

Fig. 2. Clinographic projection of the structure along *c*, showing the molecular packing.

Some very short intramolecular contact distances involving H atoms occur [S(1)···H1(C2) 2.54 (10), S(3)···H2(C12) 2.51 (11), N(1)···H(C4) 2.54 (11) and N(2)···H(C18) 2.54 (11) Å], the S···H and N···H van der Waals distances being 3.00 and 2.75 Å, respectively (Bondi, 1964)]. Since the observed *X*···

H—C angles (*X* = S, N) are less than 117° these close contacts probably do not involve hydrogen bonding. There are no unusual intermolecular *X*···H interactions and the crystal cohesion is thus dominated by normal van der Waals forces. A clinographic projection of the structure showing the molecular packing is shown in Fig. 2.

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Structure of Dichloro[2,5-dimethyl-1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-diazahexane-*N,N',N'',N'''*]cadmium(II)

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Abstract. [CdCl₂(C₁₆H₂₈N₆)], *M_r* = 487.76, orthorhombic, *Pbcn*, *a* = 15.936 (2), *b* = 8.4044 (8), *c* = 15.454 (2) Å, *V* = 2069.8 Å³, *Z* = 4, *D_x* =

1.565 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 13.1 cm⁻¹, *F*(000) = 989.1, *T* = 295 K, molecular symmetry *C*_{2v}, *R* = 0.031 for 1747 significant reflections. The coordination of the cadmium atoms is distorted octahedral, although no unusual bond lengths or angles occur [Cd—Cl 2.501 (1) Å, Cd—N 2.478 (3) and 2.431 (3) Å]. The coordination geometry is similar to

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that of a similar nickel compound, although the Cd coordination octahedron is more distorted than that of Ni.

Introduction. Recently a series of compounds of general formula $M(\text{debd})X_2$ has been synthesized (Paap, Driessen, Reedijk, Kojić-Prodić & Spek, 1985), where $\text{debd} = 2,5\text{-dimethyl-1,6-(3,5-dimethyl-1-pyrazolyl)-2,5-diazahexane}$, M is a first-row transition metal and X is thiocyanate, azide or halide. With chloride and bromide only compounds with manganese and cadmium could be synthesized, which is probably due to steric factors. The cadmium compound was expected to have a structure similar to that of $\text{Ni}(\text{debd})(\text{N}_3)_2$, whose crystal structure has been determined previously (Paap *et al.*, 1985). To prove this and to investigate how debd chelates to large metal ions, the structure of $\text{Cd}(\text{debd})\text{Cl}_2$ was determined.

Experimental. Crystals obtained from methanolic solution; crystal dimensions approximately $0.25 \times 0.15 \times 0.10$ mm; cell constants from setting angles of 24 reflections ($10 < \theta < 12^\circ$) centered on Enraf-Nonius CAD-4 four-circle diffractometer (graphite-monochromated $\text{Mo K}\alpha$). Azimuth scan type, $2 < \theta < 30^\circ$; intensities corrected for Lorentz and polarization effects; 3421 reflections measured, 3418 independent, $R_{\text{int}} = 0.0056$; $h = 0-22$, $k = 0-11$, $l = 0-21$; 1747 reflections with $I > 2\sigma(I)$ considered observed; position of Cd derived from Patterson synthesis, those of other atoms from subsequent Fourier maps. Full-matrix least-squares refinement (F values) with anisotropic thermal parameters for non-hydrogen atoms. H atoms located from difference Fourier maps and refined isotropically. All H atoms assigned same B value which was refined. $R = 0.0312$, $wR = 0.0435$, $w = 1/\sigma^2(F)$, $S = 1.515$, $A_{\text{max}}/\sigma < 0.01$. Maximum $\Delta\rho$ excursion in final difference Fourier map $0.89 \text{ e } \text{Å}^{-3}$, within 0.9 Å of Cd. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Programs written or modified by Mr E. W. Rutten-Ceulemans and Dr R. A. G. de Graaff used on the Leiden University Amdahl V7B computer.

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.* Bond lengths and angles are given in Table 2. An ORTEP drawing (Johnson, 1965) of the molecule indicating the atomic numbering scheme is shown in Fig. 1. H atoms have been omitted for clarity.

* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42782 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^5$ for Cd, $\times 10^4$ for all other atoms) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$ for Cd, $\text{Å}^2 \times 10^2$ for all other atoms) with *e.s.d.*'s in parentheses

	$B_{\text{eq}} = (8/3) \pi^2 \text{ trace } \bar{U}$			
	x	y	z	B_{eq}
Cd(1)	0	807 (1)	25000	2796 (9)
Cl(2)	163 (1)	1941 (1)	1248 (1)	472 (2)
N(3)	152 (1)	-2275 (3)	3452 (2)	303 (6)
C(4)	292 (3)	-3686 (4)	2892 (3)	376 (8)
C(5)	-567 (2)	-2497 (5)	4028 (3)	437 (10)
C(10)	878 (2)	-1917 (5)	3987 (2)	386 (9)
N(11)	1598 (1)	-1512 (3)	3437 (2)	319 (6)
N(12)	1463 (2)	-641 (4)	2713 (2)	330 (7)
C(13)	2220 (2)	-534 (4)	2333 (2)	357 (8)
C(14)	2816 (2)	-1317 (4)	2834 (3)	409 (9)
C(15)	2404 (2)	-1940 (4)	3529 (2)	349 (7)
C(16)	2330 (3)	286 (6)	1497 (3)	485 (11)
C(17)	2725 (3)	-2877 (6)	4281 (3)	486 (11)

Table 2. Intramolecular distances (Å) and angles ($^\circ$)

Coordination sphere			
Cd-Cl	2.5012 (9)		
Cd-N(3)	2.478 (3)		
Cd-N(12)	2.431 (3)		
Cl-Cd-N(12)	99.25 (7)	N(3)-Cd-N(12)	68.08 (9)
Cl-Cd-N(3)	161.50 (7)	N(3)-Cd-N(3)	74.0 (1)
Cl-Cd-N(3)	92.87 (7)	N(3)-Cd-N(12)	88.57 (9)
Cl-Cd-N(12)	98.68 (7)	N(12)-Cd-N(12)	151.1 (2)
Cl-Cd-Cl	102.64 (5)		
debd ligand			
N(3)-C(5)	1.463 (5)	C(15)-C(14)	1.362 (5)
N(3)-C(4)	1.486 (5)	C(14)-C(13)	1.391 (5)
N(3)-C(10)	1.454 (4)	C(13)-C(16)	1.475 (6)
C(10)-N(11)	1.467 (4)	C(13)-N(12)	1.345 (4)
N(11)-C(15)	1.342 (4)	N(12)-N(11)	1.355 (4)
C(15)-C(17)	1.494 (6)	C(4)-C(4)	1.528 (8)
Cd(1)-N(12)-N(11)	113.5 (2)	N(12)-N(11)-C(15)	112.6 (3)
Cd(1)-N(12)-C(13)	141.7 (2)	N(11)-C(10)-N(3)	109.9 (3)
N(12)-C(13)-C(16)	121.3 (4)	C(10)-N(3)-C(5)	107.7 (3)
N(12)-C(13)-C(14)	109.8 (3)	C(10)-N(3)-C(4)	112.2 (3)
C(13)-C(14)-C(15)	107.0 (3)	N(3)-C(4)-C(4)	111.8 (3)
C(14)-C(15)-C(17)	130.6 (3)	Cd(1)-N(3)-C(10)	104.5 (2)
C(14)-C(15)-N(11)	106.0 (3)	Cd(1)-N(3)-C(5)	112.8 (2)
N(11)-C(15)-C(17)	123.4 (3)	Cd(1)-N(3)-C(4)	107.8 (2)
N(12)-N(11)-C(10)	118.7 (3)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$

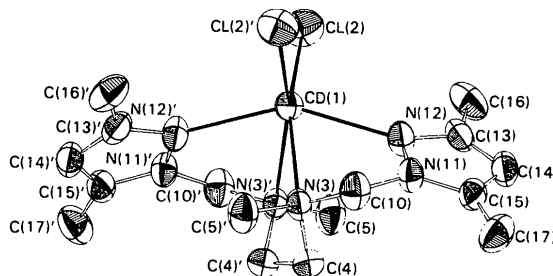


Fig. 1. ORTEP representation of $\text{Cd}(\text{debd})\text{Cl}_2$, indicating the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

As expected, the molecule has a symmetrical *cis* coordination analogous to that of Ni(debd)(N₃)₂ (Paap *et al.*, 1985). The Cd—Cl and the Cd—N bonds are comparable with literature values (Cannas, Marongiu & Saba, 1980; Kleywegt, Wiesmeijer, Van Driel, Driessen, Reedijk & Noordik, 1985). The pyrazole rings are planar to within 0.02 Å. Comparison of the ligand geometry of the title compound with that of Ni(debd)(N₃)₂ shows no significant differences between the two. However, the metal coordination spheres differ significantly. The Cd octahedron is more distorted than the Ni octahedron. This can be seen from comparison of the N(12)—M—N(12') angle, which is 151° in the Cd compound and 171° in the Ni compound. The steric constraints of the ligand obviously make it more suitable to accommodate the smaller Ni²⁺ ion (coordination distances ~2.15 Å) than the larger Cd²⁺ ion (coordination distances ~2.50 Å). On the other hand, the more distorted octahedron is able to accommodate the larger Cl⁻ anions, which do not bind to the smaller ion in combination with the debd ligand.

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Structure of Tris- μ -[bis(8-quinolinolato)hydrogen(I)-N,O]-dinickel(II) Thiocyanate Monohydrate

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Abstract. [Ni₂{H(C₉H₆NO)₂}₃](SCN).H₂O, *M_r* = 1061.4, monoclinic, *C2/c*, *a* = 21.269 (3), *b* = 15.004 (1), *c* = 15.481 (2) Å, β = 101.732 (9)°, *V* = 4837.2 (9) Å³, *Z* = 4, *D_m* = 1.47 (1), *D_x* = 1.46 Mg m⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 0.88 mm⁻¹, *F*(000) = 2192, *T* = 298 K, *R* = 0.045 for 4747 unique observed reflections. The crystal contains dinuclear cations made up of two Ni complexes joined face to face by three strong O—H...O hydrogen bonds of distances 2.402 (2) and 2.448 (2) Å. The counter SCN⁻ is orientationally disordered, its N atom lying on a twofold (2) axis and the remaining C and S atoms each being located on the two sites related by 2 symmetry. A water molecule is hydrogen-bonded to an SCN⁻ ion to form an O(*W*)...N—C—S linear array. These dinuclear cations and the disordered, hydrated thiocyanate anions are arranged in the NaCl-type structure.

Introduction. In previous papers the crystal structures of the novel dimeric nickel 8-quinolinol complexes with triiodide and perchlorate anions were reported (Kiriyaama, Fukuda, Yamagata & Sekido, 1985; Kiriyaama, Yamagata, Yonetani & Sekido, 1986). Both structures contain the unique dinuclear cation in which two nickel complexes with three bidentate 8-quinolinol ligands in facial conformation are joined face to face by three very strong O—H...O hydrogen bonds. These facts suggest that the hydrogen-bonded dinuclear cations are essential for the nickel 8-quinolinol complexes in the presence of anions and excess 8-quinolinol in organic solvents. The present structural study was extended to the corresponding thiocyanate complex. Better crystals were obtained and a more accurate structure determination could be carried out.

Experimental. Yellow nickel(II) chloride (10 mmol in 30 ml of ethanol) and 8-quinolinol (60 mmol in 30 ml of ethanol) were added to a sodium thiocyanate solution (20 mmol in 200 ml ethanol) dropwise with stirring.

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