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Structures of Bis(1,4,7-triazacyclononane)cadmium(II) Diperchlorate, $[Cd(tacn)_2](ClO_4)_2$ (1), and Bis(1,4,7-triazacyclononane)cadmium(II) Bis(tetraphenylborate) Bis(dimethyl sulfoxide) Solvate, $[Cd(tacn)_2](BPh_4)_2.2(CH_3)_2SO$ (2)

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Abstract. (1) $[Cd(C_6H_{15}N_3)_2](ClO_4)_2$, $M_r = 569.7$, triclinic, $P\bar{1}$, $a = 9.228\,(1)$, $b = 9.533\,(1)$, $c = 14.095\,(2)$ Å, $\alpha = 80.45\,(1)$, $\beta = 89.79\,(1)$, $\gamma = 62.45\,(1)°$, $V = 1080.3$ Å^3, $Z = 2$, $D_m = 1.76$, $D_x = 1.751$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 12.58$ cm^{-1}, $F(000) = 580$, $T = 297$ K, $R = 0.029$ for 3512 unique reflections with $I > 2\sigma(I)$. (2) $[Cd(C_6H_{15}N_3)_2][B(C_6H_5)_4]_2.2(CH_3)_2SO$, $M_r = 1165.6$, triclinic, $P\bar{1}$, $a = 11.298\,(2)$, $b = 11.364\,(2)$, $c = 13.936\,(3)$ Å, $\alpha = 74.78\,(1)$, $\beta = 71.05\,(1)$, $\gamma = 67.45\,(1)°$, $V = 1543.3$ Å^3, $Z = 1$, $D_m = 1.26$, $D_x = 1.254$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.34$ cm^{-1}, $F(000) = 614$, $T = 297$ K, $R = 0.040$ for 4977 unique reflections with $I > 2\sigma(I)$. The 1,4,7-triazacyclononane (tacn) macrocycles act as tridentate ligands. In both compounds, the $[Cd(tacn)_2]^{2+}$ complexes are located on crystallographic centres of inversion. Each Cd ion is surrounded by an N_6 coordination polyhedron which can be described as a trigonally elongated octahedron. The average Cd—N bond distances are 2.36 (1) Å [range 2.351 (3)–2.382 (3) Å] for (1) and 2.36 (6) Å [range 2.301 (8)–2.443 (8) Å] for (2).

Introduction. Very few homoleptic cadmium complexes of non-aromatic nitrogen ligands have been structurally characterized. Examples are $[Cd(NH_3)_6]^{2+}$ (Yamaguchi & Ohtaki, 1979), $[Cd(H_2NCH_2CH_2NH_2)_3]^{2+}$ (Breitwieser, Göttlicher & Paulus, 1984; Liu & Huang, 1986) and the eight-coordinate complex $[Cd(C_{12}H_{22}N_6)_2]^{2+}$ (Strasdeit & Pohl, 1988). In a study on the structural properties of this type of complex, we have prepared some new coordination compounds containing $[CdL_2]^{2+}$ [L = 4-azaheptane-1,7-diamine (dipropylenetriamine), 1,4,7-triazacyclononane (tacn), 1,4,7,10-tetraazacyclododecane (cyclen)] and $[CdL_2]^{2+}$ ions [L = 3,6,9,12-tetraazatetradecane-1,14-diamine (linear pentaethylenehexamine)], and determined their X-ray structures. Some of these compounds are also interesting from a bioinorganic point of view, as several aliphatic polyamines occur in organisms (Oshima, 1983; Tabor & Tabor, 1984; Kuehn, Rodriguez-Garay, Bagga & Phillips, 1990) where they are potential ligands for metal ions.

In the present paper we describe the isolation and the molecular structure of $[Cd(tacn)_2]^{2+}$ as ClO_4^- salt (1). Compound (2) was also studied, but disorder of the complex cation prevented accurate structural data.

Experimental. Compound (1). A solution of $Cd(ClO_4)_2.6H_2O$ (0.21 g, 0.5 mmol) in methanol (20 ml) was added dropwise to a stirred solution of tacn (0.13 g, 1.0 mmol) in methanol (20 ml). On standing at *ca* 273 K for 24 h colourless crystals of (1) formed. The density was measured by flotation in tetrachloromethane/bromoform. It should be mentioned that by reaction with tacn.3HBr + 3NaOH instead of the free amine, (1) could not be obtained.

Diffraction data of a rhombic crystal of dimensions 0.42 × 0.30 × 0.21 mm were collected with a Siemens/Stoe AED-2 automated four-circle diffractometer. Cell constants were derived from least-squares refinement of the setting angles of 38 reflections in the range $31.5 < 2\theta < 38.4°$. 4661 reflections were measured in the range $3 < 2\theta < 52°$; ω–2θ scan mode; $0 \leq h \leq 11$, $-11 \leq k \leq 11$, $-17 \leq l \leq 17$. Three standard reflections (511, $01\bar{8}$ and 044) were measured every 45 min; maximum loss in intensity 8%. Corrections for decay and Lp effects; no absorption correction, as no significant absorption effects occurred; 4235 unique reflections; $R_{\text{int}} = 0.011$; 3512 reflections with $I > 2\sigma(I)$ were used in the refinement.

The structure was solved by direct methods. H-atom positions in NH groups were taken from difference syntheses and refined ($U = 0.06$ Å^2). The H atoms of the CH_2 groups were included at idealized positions (C—H 1.08 Å, $U = 0.07$ Å^2). Aniso-

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Table 1. *Fractional atomic coordinates and equivalent isotropic displacement factors* ($Å^2 \times 100$) *for* (1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cd(1)	0.0	1.0	0.0	3.55 (1)
Cd(2)	0.5	0.0	0.5	3.75 (1)
Cl(1)	0.07360 (9)	0.83507 (9)	0.36935 (5)	3.96 (2)
Cl(2)	0.42484 (12)	0.21103 (16)	0.82826 (8)	7.36 (3)
O(1)	0.2166 (4)	0.6958 (4)	0.3548 (2)	8.1 (1)
O(2)	0.1085 (5)	0.9652 (4)	0.3593 (3)	10.1 (1)
O(3)	−0.0562 (4)	0.8719 (5)	0.3000 (2)	9.7 (1)
O(4)	0.0295 (4)	0.8089 (4)	0.4640 (2)	8.6 (1)
O(5)	0.3406 (6)	0.1251 (8)	0.8178 (4)	16.8 (2)
O(6)	0.5748 (5)	0.1462 (6)	0.7881 (4)	13.4 (2)
O(7)	0.4466 (7)	0.2148 (9)	0.9239 (3)	17.8 (3)
O(8)	0.3286 (9)	0.3651 (7)	0.7869 (5)	20.9 (2)
N(1)	−0.0592 (3)	0.8724 (3)	−0.1130 (2)	4.26 (6)
N(2)	0.0137 (4)	0.7657 (3)	0.0942 (2)	4.63 (7)
N(3)	0.2591 (3)	0.7906 (3)	−0.0243 (2)	4.74 (7)
N(4)	0.5734 (3)	0.1114 (3)	0.3555 (2)	4.04 (6)
N(5)	0.4725 (4)	0.2466 (3)	0.5303 (2)	4.52 (6)
N(6)	0.2482 (3)	0.1928 (3)	0.4161 (2)	4.26 (6)
C(1)	−0.1456 (5)	0.7948 (5)	−0.0566 (3)	5.37 (9)
C(2)	−0.0488 (5)	0.6861 (4)	0.0362 (3)	5.29 (9)
C(3)	0.1905 (5)	0.6681 (4)	0.1279 (2)	5.94 (9)
C(4)	0.3007 (4)	0.6404 (4)	0.0449 (3)	5.49 (8)
C(5)	0.2410 (4)	0.7796 (4)	−0.1270 (2)	5.03 (8)
C(6)	0.0932 (4)	0.7586 (4)	−0.1512 (2)	4.88 (8)
C(7)	0.6512 (4)	0.1988 (4)	0.3924 (3)	4.65 (8)
C(8)	0.5412 (4)	0.3179 (4)	0.4534 (3)	4.63 (8)
C(9)	0.2919 (4)	0.3411 (4)	0.5342 (3)	5.36 (9)
C(10)	0.1954 (4)	0.3507 (4)	0.4435 (3)	5.36 (9)
C(11)	0.2785 (4)	0.1903 (5)	0.3139 (2)	5.16 (9)
C(12)	0.4277 (4)	0.2136 (5)	0.2867 (2)	5.08 (8)
H(N1)	−0.124 (5)	0.943 (5)	−0.158 (3)	
H(N2)	−0.030 (5)	0.777 (5)	0.141 (3)	
H(N3)	0.333 (5)	0.822 (5)	−0.020 (3)	
H(N4)	0.641 (5)	0.036 (5)	0.331 (3)	
H(N5)	0.524 (5)	0.240 (5)	0.583 (3)	
H(N6)	0.187 (5)	0.159 (5)	0.426 (3)	

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement factors* ($Å^2 \times 100$) *for* (2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cd	0.5	0.5	0.5	5.50 (1)
N(1*A*)*	0.6106 (5)	0.3806 (5)	0.3669 (4)	7.6 (1)
N(2*A*)*	0.7309 (6)	0.4626 (7)	0.4812 (5)	9.1 (2)
N(3*A*)*	0.5758 (6)	0.2899 (5)	0.5841 (4)	8.1 (1)
N(1*B*)*	0.3082 (8)	0.5464 (8)	0.6381 (5)	7.8 (2)
N(2*B*)*	0.3333 (7)	0.6267 (8)	0.4202 (5)	7.7 (2)
N(3*B*)*	0.4542 (10)	0.7202 (9)	0.5236 (8)	9.5 (3)
S(*A*)*	0.6336 (2)	0.7057 (2)	0.0985 (1)	9.95 (5)
S(*B*)*	0.5029 (3)	0.6284 (3)	0.1045 (2)	7.81 (7)
S(C)*	0.5681 (17)	0.6642 (15)	0.1257 (13)	10.2 (4)†
O(*A*C)*	0.6063 (5)	0.6772 (5)	0.2126 (3)	13.4 (2)
O(*B*C)*	0.4975 (7)	0.5875 (7)	0.2178 (4)	10.3 (2)
B	0.2554 (3)	0.2446 (3)	0.2783 (2)	5.50 (7)
C(*A*)*	0.6348 (17)	0.5828 (11)	0.0509 (8)	16.2 (4)
C(*B*)*	0.4384 (16)	0.8008 (18)	0.0896 (14)	9.3 (6)†
C(*A*C)*	0.4903 (8)	0.8179 (7)	0.0723 (5)	9.2 (2)
C(*B*C)*	0.6638 (26)	0.5579 (24)	0.0504 (21)	15.4 (10)†
C(1*A*)*	0.7554 (6)	0.3701 (8)	0.3285 (5)	8.8 (2)
C(2*A*)*	0.7916 (10)	0.4383 (17)	0.3799 (12)	16.9 (7)
C(3*A*)*	0.7861 (5)	0.3337 (9)	0.5449 (5)	9.8 (2)
C(4*A*)*	0.6860 (7)	0.2826 (10)	0.6229 (6)	9.8 (2)
C(5*A*)*	0.6243 (10)	0.1956 (7)	0.5105 (8)	11.5 (3)
C(6*A*)*	0.5873 (13)	0.2590 (7)	0.4060 (9)	9.8 (3)
C(1*B*)*	0.2012 (22)	0.5533 (21)	0.6152 (20)	12.0 (7)†
C(2*B*)*	0.2288 (16)	0.5783 (16)	0.4899 (13)	9.9 (5)†
C(3*B*)*	0.3307 (20)	0.7612 (16)	0.4041 (13)	11.6 (6)†
C(4*B*)*	0.4135 (15)	0.7868 (17)	0.4286 (13)	11.6 (5)†
C(5*B*)*	0.3467 (15)	0.7588 (17)	0.6133 (15)	11.9 (7)†
C(6*B*)*	0.3233 (15)	0.6403 (11)	0.6837 (9)	9.4 (3)†
C(7)	0.0926 (3)	0.1016 (2)	0.3523 (2)	6.17 (6)
C(8)	0.0258 (3)	0.0277 (3)	0.3416 (3)	7.59 (8)
C(9)	0.0436 (4)	−0.0015 (3)	0.2473 (3)	8.85 (10)
C(10)	0.1292 (4)	0.0437 (4)	0.1637 (3)	10.04 (12)
C(11)	0.1962 (4)	0.1176 (4)	0.1749 (2)	8.40 (10)
C(12)	0.1798 (3)	0.1509 (3)	0.2693 (2)	5.84 (6)
C(13)	0.1342 (3)	0.3236 (3)	0.4612 (2)	6.44 (7)
C(14)	0.1127 (3)	0.3106 (3)	0.5671 (2)	6.68 (7)
C(15)	0.1981 (3)	0.2135 (3)	0.6175 (2)	5.87 (6)
C(16)	0.3057 (3)	0.1299 (3)	0.5613 (2)	6.85 (7)
C(17)	0.3263 (3)	0.1443 (3)	0.4556 (2)	6.24 (7)
C(18)	0.2400 (2)	0.2396 (2)	0.4015 (2)	4.99 (5)
C(19)	0.4960 (3)	0.2670 (3)	0.1750 (2)	7.36 (8)
C(20)	0.6316 (4)	0.2152 (4)	0.1349 (3)	9.53 (12)
C(21)	0.6925 (3)	0.0864 (4)	0.1374 (3)	9.05 (11)
C(22)	0.6170 (3)	0.0059 (4)	0.1806 (3)	8.31 (9)
C(23)	0.4807 (3)	0.0581 (3)	0.2214 (2)	6.86 (7)
C(24)	0.4145 (3)	0.1895 (2)	0.2210 (2)	5.46 (6)
C(25)	0.2179 (3)	0.4978 (3)	0.2380 (2)	7.52 (8)
C(26)	0.1651 (4)	0.6243 (3)	0.1935 (3)	9.65 (11)
C(27)	0.0758 (5)	0.6535 (4)	0.1372 (3)	11.57 (12)
C(28)	0.0382 (4)	0.5572 (4)	0.1260 (3)	10.65 (11)
C(29)	0.0927 (3)	0.4303 (3)	0.1699 (2)	8.20 (8)
C(30)	0.1859 (3)	0.3945 (3)	0.2267 (2)	6.15 (7)

* Disordered atoms with occupancies: N(1*A*), N(2*A*), N(3*A*), S(*A*), C(*A*), C(1*A*)–C(6*A*) 0.60; N(1*B*), N(2*B*), N(3*B*), C(*B*C), C(1*B*)–C(6*B*) 0.40; S(*B*), C(*B*) 0.32; S(C) 0.08; O(*A*C) 0.64; O(*B*C) 0.36; C(*A*C) 0.68.

† U_{iso}.

tropic refinement of all non-H atoms; $\sum w(|F_o| - |F_c|)^2$ was minimized, $w = k/[\sigma^2(F_o) + 0.0002F_o^2]$, $k = 1.6458$; full-matrix least-squares refinement (on F) of 283 parameters converged at $R = 0.029$, $wR = 0.032$, $(\Delta/\sigma)_{max} = 0.001$ in final refinement cycle; residual electron density in the range −0.51 to 0.62 e $Å^{-3}$.

Compound (2). $Cd(O_2CCH_3)_2.2H_2O$ (0.27 g, 1.0 mmol) was added to a solution of tacn.3HBr (0.74 g, 2.0 mmol) and NaOH (0.27 g, 6.7 mmol) in methanol (25 ml). After addition of $NaBPh_4$ (0.68 g, 2.0 mmol) a white precipitate formed which was isolated, thoroughly washed with methanol and dried *in vacuo*. A sample (0.1 g) was dissolved in dimethyl sulfoxide (*ca* 1.5 ml) in a test tube. Colourless crystals of (2) were grown by layering methanol over this solution. Their density was determined by flotation in toluene/chloroform.

Diffraction data of a crystal fragment of dimensions 0.68 × 0.38 × 0.23 mm were collected; diffractometer as for (1). Cell constants were obtained from least-squares refinement of 28 reflections in the range $25.0 < 2\theta < 29.4°$. 5670 reflections were measured in the range $3 < 2\theta < 50°$; ω–2θ scan mode; $-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $0 \leq l \leq 16$. Three standard reflections ($0\bar{5}1$, 544 and $0\bar{1}7$) were measured every 45 min. Corrections for a small loss of intensity (maximum 3%) and Lp effects; no absorption correction, as no significant absorption effects were observed; 5427 unique reflections; $R_{int} = 0.012$; 4977 reflections with $I > 2\sigma(I)$ were used in the refinement.

The structure was solved in space group $P\bar{1}$ by tentatively placing the Cd atom at $x = 0.5$, $y = 0.5$, $z = 0.5$. All H atoms within the cation and the anion were given idealized positions [N—H and C—H 1.08 Å, $U(NH) = 0.11$ $Å^2$, $U(CH_2) = 0.16$ $Å^2$, $U(CH) = 0.10$ $Å^2$]. The dimethyl sulfoxide molecule was described as triply disordered. Its H atoms were not included. All non-H atoms were anisotropically

Table 3. *Selected bond distances* (Å) *and angles* (°) *for* (1)

Cd(1)—N(1)	2.362 (3)	Cd(2)—N(4)	2.382 (3)
Cd(1)—N(2)	2.351 (3)	Cd(2)—N(5)	2.357 (3)
Cd(1)—N(3)	2.372 (3)	Cd(2)—N(6)	2.351 (3)
N(1)—Cd(1)—N(2)	76.0 (1)	N(4)—Cd(2)—N(5)	76.1 (1)
N(1)—Cd(1)—N(3)	75.4 (1)	N(4)—Cd(2)—N(6)	75.5 (1)
N(2)—Cd(1)—N(3)	75.3 (1)	N(5)—Cd(2)—N(6)	76.1 (1)
N(1)—Cd(1)—N(2$^{\text{i}}$)	104.0 (1)	N(4)—Cd(2)—N(5$^{\text{ii}}$)	103.9 (1)
N(1)—Cd(1)—N(3$^{\text{i}}$)	104.6 (1)	N(4)—Cd(2)—N(6$^{\text{ii}}$)	104.5 (1)
N(2)—Cd(1)—N(3$^{\text{i}}$)	104.7 (1)	N(5)—Cd(2)—N(6$^{\text{ii}}$)	103.9 (1)

Symmetry code: (i) $-x, 2-y, -z$; (ii) $1-x, -y, 1-z$.

Table 4. *Selected bond distances* (Å) *and angles* (°) *for* (2)

Cd N(1*A*)	2.315 (5)	Cd N(1*B*)	2.372 (8)
Cd—N(2*A*)	2.413 (6)	Cd—N(2*B*)	2.301 (8)
Cd—N(3*A*)	2.328 (5)	Cd—N(3*B*)	2.443 (8)
N(1*A*)—Cd—N(2*A*)	75.6 (2)	N(1*B*)—Cd—N(2*B*)	76.2 (2)
N(1*A*)—Cd—N(3*A*)	76.6 (2)	N(1*B*)—Cd—N(3*B*)	73.5 (3)
N(2*A*)—Cd—N(3*A*)	75.9 (2)	N(2*B*)—Cd—N(3*B*)	74.5 (3)
N(1*A*)—Cd—N(2*A*$^{\text{i}}$)	104.4 (2)	N(1*B*)—Cd—N(2*B*$^{\text{i}}$)	103.8 (2)
N(1*A*)—Cd—N(3*A*$^{\text{i}}$)	103.4 (2)	N(1*B*)—Cd—N(3*B*$^{\text{i}}$)	106.5 (3)
N(2*A*)—Cd—N(3*A*$^{\text{i}}$)	104.1 (2)	N(2*B*)—Cd—N(3*B*$^{\text{i}}$)	105.5 (3)

Symmetry code: (i) $1-x, 1-y, 1-z$.

refined except the S atom S(C) (occupancy 0.08) and eight C atoms with occupancies smaller than 0.60. Quantity minimized and definition of w as for (1), $k = 0.9631$; full-matrix least-squares refinement (on F) of 430 parameters converged at $R = 0.040$, $wR = 0.039$; $(\Delta/\sigma)_{\max} = 0.002$ in final refinement cycle; residual electron density between -0.20 and $0.35\ \text{e Å}^{-3}$.

Computer programs used were *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986) and *SCHAKAL86* (Keller, 1986); scattering factors inlaid in *SHELX76*, except those for Cd which were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Refined atomic coordinates and isotropic displacement factors of (1) and (2) are listed in Tables 1 and 2, respectively.* Bond distances and angles within the CdN_6 coordination units of the $[Cd(tacn)_2]^{2+}$ complexes are given in Tables 3 and 4. Both compounds have ionic structures. They consist of complex cations and ClO_4^- (1) and BPh_4^- (2) anions, respectively. In addition, (2) contains dimethyl sulfoxide molecules. There are no O···N distances that clearly indicate hydrogen bonding, except perhaps one $(CH_3)_2SO$···N contact of 2.93 Å in (2).

Each Cd ion is sandwiched between two tridentate tacn macrocycles. In crystals of (1) there are two symmetry independent $[Cd(tacn)_2]^{2+}$ cations situated on centres of inversion. The $[Cd(tacn)_2]^{2+}$ cation of (2) also possesses crystallographically imposed inversion symmetry. Additionally, the complex Cd cations of both compounds have approximate threefold rotational symmetry; the non-crystallographic axis passes through the Cd atom and the centres of the ligands. As a representative example, one of the $[Cd(tacn)_2]^{2+}$ complexes is shown in Fig. 1. In (2) a disorder occurs with the ligand having two alternative positions which are twisted by *ca* 56° with respect to each other (Fig. 2). The split atom positions are occupied in a 3:2 ratio (*A*:*B*).

Some other six-coordinate complexes of the type $[M(tacn)_2]^{n+}$ have been structurally characterized

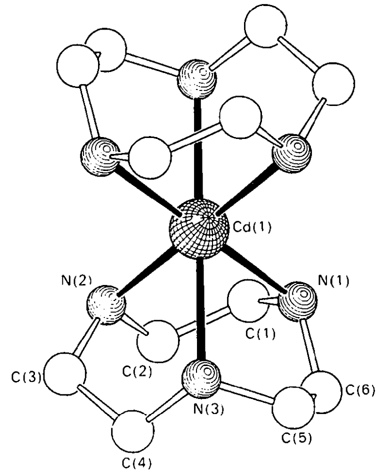

Fig. 1. Perspective view of the $[Cd(tacn)_2]^{2+}$ complex 1 in compound (1) with atomic numbering scheme. The structures of complex 2 in (1) and complexes *A* and *B* in (2) are very similar.

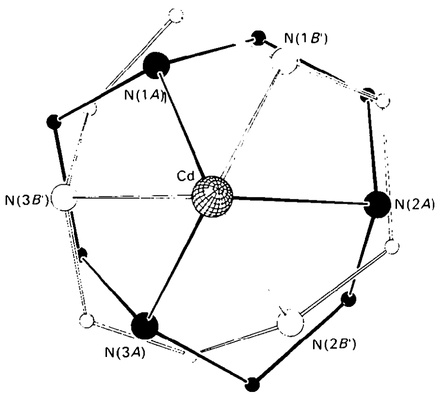

Fig. 2. The disorder of the tacn ligand in (2). The interpenetrating alternative positions *A* (filled atoms and bonds) and *B* (open atoms and bonds) are shown. The symmetry-related ligand at the Cd atom is omitted for clarity. Symmetry code as in Table 4.

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* Structure factors, anisotropic thermal parameters, calculated H-atom coordinates, full lists of bond lengths and angles and additional plots have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54616 (91 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Chaudhuri & Wieghardt, 1987). For small metal ions ($M = Co^{III}$, Ni^{III}) the M—N bonds are stretched as a result of interligand and intraligand H···H repulsions (Thöm, Boeyens, McDougall & Hancock, 1984; Wieghardt *et al.*, 1986). The bond stretching can be substantial; for example, from 1.925 to 1.97 Å for the Co^{III}—N bond. A metal ion with the M—N bond length of 2.08 Å fits ideally between two tacn ligands. For larger metal ions like Cd^{2+} a, possibly small, M—N bond compression is predicted. It results from attractive van der Waals forces and the resistance of N—M—N bond angles to compression (Thöm *et al.*, 1984). For (1) and (2) we observe mean Cd—N bond lengths of 2.36 (1) and 2.36 (6) Å, respectively. The mean N—M—N angles within the chelate rings are 75.7 (4) and 75 (1)°, respectively. Comparison with the other CdN_6-type complexes mentioned in the *Introduction* does not indicate any statistically significant Cd—N bond compression in the case of $[Cd(tacn)_2]^{2+}$.

The N_6 coordination polyhedron of $[Cd(tacn)_2]^{2+}$ can be described as an octahedron strongly elongated along one of its threefold axes of rotation. Due to the position on a centre of inversion, three N—Cd—N angles are exactly 180°. Another consequence of the crystallographically imposed inversion symmetry is the fact that ligands bonded to the same Cd atom must be enantiomeric. Thus, the five-membered CdN_2C_2 chelate rings have λ conformation in one ligand and δ conformation in the adjacent one. The tacn macrocycles have the following average bond lengths (ranges of individual values in parentheses): (1) N—C 1.479 (7) [1.468 (4)–1.490 (4)], C—C 1.522 (7) [1.512 (5)–1.531 (5) Å]; (2) N—C 1.46 (5) [1.32 (2)–1.52 (1)], C—C 1.47 (13) [1.24 (2)–1.64 (3) Å]. The remaining parts of the structures do not show any unusual features.

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Structure of *nido*-$[8,8,8\text{-}(PMe_2Ph)_3\text{-}8,7\text{-}RhSB_9H_{10}]$

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Abstract. 8,8,8-Tris(dimethylphenylphosphine)-7-thia-8-rhoda-9,10-μH-*nido*-undecaborane(10), $C_{24}H_{43}B_9P_3RhS$, $M_r = 656.8$, monoclinic, $P2_1/c$, $a = 15.794$ (2), $b = 12.020$ (3), $c = 17.119$ (2) Å, $\beta = 98.21$ (1)°, $V = 3217$ (2) Å^3, $Z = 4$, $D_x = 1.35$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 7.5$ cm^{-1}, $F(000) = 1352$, $T = 294$ K, $R = 0.022$ for 5421 observed

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