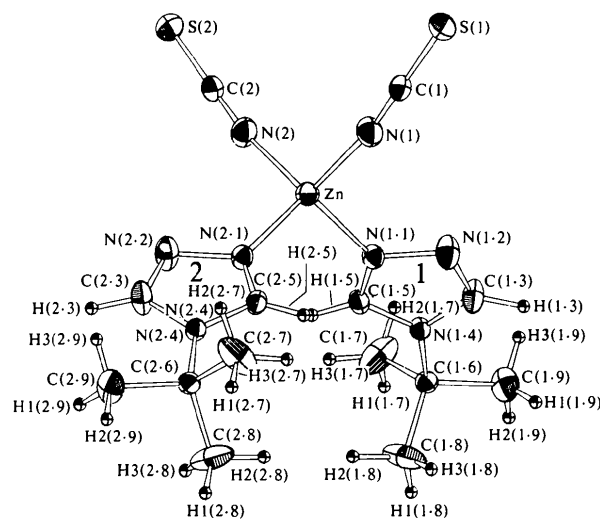
* N(2), C(2) and S(2) and related to N(1), C(1) and S(1) respectively by the symmetry operation $-x, y, \frac{1}{2} - z$.† Triazole group 2 is related to triazole 1 by the symmetry operation $-x, y, \frac{1}{2} - z$.

Fig. 1. An ORTEP (Johnson, 1965) drawing of the mononuclear unit Zn(*t*-Butrz)₂(NCS)₂ with atomic labelling. In this figure and in Fig. 2 the H atoms are depicted with the same small isotropic temperature factor for reasons of clarity. N(2), C(2) and S(2) are related to N(1), C(1) and S(1) respectively by the symmetry operation $-x, y, \frac{1}{2} - z$. Triazole group 2 is related to triazole group 1 by the same symmetry operation.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates and isotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36795 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and angles (°) of the triazole rings in $\text{Zn}(t\text{-Butrz})_2(\text{NCS})_2$ (A) and in $\text{Co}_2(\text{Phtrz})_5(\text{NCS})_4 \cdot 2 \cdot 7\text{H}_2\text{O}$ (B) (Engelfriet et al., 1980), 1,2,4-triazole (C) (Deuschl, 1965) and $\text{Mn}(\text{trz}) \cdot \text{SO}_4 \cdot 4\text{H}_2\text{O}$ (D) (Gorter & Engelfriet, 1981)

A, B1 and D are non-bridging monodentate triazole groups; B2 is a bridging triazole group.

	A	B1	B2	C	D
N(1,1)–N(1,2)	1.378 (3)	1.382 (7)	1.371 (7)	1.35 (1)	1.357 (3)
N(1,2)–C(1,3)	1.306 (4)	1.294 (9)	1.291 (7)	1.33 (1)	1.312 (4)
C(1,3)–N(1,4)	1.342 (4)	1.347 (9)	1.348 (7)	1.35 (1)	1.355 (4)
N(1,4)–C(1,5)	1.335 (3)	1.334 (8)	1.351 (8)	1.35 (1)	1.324 (4)
C(1,5)–N(1,1)	1.297 (4)	1.308 (9)	1.307 (8)	1.34 (1)	1.311 (4)
N(1,1)–N(1,2)–C(1,3)	105.1 (3)	106.1 (5)	107.1 (5)	101.8 (9)	102.2 (3)
N(1,2)–C(1,3)–N(1,4)	112.5 (3)	112.0 (6)	111.5 (5)	114.5 (9)	114.6 (3)
C(1,3)–N(1,4)–C(1,5)	103.4 (3)	104.1 (6)	103.8 (5)	104.3 (9)	102.5 (3)
N(1,4)–C(1,5)–N(1,1)	111.8 (3)	110.8 (6)	111.0 (5)	107.1 (9)	110.4 (3)
C(1,5)–N(1,1)–N(1,2)	107.2 (3)	107.0 (5)	106.6 (5)	112.2 (9)	110.4 (3)

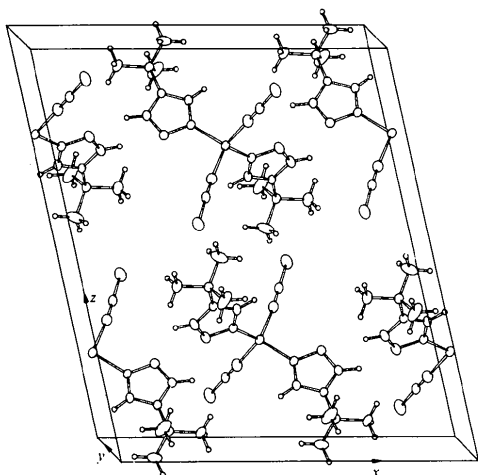


Fig. 2. The intermolecular arrangement of $\text{Zn}(t\text{-Butrz})_2(\text{NCS})_2$.

by the metal ion. In 4-substituted triazoles the π electrons seem to be predominantly located between N(1,1)–C(1,5) and N(1,2)–C(1,3), which makes these distances shorter (more double-bond character) and the remaining bonds longer.

The packing of the molecules in the crystal lattice is determined only by van der Waals contacts. No unusual contacts have been found.

All calculations were carried out on the Leiden University Amdahl V7B computer, using a set of computer programs written or modified by Mrs E. W. Rutten-Keulemans and Dr R. A. G. de Graaff. The authors are indebted to Professor J. Reedijk for his interest in this study. The investigations were supported in part by the Netherlands Organization for Chemical Research (SON), with financial aid from the Nether-

lands Organization for the Advancement of Pure Research (ZWO).

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