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1,2,4-Triazole Complexes. IX.* The Structure of Tris-μ-(4-phenyl-1,2,4-triazole-N^1,N^2)-bis[bis(isothiocyanato)(4-phenyl-1,2,4-triazole-N^1)cobalt(II)] Hydrate, $Co_2(C_8H_7N_3)_5(NCS)_4.xH_2O$ ($x \simeq 2{\cdot}7$)

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Abstract

The crystal structure of Co_2(4-phenyl-1,2,4-triazole)$_5$(NCS)$_4$.2·7 H_2O, $C_{44}H_{35}Co_2N_{19}S_4$.2·7 H_2O, has been determined by single-crystal X-ray diffraction techniques. The compound is orthorhombic, space group *Pbca*, with $a = 16{\cdot}855$ (2), $b = 17{\cdot}841$ (2), $c = 34{\cdot}355$ (4) Å and $Z = 8$, $D_m = 1{\cdot}447$ (4) Mg m^{-3}. Data were collected with a four-circle diffractometer using Mo $K\alpha$ radiation. The structure was solved by Patterson and Fourier techniques and was refined by block-diagonal least squares to a final $R = 0{\cdot}037$ ($R_w = 0{\cdot}045$) for 5089 independent significant reflexions. The compound consists of dimeric units in which two Co^{II} ions are bridged by three phenyltriazole groups. Two N-donating NCS$^-$ groups and a phenyltriazole group coordinating by only one N atom complete the CoN$_6$ octahedra. The NCS$^-$ groups coordinated to one of the two Co^{II} ions are disordered. Between the dimeric units there are large voids containing solvent molecules.

Introduction

Very recently, a series of compounds was discovered at our laboratory for which chemical analysis yielded the approximate composition M^{II}(Phetrz)$_{2{\cdot}5}$(NCS)$_2$ (Haasnoot & Groeneveld, 1980). Here, M is a first-row transition metal and Phetrz stands for 4-phenyl-1,2,4-triazole. The stoichiometry of these Phetrz complexes is thus identical to that of Mn_2(Metrz)$_5$(NCS)$_4$. In a previous paper (Engelfriet, Verschoor & Vermin, 1979), it was shown that the latter compound consists of dimeric units in which two Mn^{II} ions are bridged by three 1,2-coordinating Metrz groups. From the structural formula of Phetrz (Fig. 1), we expected that with this ligand a similar type of compound would be formed.

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[*] Part VIII: Engelfriet, Groeneveld, Groenendijk, Smit & Nap (1980).

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The dimeric character of the orange-red $Co(Phetrz)_{2.5}(NCS)_2$ could be confirmed by magnetic-susceptibility measurements on a polycrystalline sample (Engelfriet & Groeneveld, 1980). Nevertheless, for a number of reasons it was thought worthwhile to determine the structure of this compound: Weissenberg photographs of a single crystal showed an unusually large unit cell, probably containing eight dimeric units; the compound turns blue on powdering as well as on heating to ~460 K, indicating a change of the coordination of Co^{II} from octahedral to tetrahedral. Magnetic-susceptibility measurements on a single crystal cannot be interpreted properly without more detailed knowledge of the complete structure.

Experimental

Single crystals were grown from an aqueous solution containing stoichiometric amounts of $Co(NO_3).6H_2O$, Phetrz and NH_4NCS. Zero- and upper-level Weissenberg photographs showed the space group to be *Pbca* and yielded approximate cell parameters. A crystal (approximate size 0·50 × 0·29 × 0·21 mm) was then mounted on an Enraf–Nonius four-circle diffractometer. Mo $K\alpha$ radiation, monochromated by graphite, was used for determining the precise unit-cell parameters and the reflexion intensities. The data were corrected for Lorentz and polarization effects. Azimuth scans of the reflexions $2\bar{3}5$ and $4,\bar{6},10$ showed only small intensity variations, ranging from 97 to 103 and from 98 to 102% respectively. It was therefore considered not necessary to correct for absorption. 16491 reflexions were measured. After averaging equivalent reflexions, 8089 independent reflexions were obtained, of which 5089 had $I > 2\sigma(I)$ (calculated from counting statistics, inaccuracies in the attenuation factors and the neglect of absorption effects). After reduction to F_o values, a Wilson plot was calculated, from which starting values were obtained for the scale parameter and the overall isotropic thermal parameter B.

Solution and refinement of the structure

All calculations were carried out on the Leiden University IBM 370-158 computers, 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 $w = (\sigma_F)^{-2}$. Discrepancy indices referred to are $R = \sum |\Delta F|/|F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$.

The positions of the non-hydrogen atoms were found from three-dimensional Patterson and Fourier syntheses. The structure appears to consist of Co^{II} ions, bridged by three Phetrz groups. Each Co^{II} ion is further connected to two N-donating NCS^- groups and a non-bridging Phetrz group.

Five cycles of block-diagonal isotropic refinement yielded $R = 0.15$ ($R_w = 0.21$). The parameters of each Phetrz group and those of the Co^{II} ions and NCS^- groups were allocated to separate blocks. Analysis of the results of further cycles and subsequent difference-Fourier maps showed that the NCS^- groups attached to one of the Co^{II} ions [denoted Co(1)] are disordered. This disorder was accounted for by introducing alternative C and S atoms for these NCS^- groups and refinement of the occupation rate. The difference-Fourier syntheses further revealed the presence of peaks at fairly large distances (>2·2 Å) from the atoms introduced so far. Because the infrared spectrum showed a small amount of water to be present, these peaks were assigned to H_2O molecules. The occupation rates were chosen in such a way that the isotropic thermal parameters gave reasonable values. The H atoms of the Phetrz groups were placed on calculated positions at a C—H distance of 0·95 Å. They were given B values which were kept 1 Å^2 higher than those of the corresponding ring atoms.

Refining the Co and S atoms anisotropically and the other non-hydrogen atoms isotropically, we found $R = 0.062$ ($R_w = 0.076$). Because the geometries of some of the trz and phenyl rings showed unusual features, further cycles were calculated with slack constraints (Waser, 1963) imposed upon the distances between neighbouring atoms of the Phetrz groups. The constraints were found by averaging supposedly equivalent distances and were, if necessary, adjusted after each cycle. This procedure yielded $R = 0.058$ ($R_w = 0.072$) after four cycles. Next, four cycles were calculated in which all non-hydrogen atoms (except the H_2O molecules) were refined with anisotropic thermal parameters. In these cycles the atoms of the trz and phenyl rings were allocated to separate blocks. Lastly, after four cycles without constraints, $R = 0.037$ ($R_w = 0.045$) was obtained. Release of the constraints appeared to result in slightly irregular geometries for some Phetrz groups. In view of the large e.s.d.'s this was not considered alarming.

A final difference-Fourier synthesis showed 15 peaks with heights ranging from 1·2 to 1·7 e Å^{-3} and one of 2·1 e Å^{-3} (statistical height = 0·56 e Å^{-3}). This will be discussed further in the next section.

Positional parameters, isotropic thermal parameters and occupation rates are given in Tables 1 and 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35205 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (×10⁴) *and isotropic temperature factors* (Å²) *of the non-hydrogen atoms and the water molecules*

Multiplicities are 8, unless otherwise stated.

	x	*y*	*z*	B_{iso}	Mult.
Co(1)	340·1 (3)	3170·9 (3)	1342·9 (1)	3·35 (2)	
Co(2)	536·2 (3)	1036·6 (3)	1106·3 (1)	3·20 (2)	
N(1)	511 (2)	4048 (2)	937 (1)	5·3 (1)	
C(1)	1059 (7)	4471 (5)	835 (3)	5·5 (3)	4·00 (2)
C(1*A*)	325 (7)	4470 (5)	686 (3)	5·9 (3)	4·00 (2)
S(1)	1829 (2)	4981 (2)	718 (1)	10·4 (1)	4·00 (2)
S(1*A*)	155 (3)	5088 (2)	368 (1)	15·1 (2)	4·00 (2)
N(2)	−649 (2)	3708 (2)	1588 (1)	4·7 (1)	
C(2)	−1103 (20)	4012 (20)	1812 (12)	4·1 (4)	2·7 (1)
C(2*A*)	−928 (8)	3827 (8)	1879 (6)	4·1 (4)	5·3 (1)
S(2)	−1652 (7)	4425 (12)	2114 (6)	10·6 (3)	2·7 (1)
S(2*A*)	−1357 (3)	3979 (4)	2292 (1)	7·1 (2)	5·3 (1)
N(3)	789 (2)	635 (2)	555 (1)	4·3 (1)	
C(3)	965 (2)	499 (2)	241 (1)	3·7 (1)	
S(3)	1216·9 (9)	319·1 (7)	−212·0 (4)	6·10 (5)	
N(4)	1227 (2)	209 (2)	1359 (1)	4·5 (1)	
C(4)	1377 (2)	−370 (3)	1481 (1)	3·8 (1)	
S(4)	1576·6 (9)	−1197·0 (7)	1659·4 (4)	6·13 (1)	
N(1,1)	180 (2)	2268 (2)	1746 (1)	3·7 (1)	
N(1,2)	286 (2)	1515 (2)	1672 (1)	3·7 (1)	
C(1,3)	216 (2)	1160 (2)	2002 (1)	4·3 (1)	
N(1,4)	81 (2)	1657 (2)	2295 (1)	4·1 (1)	
C(1,5)	59 (2)	2336 (2)	2117 (1)	4·3 (1)	
C(1,6)	−7 (3)	1513 (3)	2706 (1)	4·6 (1)	
C(1,7)	413 (4)	947 (3)	2870 (1)	6·2 (2)	
C(1,8)	329 (4)	804 (3)	3268 (2)	7·8 (2)	
C(1,9)	−177 (4)	1252 (3)	3481 (1)	7·7 (2)	
C(1,10)	−575 (4)	1834 (3)	3318 (1)	7·9 (2)	
C(1,11)	−502 (3)	1964 (3)	2923 (1)	6·3 (2)	
N(2,1)	1375 (2)	2604 (2)	1133 (1)	4·0 (1)	
N(2,2)	1480 (2)	1850 (2)	1059 (1)	3·4 (1)	
C(2,3)	2191 (2)	1771 (2)	917 (1)	3·5 (1)	
N(2,4)	2566 (2)	2440 (2)	889 (1)	3·0 (1)	
C(2,5)	2030 (2)	2942 (2)	1029 (1)	3·6 (1)	
C(2,6)	3314 (2)	2605 (2)	710 (1)	3·2 (1)	
C(2,7)	3811 (2)	2025 (2)	607 (1)	4·6 (1)	
C(2,8)	4512 (2)	2183 (3)	417 (1)	5·1 (1)	
C(2,9)	4708 (2)	2916 (3)	326 (1)	5·0 (1)	
C(2,10)	4213 (2)	3481 (3)	432 (1)	4·6 (1)	
C(2,11)	3508 (2)	3335 (2)	622 (1)	3·9 (1)	
N(3,1)	−406 (2)	2553 (2)	953 (1)	3·6 (1)	
N(3,2)	−247 (2)	1833 (2)	837 (1)	3·4 (1)	
C(3,3)	−818 (2)	1628 (2)	610 (1)	3·4 (1)	
N(3,4)	−1363 (2)	2175 (2)	568 (1)	3·4 (1)	
C(3,5)	−1076 (2)	2742 (2)	788 (1)	3·9 (1)	
C(3,6)	−2096 (2)	2134 (2)	357 (1)	3·5 (1)	
C(3,7)	−2449 (2)	1456 (3)	308 (1)	4·9 (1)	
C(3,8)	−3150 (3)	1405 (3)	99 (1)	5·7 (2)	
C(3,9)	−3487 (3)	2034 (3)	−52 (1)	5·4 (2)	
C(3,10)	−3140 (3)	2716 (3)	4 (1)	5·1 (2)	
C(3,11)	−2436 (2)	2774 (2)	208 (1)	4·5 (1)	
N(4,1)	1088 (2)	3746 (2)	1753 (1)	4·0 (1)	
N(4,2)	1403 (2)	3407 (2)	2079 (1)	5·1 (1)	
C(4,3)	1719 (3)	3933 (3)	2281 (1)	5·3 (1)	
N(4,4)	1639 (2)	4611 (2)	2110 (1)	4·2 (1)	
C(4,5)	1247 (2)	4462 (2)	1780 (1)	4·0 (1)	
C(4,6)	1919 (2)	5329 (2)	2248 (1)	4·6 (1)	
C(4,7)	1761 (3)	5516 (3)	2628 (1)	5·8 (2)	
C(4,8)	2049 (4)	6209 (3)	2763 (2)	7·6 (2)	
C(4,9)	2463 (4)	6670 (3)	2523 (2)	5·1 (2)	
C(4,10)	2604 (3)	6474 (3)	2146 (2)	6·8 (2)	
C(4,11)	2334 (3)	5784 (3)	2006 (2)	5·8 (1)	
N(5,1)	−480 (2)	308 (2)	1188 (1)	3·7 (1)	
N(5,2)	−1250 (2)	556 (2)	1240 (1)	5·6 (1)	
C(5,3)	−1683 (2)	−41 (3)	1272 (1)	5·7 (1)	
N(5,4)	−1247 (2)	−672 (2)	1247 (1)	3·8 (1)	
C(5,5)	−502 (2)	−425 (2)	1191 (1)	3·9 (1)	
C(5,6)	−1515 (2)	−1440 (2)	1268 (1)	4·0 (1)	
C(5,7)	−2190 (3)	−1600 (3)	1470 (1)	6·1 (2)	
C(5,8)	−2459 (3)	−2334 (3)	1482 (2)	7·0 (2)	
C(5,9)	−2063 (4)	−2882 (3)	1303 (2)	6·6 (2)	
C(5,10)	−1407 (4)	−2712 (3)	1096 (2)	4·1 (2)	
C(5,11)	−1126 (3)	−1985 (3)	1076 (1)	6·1 (2)	
H_2O(1)	164 (4)	4274 (4)	2880 (2)	8·0 (2)	6
H_2O(2)	−62 (9)	4315 (8)	2711 (4)	8·4 (4)	3
H_2O(3)	3520 (6)	4731 (5)	4018 (3)	7·8 (4)	4
H_2O(4)	3935 (15)	4815 (14)	4276 (8)	11·5 (7)	2
H_2O(5)	2996 (14)	4549 (12)	5183 (7)	11·2 (6)	2
H_2O(6)	2814 (10)	4873 (10)	5606 (5)	6·9 (4)	2
H_2O(7)	3139 (10)	4490 (9)	4328 (6)	6·6 (4)	2
H_2O(8)	3264 (11)	4466 (11)	4712 (6)	8·6 (5)	2

Table 2. *Fractional coordinates* (*calculated*) *of the hydrogen atoms* (×10⁴)

The numbers in parentheses after the atom symbol are those of the atoms to which the H atoms are attached.

	x	*y*	*z*
H(1,3)	253	632	2033
H(1,5)	−34	2797	2248
H(1,7)	761	651	2715
H(1,8)	611	407	3389
H(1,9)	−244	1150	3751
H(1,10)	−899	2148	3475
H(1,11)	−792	2357	2802
H(2,3)	2417	1305	842
H(2,5)	2120	3466	1049
H(2,7)	3673	1522	669
H(2,8)	4861	1788	345
H(2,9)	5187	3021	191
H(2,10)	4357	3984	375
H(2,11)	3158	3731	690
H(3,3)	−851	1151	488
H(3,5)	−1327	3215	819
H(3,7)	−2215	1020	417
H(3,8)	−3396	932	60
H(3,9)	−3966	1998	−197
H(3,10)	−3386	3153	−98
H(3,11)	−2189	3248	244
H(4,3)	1979	3856	2523
H(4,5)	1103	4827	1592
H(4,7)	1468	5190	2793
H(4,8)	1956	6354	3025
H(4,9)	2653	7136	2618
H(4,10)	2887	6805	1980
H(4,11)	2439	5636	1746
H(5,3)	−2241	−35	1309
H(5,5)	−53	−740	1158
H(5,7)	−2472	−1213	1601
H(5,8)	−2932	−2450	1620
H(5,9)	−2240	−3386	1320
H(5,10)	−1133	−3099	962
H(5,11)	−669	−1862	929

Discussion

The structure consists of pairs of Co^{II} ions that are bridged by three 1,2- coordinating Phetrz groups. Each Co^{II} ion is further coordinated to two NCS^- groups and a Phetrz group coordinating by only one N atom

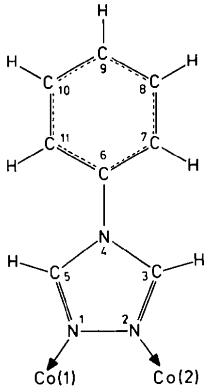

Fig. 1. The structural formula and the numbering system of 4-phenyl-1,2,4-triazole in $Co_2(Phetrz)_5(NCS)_4.2\cdot7H_2O$.

Table 3. *Distances* (Å) *and angles* (°) *in a dimeric unit, except* Phetrz *groups*

Co(1)–Co(2)	3·907 (1)	Co(2)–N(3)	2·070 (7)
Co(1)–N(1)	2·115 (6)	–N(4)	2·071 (6)
–N(2)	2·099 (6)	–N(1,2)	2·165 (4)
–N(1,1)	2·142 (5)	–N(2,2)	2·159 (5)
–N(2,1)	2·141 (5)	–N(3,2)	2·148 (5)
–N(3,1)	2·144 (5)	–N(5,1)	2·169 (5)
–N(4,1)	2·150 (6)	N(3)–C(3)	1·145 (9)
N(1)–C(1)	1·24 (2)	N(4)–C(4)	1·145 (9)
–C(1*A*)	1·19 (2)	C(3)–S(3)	1·643 (7)
C(1)–S(1)	1·64 (2)	C(4)–S(4)	1·631 (7)
C(1*A*)–S(1*A*)	1·58 (2)		
N(2)–C(2)	1·22 (6)	C(1)···C(1*A*)	1·34 (2)*
–C(2*A*)	1·12 (3)	C(2)···C(2*A*)	0·50 (6)*
C(2)–S(2)	1·57 (6)	S(1)···S(1*A*)	3·07 (1)*
C(2*A*)–S(2*A*)	1·70 (6)	S(2)···S(2*A*)	1·12 (3)*
N(1)–Co(1)–N(2)	92·0 (2)	N(3)–Co(2)–N(4)	91·2 (2)
–N(1,1)	178·8 (2)	–N(1,2)	177·0 (2)
–N(2,1)	91·0 (2)	–N(2,2)	90·7 (2)
–N(3,1)	92·7 (2)	–N(3,2)	87·8 (2)
–N(4,1)	89·9 (2)	–N(5,1)	94·2 (2)
N(2)–Co(1)–N(1,1)	89·0 (2)	N(4)–Co(2)–N(1,2)	90·8 (2)
–N(2,1)	176·0 (2)	–N(2,2)	95·5 (2)
–N(3,1)	91·1 (2)	–N(3,2)	175·7 (2)
–N(4,1)	89·2 (2)	–N(5,1)	87·9 (2)
N(1,1)–Co(1)–N(2,1)	88·0 (2)	N(1,2)–Co(2)–N(2,2)	86·9 (2)
–N(3,1)	86·8 (2)	–N(3,2)	90·4 (2)
–N(4,1)	90·5 (2)	–N(5,1)	88·0 (2)
N(2,1)–Co(1)–N(3,1)	91·4 (2)	N(2,2)–Co(2)–N(3,2)	88·6 (2)
–N(4,1)	88·2 (2)	–N(5,1)	173·9 (2)
N(3,1)–Co(1)–N(4,1)	177·3 (2)	N(3,2)–Co(2)–N(5,1)	88·1 (2)
Co(1)–N(1,1)–C(1,5)	125·9 (5)	Co(2)–N(1,2)–C(1,3)	127·4 (5)
–N(1,2)	126·6 (3)	–N(1,1)	125·1 (3)
–N(2,1)–C(2,5)	124·2 (4)	–N(2,2)–C(2,3)	129·3 (4)
–N(2,2)	128·8 (4)	–N(2,1)	123·2 (4)
–N(3,1)–C(3,5)	130·1 (4)	–N(3,2)–C(3,3)	122·0 (4)
–N(3,2)	123·2 (4)	–N(3,1)	128·0 (3)
–N(4,1)–C(4,5)	129·3 (5)	–N(5,1)–C(5,5)	128·5 (4)
–N(4,2)	123·2 (4)	–N(5,2)	124·6 (4)
Co(1)–N(1)–C(1)	137·4 (8)	Co(2)–N(3)–C(3)	171·5 (5)
–N(1)–C(1*A*)	155·8 (9)	–N(4)–C(4)	157·3 (5)
–N(2)–C(2)	164 (3)		
–N(2)–C(2*A*)	141 (1)		
N(1)–C(1)–S(1)	175 (1)	N(3)–C(3)–S(3)	179·0 (5)
–C(1*A*)–S(1*A*)	174 (1)	N(4)–C(4)–S(4)	179·0 (6)
N(2)–C(2)–S(2)	177 (5)		
–C(2*A*)–S(2*A*)	178 (2)		

* Distances between alternative positions of disordered atoms.

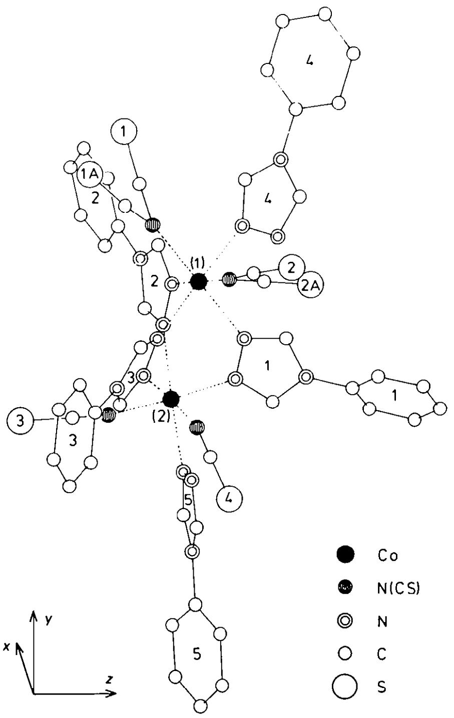

Fig. 2. A *FIGATOM* (Langlet, 1962) drawing of the binuclear unit of $Co_2(Phetrz)_5(NCS)_4.2\cdot7H_2O$. The H atoms and the disordered H_2O molecules have been omitted.

[N(1)]. The NCS^- groups attached to Co(1) are found to be disordered.

The numbering of the Phetrz groups is given in Fig. 1. One dimeric unit is depicted in Fig. 2, which also gives the numbering of the Phetrz and NCS^- groups. Relevant distances and angles are given in Tables 3 and 4. (E.s.d.'s in these and the following tables have been calculated from the e.s.d.'s in the fractional coordinates multiplied by a factor of 1·5 to account for the underestimation of the e.s.d.'s in block-diagonal least-squares refinement.)

The CoN_6 octahedra are fairly distorted, as can be seen from Table 3. Table 4 shows that the geometries of the trz rings in the Phetrz groups are less regular than those in the Metrz groups of $Mn_2(Metrz)_5(NCS)_4$. Considering the large e.s.d.'s, however, there is reasonable agreement.

The trz rings are quite planar (Table 5). The phenyl rings are somewhat less planar and highly distorted, which may partly be due to steric hindrance. The rather large angles between the phenyl and trz planes in the Phetrz groups (Table 6) indicate that between N(4) and C(6) mainly σ bonding will be present.

There are large voids between the dimeric units, containing disordered H_2O molecules. From the measured density $D_m = 1\cdot447$ (4) Mg m^{-3} (determined by the flotation method), the number of water

Table 4. *Bond lengths* (Å) *and angles* (°) *in the* Phetrz *groups in* $Co_2(Phetrz)_5(NCS)_4.2{\cdot}7\ H_2O$ *and in the* Metrz *groups in* $Mn_2(Metrz)_5(NCS)_4$ (*Engelfriet, Verschoor & Vermin*, 1979)

	Phetrz 1*	Phetrz 2*	Phetrz 3*	Phetrz 4†	Phetrz 5†	Metrz 1*	Metrz 2*	Metrz 3†
N(1)–N(2)	1·379 (8)	1·381 (8)	1·371 (7)	1·379 (9)	1·382 (7)	1·382 (3)	1·383 (3)	1·375 (4)
N(2)–C(3)	1·304 (8)	1·302 (7)	1·291 (7)	1·283 (9)	1·294 (9)	1·301 (4)	1·306 (3)	1·287 (6)
C(3)–N(4)	1·360 (8)	1·353 (8)	1·348 (7)	1·352 (9)	1·347 (9)	1·338 (4)	1·341 (3)	1·339 (5)
N(4)–C(5)	1·357 (8)	1·359 (7)	1·351 (8)	1·337 (9)	1·334 (8)	1·334 (4)	1·341 (3)	1·331 (5)
C(5)–N(1)	1·296 (5)	1·308 (7)	1·307 (8)	1·309 (9)	1·308 (9)	1·300 (4)	1·306 (3)	1·296 (5)
N(4)–C(6)	1·443 (5)	1·434 (7)	1·436 (7)	1·444 (9)	1·445 (9)	1·476 (4)	1·458 (5)	1·469 (6)
C(6)–C(7)	1·36 (1)	1·376 (9)	1·359 (9)	1·37 (1)	1·36 (1)			
C(7)–C(8)	1·40 (1)	1·38 (1)	1·39 (1)	1·41 (1)	1·39 (1)			
C(8)–C(9)	1·38 (1)	1·38 (1)	1·36 (1)	1·36 (1)	1·33 (1)			
C(9)–C(10)	1·36 (1)	1·36 (1)	1·36 (1)	1·36 (1)	1·35 (1)			
C(10)–C(11)	1·38 (1)	1·38 (1)	1·38 (1)	1·40 (1)	1·38 (1)			
C(11)–C(6)	1·38 (1)	1·377 (8)	1·376 (9)	1·36 (1)	1·35 (1)			
N(1)–N(2)–C(3)	107·5 (4)	107·0 (5)	107·1 (5)	106·3 (5)	106·1 (5)	106·2 (3)	106·5 (2)	105·1 (3)
N(2)–C(3)–N(4)	110·0 (6)	111·2 (5)	111·5 (5)	112·1 (6)	112·0 (6)	111·4 (3)	110·0 (2)	112·1 (3)
C(3)–N(4)–C(5)	104·7 (4)	104·2 (5)	103·8 (5)	103·8 (6)	104·1 (6)	104·6 (3)	105·0 (3)	103·7 (3)
N(4)–C(5)–N(1)	110·8 (6)	110·7 (5)	111·0 (5)	110·9 (6)	110·8 (6)	111·3 (3)	111·0 (2)	111·6 (3)
C(5)–N(1)–N(2)	107·0 (5)	106·9 (5)	106·6 (5)	106·8 (6)	107·0 (5)	106·6 (3)	106·5 (2)	106·5 (3)
C(5)–N(4)–C(6)	126·6 (5)	126·9 (5)	129·0 (5)	128·0 (6)	127·6 (6)	128·1 (3)	127·5 (2)	128·8 (4)
C(3)–N(4)–C(6)	128·7 (6)	128·5 (5)	127·1 (5)	128·1 (6)	128·3 (5)	127·3 (3)	127·5 (2)	127·4 (4)
C(7)–C(6)–N(4)	118·9 (6)	119·4 (5)	119·0 (5)	117·7 (6)	119·0 (6)			
C(11)–C(6)–N(4)	119·1 (6)	119·8 (5)	120·3 (5)	119·9 (6)	120·4 (6)			
C(6)–C(7)–C(8)	119·2 (7)	119·3 (6)	119·7 (7)	117·4 (7)	119·0 (7)			
C(7)–C(8)–C(9)	118·5 (8)	120·3 (6)	120·0 (8)	120·6 (9)	121·0 (7)			
C(8)–C(9)–C(10)	121·8 (7)	119·6 (6)	120·2 (7)	120·8 (9)	119·2 (7)			
C(9)–C(10)–C(11)	119·4 (8)	121·0 (6)	120·5 (7)	119·8 (8)	121·3 (7)			
C(10)–C(11)–C(6)	119·1 (7)	119·2 (6)	118·9 (7)	119·0 (7)	119·0 (7)			
C(11)–C(6)–C(7)	121·9 (5)	120·7 (6)	120·8 (6)	122·4 (7)	120·5 (7)			

* Bridging groups.
† Non-bridging groups.

Table 5. *Distances* (10^{-3} Å) *from the ring atoms and the coordinated metal atoms to the least-squares planes* (*of non-hydrogen* trz *and phenyl atoms*) *of the* Phetrz *groups*

	Ring 1	Ring 2	Ring 3	Ring 4	Ring 5
trz rings					
N(1)	2 (1)	−1 (1)	1 (1)	−4 (1)	−3 (1)
N(2)	−5 (1)	2 (1)	−2 (1)	3 (2)	0 (2)
C(3)	6 (2)	−3 (2)	2 (2)	0 (2)	3 (2)
N(4)	−5 (1)	2 (1)	−1 (1)	−2 (1)	−5 (1)
C(5)	2 (2)	0 (2)	0 (2)	4 (2)	5 (2)
C(6)*	−43 (2)	144 (2)	−73 (2)	1 (2)	−2 (2)
Co(1)*	−217 (1)	98 (1)	−41 (1)	−280 (1)	—
Co(2)*	−48 (1)	256 (1)	−569 (1)	—	23 (1)
Phenyl rings					
C(6)	9 (2)	0 (2)	7 (2)	−6 (2)	−13 (2)
C(7)	−10 (3)	0 (2)	−8 (2)	8 (2)	4 (2)
C(8)	−1 (3)	−3 (2)	1 (2)	−4 (3)	9 (3)
C(9)	14 (3)	6 (2)	6 (2)	−2 (3)	−13 (3)
C(10)	−15 (3)	−6 (2)	−7 (2)	3 (3)	4 (3)
C(11)	4 (3)	4 (2)	1 (2)	1 (2)	9 (2)
N(4)*	3 (1)	76 (1)	22 (1)	−22 (1)	17 (1)

* Not included in the calculation of the least-squares plane.

Table 6. *Angles between least-squares planes of bridging* trz *units and those between a* trz *plane and the phenyl ring attached to it* (°)

trz(1), trz(2)	118·0 (2)
trz(2), trz(3)	126·1 (2)
trz(3), trz(1)	114·3 (2)
trz(1), $\varphi(1)$	33·1 (4)
trz(2), $\varphi(2)$	13·5 (3)
trz(3), $\varphi(3)$	27·8 (3)
trz(4), $\varphi(4)$	48·3 (4)
trz(5), $\varphi(5)$	27·6 (4)

molecules per dimer is calculated as 2·7 (3). This number is in good agreement with the value of 2·6 obtained from the estimated occupation rates of the H_2O molecules in the least-squares refinement.

Fig. 3 presents a projection on $x = 0$ of a pair of Co^{II} ions and the H_2O molecules surrounding the corresponding dimeric unit. The figure clearly shows that there are two voids, one containing $H_2O(1)$ and $H_2O(2)$, and the other the remaining H_2O molecules. Further, it can be seen that the remaining peaks in the

Table 7. *Distances* (Å) (<4·0 Å) *between* H_2O *molecules and between* H_2O *molecules and nearest atoms in a dimeric unit*

Distances between H_2O molecules and non-sulphur atoms are ≤3·0 Å only.

H_2O(1)–H_2O(2)	0·70 (2)	H_2O(1)– H(1,3)	2·54 (1)
H_2O(3)–H_2O(4)	1·14 (4)	– H(4,7)	2·76 (1)
–H_2O(7)	1·31 (3)	H_2O(2)– H(1,3)	2·53 (2)
–H_2O(8)	2·47 (3)	H_2O(3)– H(1,8)	2·88 (2)
H_2O(4)–H_2O(5)	3·53 (5)	– H(3,5)	2·77 (2)
–H_2O(7)	1·47 (4)	– H(5,3)	2·47 (2)
–H_2O(8)	1·98 (5)	H_2O(4)– C(1*A*)	2·42 (4)
H_2O(5)–H_2O(6)	1·59 (4)	– H(3,5)	2·91 (4)
H_2O(5)–H_2O(7)	2·95 (5)	H_2O(5)– H(2,3)	2·90 (3)
–H_2O(8)	1·68 (5)	– H(2,7)	2·78 (3)
H_2O(7)–H_2O(8)	1·34 (4)	– H(3,8)	2·69 (3)
		– H(3,11)	2·76 (3)
H_2O(1)–S(2*A*)	3·31 (1)	H_2O(6)– C(1)	2·37 (3)
–S(4)	3·44 (1)	– H(2,3)	2·35 (3)
H_2O(2)–S(2)	3·38 (3)	– H(2,7)	2·89 (3)
–S(2*A*)	2·68 (2)	– H(2,11)	3·00 (3)
–S(4)	3·47 (2)	H_2O(7)– H(3,5)	2·50 (3)
H_2O(3)–S(1*A*)	3·53 (2)	– H(3,11)	2·72 (3)
–S(2)	3·94 (3)	– H(5,3)	2·79 (3)
H_2O(4)–S(1*A*)	2·44 (4)	H_2O(8)– H(3,5)	2·96 (3)
H_2O(5)–S(1)	2·04 (3)	– H(3,8)	2·74 (3)
–S(1*A*)	3·25 (4)	– H(3,11)	2·31 (3)
–S(3)	3·30 (4)		
H_2O(6)–S(1)	0·76 (3)		
–S(1*A*)	3·52 (3)		
–S(3)	3·91 (3)		
H_2O(7)–S(1*A*)	3·71 (3)		
–S(3)	3·62 (3)		
H_2O(8)–S(1)	3·60 (3)		
–S(1*A*)	3·58 (3)		
	3·39 (3)		
–S(3)	3·48 (3)		

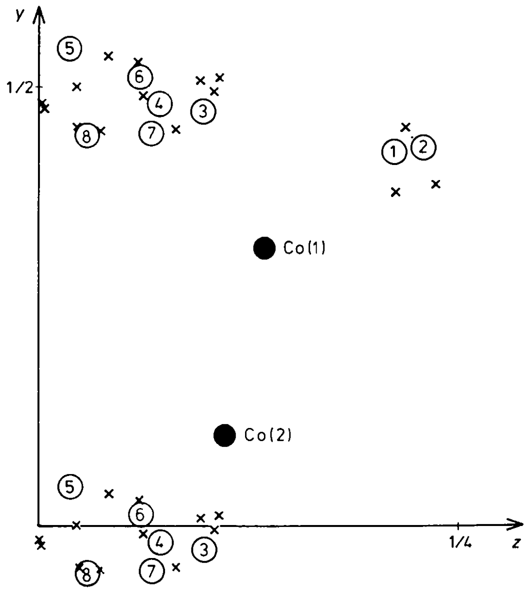

Fig. 3. Projection on $x = 0$ of the Co^{II} ions (black circles) of a dimeric unit and the surrounding H_2O molecules (open circles). The crosses indicate the remaining peaks in the final difference-Fourier synthesis.

Table 8. *Intermolecular distances* (Å) (<3·0 Å) *between neighbouring dimeric units*

S(1)–H(2,3)	2·716 (5)	C(4)–H(4,11)	2·833 (7)
–H(2,7)	2·882 (5)	C(1,9)–H(4,5)	2·994 (7)
S(1*A*)–S(1*A*)	2·603 (7)	C(2,3)–H(3,10)	2·979 (5)
		C(2,9)–H(5,11)	2·658 (5)
C(2)–H(1,8)	2·71 (4)	C(3,9)–H(2,9)	2·966 (7)
–H(5,7)	2·54 (4)	C(3,10)–H(2,9)	2·943 (6)
C(2*A*)–H(5,7)	2·86 (2)	H(1,9)–H(2,7)	2·783 (6)
S(2)–H(1,7)	2·72 (2)	–H(5,10)	2·855 (9)
–H(4,3)	2·81 (2)	H(2,8)–H(3,9)	2·742 (6)
–H(5,7)	2·57 (2)	H(2,9)–H(3,9)	2·673 (7)
S(2*A*)–H(4,3)	2·89 (1)	–H(3,10)	2·613 (6)
C(3)–H(2,10)	2·795 (6)	–H(5,11)	2·670 (5)
–H(3,10)	2·688 (6)	H(2,10)–H(5,5)	2·976 (5)
S(3)–H(3,3)	2·857 (4)	–H(3,3)	2·995 (5)
N(4)–H(4,11)	2·720 (6)	H(4,8)–H(5,8)	2·464 (8)
		–H(5,9)	2·67 (1)
		H(4,9)–H(5,8)	2·892 (9)

difference Fourier map after least-squares refinement are lying within the voids. These peaks may be due to H atoms of H_2O molecules and to H_2O molecules with a very low occupation rate. It seems likely that the H_2O molecules are connected to the nearest S atoms by hydrogen bonding. O–S distances in the range 3·2–3·6 Å are reasonable for O–H···S bonding (Hamilton & Ibers, 1968). Table 7 shows that for most of the H_2O molecules there is an O–S distance within this range. The occurrence of O–S distances that are much shorter than 3·2 Å can be related to disorder in the NCS^- groups, *e.g.* H_2O(6) will be absent when S(1) is present. Furthermore, the short distances between some of the H_2O molecules suggest that O–H···O bridging may also be present. All other intermolecular bonding (see Tables 7 and 8) will probably be of the van der Waals type.

As regards the presence of solvent molecules in the structure, it is interesting to mention here that compounds slightly differing from the present one can be prepared from other polar solvents like MeCN, MeOH and EtOH (Haasnoot & Groeneveld, 1980). Their infrared spectra, which show the presence of solvent molecules, are very similar to that of the title compound; probably they also consist of dimers. These compounds too, turn blue on powdering. Examination of a crystal obtained from MeCN showed it to be monoclinic with $a = 15{\cdot}62$, $b = 18{\cdot}64$, $c = 19{\cdot}53$ Å, $\beta = 109{\cdot}3°$, with four dimeric formula units per cell. From the measured density, $D_m = 1{\cdot}436$ (5) Mg m^{-3}, it can be calculated that the compound might contain two molecules of MeCN per dimer, although the presence of H_2O cannot be excluded. Most of the MeCN appeared to have gone after a few months, leading to disintegration of the crystals. Thus, the solvent molecules seem to play an essential role in stabilizing these structures. This is further supported by the observation that from polar solvents consisting of larger molecules than the ones previously mentioned, like dioxane and DMF, only blue powders could be obtained, indicating the presence of tetrahedrally coordinated Co^{II}. Apparently, the size of these solvent molecules is unsuitable for stabilizing a structure with dimeric units.

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