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which can yield large anisotropy components in the spin Hamiltonian. However, we may assume that at high temperature it is possible to treat the spin state of cobalt(II) with an effective $S = {}^3/_2$ and a g value sensibly different from 2. In this scheme the total spin states for the $(CoNITEt)_2$ clusters are $S = 2$ for antiferromagnetic and $S = 4$ for ferromagnetic coupling. The latter can be immediately discarded, because, even with a spin-only formalism, which clearly underestimates the cobalt contribution, it requires $\chi T = 5$ emu K mol^{-1}, much larger than the experimental value. Therefore, it can be reasonably assumed that also in $Co(hfac)_2NITEt$ the intracluster coupling is antiferromagnetic. In fact, for $S = 2$ the limit χT value can be reproduced by using for the cluster $g = 2.68$. This value, in turn, can be used to calculate the individual g value for cobalt, $g_{Co} = 2.54$, which yields a simple ion χT value of 3.03 emu K mol^{-1}, in excellent agreement with values ranging from 2.82 to 3.30 emu K mol^{-1} found in a series of adducts of cobalt(II) complexes of β-diketonates. The fact that the χT curve is essentially flat at high temperature shows that the ground $S = 2$ level of the cluster is the only one to be populated even at room temperature. It seems further that J must be at least as in the nickel derivative.

The low-temperature magnetic behavior is more difficult to analyze, because the single-ion cobalt(II) energy levels become largely depopulated, until eventually a single Kramers doublet is occupied. In this limit antiferromagnetic coupling within the cluster yields a nonmagnetic ground state. Therefore, the low χT value observed at 5 K may be justified by both intra- and intermolecular effects. However, by analogy with the nickel derivative, it can be assumed that intermolecular effects play a significant role.

The extent of the coupling between both metal ions and radicals is fairly large. This is easily understood on the basis of exchange pathways involving the $x^2 - y^2$ and z^2 orbitals of the metals and the π^* orbitals of the radicals. Indeed, the structure shows that the latter lie practically in the Co_2O_2 plane, thus maximizing the overlap with the $x^2 - y^2$ and z^2 orbitals. It must be recalled here that copper(II) complexes in which the nitroxide is equatorially bound all show very strong antiferromagnetic coupling.[32-35]

Conclusions. The present investigation has shown the versatility of the nitronyl nitroxide radicals in yielding complex architectures of magnetic structures with transition-metal ions. It is confirmed that, although the magnetic orbital can overlap with appropriate magnetic orbitals on the metals, the spin pairing is incomplete, and finite coupling constants can be observed.

Registry No. $Co(hfac)_2NITEt$, 113218-91-0; $Ni(hfac)_2NITEt$, 113218-92-1; $Co(hfac)_2$, 19648-83-0; $Ni(hfac)_2$, 14949-69-0.

Supplementary Material Available: Tables SI and SIII (anisotropic thermal parameters and derived hydrogen positions for $[Co(hfac)_2NITEt]_2$, respectively) and Tables SIV and SV (observed values of the χT product for the cobalt and nickel derivatives, respectively) (5 pages); Table SII (calculated and observed structural factors for the cobalt derivative) (17 pages). Ordering information is given on any current masthead page.

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Contribution from the Fachbereich Chemie, Universität Oldenburg, D-2900 Oldenburg, FRG,
and Department of Chemistry, Gorlaeus Laboratories, Leiden University, 2300 RA Leiden, The Netherlands

Synthetic and Structural Studies on the Novel Nitrogen Ligand 2,5,8,10,13,16-Hexaazapentacyclo[8.6.1.$1^{2,5}$.$0^{9,18}$.$0^{13,17}$]octadecane and Its Reaction Products with Methanolic Cadmium Halogenide Solutions: C_i-$C_{12}H_{22}N_6$, $[CdX_2(C_2\text{-}C_{12}H_{22}N_6)]$ (X = Cl, Br, I), and $[CdI_2(C_{12}H_{23}N_6OCH_3)]$

Henry Strasdeit,*[1a] Wolfgang Saak,[1a] Siegfried Pohl,[1a] Willem L. Driessen,[1b] and Jan Reedijk[1b]

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Ethanolic solutions of diethylenetriamine and aqueous glyoxal react to give the novel 2:2 condensation product C_i-$C_{12}H_{22}N_6$ (**1**). In methanol equimolar amounts of **1** and CdX_2 (X = Cl, Br, I) yield $[CdCl_2(C_2\text{-}C_{12}H_{22}N_6)]$ (**2**), $[CdBr_2(C_2\text{-}C_{12}H_{22}N_6)]\cdot 2MeOH$ (**3**), and $[CdI_2(C_2\text{-}C_{12}H_{22}N_6)]\cdot 2MeOH$ (**4**), respectively. On small variations in the CdI_2/**1**/MeOH system the compound $[CdI_2(C_{12}H_{23}N_6OCH_3)]\cdot MeOH$ (**5**) crystallizes instead of **4**. All five products have been structurally characterized by single-crystal X-ray diffraction (space group; unit cell parameters; Z; R, R_w (%)). **1**: $P2_1/c$; a = 7.415 (1) Å, b = 5.780 (1) Å, c = 14.196 (1) Å, β = 98.32 (1)°; 2; 3.5, 3.9. **2**: $Pbcn$; a = 15.840 (1) Å, b = 7.968 (1) Å, c = 12.868 (1) Å; 4; 2.2, 2.4. **3**: $C2/c$; a = 21.795 (2) Å, b = 7.885 (1) Å, c = 18.023 (1) Å, β = 137.77 (1)°; 4; 2.8, 3.0. **4**: $Pccn$; a = 9.232 (1) Å, b = 14.571 (1) Å, c = 16.465 (1) Å; 4; 3.0, 3.1. **5**: $P2_1/c$; a = 15.986 (1) Å, b = 9.142 (1) Å, c = 15.289 (1) Å, β = 97.17 (1)°; 4; 3.9, 3.8. The centrosymmetric hexaamine (or "tetraaminal") molecules in solid **1** are pentacyclic with three C_4N_2 and two C_3N_2 rings. In methanolic CdX_2 solutions they undergo a configurational change to the axially symmetric "C_2" form. C_2-$C_{12}H_{22}N_6$ acts as a tetradentate ligand in the six-coordinate $[CdX_2(C_{12}H_{22}N_6)]$ complexes, which are situated on crystallographic twofold axes in **2**–**4**. Two of the Cd–N bonds are "normal" (2.369 (2) (**2**), 2.336 (3) (**3**), 2.372 (4) Å (**4**)), while the other two are "secondary" bonds (2.625 (2) (**2**), 2.736 (3) (**3**), 2.739 (4) Å (**4**)). The coordination polyhedra are derived from distorted N_2X_2 tetrahedra by insertion of the two weakly bonded N atoms near the N···N tetrahedral edge. Geometrical changes with increasing softness of the halogenide and the comparison of calculated and experimental (2.468 (1) (**2**), 2.586 (1) (**3**), 2.774 (1) Å (**4**)) Cd–X bond lengths suggest a high electron density at the metal atom in the iodo complex. This is consistent with the observed lowering of the Cd coordination number from 6 to 5 by formation of $[CdI_2(C_{12}H_{23}N_6OCH_3)]$. The tridentate $C_{12}H_{23}N_6OCH_3$ ligand in **5** is derived from C_i-$C_{12}H_{22}N_6$ by covalent addition of methanol. Addition and elimination of methanol is a plausible pathway for the observed $C_i \rightarrow C_2$ transformation of $C_{12}H_{22}N_6$ on coordination. The Cd atom in **5** has a distorted-square-pyramidal N_3I_2 environment (Cd–N: 2.325 (7), 2.393 (5), 2.506 (5) Å; Cd–I: 2.775 (1) (apical), 2.812 (1) Å (basal)). In all five compounds hydrogen bonding is present (N–H···N (**1**); O–H···N, N–H···O (**3**, **4**)) or at least possible (N–H···Cl (**2**), O–H···N (**5**)).

Introduction

The mobilization and immobilization of cadmium in the environment, in organisms, and in some technical processes can depend significantly on the complexation by chelating organic molecules, especially by those containing nitrogen or sulfur donor atoms. For example, anthropogenic chelators released into the environment, humic acids, and several types of chelators produced by microorganisms contribute to the transfer of cadmium between solid and aqueous phases.[2]

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(1) (a) Universität Oldenburg. (b) Leiden University.

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Though Cd probably does not have any biological function, the body of a normal human adult usually contains 7 to >33 mg of it,[3] mainly in metallothioneins, where it is tightly bonded to cysteinyl sulfur atoms.[4] In special cases of cadmium poisoning the so-called "chelation therapy" can be applied in which synthetic chelators like ethylenediaminetetraacetate, diethylenetriaminepentaacetic acid, 2,3-dimercapto-1-propanol (BAL), 2,3-dimercapto-1-propanesulfonic acid, and 2,3-dimercaptosuccinic acid are given as potential antidotes.[5] Further examples of applied cadmium coordination chemistry are found in wastewater treatment and organic separation problems. Conventional ion exchangers and chelating resins[6] are widely used to remove heavy metals, including cadmium, from wastewaters. However, there is a lack of highly Cd(II)-selective chelating resins that meet the practical demands, e.g. usability within a wide pH range, chemical and mechanical stability, and low costs. Complexes of Cd(II) and nitrogen-containing ligands have been successfully used in ligand-exchange chromatography for the separation of sulfa drugs, dipeptides,[7] and optical isomers of dansyl amino acids.[8] These examples illustrate the practical importance of cadmium coordination chemistry and the need for further research in this field.

As a rule homoleptic cadmium complexes with monodentate ligands reveal no unusual structural features. However, when the ligands and ligand combinations become more complicated, Cd(II) accepts various different ligand surroundings. The adducts of cadmium halogenides and two novel chelating ligands described in the present paper are examples of this unique behavior. The interplay of steric and electronic factors results in systematic structural changes in the series of six-coordinate $[CdX_2(C_{12}H_{22}N_6)]$ complexes (X = Cl, Br, I). In the iodide system six-coordination in $[CdI_2(C_{12}H_{22}N_6)]$ and five-coordination in $[CdI_2(C_{12}H_{23}N_6OCH_3)]$ are equally favored.

Experimental Section

Solvents used were ethanol (99% and anhydrous, respectively) denatured by petroleum ether, and reagent-grade methanol (≥99.8%, ≤0.05% H_2O, Merck), chloroform (99.0–99.4%, Merck), and diethyl ether (>99.8%, Fluka). Glyoxal (~40% in H_2O) and diethylenetriamine (>97%) were obtained from Fluka. Anhydrous $CdCl_2$ (Merck), $CdBr_2$ (Strem), and CdI_2 (Riedel-de Haën) had 99% purity.

Elemental analyses were performed by the Microanalytical Laboratory, Beller, Göttingen, FRG. Infrared spectra were measured with a Beckman IR-4220 spectrophotometer. Only the strongest IR bands are given. The ^{13}C CP/MAS NMR spectrum was obtained on a Bruker MSL-400 instrument. Mass spectra were measured with a Finnigan MAT 212 instrument equipped with an SS 300 data system.

Syntheses. C_{r}-$C_{12}H_{22}N_6$ **(1).**[9] A 43-mL (0.40-mol) sample of diethylenetriamine was poured into a stirred solution of 58 g of a ~40% aqueous solution of glyoxal (0.40 mol) in 500 mL of ethanol. The temperature increased to about 45 °C. The light yellow reaction mixture was stirred for 1 h. Then its volume was reduced to ~60 mL by rotary evaporation at 40 °C. The crystallization of the product started during or shortly after this procedure. After it stood at room temperature for 48 h and at −2 °C for an additional 1 day, the viscous mass was diluted with 50 mL of ice-cold anhydrous ethanol. The product was isolated on a glass filter, washed with a small amount of cold anhydrous ethanol and with ether, and dried in vacuo. A total of 6 g (12%) of a white microcrystalline powder was obtained; mp ~229 °C dec. This product was used in the preparation of the Cd complexes. Anal. Calcd for $C_{12}H_{22}N_6$: C, 57.57; H, 8.86; N, 33.57. Found: C, 57.64; H, 8.96; N, 33.56. IR (KBr): 3250, 3240, 2925, 2795, 1400, 1335, 1259, 1171, 1139, 1054, 956, 838 cm^{-1}. ^{13}C NMR (solid state, CP/MAS): 79.7, 69.7 ppm (CH); 54.6, 50.3, 48.4, 40.7 ppm (CH_2). Mass spectrum (electron impact, 30 eV, 150 °C): *m/e* 250 (M^+, highest peak). **1** can be sublimed at 120–150 °C and 0.1 Torr.

Caution! Without dilution diethylenetriamine and the 40% aqueous solution of glyoxal react very vigorously.

$[CdCl_2(C_2\text{-}C_{12}H_{22}N_6)]$ (2). A 1.00-g (4.0-mmol) sample of $C_{12}H_{22}N_6$ was added to a solution of 0.73 g (4.0 mmol) of $CdCl_2$ in 300 mL of methanol without stirring or shaking. At this stage the lower part of the solution was cloudy. The solution was allowed to stand undisturbed at room temperature. During the next few days the ligand dissolved, and **2** crystallized as colorless distorted hexagonal plates. After 1 week, the product was isolated on a large-pored glass filter, thoroughly washed with methanol, and dried in vacuo; yield 1.48 g (85%). Anal. Calcd for $C_{12}H_{22}CdCl_2N_6$: C, 33.24; H, 5.11; Cd, 25.92; Cl, 16.35; N, 19.38. Found: C, 33.45; H, 5.09; Cd, 25.82; Cl, 16.42; N, 19.54. IR (KBr): 3240, 2875, 1451, 1299, 1282, 1159, 1088, 1051, 910 cm^{-1}.

$[CdBr_2(C_2\text{-}C_{12}H_{22}N_6)]\cdot 2MeOH$ (3). The preceding method was used with 1.09 g (4.0 mmol) of $CdBr_2$. Drying in vacuo was limited to a few seconds to avoid the loss of crystal methanol. A total of 1.95 g (83%) of colorless crystals was obtained. The rapid loss of methanol on exposure to laboratory air affected the analytical data and the infrared spectrum, which was nearly identical with that of **2**. Anal. Calcd for $C_{14}H_{30}Br_2CdN_6O_2$: C, 28.66; H, 5.15; Br, 27.24; Cd, 19.16; N, 14.33. Found: C, 28.47; H, 4.93; Br, 28.42; Cd, 19.49; N, 15.07. IR (KBr): 3235, 2870, 2855, 1449, 1299, 1281, 1161, 1090, 1052, 910 cm^{-1}.

$[CdI_2(C_2\text{-}C_{12}H_{22}N_6)]\cdot 2MeOH$ (4). A 1.46-g (4.0-mmol) sample of CdI_2 was dissolved in a solution of 1.00 g (4.0 mmol) of $C_{12}H_{22}N_6$ in 600 mL of methanol. When the mixture stood at room temperature, white needles of **4** formed. After 5 days the product was isolated on a glass filter, washed with methanol, and dried in vacuo for a short period; yield 1.87 g (69%). Anal. Calcd for $C_{14}H_{30}CdI_2N_6O_2$: C, 24.70, H, 4.44; Cd, 16.52; I, 37.29; N, 12.35. Found: C, 24.84; H, 4.49; Cd, 16.45; I, 37.31; N, 12.49. IR (KBr): 3210, 3190, 2875, 2860, 1305, 1159, 1142, 1087, 1055, 1026, 908, 794 cm^{-1}.

$[CdI_2(C_{12}H_{23}N_6OCH_3)]\cdot MeOH$ (5). A 1.46-g (4.0-mmol) sample of CdI_2 was dissolved in a solution of 1.00 g (4.0 mmol) of $C_{12}H_{22}N_6$ in 200 mL of methanol. When the mixture stood at −2 °C, **5** crystallized as white rhombic plates. After 2 weeks the product was isolated on a glass filter, washed with a small amount of methanol, and dried in vacuo for a short period; yield 1.14 g (42%). Anal. Calcd for $C_{14}H_{30}CdI_2N_6O_2$: C, 24.70; H, 4.44; Cd, 16.52; I, 37.29; N, 12.35. Found: C, 25.32; H, 4.58; Cd, 16.17; I, 37.18; N, 12.29. IR (KBr): 3330, 3310, 3270, 2940, 2860, 1199, 1167, 1112, 1060, 1045, 1031, 963, 870 cm^{-1}.

X-ray Structure Determinations. Suitable single crystals of **1** were grown by vapor diffusion of ether into a solution of microcrystalline **1** (0.3 g) in chloroform (10 mL) at room temperature. The starting material and the recrystallized product were infrared and X-ray isomorphous.[10] Cooling a saturated solution of **1** in chloroform to −30 °C afforded crystals that decayed very rapidly on exposure to laboratory air. These crystals were orthorhombic with a = 9.718 (8) Å, b = 11.005 (8) Å, and c = 20.185 (10) Å. On the basis of their mass spectrum, unit cell volume, and weight loss in vacuo their most probable composition is "$C_{12}H_{22}N_6\cdot 2CHCl_3$". Single crystals of the Cd complexes **2**–**5** were obtained from preparations identical with or very similar to those described under Syntheses.

Single crystals of all five compounds were sealed into thin-walled glass capillaries. In the case of **3** a drop of methanol was added to avoid decomposition of the crystal. The crystals were mounted on a Siemens/STOE AED2 automated four-circle diffractometer. Graphite-monochromated Mo Kα radiation was used. Accurate lattice parameters were determined by measuring the centers of typically 36 reflections including Friedel pairs. The crystal data are summarized in Table I together with details of the data collections and structure refinements.

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(10) Diffraction data of polycrystalline **1** were measured on a Philips PW1710 automated powder diffractometer system (Cu Kα radiation, 10° ≤ 2θ ≤ 70°); *d* spacings are as follows (approximate relative intensities): 7.38 (100), 7.06 (50), 5.52 (39), 5.37 (73), 4.76 (17), 4.56 (37), 4.46 (72), 4.23 (7), 4.00 (90), 3.67 (30), 3.48 (7), 3.38 (5), 3.08 (5), 3.01 (8), 2.96 (5), 2.68 (6), 2.47 (8), 2.28 (5), 2.23 (6), 2.15 (6), 2.13 (5), 2.02 (4), and 1.76 Å (4).

Table I. Crystal Data and Details of Intensity Collections and Structure Refinements for $C_{12}H_{22}N_6$ (**1**), $[CdCl_2(C_{12}H_{22}N_6)]$ (**2**), $[CdBr_2(C_{12}H_{22}N_6)]\cdot 2MeOH$ (**3**), $[CdI_2(C_{12}H_{22}N_6)]\cdot 2MeOH$ (**4**), and $[CdI_2(C_{12}H_{23}N_6OCH_3)]\cdot MeOH$ (**5**)

	1	**2**	**3**	**4**	**5**
formula	$C_{12}H_{22}N_6$	$C_{12}H_{22}CdCl_2N_6$	$C_{14}H_{30}Br_2CdN_6O_2$	$C_{14}H_{30}CdI_2N_6O_2$	$C_{14}H_{30}CdI_2N_6O_2$
fw	250.35	433.66	586.65	680.65	680.65
a, Å	7.415 (1)	15.840 (1)	21.795 (2)	9.232 (1)	15.986 (1)
b, Å	5.780 (1)	7.968 (1)	7.885 (1)	14.571 (1)	9.142 (1)
c, Å	14.196 (1)	12.868 (1)	18.023 (1)	16.465 (1)	15.289 (1)
β, deg	98.32 (1)		137.77 (1)		97.17 (1)
V, Å^3	602.0	1624.1	2081.7	2214.9	2216.9
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Z	2	4	4	4	4
d_{calcd}, g/cm^3	1.381	1.774	1.872	2.041	2.039
d_{obsd},^{a} g/cm^3	1.38	1.78	1.88	2.06	2.05
space group	$P2_1/c$	*Pbcn*	$C2/c$	*Pccn*	$P2_1/c$
cryst dimens, mm	1.14 × 0.32 × 0.29	0.57 × 0.27 × 0.19	1.06 × 0.30 × 0.25	0.61 × 0.15 × 0.15	0.46 × 0.30 × 0.08
μ(Mo Kα), cm^{-1}	0.52	16.3	48.1	37.4	37.4
scan speed, deg/min	1.0–4.8	0.5–3.6	0.6–3.6	0.6–3.6	0.6–3.6
2θ limits, deg	$3 \le 2\theta \le 52$	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 52$	$3 \le 2\theta \le 50$
index range	$+h,+k,\pm l$	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,+l$	$\pm h,-k,+l$
total no. of rflns	1410	1678	2046	2505	4333
rflns used ($I > 2\sigma(I)$)	982	1170	1644	1649	3010
no. of variables	126	129	129	129	225
R (R_w),^{b} %	3.5 (3.9)	2.2 (2.4)	2.8 (3.0)	3.0 (3.1)	3.9 (3.8)

[a] Determined by flotation in CCl_4/toluene (**1**) and in 1,2-dibromoethane/methanol (**2–5**), respectively. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

The intensity data were collected by the ω–2θ step scan technique at 23 ± 1 °C. Three check reflections were measured every 45 min. During the data collection, the raw data were corrected for the background intensities, variation of measuring time, filter attenuation factor, and dead time of the scintillation counter. Subsequently the data were scaled with respect to the standard reflections. Lorentz–polarization corrections and in the case of **3** and **5** an empirical absorption correction (ψ-scan) were applied.

All structures were solved by direct methods with use of the structure-solution program SHELXS-86.[11] Other computer programs used were SHELX[12] and ORTEP.[13] In the refinements the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized, *w* being defined as $w = k/(\sigma^2(F_o) + gF_o^2)$ with $g = 0.0001$ for **1** and 0.0002 for **2–5**, respectively. Atomic scattering factors for spherical neutral free (all except H) and bonded (H) atoms as well as anomalous scattering contributions were taken from a standard source.[14] All non-hydrogen atoms except those of the methanol molecule in **5** were refined anisotropically. Further details of the individual structure refinements are given in the following.

(a) $C_{12}H_{22}N_6$. From the systematic absences the space group could be unambiguously determined as $P2_1/c$ (No. 14). Starting values for all H atom coordinates were taken from difference Fourier maps. In the final refinement the positional parameters and the isotropic temperature factors of all H atoms were included.

(b) $[CdCl_2(C_{12}H_{22}N_6)]$. The observed systematic absences were characteristic of the space group *Pbcn* (No. 60). All H atom positions were found in difference Fourier maps and were refined. The temperature factors of the H atoms were fixed at $U = 0.05$ Å^2.

(c) $[CdBr_2(C_{12}H_{22}N_6)]\cdot 2MeOH$. On the basis of the systematic absences and *E* statistics the centrosymmetric space group $C2/c$ (No. 15) was chosen. This choice was confirmed by the successful structure refinement, which converged at $R = 2.8\%$. The positions of the H atom at N(1) and the H atoms in the methanol molecule were taken from difference Fourier syntheses and refined. The corresponding *U* values were fixed at 0.05 (H(N1)) and 0.09 Å^2 (H(O), H(7A), H(7B), H(7C)), respectively. The remaining H atoms were given idealized positions and *U* values of 0.05 Å^2 in CH groups and 0.07 Å^2 in CH_2 groups, respectively. Probably due to the large monoclinic angle of 137.77 (1)°, 60 elements of the correlation matrix were larger than 0.5, the maximum value being 0.864. Nevertheless, the refinement proceeded smoothly.

(d) $[CdI_2(C_{12}H_{22}N_6)]\cdot 2MeOH$. The observed systematic absences uniquely define the space group *Pccn* (No. 56). The H atoms were treated as described above for the bromine compound.

Table II. Atomic Coordinates for $C_{12}H_{22}N_6$

atom	*x*	*y*	*z*
N(1)	0.53950 (16)^a	−0.09528 (22)	0.19564 (8)
N(2)	0.78543 (14)	0.07516 (19)	0.07430 (7)
N(3)	0.55704 (14)	0.22397 (18)	−0.03655 (7)
C(1)	0.59564 (17)	0.15573 (22)	0.06324 (9)
C(2)	0.46863 (17)	−0.02029 (22)	0.09867 (9)
C(3)	0.73311 (20)	−0.16030 (26)	0.20706 (10)
C(4)	0.85466 (19)	0.02370 (26)	0.17307 (10)
C(5)	0.87629 (18)	0.26335 (26)	0.03042 (11)
C(6)	0.72703 (19)	0.34840 (25)	−0.04961 (11)
H(N1)	0.5265 (23)	0.0284 (32)	0.2342 (13)
H(1)	0.5903 (17)	0.2983 (23)	0.1011 (9)
H(2)	0.3513 (18)	0.0582 (23)	0.1017 (9)
H(3A)	0.7433 (21)	−0.3028 (28)	0.1704 (11)
H(3B)	0.7711 (20)	−0.1916 (26)	0.2732 (11)
H(4A)	0.9803 (24)	−0.0345 (30)	0.1779 (11)
H(4B)	0.8528 (21)	0.1666 (27)	0.2133 (11)
H(5A)	0.9852 (23)	0.2083 (27)	0.0036 (11)
H(5B)	0.9125 (23)	0.3882 (32)	0.0756 (12)
H(6A)	0.7065 (22)	0.5170 (30)	−0.0443 (11)
H(6B)	0.7555 (21)	0.3163 (26)	−0.1141 (12)

[a] In this and succeeding tables numbers in parentheses are estimated standard deviations.

Table III. Atomic Coordinates for $[CdCl_2(C_{12}H_{22}N_6)]$

atom	*x*	*y*	*z*
Cd	0.00	0.49223 (3)	0.25
Cl	0.07541 (5)	0.30932 (9)	0.12613 (6)
N(1)	−0.08649 (13)	0.63742 (28)	0.12963 (18)
N(2)	−0.17198 (14)	0.85695 (30)	0.26981 (17)
N(3)	−0.04183 (13)	0.77775 (26)	0.33770 (15)
C(1)	−0.0821 (2)	0.8730 (4)	0.2517 (2)
C(2)	−0.0492 (1)	0.8047 (3)	0.1493 (2)
C(3)	−0.1799 (2)	0.6467 (4)	0.1331 (3)
C(4)	−0.2061 (2)	0.6907 (4)	0.2412 (2)
C(5)	−0.1768 (2)	0.8819 (4)	0.3834 (2)
C(6)	−0.0978 (2)	0.7944 (5)	0.4286 (2)
H(N1)	−0.071 (2)	0.605 (4)	0.072 (2)
H(1)	−0.069 (3)	0.980 (4)	0.256 (2)
H(2)	−0.061 (2)	0.889 (4)	0.093 (2)
H(3A)	−0.199 (2)	0.543 (4)	0.115 (3)
H(3B)	−0.198 (2)	0.735 (4)	0.085 (2)
H(4A)	−0.189 (2)	0.602 (4)	0.290 (2)
H(4B)	−0.267 (3)	0.697 (5)	0.245 (2)
H(5A)	−0.174 (2)	1.009 (4)	0.397 (3)
H(5B)	−0.233 (2)	0.833 (4)	0.409 (2)
H(6A)	−0.072 (2)	0.852 (4)	0.481 (2)
H(6B)	−0.115 (2)	0.681 (4)	0.456 (3)

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(11) Sheldrick, G. M. "SHELXS-86"; Universität Göttingen: Göttingen, FRG, 1986.

(12) Sheldrick, G. M. "SHELX-76, Program for Crystal Structure Determination", University of Cambridge: Cambridge, England, 1976.

(13) Johnson, C. K. "ORTEP-II"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(14) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table IV. Refined Atomic Coordinates for $[CdBr_2(C_{12}H_{22}N_6)]\cdot 2MeOH$

atom	*x*	*y*	*z*
Cd	0.50	0.17589 (4)	0.75
Br	0.43684 (3)	0.35399 (5)	0.80244 (4)
N(1)	0.3639 (2)	0.0242 (4)	0.6157 (2)
N(2)	0.4061 (2)	-0.2009 (4)	0.5339 (2)
N(3)	0.5372 (2)	-0.1278 (3)	0.7163 (2)
C(1)	0.4498 (2)	-0.2199 (4)	0.6455 (3)
C(2)	0.3981 (2)	-0.1476 (4)	0.6649 (3)
C(3)	0.3079 (3)	0.0214 (6)	0.4976 (3)
C(4)	0.3687 (3)	-0.0300 (5)	0.4879 (3)
C(5)	0.4845 (3)	-0.2297 (5)	0.5534 (3)
C(6)	0.5693 (3)	-0.1535 (5)	0.6681 (3)
O	0.2838 (2)	-0.4850 (5)	0.4067 (3)
C(7)	0.3054 (4)	-0.5711 (8)	0.3609 (5)
H(N1)	0.330 (3)	0.061 (5)	0.623 (3)
H(O)	0.315 (4)	-0.396 (7)	0.439 (5)
H(7A)	0.267 (4)	-0.652 (7)	0.316 (5)
H(7B)	0.317 (4)	-0.507 (7)	0.325 (4)
H(7C)	0.362 (4)	-0.644 (6)	0.417 (5)

Table V. Refined Atomic Coordinates for $[CdI_2(C_{12}H_{22}N_6)]\cdot 2MeOH$

atom	*x*	*y*	*z*
Cd	0.25	0.25	0.44287 (3)
I	0.48722 (5)	0.21202 (3)	0.54065 (2)
N(1)	0.3035 (4)	0.3847 (3)	0.3678 (2)
N(2)	0.0596 (4)	0.3950 (3)	0.2601 (2)
N(3)	0.1074 (4)	0.2438 (3)	0.2971 (2)
C(1)	0.1687 (5)	0.3222 (3)	0.2516 (3)
C(2)	0.3176 (5)	0.3431 (3)	0.2862 (2)
C(3)	0.2099 (6)	0.4676 (3)	0.3645 (3)
C(4)	0.0590 (5)	0.4386 (3)	0.3407 (3)
C(5)	-0.0768 (5)	0.3422 (4)	0.2471 (3)
C(6)	-0.0513 (5)	0.2475 (4)	0.2856 (3)
O	0.4040 (5)	-0.0347 (3)	0.1453 (3)
C(7)	0.3308 (8)	-0.0114 (6)	0.0746 (5)
H(N1)	0.392 (5)	0.400 (4)	0.384 (3)
H(O)	0.410 (7)	0.018 (4)	0.177 (4)
H(7A)	0.252 (7)	0.021 (5)	0.083 (4)
H(7B)	0.313 (7)	-0.076 (5)	0.060 (4)
H(7C)	0.396 (8)	0.033 (5)	0.045 (4)

(e) $[CdI_2(C_{12}H_{23}N_6OCH_3)]\cdot MeOH$. From the systematic absences the space group was unambiguously determined as $P2_1/c$ (No. 14). Difference Fourier maps revealed the positions of the H atoms at N(1) and N(6). These positions were refined and the corresponding *U* values fixed at 0.08 Å^2. Idealized positions were calculated for all H atoms in CH and CH_2 groups. The temperature factors of these H atoms were fixed at 0.07 Å^2. The H atoms of the C(13) methyl group and of the methanol molecule were not included in the final structural model.

The final positional parameters for the compounds **1**–**5** are listed in Tables II–VI. The atom-labeling schemes are shown in Figures 1–3. Lists of thermal parameters, bond lengths and angles that are not given in Tables VII–IX, calculated hydrogen atom coordinates, and observed and calculated structure factors are available as supplementary material.

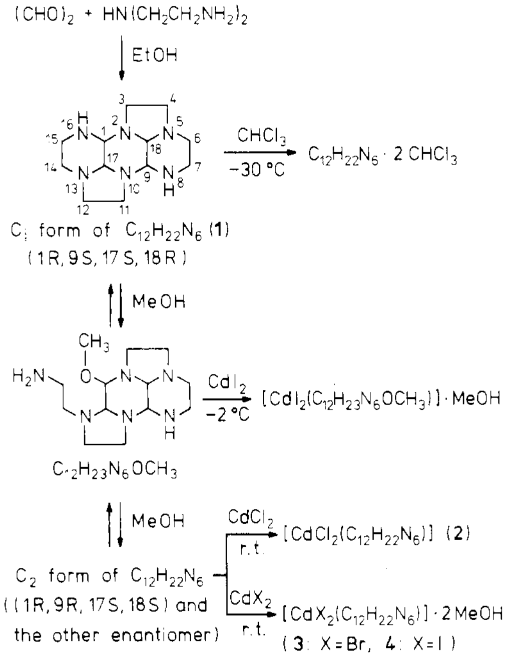
Results and Discussion

Reactions. The reactions that have been studied are summarized in Scheme I. From equimolar solutions of diethylenetriamine and aqueous glyoxal in ethanol the crystalline 2:2 condensation product C_i-$C_{12}H_{22}N_6$ (**1**) was prepared for the first time. It was isolated in low yield. No other solid products, particularly no Schiff bases, were observed. Molecules of **1** are pentacyclic and have four asymmetric carbon atoms.[15] In the crystals, before as well as after recrystallization from chloroform/ether, the molecules are centrosymmetric. Consequently, one of the two possible meso forms is present. The prefix "C_i" denotes the point symmetry.

Table VI. Refined Atomic Coordinates for $[CdI_2(C_{12}H_{23}N_6OCH_3)]\cdot MeOH$

atom	*x*	*y*	*z*
Cd	0.85055 (3)	0.48220 (5)	0.58641 (3)
I(1)	0.93953 (3)	0.21615 (6)	0.59599 (4)
I(2)	0.78017 (4)	0.51488 (6)	0.41221 (3)
N(1)	0.9706 (5)	0.6244 (9)	0.6216 (6)
N(2)	0.8021 (4)	0.7083 (6)	0.6579 (4)
N(3)	0.6558 (4)	0.6870 (6)	0.6754 (4)
N(4)	0.7384 (3)	0.4053 (5)	0.6659 (3)
N(5)	0.6027 (4)	0.3598 (6)	0.6884 (4)
N(6)	0.5352 (4)	0.5931 (7)	0.5839 (4)
C(1)	0.9511 (5)	0.7753 (8)	0.6484 (5)
C(2)	0.8805 (5)	0.7706 (9)	0.7056 (5)
C(3)	0.7542 (5)	0.8205 (8)	0.5996 (5)
C(4)	0.6694 (5)	0.8333 (8)	0.6377 (6)
C(5)	0.7346 (5)	0.2478 (7)	0.6918 (5)
C(6)	0.6414 (5)	0.2157 (8)	0.7023 (6)
C(7)	0.5114 (5)	0.3658 (9)	0.6619 (5)
C(8)	0.4882 (5)	0.5246 (9)	0.6495 (6)
C(9)	0.6259 (4)	0.5836 (7)	0.6043 (4)
C(10)	0.6512 (4)	0.4277 (7)	0.6254 (4)
C(11)	0.7420 (4)	0.6570 (7)	0.7194 (4)
C(12)	0.7533 (4)	0.4980 (7)	0.7455 (4)
O(1)	0.8375 (3)	0.4733 (6)	0.7827 (3)
C(13)	0.8483 (6)	0.4752 (11)	0.8778 (5)
O(2)	0.5416 (5)	0.3801 (8)	0.9724 (5)
C(14)	0.6058 (8)	0.4177 (13)	0.9198 (8)
H(N1A)	1.010 (6)	0.623 (10)	0.582 (6)
H(N1B)	1.003 (6)	0.587 (10)	0.674 (6)
H(N6)	0.520 (6)	0.558 (9)	0.524 (6)

Scheme I



At room temperature methanolic solutions of **1** and CdX_2 (X = Cl, Br, I) give the compounds $[CdCl_2(C_2\text{-}C_{12}H_{22}N_6)]$ (**2**), $[CdBr_2(C_2\text{-}C_{12}H_{22}N_6)]\cdot 2MeOH$ (**3**), and $[CdI_2(C_2\text{-}C_{12}H_{22}N_6)]\cdot 2MeOH$ (**4**), respectively, in good yields. In all three compounds the hexaamine has an axially symmetric configuration. This is only possible after isomerization. An indication of how the configurational change from the C_i to the C_2 form may occur was obtained from the $CdI_2/C_{12}H_{22}N_6/MeOH$ system. When the concentrations of the starting materials were 3 times as high as in the preparation of **4** and the temperature was lowered to −2 °C, the compound $[CdI_2(C_{12}H_{23}N_6OCH_3)]\cdot MeOH$ (**5**) could be crystallized as the only product. The new ligand $C_{12}H_{23}N_6OCH_3$ is formed by covalent addition of methanol to C_i-$C_{12}H_{22}N_6$. It contains a methoxy group at one of the asymmetric carbon atoms. The reverse reaction may result in a configurational change

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[15] For related bi-, tri-, and tetracyclic molecules see: Jaźwiński, J.; Koliński, R. A. *Tetrahedron Lett.* **1981**, *22*, 1711 and references therein. Riddell, F. G.; Murray-Rust, P. *J. Chem. Soc., Chem. Commun.* **1970**, 1075. Suh, M. P.; Kang, S.; Shin, W. *Proc. Int. Conf. Coord. Chem.* **1987**, *25*, 450. Suh, M. P.; Shin, W.; Kim, H.; Koo, C. H. *Inorg. Chem.* **1987**, *26*, 1846.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for the $C_{12}H_{22}N_6$ Groups in the Compounds **1–4**

	1	**2**	**3**	**4**
N(1)–C(2)	1.466 (2)	1.480 (3)	1.483 (4)	1.480 (5)
N(1)–C(3)	1.470 (2)	1.483 (4)	1.475 (4)	1.487 (6)
N(2)–C(1)	1.469 (2)	1.448 (3)	1.462 (4)	1.469 (6)
N(2)–C(4)	1.452 (2)	1.477 (4)	1.472 (5)	1.471 (6)
N(2)–C(5)	1.465 (2)	1.477 (4)	1.484 (5)	1.492 (6)
N(3)–C(1)	1.458 (2)	1.486 (3)	1.478 (4)	1.479 (5)
N(3)–C(2′)	1.467 (2)	1.467 (3)	1.457 (4)	1.453 (5)
N(3)–C(6)	1.486 (2)	1.475 (3)	1.478 (5)	1.478 (6)
C(1)–C(2)	1.521 (2)	1.518 (4)	1.517 (5)	1.519 (6)
C(3)–C(4)	1.517 (2)	1.494 (4)	1.514 (5)	1.508 (7)
C(5)–C(6)	1.547 (2)	1.546 (4)	1.547 (6)	1.537 (7)
Cd–N(1)–C(2)		95.6 (1)	99.1 (2)	98.7 (3)
Cd–N(1)–C(3)		125.6 (2)	124.2 (2)	124.8 (3)
C(2)–N(1)–C(3)	113.0 (1)	110.4 (2)	111.2 (3)	110.6 (4)
C(1)–N(2)–C(4)	111.6 (1)	113.5 (2)	113.2 (3)	113.6 (4)
C(1)–N(2)–C(5)	102.2 (1)	101.4 (2)	101.3 (3)	101.1 (3)
C(4)–N(2)–C(5)	116.3 (1)	110.4 (2)	109.5 (3)	110.4 (4)
Cd–N(3)–C(1)		103.4 (1)	102.6 (2)	103.5 (2)
Cd–N(3)–C(2′)		85.8 (1)	83.8 (2)	84.7 (2)
Cd–N(3)–C(6)		124.8 (2)	126.7 (2)	126.0 (3)
C(1)–N(3)–C(2′)	110.9 (1)	115.6 (2)	116.2 (3)	115.4 (3)
C(1)–N(3)–C(6)	101.6 (1)	106.6 (2)	107.1 (3)	106.7 (4)
C(2′)–N(3)–C(6)	110.6 (1)	119.2 (2)	118.9 (3)	119.2 (4)
N(2)–C(1)–N(3)	103.9 (1)	104.9 (2)	104.4 (3)	104.3 (4)
N(2)–C(1)–C(2)	112.5 (1)	116.5 (2)	116.1 (3)	116.1 (4)
N(3)–C(1)–C(2)	117.3 (1)	108.4 (2)	108.6 (3)	108.1 (3)
N(1)–C(2)–C(1)	110.7 (1)	109.5 (2)	109.6 (3)	110.0 (4)
N(1)–C(2)–N(3′)	109.0 (1)	106.3 (2)	107.0 (3)	106.7 (4)
N(3′)–C(2)–C(1)	111.8 (1)	106.9 (2)	107.6 (3)	107.6 (4)
N(1)–C(3)–C(4)	113.7 (1)	108.4 (2)	108.1 (3)	108.5 (4)
N(2)–C(4)–C(3)	107.9 (1)	109.9 (2)	110.3 (3)	110.6 (4)
N(2)–C(5)–C(6)	102.9 (1)	105.7 (2)	106.5 (3)	105.9 (4)
N(3)–C(6)–C(5)	106.5 (1)	103.2 (2)	102.8 (3)	103.7 (4)

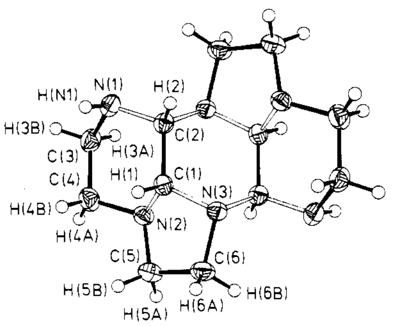

Figure 1. Structure of the C_i-$C_{12}H_{22}N_6$ molecule in **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids. The *U* values of the hydrogen atoms have been reduced to 0.01 Å^2 for clarity. Bonds within the glyoxal and diethylenetriamine fragments are represented by solid lines.

at this C atom. So it is reasonable to assume that the addition and elimination of methanol provides at least one possible way for the $C_i \rightarrow C_2$ transformation of $C_{12}H_{22}N_6$. It should be mentioned that **4** and **5**, although being entirely different compounds, have the same empirical formula.

X-ray Structures. (a) Hexaamine Groups. Selected bond lengths and angles of the free $C_{12}H_{22}N_6$ in **1** and of its complex-bound forms in **2-4** are compared in Table VII. ORTEP plots of **1** and of the $[CdX_2(C_{12}H_{22}N_6)]$ complexes in **2-4** are shown in Figures 1 and 2, respectively. Important features of the $C_{12}H_{22}N_6$ groups are as follows: The molecules are situated on a crystallographic center of inversion (**1**) and on crystallographic twofold axes (**2-4**), respectively. They contain three C_4N_2 6-rings with the nitrogen atoms in 1,4-positions and two C_3N_2 5-rings with the nitrogen atoms in 1,3-positions. The central N atom and one of the terminal N atoms of each diethylenetriamine fragment have become parts of tertiary amine groups; the other formerly primary N atom is now a secondary one. As expected, the angles within the 5-rings are smaller than the ideal tetrahedral angle, while the angles C(1)–N(3)–C(2′), C(2′)–N(3)–C(6), and N(2)–C(1)–C(2), which are exocyclic with respect to the 5-rings, are larger, especially in the complex-bound molecules.

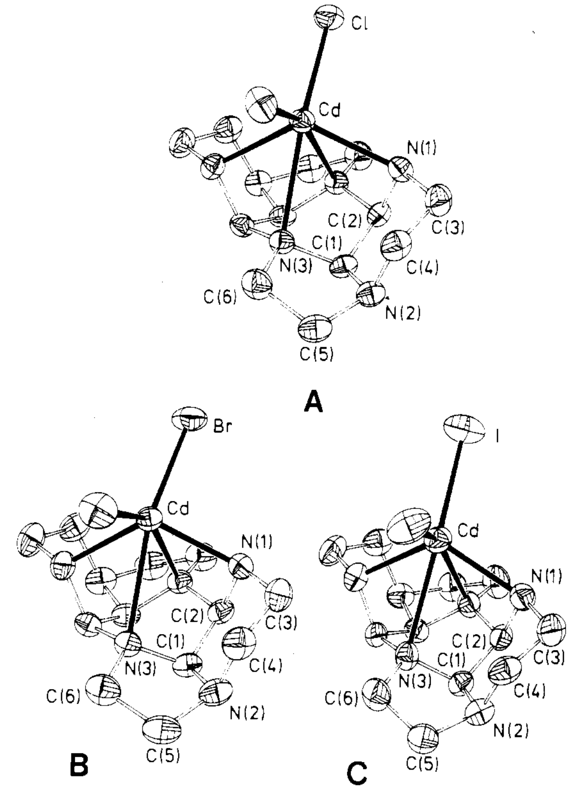

Figure 2. Structures of the $[CdX_2(C_2\text{-}C_{12}H_{22}N_6)]$ complexes in **2** (A, X = Cl), **3** (B, X = Br), and **4** (C, X = I) showing the atom-labeling scheme and 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

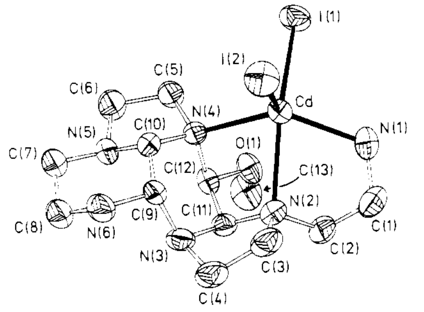

Figure 3. Structure of the $[CdI_2(C_{12}H_{23}N_6OCH_3)]$ complex in **5** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Inspection of Table VII reveals significant differences in bond lengths and angles between the $C_{12}H_{22}N_6$ molecules in the free C_i form and those in the $[CdX_2(C_2\text{-}C_{12}H_{22}N_6)]$ complexes. It is not clear to what extent the binding of the $\{CdX_2\}$ groups contributes to these differences. The only part of the molecule in which an influence of the metal binding can undoubtedly be seen is the Cd–N(3)–C(1)–N(2) fragment. On binding of Cd to N(3) the N(3)–C(1) bond is lengthened from 1.458 (2) Å in **1** to 1.486 (3) Å in **2**. Obviously as a compensation the N(2)–C(1) bond is shortened from 1.469 (2) to 1.448 (3) Å. These effects, however, are less pronounced in **3** and **4**. This is consistent with the fact that the Cd–N(3) bonds in **3** and **4** are weaker than in **2**. Except for the bond lengths N(2)–C(1) and C(3)–C(4) and the Cd–N–C angles corresponding metrical data of the C_2-$C_{12}H_{22}N_6$ ligands in **2-4** are the same within 2σ.

Bond distances and angles in the $C_{12}H_{23}N_6OCH_3$ ligand of **5** are given in Table S-VIII of the supplementary material. This ligand is derived from C_i-$C_{12}H_{22}N_6$ by solvolysis with methanol: one of the N(1)–C(2) bonds is cleaved, and NH_2 and OCH_3

Table VIII. Selected Interatomic Distances (Å) and Angles (deg) in the Cd Coordination Spheres of the $[CdX_2(C_{12}H_{22}N_6)]$ Complexes

	X = Cl (**2**)	X = Br (**3**)	X = I (**4**)
Cd–X	2.468 (1)	2.586 (1)	2.774 (1)
Cd–N(1)	2.369 (2)	2.336 (3)	2.372 (4)
Cd–N(3)	2.625 (2)	2.736 (3)	2.739 (4)
N(1)···N(1′)	4.136 (3)	4.013 (4)	4.048 (5)
N(3)···N(3′)	2.617 (3)	2.649 (4)	2.639 (5)
X–Cd–X′	107.62 (4)	114.22 (3)	109.04 (3)
X–Cd–N(1)	98.4 (1)	92.6 (1)	107.6 (1)
X–Cd–N(1′)	115.5 (1)	120.7 (1)	107.6 (1)
X–Cd–N(3)	155.7 (1)	151.8 (1)	151.8 (1)
X–Cd–N(3′)	96.4 (1)	93.9 (1)	97.8 (1)
N(1)–Cd–N(1′)	121.5 (1)	118.4 (1)	117.2 (1)
N(1)–Cd–N(3)	73.3 (1)	71.3 (1)	70.8 (1)
N(1)–Cd–N(3′)	56.1 (1)	54.8 (1)	54.3 (1)
N(3)–Cd–N(3′)	59.8 (1)	57.9 (1)	57.6 (1)

Table IX. Bond Lengths (Å) and Angles (deg) in the Cd Coordination Sphere of $[CdI_2(C_{12}H_{23}N_6OCH_3)]\cdot MeOH$

Cd–I(1)	2.812 (1)	Cd–N(1)	2.325 (7)
Cd–I(2)	2.775 (1)	Cd–N(2)	2.506 (5)
		Cd–N(4)	2.393 (5)
I(1)–Cd–I(2)	106.55 (4)	I(2)–Cd–N(2)	102.7 (1)
I(1)–Cd–N(1)	94.2 (2)	I(2)–Cd–N(4)	106.2 (1)
I(1)–Cd–N(2)	150.8 (1)	N(1)–Cd–N(2)	74.3 (2)
I(1)–Cd–N(4)	97.2 (1)	N(1)–Cd–N(4)	134.1 (3)
I(2)–Cd–N(1)	112.7 (2)	N(2)–Cd–N(4)	74.3 (2)

groups are formed. The characteristic step shape of the C_i-$C_{12}H_{22}N_6$ molecule is retained as can be seen from Figure 3.

(b) Cd Coordination Spheres. Cd–ligand distances and the bond angles at the Cd atoms in the $[CdX_2(C_{12}H_{22}N_6)]$ complexes and in $[CdI_2(C_{12}H_{23}N_6OCH_3)]$ are given in Tables VIII and IX, respectively. One of the coordination hemispheres in the $[CdX_2(C_{12}H_{22}N_6)]$ complexes is filled by the hexaamine acting as a tetradentate ligand. The other one is occupied by two terminal halogenide ligands. Hence, the metal is six-coordinate in a N_4X_2 environment. The coordination polyhedron is derived from a distorted tetrahedron formed by the atoms X, X′, N(1), and N(1′). Two additional bonds, namely Cd–N(3) and Cd–N(3′), are inserted near the N(1)···N(1′) edge. This description is consistent with the values of the angles X–Cd–X′, X–Cd–N(1), X–Cd–N(1′), and N(1)–Cd–N(1′) and with the fact that the Cd–N(3) bond is a long ("secondary") bond. From the angular criterion the least distorted X, X′, N(1), N(1′) tetrahedron is found in the iodo complex. In the chloro and bromo complexes the $\{CdX_2\}$ groups are twisted around the twofold axes. This results in smaller X–Cd–N(1) (98.4 (1) and 92.6 (1)°, respectively) and larger X–Cd–N(1′) angles (115.5 (1) and 120.7 (1)°, respectively), compared with those of an ideal tetrahedron.

There are two types of small N–Cd–N angles in the $[CdX_2(C_{12}H_{22}N_6)]$ complexes. One is within the four-membered chelate ring that consists of the atoms Cd, N(1), C(2), and N(3′). With such small rings a small angle at the Cd atom is not unexpected. The other one, however, is within the five-membered chelate ring consisting of the atoms Cd, N(3), C(1), C(2), and N(3′). This kind of ring generally adopts a conformation in which the N–Cd–N angle is near 75°. Examples are found in the complexes $[Cd(en)_3]^{2+}$ (74.5 (3) and 76.6 (3)°)[16] and $[Cd_2(apa)_2Cl_4]$ (77.5 (8)°).[17] In the $[CdX_2(C_{12}H_{22}N_6)]$ complexes the angle N(3)–Cd–N(3′) is only 59.8 (1) (**2**), 57.9 (1) (**3**), and 57.6 (1)° (**4**), respectively. This is a consequence of the rigid geometry of the ligand causing two very long Cd–N bonds and an unusually large displacement of the Cd atom from the N–C–C–N least-squares plane.

From literature data the length of a "standard" Cd–N(aliphatic amine) bond is estimated at 2.33 ± 0.05 Å.[18] The Cd–N(1) bond lengths in **2**–**4** are within this range, while the Cd–N(3) bonds are substantially longer (2.625 (2), 2.736 (3), and 2.739 (4) Å, respectively). The limit for zero bond formation between Cd and N should be at ~3.1 Å. This approximate value is the sum of the nonpolar covalent radius of Cd (1.493 Å,[19] which is close to the metallic radius of 1.52 Å[20]) and the van der Waals radius of N.[21] From general trends in bond-length/bond-order (energy) relations one can estimate that the Cd–N(3) bond in the chloro complex is about half as strong as the standard Cd–N bond; the Cd–N(3) bonds in the bromo and iodo complexes are even weaker. It should be noticed that the standard bond might well have a σ bond order below unity.

There are some indications that with increasing softness of the halogenide the N_4X_2 coordination in $[CdX_2(C_{12}H_{22}N_6)]$ becomes less favorable due to an increase of electron density at the cadmium:

(i) Substitution of chloride by the softer bromide ion is accompanied by geometrical changes that are directed toward a lowering of the coordination number from 6 to 4. The bonds Cd–N(3) and Cd–N(3′) are lengthened by 0.111 Å, and the atoms N(1) and N(1′), which together with X and X′ form the primary coordination sphere, move closer to the central atom by 0.033 Å. Within the hexaamine the distance N(1)···N(1′) decreases by 0.123 Å. However, the ability of the ligand to increase its "bending" is probably very limited. We suppose that the displacement of N(3) and N(3′) from the coordination sphere cannot continue in the iodo complex because of this steric restriction. Instead the Cd–N(1) bond length increases slightly.

(ii) On the basis of Sanderson's principle of electronegativity equalization[19] the following values of the partial charges at the halogen atoms and of the Cd–X bond lengths were calculated: X = Cl, –0.292, 2.466 Å; X = Br, –0.247, 2.565 Å; X = I, –0.166, 2.680 Å. In general, Sanderson's method is far less useful for coordination compounds than for simple molecules. In this special case, however, valuable information can be obtained from the comparison of calculated and experimental data for complexes of the *same* type. The calculated Cd–Cl bond length is in excellent agreement with the experimental value of 2.468 (1) Å, while the calculated Cd–Br and especially the Cd–I bond lengths are smaller than the observed values of 2.586 (1) and 2.774 (1) Å, respectively. Obviously the partial charge at the iodine atom and thus the iodine radius are larger than those calculated. In terms of the electronegativity-equalization model this can be explained by an unusually low electronegativity of the Cd in **4** caused by a comparatively high electron density. The iodine atoms are not involved in hydrogen bonding, which otherwise would have offered an alternative explanation of the difference between the calculated and the observed Cd–I bond lengths.

(iii) The six-coordinate complex $[CdI_2(C_{12}H_{22}N_6)]$ and the

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(16) Liu, S.; Huang, J. *Huaxue Xuebao* **1986**, *44*, 288.

(17) Cannas, M.; Marongiu, G.; Saba, G. *J. Chem. Soc., Dalton Trans.* **1980**, 2090. apa = (2-aminoethyl)(3-aminopropyl)amine.

(18) This value is the mean of 29 bond lengths involving nonbridging aliphatic N atoms in the following six-coordinate Cd complexes. Minimum and maximum values were 2.25 (1) and 2.44 (1) Å, respectively. $[Cd(en)_3]^{2+}$: Fujita, T.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 930. See also ref 16. $Cd(dien)(SCN)_2$: Cannas, M.; Carta, G.; Cristini, A.; Marongiu, G. *Inorg. Chem.* **1977**, *16*, 228. $Cd(dien)Cl_2$, $[Cd_2(apa)_2Cl_4]$, $[Cd_2(bpa)_2Cl_4]$ (bpa = bis(3-aminopropyl)amine): Reference 17. $\{NH_2(CH_2)_3NH_2\}CdCl_2$: Andreetti, G. D.; Cavalca, L.; Pellinghelli, M. A.; Sgarabotto, P. *Gazz. Chim. Ital.* **1971**, *101*, 488. $Cd\{NH_2(CH_2)_6NH_2\}Ni(CN)_4\cdot o\text{-}CH_3C_6H_4NH_2$: Hasegawa, T.; Nishikiori, S.; Iwamoto, T. *J. Inclusion Phenom.* **1984**, *2*, 351. $Cd\{NH_2(CH_2)_4NH_2\}Ni(CN)_4\cdot nG$, G = 2,5-$(CH_3)_2C_6H_3NH_2$ (n = 1): Nishikiori, S.; Iwamoto, T. *J. Inclusion Phenom.* **1984**, *2*, 341. G = C_4H_4NH (n = 1), $C_6H_5NH_2$ (n = 1.5), $C_6H_5N(CH_3)_2$ (n = 1): Nishikiori, S.; Iwamoto, T. *Inorg. Chem.* **1986**, *25*, 788.

(19) Sanderson, R. T. *Polar Covalence*; Academic: New York, 1983.

(20) In metallic cadmium there are two sets of distances between neighboring atoms. The corresponding bond radii are 1.487 and 1.643 Å: Wells, A. F. *Structural Inorganic Chemistry*; Clarendon: Oxford, 1984; Chapter 29.

(21) Well aware of the fact that atomic shapes can be nonspherical, throughout this paper we use the following *isotropic* values of the van der Waals radii. H (bonded to strongly electronegative elements), 1.0 Å: Baur, W. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1456. N, 1.6 Å; O, 1.5 Å; Cl, 1.7 Å: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1985**, *B41*, 274.

five-coordinate $[CdI_2(C_{12}H_{23}N_6OCH_3)]$ are formed under very similar conditions. In fact, when the temperature and concentrations were adjusted between the values given for the preparations of pure **4** and **5**, mixtures containing variable amounts of both compounds were obtained. In the chloride and bromide systems no complexes with coordination numbers lower than 6 were observed. The tendency of the $\{CdI_2\}$ group to decrease the number of atoms in the Cd coordination sphere is not inconsistent with the idea of a destabilization of the $[CdI_2(C_{12}H_{22}N_6)]$ complex by a high electron density at the metal center.

The N_3I_2 coordination polyhedron of the complex $[CdI_2(C_{12}H_{23}N_6OCH_3)]$ in **5** consists of the atoms N(1), N(2), N(4), I(1), and I(2). It is best described as a distorted square pyramid with I(2) as the apical atom. The distortion in five-coordinate complexes can be quantified by the "degree of trigonality" defined as $\tau = (\beta - \alpha)/60$, where β is the largest and α the second largest of the L_{basal}–M–L_{basal} angles.[22] In the present case we find β = 150.8 (1)° (I(1)–Cd–N(2)) and α = 134.1 (3)° (N(1)–Cd–N(4)) and thus τ = 0.28; the limiting values are τ = 0 for an ideal tetragonal geometry and τ = 1 for an ideal trigonal-bipyramidal geometry. The angles α and β are relatively small. For this situation in a d^{10} system calculations predict that the apical M–L bond will be stronger than the basal bonds.[23] Consistent with this prediction, in $[CdI_2(C_{12}H_{23}N_6OCH_3)]$ the apical Cd–I(2) bond is significantly shorter than the basal Cd–I(1) bond (2.775 (1) vs 2.812 (1) Å).

The Cd–N(2) bond is 0.18 Å longer than the Cd–N standard bond (see above) but is still considerably shorter than the secondary bonds in the $[CdX_2(C_{12}H_{22}N_6)]$ complexes. In these complexes the weak Cd–N bonds are situated opposite to the halogenide atoms. Similarly the weakened Cd–N(2) bond in $[CdI_2(C_{12}H_{23}N_6OCH_3)]$ is trans to a Cd–I bond.

In **5** the oxygen atom O(1) is in the vicinity of Cd but should be considered nonbonded. The Cd···O(1) distance of 3.036 (5) Å is nearly as large as the Cd···C(12) distance of 3.049 (7) Å. The limit for bonding interaction between Cd and O, estimated in the same way as above for Cd and N, is at ~3.0 Å. Furthermore, the angles at O(1), e.g. Cd···O(1)–C(12) = 77.1 (3)°, do not indicate coordinative bonding to Cd.

(c) Hydrogen Bonding. In **1** the intermolecular distance of the hydrogen atom H(N1) to N(1″) (1 – *x*, 0.5 + *y*, 0.5 – *z*) is 2.47 (2) Å, which is less than the van der Waals distance of 2.6 Å.[21] The distance N(1)···N(1″) is 3.367 (2) Å. The angles at N(1″) involving H(N1) are 89 (1), 114 (1), and 125 (1)°. The angle N(1)–H(N1)···N(1″) is 167 (1)°. These geometrical data together with the presence of an intense and split ν(NH) band in the infrared spectrum at 3250/3240 cm^{-1} are indicative of hydrogen bonding.[24] The result is infinite ···N–H···N–H··· chains along the crystallographic *b* direction.

In compound **2** there is possibly a weak bonding interaction between H(N1) and Cl″ (–*x*, 1 – *y*, –*z*). The distance N(1)···Cl″ (3.323 (3) Å) is about equal to the sum of the van der Waals radii (3.3 Å).[21] The angles N(1)–H(N1)···Cl″ and H(N1)···Cl″–Cd″ are 141 (2) and 117 (2)°, respectively.

The hydrogen bridge systems in **3** and **4** resemble each other. In both compounds the methanol molecule acts as acceptor and donor in two hydrogen bonds to two $[CdX_2(C_{12}H_{22}N_6)]$ complexes. In **3** the O···N(2) distance is 2.886 (5) Å (O–H(O)···N(2) = 172 (4)°) and the distance O···N(1″) is 2.949 (5) Å (O···H(N1″)–N(1″) = 142 (4)°; N(1″) and H(N1″) are at 0.5 – *x*, –0.5 – *y*, 1 – *z*). The corresponding values for **4** are O···N(2′) = 2.798 (6) Å, O–H(O)···N(2′) = 165 (4)°, O···N(1″) = 2.952 (6) Å, and O···H(N1″)–N(1″) = 147 (4)° (N(2′) is at 0.5 – *x*, 0.5 – *y*, *z*; N(1″) and H(N1″) are at 1 – *x*, 0.5 + *y*, 0.5 – *z*).

Finally, in compound **5** the oxygen atom O(2) of the methanol molecule has relatively short contacts of 2.75 (1) Å to its symmetry equivalent at 1 – *x*, 1 – *y*, 1 – *z* and of 2.98 (1) Å to N(6′) (1 – *x*, –0.5 + *y*, 1.5 – *z*). The hydrogen atom H(O2) could not be located. However, from geometrical considerations the presence of a O(2)–H(O2)···N(6′) bridge is more likely than a dimerization of the methanol molecules through hydrogen bridges.

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Registry No. **1**, 113585-93-6; **1**·$2CHCl_3$, 113666-13-0; **2**, 113585-86-7; **3**, 113585-88-9; **4**, 113585-90-3; **5**, 113585-92-5; MeOH, 67-56-1; $(CHO)_2$, 107-22-2; $HN(CH_2CH_2NH_2)_2$, 111-40-0.

Supplementary Material Available: Tables of thermal parameters, additional bond lengths and angles, and calculated hydrogen atom coordinates (6 pages); tables of observed and calculated structure factors (51 pages). Ordering information is given on any current masthead page.

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