ne sont entourés que de 12 voisins (environnement ico-saédrique: 7,6–10,3 Å). Toutes ces remarques viennent ainsi justifier le comportement particulier déjà signalé pour Cr(1), quant à son orientation et son mode de cohésion intermoléculaire.

Cette description met donc en évidence que (+)-[Cr(en)$_3$]Br$_3$.0,6H$_2$O possède un arrangement structural de ses ions complexes, de type pseudocubique, correspondant à une maille cristalline construite sur les trois axes orthorhombiques [100], [011] et [01$\bar{1}$] (paramètres: 21,02, 22,5 et 22,5 Å). Il est particulièrement intéressant de constater que (+)-[Cr(en)$_3$]Br$_3$.0,6H$_2$O est, dans sa forme ortho-rhombique, quasiment isostructural de (−)-[Rh(en)$_3$]Cl$_3$ cubique ($a = 21,675$ Å, $F4_132$) (Whuler, 1978). Nous montrerons dans un prochain article que, malgré son originalité, ce type d'arrangement cristallin s'intègre parfaitement dans une filiation structurale commune à un très grand nombre de complexes [M(en)$_3$]X_m.nH$_2$O.

Nous remercions M B. Bachet pour sa contribution efficace, apportée lors des mesures diffractométriques.

Références

BROUTY, C. (1978). Thèse de Doctorat d'Etat, Paris, Université Pierre et Marie Curie.
BROUTY, C., SPINAT, P. & WHULER, A. (1977). Acta Cryst. B33, 3453–3460.
BROUTY, C., SPINAT, P., WHULER, A. & HERPIN, P. (1977). Acta Cryst. B33, 1913–1920.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
CRAMER, R. E. & HUNEKE, J. T. (1978). Inorg. Chem. 17(2), 365–374.

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–323.
DUESLER, E. N. & RAYMOND, K. N. (1978). Inorg. Chim. Acta, 30, 87–95.
FULLER, W. (1959). J. Phys. Chem. 63, 1705–1717.
GALSBØL, F. (1970). Inorg. Synth. 12, 269.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.
HAMILTON, W. C. & IBERS, J. A. (1968). Hydrogen Bonding in Solids, pp. 14–16. New York: Benjamin.
IWATA, M., NAKATSU, K. & SAITO, Y. (1969). Acta Cryst. B25, 2562–2571.
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KUSHI, Y., KURAMOTO, M. & YONEDA, H. (1976). Chem. Lett. 1976, 135.
NAKATSU, K. (1962). Bull. Chem. Soc. Jpn. 35, 832.
PAULING, L. (1960). The Nature of the Chemical Bond, pp. 257–264. Ithaca: Cornell Univ. Press.
RAYMOND, K. N., CORFIELD, P. W. R. & IBERS, J. A. (1968a). Inorg. Chem. 7, 1362–1373.
RAYMOND, K. N., CORFIELD, P. W. R. & IBERS, J. A. (1968b). Inorg. Chem. 7, 842–844.
RAYMOND, K. N. & IBERS, J. A. (1968). Inorg. Chem. 7, 2333–2338.
SPINAT, P., WHULER, A. & BROUTY, C. (1979). C. R. Acad. Sci. 288, 209–212.
WALLWORK, S. C. (1962). Acta Cryst. 15, 758–759.
WHULER, A. (1978). Thèse de Doctorat d'Etat, Paris, Université Pierre et Marie Curie.
WHULER, A., BROUTY, C. & SPINAT, P. (1977). Acta Cryst. B33, 2877–2885.
WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1975). Acta Cryst. B31, 2069–2076.
WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1976). Acta Cryst. B32, 2238–2239.
WHULER, A., SPINAT, P. & BROUTY, C. (1978). Acta Cryst. B34, 793–799.

1,2,4-Triazole Complexes.

V.* The Crystal Structure of the Layered Compound poly-Bis(thiocyanato-N)bis-μ-(1,2,4-triazole-N²,N⁴)cobalt(II) and its Zinc(II) and Copper(II) Analogues

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Abstract

The crystal structures of $M^{II}(C_2H_3N_3)_2(NCS)_2$ with M = Co, Zn and Cu have been determined by single-crystal X-ray diffraction techniques. The Co compound is orthorhombic, space group $Aba2$, with $a = 7.801$ (2), $b = 16.331$ (2), $c = 9.738$ (1) Å and $Z = 4$. The Zn compound is also orthorhombic, space group $Pbcn$, with $a = 7.897$ (2), $b = 9.816$ (1), $c = 16.224$ (6) Å, with $Z = 4$. The Cu compound is mono-

* Part IV: Engelfriet & Groeneveld (1978).

clinic, space group $P2_1/n$, with $a = 10\cdot084$ (7), $b = 7\cdot682$ (5), $c = 9\cdot126$ (6) Å and $\beta = 116\cdot43$ (7)°, with $Z = 2$. Data were collected with a three-circle diffractometer using Mo $K\alpha$ radiation. The structures were solved and refined by conventional heavy-atom techniques and least-squares refinements. The R values obtained in the final least-squares cycles were $0\cdot024$ ($R_w = 0\cdot033$, 858 reflexions), $0\cdot035$ ($R_w = 0\cdot040$, 1510 reflexions) and $0\cdot034$ ($R_w = 0\cdot041$, 1217 reflexions) for the Co, Zn and Cu compounds respectively. All three compounds exhibit the same basic features, namely two-dimensional M^{II} networks with 2,4-bridging triazole molecules and NCS^- groups, acting as N donors, on either side of the planes. The $M^{II}N_6$ octahedra are tilted. Hydrogen bonding is shown to be present between neighbouring layers. For the Co complex, a satisfactory result could only be obtained by imposing constraints upon the triazole ring and by introducing an inversion centre, implying 50% disorder in the orientation of the triazole rings.

Introduction

The existence of two tautomeric forms for 1,2,4-triazole (trz) suggests that upon complex formation this compound may act as a 2,4- or a 1,2-bidentate coordinating ligand. In both cases it is to be expected that polynuclear complexes may be formed, with the trz molecule acting as a bridging ligand. Up to now the structures of two such complexes have been reported, namely $CuCl_2.trz$ and $Ni_3(trz)_6(H_2O)_6(NO_3)_6.$ $2H_2O$. In these compounds 1,2-bridging trz units have been found. In $CuCl_2.trz$ (Jarvis, 1962) Cu^{II} ions are bridged by Cl^- and trz groups along infinite chains. $Ni_3(trz)_6(H_2O)_6(NO_3)_6.2H_2O$ (Reimann & Zocchi, 1971) is built up of linear clusters of three Ni^{II} ions bridged by six trz molecules. From physical measurements on $Ni(trz)_2(H_2O)_2SO_4.3H_2O$ and α-

$Ni(trz)_2(NCS)_2$, it has been concluded that these compounds are also linear trimers with 1,2-bridging triazole molecules (Engelfriet, Haasnoot & Groeneveld, 1977).

Completely different results were obtained for β-$Ni(trz)_2(NCS)_2$ and related compounds with Mn, Fe, Co, Cu and Zn, which led to the assumption of a layered structure. This model was first confirmed for $Co(trz)_2(NCS)_2$ (Engelfriet et al., 1977), the structure of which will be described in this report. From powder diffraction the Mn, Fe, Co and β-Ni complexes appeared to be isomorphous (Haasnoot & Groeneveld, 1977). The powder patterns of the Cu and Zn compounds were somewhat different and in order to obtain a complete picture of this series of compounds, their structures have also been determined.

Experimental

Crystals were grown from solutions prepared according to Haasnoot & Groeneveld (1977). They are usually quite flat and often diamond shaped. In the Co compound it was found that the diamond shape corresponds to the pattern of the metal ions in the layers (see below), with the b axis perpendicular to the flat surface. Some relevant data are listed in Table 1. Unit-cell parameters for the Cu compound have also been given in the somewhat unusual space group $B2_1/c$, in order to facilitate comparison of the three complexes. Suitable crystals were selected after taking Weissenberg photographs. They were then mounted on an Enraf–Nonius three-circle single-crystal diffractometer.

Mo $K\alpha$ radiation, monochromated by graphite, was used for determining the unit-cell parameters and space groups, and for measuring the intensities. Equivalent reflexions were averaged. Reflexions with intensities less than twice the standard deviation (calculated from counting statistics) were considered not significant. All data were corrected for Lorentz and polarization effects and for absorption (de Graaff, 1973). After reduction of the intensities to F values, Wilson plots yielded approximate values for the scale parameters and the overall isotropic thermal parameters, B.

Solution and refinement of the structure

All calculations were carried out on the Leiden University IBM 370-158 computer using a set of computer programs written or modified by Mrs E. W. Rutten-Keulemans and Dr R. A. G. de Graaff. Scattering factors and anomalous-dispersion corrections were taken from International Tables for X-ray Crystallography (1974). The function minimized during the least-squares refinement was $\sum w(\Delta F)^2$, with $\Delta F = |F_o| - |F_c|$ and the weighting scheme $w = 1/\sigma_F^2$. Discrepancy indices are defined as $R = \sum |\Delta F|/\sum |F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$.

Table 1. *Crystal and diffraction data for* $M^{II}(C_2H_3N_3)_2(NCS)_2$

M	Co	Zn	Cu	
M_r	313·24	319·69	317·84	
Space group	$Aba2$	$Pbcn$	$P2_1/n$	$B2_1/c$
Lattice constants				
a (Å)	7·801 (2)	7·897 (2)	10·084 (7)	10·151 (5)
b (Å)	16·331 (2)	9·816 (1)	7·682 (5)	7·682 (5)
c (Å)	9·738 (1)	16·224 (6)	9·126 (6)	16·337 (9)
β (°)			116·43 (7)	96·37 (7)
Z	4	4	2	4
Approximate size (mm)	0·5 × 0·3 × 0·2	0·4 × 0·3 × 0·3	0·3 × 0·1 × 0·1	
Scan mode	ω	ω	θ–2θ	
θ range (°)	4–30	4–30	4·5–27·5	
Measured reflexions	3103	3480	3010	
Independent reflexions	946	1816	1446	
Significant reflexions	858	1510	1217	
Final R (R_w)	0·024 (0·033)	0·035 (0·040)	0·034 (0·041)	

Table 2. *Positional parameters and isotropic temperature factors* $(Å^2)$ *for* $M^{II}(trz)_2(NCS)_2$

	Co				Zn				Cu			
	x	y	z	B_{Iso}	x	y	z	B_{Iso}	x	y	z	B_{Iso}
M	0	0	0	1·61(9)	0	0·21426(3)	0·25	1·74(1)	0	0	0	1·99(1)
S	0·42994(9)	−0·20624(5)	−0·013(1)	4·5(1)	0·43133(9)	0·23737(8)	0·45403(5)	4·12(2)	0·1838(1)	0·4330(1)	0·7745(1)	3·69(2)
C	0·2579(2)	−0·1495(1)	−0·001(2)	2·6(6)	0·2577(3)	0·2265(2)	0·3996(1)	2·24(5)	0·1301(3)	0·2630(4)	0·8416(3)	2·36(5)
N	0·1375(3)	−0·1089(1)	0·014(2)	2·1(2)	0·1362(2)	0·2206(2)	0·3608(1)	2·61(5)	0·0924(3)	0·1436(3)	0·8895(3)	2·84(5)
N(1)	0·195(1)	0·1204(4)	0·195(1)	2·6(2)	0·1926(2)	0·4200(2)	0·1258(1)	2·63(5)	0·1686(3)	0·2782(3)	0·4297(3)	2·77(5)
N(2)	0·168(2)	0·0410(6)	0·165(2)	1·8(1)	0·1650(2)	0·3795(2)	0·2040(1)	2·29(5)	0·2870(3)	0·2968(3)	0·3976(3)	3·09(5)
C(3)	0·258(6)	0·0032(2)	0·260(4)	2·5(3)	0·2544(3)	0·4668(2)	0·2474(1)	2·74(5)	0·2445(3)	0·2091(4)	0·2608(4)	3·19(8)
N(4)	0·342(3)	0·0533(6)	0·347(2)	2·3(1)	0·3361(2)	0·5601(2)	0·2012(1)	2·27(4)	0·1089(2)	0·1372(3)	0·2057(2)	2·27(5)
C(5)	0·299(2)	0·127(4)	0·303(1)	2·7(2)	0·2953(3)	0·5267(2)	0·1254(2)	2·58(5)	0·0660(3)	0·1832(4)	0·3168(4)	2·80(6)
H(1)	0·142(4)	0·170(1)	0·141(4)	2·5(4)	0·135(4)	0·372(3)	0·075(2)	6·2(8)	0·168(5)	0·328(6)	0·514(6)	6(1)
H(3)	0·263(6)	−0·055(1)	0·269(5)	2·5(4)	0·261(3)	0·461(3)	0·307(2)	3·6(6)	0·306(4)	0·202(5)	0·209(5)	4·0(8)
H(5)	0·336(4)	0·177(2)	0·342(3)	2·5(4)	0·328(3)	0·569(3)	0·076(2)	3·7(6)	−0·021(4)	0·155(5)	0·320(4)	4·2(8)

The positions of the non-hydrogen atoms were located by the usual Patterson techniques and refined by full-matrix least squares, at first with isotropic thermal parameters. The H atoms were found from a difference Fourier synthesis after anisotropic refinement. Further cycles were computed, including the H atoms with isotropic thermal parameters, until convergence. The values of R and R_w after the last cycle are given in Table 1 and the structural parameters are listed in Table 2.*

The parameters of the Co compound and the corresponding R values were found after a more extensive procedure. The reason for this was that refinement in $Aba2$ resulted in a highly distorted triazole ring, when compared with the rings in uncoordinated triazole (Deuschl, 1965; Goldstein, Ladell & Abowitz, 1969) and in $Ni_3(trz)_6(H_2O)_6(NO_3)_6.2H_2O$ (Reimann & Zocchi, 1971). Furthermore, the parameters of the N(2) and N(4) and the N(1) and C(5) atoms were strongly correlated. When the structure determinations of the Cu and Zn complexes subsequently yielded more acceptable geometries for the trz rings, the results for the Co compound were reconsidered. At first, constraints were imposed upon the trz ring, making use of the geometries of the Cu and Zn compounds. This procedure only resulted in a slightly higher R value. Next it was assumed that disorder in the orientations of the trz rings might be present. An inversion centre was introduced, implying 50% disorder in the orientations of the rings with respect to a pseudo-twofold axis passing from H(3)–C(3) to the midpoint between N(1) and C(5). Refinement in this space group ($Abam$) with C(3) and H(3) at $x = z = \frac{1}{4}$, the NCS⁻ group at $z = 0$, and without constraints, resulted in a better ring geometry but slightly higher R values (0·031, $R_w = 0·042$). On refinement in $Abam$ with constraints, the R index dropped significantly, and after correction for extinction, the final value obtained was 0·024 ($R_w = 0·033$).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34705 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The assumption of disorder in the trz rings seems, therefore, to be justified. We have refrained from converting to a more usual setting like *Cmca*, since we see no reasons why the disorder should be exactly 50%. Besides, the degree of disorder might very well depend on the rate of growth of the crystals.

Description of the structure

Relevant distances and angles with their e.s.d.'s are given in Tables 3 and 4. Fig. 1 depicts the structure of

Table 3. *Distances* $(Å)$ *and angles* $(°)$ *(except triazole rings) in* $M^{II}(trz)_2(NCS)_2$

|	Co	Zn	Cu
M–N(2)	2·18(2)	2·210(2)	2·477(3)
M–N(4)	2·12(2)	2·142(2)	2·002(5)
M–N	2·082(2)	2·094(3)	1·984(3)
N–C	1·160(5)	1·150(4)	1·152(4)
C–S	1·635(6)	1·634(3)	1·634(3)
S–C(5)	3·42(1) / 3·56(1)*	3·773(4)	3·805(5)
S–N(1)	3·62(1) / 3·48(1)*	3·332(4)	3·303(6)
S–H(5)	2·48(3) / 2·64(3)*	2·86(3)	2·89(4)
S–H(1)	2·58(3) / 2·44(3)*	2·30(3)	2·44(6)
N(2)–M–N(2)	85·1(9)	85·56(9)	180·00(1)
N(4)–M–N(4)	91(1)	90·1(1)	179·96(1)
N–M–N	172(1)	176·6(1)	179·96(1)
N–M–N(2)	84·4(5) / 89·9(5)	88·00(7) / 89·48(7)	89·0(2) / 91·0(2)
N–M–N(4)	95·7(6) / 89·8(6)	90·83(7) / 91·59(7)	89·9(2) / 90·1(2)
N(2)–M–N(4)	92·5(7) / 173·7(4)	92·18(7) / 177·46(7)	87·5(1) / 92·5(1)
M–N–C	153·7(8)	153·9(1)	160·9(3)
N–C–S	176(2)	179·0(2)	179·9(7)
C–S–H(1)	103·5(8)	103·8(8)	102(1)
S–H(1)–N(1)	169(3)	168(2)	172(4)
C–S–H(5)	70(1)	100·2(5)	104·5(8)
S–H(5)–C(5)	166(3)	164(2)	171(3)
H(1)–S–H(5)	71(1)	70(1)	71(1)

* Calculated with the S atom at $x,y,\bar{z}$.

Table 4. *Bond lengths* (Å) *and angles* (°) *in the triazole rings in* $M^{II}(trz)_2(NCS)_2$, *with* M = Co, Zn *and* Cu, *in uncoordinated triazole and in two other complexes containing triazole*

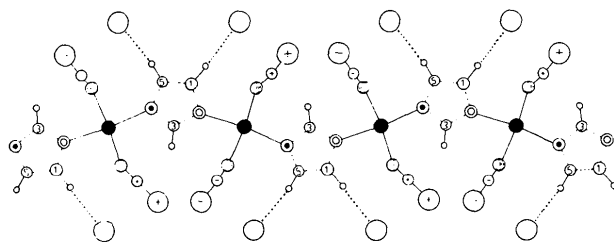|	Co*	Zn	Cu	trz (118 K)[a]	trz (293 K)[b]	Mn(trz)-(H₂O)₄SO₄[c]	Ni(trz)₂-(NO₃)₂(H₂O)₈/₃[d]
N(1)–N(2)	1·35 (1)	1·346 (2)	1·357 (7)	1·359 (3)	1·354 (14)	1·355 (4)	1·379 (5)
N(2)–C(3)	1·31 (4)	1·314 (3)	1·312 (8)	1·323 (3)	1·330 (14)	1·313 (4)	1·312 (6)
C(3)–N(4)	1·35 (4)	1·348 (3)	1·347 (4)	1·359 (3)	1·353 (14)	1·354 (4)	1·346 (6)
N(4)–C(5)	1·32 (6)	1·313 (4)	1·320 (9)	1·324 (3)	1·352 (14)	1·323 (4)	1·351 (6)
C(5)–N(1)	1·33 (4)	1·325 (3)	1·310 (5)	1·331 (3)	1·344 (14)	1·313 (5)	1·314 (6)
H(1)–N(1)	1·05 (2)	1·05 (3)	0·87 (6)	1·03 (3)	not found	0·83 (3)	–
H(3)–C(3)	0·95 (2)	0·97 (3)	0·94 (5)	0·93 (3)	1·07 (14)	0·89 (4)	–
H(5)–C(5)	0·95 (6)	0·94 (3)	0·92 (4)	0·93 (3)	1·07 (14)	0·91 (4)	–
N(1)–N(2)–C(3)	103 (1)	103·0 (2)	101·8 (4)	102·1 (2)	101·8 (9)	102·1 (2)	107·2 (3)
N(2)–C(3)–N(4)	114·6 (9)	113·7 (2)	114·4 (6)	114·6 (2)	114·5 (9)	114·7 (2)	109·8 (3)
C(3)–N(4)–C(5)	103 (2)	103·5 (2)	103·3 (5)	103·0 (2)	104·3 (9)	102·4 (3)	106·1 (3)
N(4)–C(5)–N(1)	110 (4)	110·0 (2)	109·8 (4)	110·1 (2)	107·1 (9)	110·5 (3)	109·8 (3)
C(5)–N(1)–N(2)	110 (3)	109·7 (2)	110·6 (5)	110·2 (2)	112·2 (9)	110·3 (2)	107·2 (3)

References: (a) Goldstein *et al.* (1969), (b) Deuschl (1965), (c) Gorter (1979), (d) Reimann & Zocchi (1971).

* Refined with constraints.
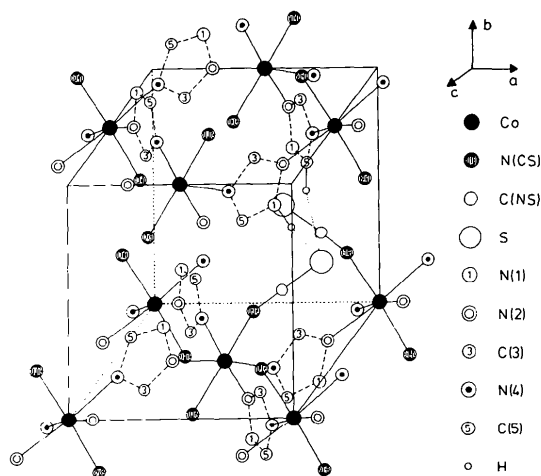
Fig. 1. The crystal structure of Co(trz)₂(NCS)₂. The top half of the unit cell has been omitted. For clarity only two isothiocyanate groups and two H atoms are shown. The numbers of the H atoms are those of the ring atoms to which they are attached. Possible interlayer hydrogen bonding is indicated by dotted lines. All figures have been generated using the crystallographic plotting program *FIGATOM* (Langlet, 1972).

Fig. 2. (101) section of Co(trz)₂(NCS)₂. The atom symbols have the same meaning as in Fig. 1. The atoms shown are within 1 Å from the plane of the drawing, except for C and S atoms from NCS⁻ groups marked + or −. C(+) and S(+) are at 1·5610 and 2·536 Å above, and C(−) and S(−) are at 1·579 and 2·699 Å below the plane of the drawing.

the Co compound, irrespective of disorder. The numbering scheme is given in Fig. 2, which presents a (101) section of the structure.

Co^{II} ions occupy special positions (0,0,0) and (0,½,½). They are octahedrally coordinated by two N(2) and two N(4) atoms, originating from trz rings, and by two N atoms from NCS⁻ groups. The NCS⁻ groups lie almost in the z = 0 and z = ½ planes. The distorted CoN₆ octahedra are tilted, the angle between the (SC)N–Co–N(CS) axis and the b direction being approximately 31°. The planes of the trz molecules make an angle of 0·2° with the b axis and by

coordinating *via* their N(2) and N(4) atoms a two-dimensional layered structure is formed.

The structure of Zn(trz)₂(NCS)₂, Fig. 3, is very similar to that of the Co compound. Apart from the origin translation, the main differences in the Zn structure are: (1) the top layer in the drawing is shifted by y = 0·07, and (2) the trz rings in this layer are rotated by 180° around an axis passing from C(3) to the midpoint between N(1) and C(5). (Note that the c axis in the Co cell points in a direction opposite to that of the b axis of the Zn cell.)

The structure of the Cu complex shows a striking resemblance to the other two structures, as can be seen from Fig. 4, which represents the structure in $B2_1/c$ to facilitate comparison with the other two structures. By means of the transformation

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix}$$
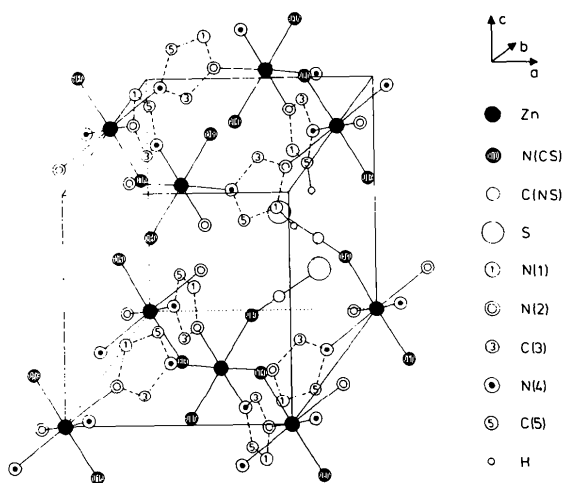
Fig. 3. The structure of $Zn(trz)_2(NCS)_2$. The origin is at (0·5, 0·2857, 0·75). Only one half of the unit cell is shown. Further omissions are the same as in Fig. 1.
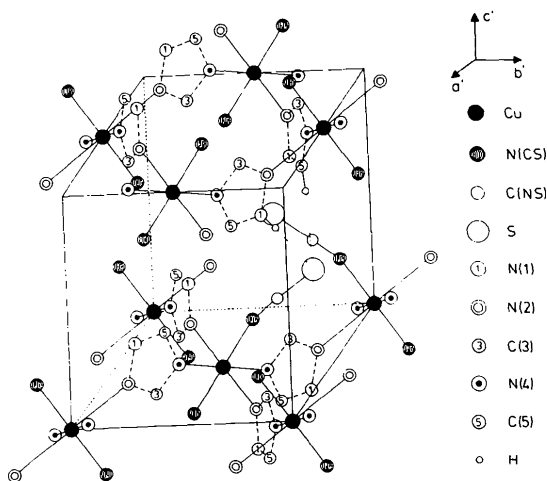

Fig. 4. The structure of $Cu(trz)_2(NCS)_2$. One half of the unit cell in $B2_1/c$ is given. The origin is at ($\frac{1}{2}$,0,$\frac{1}{2}$). Omissions are the same as in Fig. 1.

the $P2_1/n$ setting is obtained. Apart from the origin translation and the monoclinic distortion, the main difference in the Cu structure is the centrosymmetry in the environment of the Cu^{II} ions. Fig. 4 can therefore be derived from Fig. 1 by rotating the trz rings in the left half of Fig. 1 by 180° around an axis pointing from C(3) to the midpoint between N(1) and C(5). The CuN_6 octahedra clearly show Jahn–Teller deformation (see Table 3).

Interlayer bonding

Fairly short distances are found between an S atom in one layer and the H(1) and H(5) atoms in a neigh-

bouring layer. This observation and the fact that the S–H(1)–N(1) and S–H(5)–C(5) angles do not differ significantly from 180°, as can be seen from Table 3, are suggestive of hydrogen bonding. In Figs. 1–4 these possible hydrogen bonds are indicated by dotted lines.

In fact the N–S distances in the three complexes are well within the range of 3·24–3·67 Å, which is accepted for N–H···S bonding (Hamilton & Ibers, 1968). It is, however, not clear if C–H···S bonding is actually present. C is a far less common hydrogen-bond donor than N and the S–C(5) distances are fairly large, especially in the Zn and Cu compounds. It should be noted that an enlargement of the S–C(5) distance appears to be accompanied by a shortening of the S–N(1) distance.

The picture thus formed of the S atom, which is bonded in one direction to a C atom in the isothiocyanate group and hydrogen-bonded to a triazole molecule in another direction, might imply some anisotropy in its motion. This implication is in agreement with the relatively high value of U_{33} found in the Co compound. A similar situation appears to exist in the Zn and Cu compounds, in which relatively high values occur for U_{22} and U_{11} (in $B2_1/c$), respectively.

Triazole rings

Table 4 presents the trz bond lengths in the three title compounds, in uncoordinated triazole and in two other compounds containing triazole as a ligand. In $Mn(trz)(H_2O)_4SO_4$, which was recently discovered at our laboratory, the Mn^{II} ions are octahedrally coordinated

Table 5. *Distances (Å) from the ring atoms and the coordinated metal atoms to the least-squares planes (of non-hydrogen atoms) of the triazole rings in $M(trz)_2(NCS)_2$, with $M = $ Co, Zn and Cu*

The numbers of the hydrogen and metal atoms are those of the atoms to which they are attached. The equation of the plane in direct space is given by $Ax + By + Cz + D = 0$.

	A	B	C	D
Co	−0·7934	−0·0029	0·6086	0·0622
Zn	0·7925	−0·6077	−0·0521	1·4040
Cu	0·1978	−0·8290	0·5231	3·4113

	Co*	Zn	Cu
N(1)	0·002 (4)	−0·002 (1)	−0·004 (1)
N(2)	−0·005 (6)	0·000 (1)	0·002 (1)
C(3)	0·01 (1)	0·002 (1)	−0·003 (1)
N(4)	0·004 (6)	−0·004 (1)	−0·003 (1)
C(5)	0·001 (5)	0·004 (1)	0·005 (1)
H(1)	0·01 (1)	−0·03 (1)	−0·03 (2)
H(3)	0·02 (2)	0·03 (1)	−0·01 (2)
H(5)	0·00 (1)	−0·00 (1)	0·02 (2)
M(2)	0·0622 (1)	−0·0854 (4)	−0·5113 (1)
M(4)	−0·0694 (1)	0·0614 (4)	−0·0604 (1)

* Refined with constraints.

by one SO_4^{2-} group, four H_2O molecules and one triazole group, coordinating by its N(4) atom only (Gorter, 1979).

The table shows that there are no large differences between coordinated and uncoordinated trz, with the exception of the Ni complex. This compound is a different case altogether, since here the trz ring is 1,2 coordinating and therefore can be considered as existing in another tautomeric form. For the trz rings in the other four compounds, the best agreement is found with trz at low temperature, probably because the parameters at 118 K were determined more accurately than those at room temperature. The bond lengths in the coordinated triazole are systematically smaller than those in the free molecule. At least in part this may be attributed to the fact that no correction for librational motion was applied (mean correction in free triazole is 0·005 Å). Slight changes may also be caused by coordination.

Further, it should be noted that the trz rings in the Cu and Zn compounds differ somewhat. The N(1) atom of the trz ring in the Cu compound is shifted towards the C(5) atom with respect to that in the Zn compound. We have been unable to find an explanation for this.

Finally, as can be seen from Table 5, the trz rings are planar within experimental error. The metal atoms are at fairly short distances from the trz planes, except for the Cu attached to the N(2) atom.

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References

DEUSCHL, H. (1965). *Ber. Bunsenges. Phys. Chem.* **69**, 550–557.
ENGELFRIET, D. W. & GROENEVELD, W. L. (1978). *Z. Naturforsch. Teil A*, **33**, 848–854.
ENGELFRIET, D. W., HAASNOOT, J. G. & GROENEVELD, W. L. (1977). *Z. Naturforsch. Teil A*, **32**, 783–784.
GOLDSTEIN, P., LADELL, J. & ABOWITZ, G. (1969). *Acta Cryst.* B25, 135–143.
GORTER, S. (1979). To be published.
GRAAFF, R. A. G. DE (1973). *Acta Cryst.* A29, 298–301.
HAASNOOT, J. G. & GROENEVELD, W. L. (1977). *Z. Naturforsch. Teil B*, **32**, 553–558.
HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, p. 168. New York: Benjamin.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press.
JARVIS, J. A. J. (1962). *Acta Cryst.* **15**, 964–966.
LANGLET, G. A. (1972). *J. Appl. Cryst.* **5**, 66–71.
REIMANN, C. W. & ZOCCHI, M. (1971). *Acta Cryst.* B27, 682–691.

1,2,4-Triazole Complexes.

VI.* The Crystal Structure of Tris-μ-(4-methyl-1,2,4-triazole-N^1,N^2)-bis[(4-methyl-1,2,4-triazole-N^1)bis(thiocyanato-N)manganese(II)], Mn₂(C₃H₅N₃)₅(NCS)₄

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Abstract

The crystal structure of Mn₂(C₃H₅N₃)₅(NCS)₄, $C_{19}H_{25}Mn_2N_{19}S_4$, has been determined by single-crystal X-ray diffraction techniques. The compound is ortho-rhombic, space group $P2_12_12$ with $a = 12·424$ (1), $b = 14·144$ (2), $c = 9·336$ (1) Å, and $Z = 2$, $D_m = 1·532$ (2), $D_c = 1·534$ Mg m^{-3}. Data were collected with a four-circle diffractometer. The structure was solved by direct and Fourier methods and was refined by block-diagonal least squares to a final $R = 0·0251$ ($R_w = 0·0345$) for 1910 independent reflexions. The compound consists of dimeric units in which two Mn^{II} ions are bridged by three methyltriazole groups. Two N-donating NCS$^-$ groups and a methyltriazole group coordinating by only one N atom complete the MnN₆ octahedra.

Introduction

In the structures of complexes containing 1,2,4-triazole (trz) reported previously, this ligand acts as a bridging ligand, as is to be expected from its structural formula.

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* Part V: Engelfriet, den Brinker, Verschoor & Gorter (1979).