Synthesis, Spectroscopic and X-Ray Structural Characterization of $[\text{Cd}(\text{linpen})]^{2+}$, a Model for Metal Complexes of the Chelating Polymer Polyethyleneimine (linpen = Linear Pentaethylenhexamine)

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The isolation of 3,6,9,12-tetraazatetradecane-1,14-diamine (linear isomer of pentaethylenhexamine, linpen) from a technical polyamine mixture is described. In methanol, linpen acts as a hexadentate ligand towards cadmium(II). The solid compounds $[\text{Cd}(\text{linpen})](\text{BPh}_4)_2$ (**1**), $[\text{Cd}(\text{linpen})](\text{BPh}_4)_2 \cdot 2 \text{DMSO}$ (**2**) and $[\text{Cd}(\text{linpen})](\text{BF}_4)_2$ (**3**) have been isolated and characterized by elemental analysis, spectroscopy and X-ray powder diffraction. The ^{113}Cd NMR resonance of **1** is at 351 ppm (0.30 M in $\text{DMSO}-d_6$, standard: 0.10 M $\text{Cd}(\text{ClO}_4)_2$ in D_2O).

2 and **3** have been structurally characterized by single-crystal X-ray diffraction. **2**: $C2/c$; $a = 19.337(1) \text{ \AA}$, $b = 17.937(1) \text{ \AA}$, $c = 18.584(1) \text{ \AA}$, $\beta = 111.54(1)^\circ$; $Z = 4$, $R = 0.034$, $R_w = 0.033$. **3**: $P2_1/n$; $a = 8.607(1) \text{ \AA}$, $b = 14.851(2) \text{ \AA}$, $c = 15.703(2) \text{ \AA}$, $\beta = 91.21(2)^\circ$; $Z = 4$, $R = 0.083$, $R_w = 0.072$. Both compounds contain discrete $[\text{Cd}(\text{linpen})]^{2+}$ complexes. The hexamine wraps around the metal ion in a helical manner. This results in a strong distortion of the coordination polyhedron. The mean $\text{Cd}-\text{N}$ bond lengths are 2.38 Å and 2.37 Å for **2** and **3**, respectively.

Models for MN_6 centers in metal-polyethyleneimine (PEI) complexes are derived from the structure of $[\text{Cd}(\text{linpen})]^{2+}$. For example, loops at the MN_6 site in molecules of linear PEI are proposed.

Introduction

Polyethyleneimine (PEI) is a water-soluble polyamine which consists of either linear or highly branched macromolecules depending on the method of preparation [1, 2]. In the linear form only one type of functional group is present, namely the secondary amino group. In contrast to that, branched PEI contains primary, secondary and tertiary nitrogen atoms. A molar ratio of 1:2.1:1.7 has recently been determined for the three different functional groups of a commercially available PEI (Polymin P, BASF) [3].

A characteristic property of PEI is its ability to form soluble chelate complexes with several metal ions including cadmium(II) [4–7]. Indirectly, information about the metal coordination in PEI complexes should be obtainable by using appropriate low-molecular-weight amines as model ligands. We therefore studied the interaction between cadmium(II) and the PEI model 3,6,9,12-tetraazatetradecane-1,14-diamine (linear isomer of pentaethylenhexamine, linpen).

So far, $[\text{Co}(\text{linpen})]^{3+}$ is the only linpen complex whose X-ray structure has been determined [8]. The cobalt(III) ion is bonded to six nitrogen atoms forming a slightly distorted octahedron. A much stronger distortion of the coordination polyhedron can be expected for the analogous six-coordinate cadmium complex $[\text{Cd}(\text{linpen})]^{2+}$ because of the considerably larger octahedral ionic radius of $\text{Cd}(\text{II})$ as compared to $\text{Co}(\text{III})$ (0.95 vs. 0.55 Å (low spin) [9]). Actually, the existence of a 1:1 $\text{Cd}(\text{II})$ -linpen complex has been deduced from polarographic measurements in aqueous solution [10]. Therefore, the question arose whether the strongly distorted monomeric species $[\text{Cd}(\text{linpen})]^{2+}$ or instead other complexes with reduced geometrical distortions (dimers, polymers, solvent adducts with higher (>6) coordination numbers) could be isolated. The results of our study are presented in this paper.

Experimental

The following chemicals and solvents were used: 50% aqueous solution of $\text{Cd}(\text{BF}_4)_2$ (Alfa),

$\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (99%, Strem), technical pentaethylenhexamine (Aldrich), toluene-4-sulfonic acid monohydrate (Riedel-de Haën), sodium metal (Merck), reagent-grade $\text{Cd}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$ ($\geq 99\%$, Riedel-de Haën), reagent-grade sodium tetraphenylborate ($> 99.5\%$, Fluka), P_4O_{10} drying agent 'Sicapent' (Merck), methanol ($\geq 99.8\%$, Merck), chloroform (99.0–99.4%, Kraft), and dimethyl sulfoxide ($\geq 99.5\%$, Riedel-de Haën). The solvents were reagent grade.

^{13}C and ^{113}Cd NMR spectra were measured with a Bruker AM-300 instrument. IR spectra were obtained on a Beckman IR-4220 spectrophotometer. Mass spectra were recorded on a Finnigan MAT 212 instrument equipped with an SS 300 data system. A Philips PW 1710 automated powder diffractometer system ($\text{CuK}\alpha$ radiation) was used to obtain the X-ray powder diffraction data. The Cd content of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was determined by ion chromatography. The other elemental analyses were performed by the Microanalytical Laboratory Beller, Göttingen, FRG. Analytical, spectroscopic, and X-ray powder diffraction data of linpen and its cadmium compounds are compiled in Table I.

Preparation of compounds

$\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

Two flasks containing 50% aqueous solution of $\text{Cd}(\text{BF}_4)_2$ and Sicapent, respectively, were connected and evacuated. The solution was allowed to concentrate until the first crystals appeared that did not redissolve on shaking. The flasks were disconnected, and the solution was stored at -30°C overnight. Colourless crystals of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ formed which were separated from the cold mother liquor and dried in vacuo for 2 h. The product was identified as the hexahydrate by its Cd content and by comparison of its X-ray powder diffraction pattern with that of the isomorphous [11] perchlorate hexahydrate.

$\text{H}_{12}\text{B}_2\text{CdF}_8\text{O}_6$ (394.1)

Calcd Cd 28.52,

Found Cd 28.45.

3,6,9,12-Tetraazatetradecane-1,14-diamine (linpen)

Technical pentaethylenhexamine was prepurified by column distillation under reduced pressure. The fraction passing over at $160\text{--}175^\circ\text{C}/0.2\text{ mbar}$ was collected. This product was reacted with toluene-4-sulfonic acid according to a literature method to give the hexatosylate salt heptahydrate

$(\text{linpenH}_6)(\text{C}_7\text{H}_7\text{SO}_3)_6 \cdot 7\text{H}_2\text{O}$ [12]. After one recrystallization from water, the salt was dried and dehydrated over Sicapent in a vacuum desiccator; constant weight was reached after 7–10 days.

$\text{C}_{52}\text{H}_{76}\text{N}_6\text{O}_{18}\text{S}_6$ (1265.6, dehydrated form)

Calcd C 49.35 H 6.05 S 15.20,

Found C 49.35 H 6.21 S 15.08.

2.07 g (90 mmol) of sodium metal were dissolved in 250 ml of methanol. A 19.0 g (15.0 mmol) sample of $(\text{linpenH}_6)(\text{C}_7\text{H}_7\text{SO}_3)_6$ was added, and the resulting solution was stirred for 15 min. Subsequently, the solvent was removed by rotary evaporation. The residue (linpen and $\text{C}_7\text{H}_7\text{SO}_3\text{Na}$) was kept under vacuo at 60°C for 30 min and then extracted three times with a total of 200 ml of chloroform. The extracts were filtered and combined. Chloroform was evaporated, and the remaining product was dried to constant weight in vacuo at room temperature, then at 50°C , and again at room temperature. Linpen was obtained as a light-brown liquid. In some preparations it was found necessary to remove suspended material from the final product by centrifugation. Yield 3.0 g (86%).

$[\text{Cd}(\text{linpen})](\text{BPh}_4)_2$ (1)

2.67 g (10.0 mmol) of $\text{Cd}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 50 ml of methanol. To the stirred solution first 2.32 g (10.0 mmol) of linpen dissolved in 50 ml of methanol and then 6.84 g (20.0 mmol) of NaBPh_4 dissolved in 100 ml of methanol were added dropwise. The reaction mixture was allowed to stand for 1 h to complete the crystallization. The product $1 \cdot x\text{MeOH}$ was isolated on a glass filter, washed with methanol and dried in vacuo. To remove the crystal methanol completely, the substance was kept under dynamic vacuo for *ca.* 10 h. The desolvation process was monitored by ^{13}C NMR spectroscopy (methanol signal at 48.7 ppm in DMSO-d_6). **1** was obtained as a white powder. Yield 8.5 g (86%).

$[\text{Cd}(\text{linpen})](\text{BPh}_4)_2 \cdot 2\text{DMSO}$ (2)

The compound was prepared by diffusion of methanol into a solution of **1** in dimethyl sulfoxide (DMSO). Typically a 0.2 g sample of **1** was dissolved in 2 ml of DMSO, and the solution was covered with a layer of methanol in a test tube. After a few days, colourless compact crystals of **2** had formed which had edge lengths up to several millimeters. The crystals were isolated on a glass filter, washed with methanol and dried in vacuo for a short period. They are stable in air at least for some days.

[Cd(linpen)](BF₄)₂ (3)

A solution of 2.32 g (10.0 mmol) of linpen in 50 ml of methanol was added dropwise to a stirred solution of 3.94 g (10.0 mmol) of Cd(BF₄)₂ · 6H₂O in 20 ml of methanol. After the reaction mixture had stood for 1 h, the precipitate was isolated on a glass filter, washed two times with small amounts of ice-cold methanol and dried in vacuo. **3** was obtained as a white crystalline powder. Yield 3.4 g (66%).

X-ray structure determinations

Suitable single crystals of **2** and **3** were obtained by layering methanol over solutions of **1** and **3**, respectively, in dimethyl sulfoxide as described

above for **2**. The crystals were sealed into thin-walled glass capillaries and mounted on a Siemens/STOE AED2 automated four-circle diffractometer (MoK α radiation). Details of the routine procedures of data collection and reduction used in our laboratory are given elsewhere [13]. No absorption corrections were applied. Crystal data and information pertaining to data collections and structure refinements are summarized in Table II.

The structures were solved by direct methods with use of the structure-solution program SHELXS-86 [14]. Other computer programs used were SHELX [15] and SCHAKAL [16]. Atomic scattering factors for spherical neutral free (all except H) and bonded (H) atoms [17] were employed throughout the refinements. In the case of **2**, the

Table I. Analytical, spectroscopic, and X-ray powder diffraction data for linpen, [Cd(linpen)](BPh₄)₂ (**1**), [Cd(linpen)](BPh₄)₂ · 2 DMSO (**2**) and [Cd(linpen)](BF₄)₂ (**3**).

linpen	C ₁₀ H ₂₈ N ₆ (232.4) Calcd C 51.69 H 12.15 N 36.17, Found C 51.76 H 11.96 N 36.12. Mass spectrum (chemical ionization, <i>iso</i> -butane): <i>m/e</i> 233 ([M+H] ⁺). ¹³ C NMR (CDCl ₃): δ 52.5, 49.4 ^a , 49.3, 41.8. IR (5% in CCl ₄): 3310 (m), 2935 (s), 2905 (s), 2830 (s), 1450 (m), 1360 (w), 1335 (w), 1118 cm ⁻¹ (m).
1	C ₅₈ H ₆₈ B ₂ CdN ₆ (983.3) Calcd C 70.85 H 6.97 B 2.20 Cd 11.43 N 8.55, Found C 70.71 H 7.09 B 2.18 Cd 11.39 N 8.57. ¹³ C NMR (DMSO-d ₆): δ 163.4 (q, ¹ J(¹³ C, ¹¹ B) = 49 Hz), 135.6, 125.3, 121.5, 47.0, 45.5, 45.2, 44.6, 38.5. ¹¹³ Cd NMR (0.30 M in DMSO-d ₆) ^b : δ 351. IR (KBr disc): 3320 (w), 3265 (m), 3050 (m), 1577 (m), 1476 (m), 1424 (m), 756 (m), 737 (s), 711 (s), 612 cm ⁻¹ (m). X-ray diffraction ^c : 10.21(42), 9.94(100), 9.22(28), 7.24(21), 6.40(21), 6.24(58), 6.14(62), 5.89(49), 5.39(42), 5.29(38), 5.23(44), 5.11(64), 5.01(42), 4.91(30), 4.55(24), 4.43(23), 4.21(62), 4.13(27), 3.98(32), 2.85 Å (21).
2	IR (KBr disc): 3320 (m), 3270 (m), 3245 (m), 3055 (m), 2990 (m), 1578 (m), 1481 (m), 1429 (m), 1260 (m), 1132 (m), 1112 (m), 1090 (m), 1023 (s), 995 (s), 946 (s), 896 (m), 832 (m), 740 (vs), 709 (vs), 612 cm ⁻¹ (s). X-ray diffraction ^c : 12.76(50), 11.87(100), 9.21(62), 8.21(17), 7.98(52), 7.86(45), 6.52(26), 6.37(84), 6.24(21), 5.85(79), 5.52(19), 5.22(18), 5.01(39), 4.93(84), 4.80(17), 4.61(33), 4.51(43), 4.30(20), 4.22(18), 4.10(46), 3.93(46), 3.89(31), 3.82(34), 3.77(36), 3.58(49), 3.52(17), 3.49(14), 3.26(26), 3.24(32), 3.14(19), 3.00(24), 2.96(21), 2.92(25), 2.72(14), 2.70(13), 2.66(13), 2.61(17), 2.53(26), 2.39(14), 2.38(19), 2.36(14), 2.31(13), 2.13 Å (14).
3	C ₁₀ H ₂₈ B ₂ CdF ₈ N ₆ (518.4) Calcd C 23.17 H 5.44 B 4.17 Cd 21.68 F 29.32 N 16.21, Found C 23.31 H 5.37 B 4.10 Cd 21.77 F 29.1 N 16.26. ¹³ C NMR (CD ₃ CN): δ 48.2, 46.9, 46.7, 45.8, 39.8. IR (Nujol mull) ^d : 3370 (m), 3325 (m), 1590 (m), 1316 (m), 1289 (m), 1068 (s, br), 972 (m), 940 (m), 894 (m), 842 (m), 830 (m), 523 cm ⁻¹ (m). X-ray diffraction ^c : 7.56(32), 7.42(100), 6.94(55), 6.76(51), 5.39(26), 5.29(25), 4.51(20), 4.43(12), 4.30(22), 3.85(10), 3.80(29), 3.71(40), 3.47(14), 3.33(15), 2.87(13), 2.81(10), 2.77(19), 2.47(9), 2.35(9), 2.09(10), 2.07(10), 2.04 Å (10).

^a About double intensity due to the overlap of two signals; ^b 0.10 M Cd(ClO₄)₂ in D₂O as external standard (δ 0); standard/sample substitution; chemical shift corrected for the ²H lock-frequency difference between D₂O and DMSO-d₆; ^c d spacings with approximate relative intensities in parentheses; 2θ range: 5–45°; ^d In KBr discs at least partial decomposition occurs, indicated by the appearance of two additional ν (NH) bands at 3460 and 3220 cm⁻¹ and an additional δ (BF₄⁻) band at 536 cm⁻¹.

initial choice of the centrosymmetric space group $C2/c$ was confirmed by the successful structure refinement. The space group of **3** $P2_1/n$ is uniquely defined by its systematic absences.

In the final structural model of **2** the positions of all non-hydrogen atoms and of the hydrogen atoms within the ligand and the solvent molecule were refined. The H atoms of the BPh_4^- anion were included on idealized positions. All H atoms were given fixed U values of $0.09 \text{ \AA}^2$. All non-hydrogen atoms were refined anisotropically.

In the case of **3** the positions of all non-hydrogen atoms were refined. The H atoms were given idealized positions and fixed U values of $0.10 \text{ \AA}^2$. Except for the Cd atom and the N atoms, the non-hydrogen atoms were refined isotropically. Anisotropic refinement of the C atoms has also been tried. However, this resulted in unreasonable large N–C–C angles, probably due to disorder of the linpen ligand. Split atom positions gave unreasonable bond distances. Both BF_4^- anions are disordered. The severe disorder of $B(2)F_4^-$ could not be described entirely satisfactory. Final atomic coordinates for **2** and **3** are given in Tables III and IV,

respectively*. The equivalent isotropic displacement factors are defined as in ref. [18]. Their standard deviations were estimated by the method given in ref. [19] (equation (2) therein).

Results and Discussion

Reactions and spectroscopic properties

Commercially available 'pentaethylenhexamine' is a mixture of several compounds [20]. The products offered by Aldrich and Fluka show very similar ^{13}C NMR spectra with at least 22 peaks of which the four most intense ones belong to the linear isomer linpen (*cf.* Table I). Thin-layer chromatography of the Aldrich product (conditions as

* Further details of the crystal structure determinations have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, and may be obtained by quoting the deposition number CSD 56085, the authors and the literature citation.

	2	3
Formula	$C_{62}H_{80}B_2CdN_6O_2S_2$	$C_{10}H_{28}B_2CdF_8N_6$
Formula weight	1139.5	518.4
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a (Å)	19.337(1)	8.607(1)
b (Å)	17.937(1)	14.851(2)
c (Å)	18.584(1)	15.703(2)
β (°)	111.54(1)	91.21(2)
V (Å ³)	5995.7	2006.8
Z	4	4
d_{calc} (g/cm ³)	1.262	1.716
Crystal dimensions (mm)	$0.68 \times 0.53 \times 0.30$	$0.23 \times 0.19 \times 0.04$
μ (MoK α) (cm ⁻¹)	4.46	11.3
2θ limits (°)	$3 \leq 2\theta \leq 52$	$3 \leq 2\theta \leq 48$
Index range	$+h, +k, \pm l$	$+h, +k, \pm l$
Scan type	ω -2 θ scan	ω -2 θ scan
Temperature (°C)	24 ± 1	24 ± 1
No. unique data with $I > 2\sigma(I)$	4787	1562
No. parameters	399	170
g^a	0.0002	0.0002
R^b	0.034	0.083
$R^c_{w,a,c}$	0.033	0.072
Largest shift/esd for final cycle	0.001	0.067
Max/min electron density in final difference map (e/Å ³)	$+0.27/-0.18$	$+1.01/-0.85$

Table II. Crystal data and details of intensity collections and structure refinements for $[Cd(\text{linpen})](BPh_4)_2 \cdot 2\text{DMSO}$ (**2**) and $[Cd(\text{linpen})](BF_4)_2$ (**3**).

^a The weighting scheme was

$w = (\sigma^2(F_o) + gF_o^2)^{-1}$;

^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$;

^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

Table III. Atomic coordinates and equivalent isotropic displacement factors ($\times 100$) for [Cd(linpen)](BPh₄)₂ · 2 DMSO (**2**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq} (Å ²)
Cd	0.00	0.15913(1)	0.25	4.48(1)
S	0.03118(4)	0.28897(4)	0.02101(4)	6.11(2)
O	0.0147(1)	0.2414(1)	0.0793(1)	7.69(5)
N(1)	−0.0003(2)	0.0818(1)	0.1486(1)	6.55(6)
N(2)	0.1297(1)	0.1368(1)	0.2704(1)	6.08(5)
N(3)	0.0667(1)	0.2649(1)	0.3181(1)	5.90(5)
C(1)	0.0712(2)	0.0414(2)	0.1741(2)	7.38(9)
C(2)	0.1337(2)	0.0952(2)	0.2034(2)	7.38(8)
C(3)	0.1649(2)	0.2100(2)	0.2813(2)	7.01(8)
C(4)	0.1474(2)	0.2525(2)	0.3434(2)	7.27(8)
C(5)	0.0415(2)	0.3313(2)	0.2702(2)	7.42(8)
C(6)	0.1912(1)	0.4337(1)	−0.0703(1)	4.73(5)
C(7)	0.1145(1)	0.4462(1)	−0.1021(1)	6.00(6)
C(8)	0.0641(2)	0.3921(2)	−0.1457(2)	7.88(8)
C(9)	0.0894(2)	0.3240(2)	−0.1582(2)	9.28(10)
C(10)	0.1641(2)	0.3092(2)	−0.1276(2)	9.53(10)
C(11)	0.2136(2)	0.3633(1)	−0.0852(2)	6.93(7)
C(12)	0.3276(1)	0.4605(1)	0.0340(1)	4.18(5)

Table III (continued).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq} (Å ²)
C(13)	0.3824(1)	0.4385(1)	0.0063(1)	5.39(6)
C(14)	0.4462(1)	0.3996(1)	0.0503(1)	6.03(6)
C(15)	0.4575(1)	0.3805(1)	0.1250(1)	5.95(6)
C(16)	0.4056(1)	0.4015(1)	0.1554(1)	6.10(6)
C(17)	0.3424(1)	0.4413(1)	0.1113(1)	5.12(5)
C(18)	0.2119(1)	0.5515(1)	0.0240(1)	4.49(5)
C(19)	0.2067(1)	0.6288(1)	0.0186(1)	5.30(5)
C(20)	0.1742(2)	0.6717(1)	0.0601(2)	6.85(7)
C(21)	0.1463(2)	0.6384(2)	0.1100(2)	7.07(7)
C(22)	0.1494(1)	0.5616(2)	0.1176(2)	6.64(7)
C(23)	0.1808(1)	0.5193(1)	0.0744(1)	5.62(6)
C(24)	0.2691(1)	0.5504(1)	−0.0889(1)	4.61(5)
C(25)	0.2293(1)	0.5455(1)	−0.1687(1)	5.79(6)
C(26)	0.2471(2)	0.5889(2)	−0.2221(2)	7.47(8)
C(27)	0.3054(2)	0.6380(2)	−0.1974(2)	7.60(9)
C(28)	0.3463(2)	0.6442(1)	−0.1195(2)	6.67(8)
C(29)	0.3283(1)	0.6011(1)	−0.0669(2)	5.65(6)
C(30)	0.0223(2)	0.3832(2)	0.0471(2)	7.52(8)
C(31)	0.1292(2)	0.2880(2)	0.0488(3)	8.80(10)
B	0.2498(1)	0.4996(1)	−0.0246(1)	4.39(5)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(Å ²)
Cd	0.25380(14)	0.25635(10)	0.10907(8)	5.21(3) ^a
N(1)	0.4814(20)	0.2399(11)	0.1900(13)	12.0(6) ^a
N(2)	0.3283(20)	0.4054(10)	0.1493(12)	8.8(6) ^a
N(3)	0.1832(18)	0.3504(12)	−0.0100(9)	8.1(5) ^a
N(4)	0.3487(22)	0.1812(13)	−0.0142(12)	10.3(6) ^a
N(5)	0.1796(21)	0.1011(10)	0.1245(11)	8.6(5) ^a
N(6)	0.0246(18)	0.2569(13)	0.1816(11)	10.3(5) ^a
C(1)	0.555(3)	0.322(2)	0.195(2)	11.2(8)
C(2)	0.469(3)	0.396(2)	0.207(2)	13.3(10)
C(3)	0.346(3)	0.459(2)	0.075(1)	9.0(7)
C(4)	0.210(3)	0.445(2)	0.018(2)	12.6(10)
C(5)	0.271(3)	0.327(1)	−0.078(2)	9.4(7)
C(6)	0.280(3)	0.226(1)	−0.090(1)	10.3(8)
C(7)	0.326(4)	0.088(2)	−0.001(2)	14.9(11)
C(8)	0.207(3)	0.054(2)	0.042(2)	11.8(10)
C(9)	0.016(3)	0.100(2)	0.142(2)	10.9(8)
C(10)	−0.029(3)	0.169(2)	0.199(2)	12.4(9)
B(1)	0.544(4)	−0.001(2)	0.253(2)	9.6(9)
F(1A) ^b	0.598(4)	−0.040(2)	0.326(2)	11.2(10)
F(2A) ^b	0.651(5)	0.044(3)	0.220(3)	15.2(15)
F(3A) ^b	0.495(4)	−0.079(2)	0.204(2)	14.2(12)
F(4A) ^b	0.410(4)	0.041(2)	0.274(2)	11.5(9)
F(1B) ^b	0.638(5)	−0.057(3)	0.281(3)	18.0(17)
F(2B) ^b	0.601(4)	0.047(2)	0.179(2)	11.4(11)
F(3B) ^b	0.410(4)	−0.032(2)	0.216(2)	12.7(10)
F(4B) ^b	0.496(4)	0.073(2)	0.308(2)	15.5(13)
B(2)	0.286(6)	0.237(4)	0.441(3)	17.3(16)
F(5)	0.201(3)	0.309(2)	0.496(1)	20.7(9)
F(6A) ^c	0.151(3)	0.216(2)	0.396(2)	16.4(10)
F(7A) ^c	0.376(4)	0.304(2)	0.417(2)	19.0(11)
F(8A) ^c	0.332(3)	0.184(2)	0.498(2)	16.9(9)
F(6B) ^d	0.168(8)	0.175(4)	0.460(4)	12.6(11)
F(7B) ^d	0.208(7)	0.265(5)	0.358(4)	12.6(11)
F(8B) ^d	0.394(7)	0.238(4)	0.399(4)	12.6(11)

Table IV. Atomic coordinates and isotropic displacement factors ($\times 100$) for [Cd(linpen)](BF₄)₂ (**3**).

^a Equivalent isotropic displacement factor; ^b Occupancy 0.50; ^c Occupancy 0.75; ^d Occupancy 0.25; a common U value was refined for F(6B), F(7B), and F(8B).

described in ref. [12]) revealed the presence of at least five components. The complete separation of linpen from its branched isomers and other accompanying substances cannot be achieved by distillation. However, linpen can be separated as the hydrochloride [21,22] or the per-tosylate salt [12]. But to our knowledge, the isolation and spectroscopic properties of linpen itself have not yet been reported. We have obtained the compound by treatment of the per-tosylate salt with methanolic sodium methoxide solution, followed by separation from the sodium tosylate formed:

Though the column distillation is not an especially effective purification step, it turned out to be necessary.

With cadmium(II) linpen forms the 1:1 complex $[\text{Cd}(\text{linpen})]^{2+}$ which can be isolated from methanolic solutions as crystalline BPh_4^- and BF_4^- salts:

The salt **1** obtained by desolvation of $[\text{Cd}(\text{linpen})](\text{BPh}_4)_2 \cdot x\text{MeOH}$ is, at least partly, microcrystalline. Its X-ray powder diffraction pattern is still reminiscent of that of the solvate.

The direct reaction of commercial 'pentaethylenhexamine' with Cd^{2+} in methanol followed by addition of NaBPh_4 does also afford a crystalline BPh_4^- salt. However, this product contains a mixture of different ligands. Thus, complex formation with Cd^{2+} is not a suitable method to purify linpen.

Most of the spectroscopic properties of linpen and its cadmium compounds **1–3** are unexceptional (see Table I). Worth mentioning is the $\nu(\text{SO})$ band at 1023 cm^{-1} in the infrared spectrum of **2**. It is lowered by 32 cm^{-1} compared to the position in free DMSO (1055 cm^{-1} [23]). This shift can be attributed to hydrogen bonding involving the O atom of the DMSO molecule and an NH group of the linpen ligand (see below).

The ^{113}Cd NMR signal of $[\text{Cd}(\text{linpen})]^{2+}$ is observed at 351 ppm. An almost equal value of 348 ppm has been reported for the ethylenediamine complex $[\text{Cd}(\text{en})_3]^{2+}$ [24]. Apparently, neither the different angular distortion of the CdN_6 coordination unit nor the different number of chelate rings seems to influence the chemical shift significantly. However, the contribution of secondary amine donors to the ^{113}Cd chemical shift is known to be smaller than that of primary ones [25]. Therefore, one would expect a considerably smaller value for $[\text{Cd}(\text{linpen})]^{2+}$ than for $[\text{Cd}(\text{en})_3]^{2+}$. At least one effect must be operative that compensates for this chemical-shift difference caused by the different donor sets. The chelate ring size which is of crucial importance to the chemical shift [24] is the same in both complexes.

Description of structures

Crystals of **2** consist of $[\text{Cd}(\text{linpen})]^{2+}$ cations, BPh_4^- anions and DMSO molecules. Crystals of **3** contain $[\text{Cd}(\text{linpen})]^{2+}$ cations and BF_4^- counterions. The metrical data of the CdN_6 coordination units given in Table V show the close structural similarities between the Cd complexes in both compounds. The complexes are depicted in Fig. 1. Since the structure determination of **3** is less accurate (see Experimental), we will essentially confine ourselves to the discussion of the structure of **2**.

$[\text{Cd}(\text{linpen})]^{2+}$ has a helical structure. The linpen molecule wraps around the metal ion and acts as a hexadentate ligand. This results in five 'fused' five-membered chelate rings. The ring conformations are $\delta\lambda\lambda\lambda\delta$ (and $\lambda\delta\delta\delta\lambda$ for the enantiomer) in the

case of **2**, and $\lambda\lambda\lambda\lambda\delta$ (and $\delta\delta\delta\delta\lambda$) for **3**. The conformational difference between the first and the fifth ring of the $[\text{Cd}(\text{linpen})]^{2+}$ complex in **3** is the only strong deviation from C_2 symmetry. In **2** the complex has crystallographically imposed C_2 symmetry.

The Cd–N bond lengths in **2** range from 2.338(2) to 2.429(2) Å. The mean value is 2.38 Å. This is only slightly larger than the average Cd–N bond lengths in $[\text{Cd}(\text{en})_3]^{2+}$ (2.37 Å, primary N atoms as donors [26,27]) and in $[\text{Cd}(\text{tacn})_2]^{2+}$ (2.36 Å, secondary N atoms as donors, tacn = 1,4,7-triazacyclononane [28]). The small intra-chelate N–Cd–N angles (mean value: 74.0°) together with the ‘fusion’ of the chelate rings cause severe distortions from ideal geometries (octahedral and trigonal-prismatic). A complex having a similar distortion around one of its Cd atoms is $[\text{Cd}_2(\text{[30]aneN}_{10})\text{Cl}_2]^{2+}$ [29].

In **2** the $[\text{Cd}(\text{linpen})]^{2+}$ complex forms two hydrogen bonds to adjacent DMSO molecules (see Fig. 2). The N···O distance within the N–H···O

Fig. 2. Structure and atomic labelling scheme of the $[\text{Cd}(\text{linpen})]^{2+} \cdot 2 \text{DMSO}$ aggregate in **2**. Hydrogen bonds are shown as broken lines. A crystallographic twofold axis of rotation passes through the Cd atom and is perpendicular to the projection plane. Hydrogen atom are omitted for clarity except those involved in hydrogen bonding.

system is 2.92 Å and is thus significantly shorter than the sum of the van der Waals radii (3.07 Å [30], 3.14 Å [31]).

Table V. Bond distances (Å) and angles (°) for the CdN_6 coordination units of $[\text{Cd}(\text{linpen})](\text{BPh}_4)_2 \cdot 2 \text{DMSO}$ (**2**) and $[\text{Cd}(\text{linpen})](\text{BF}_4)_2$ (**3**)^a.

2		3	
Cd–N(1)	2.338(2)	Cd–N(1)	2.33(1)
		Cd–N(6)	2.30(1)
Cd–N(2)	2.429(2)	Cd–N(2)	2.39(2)
		Cd–N(5)	2.41(2)
Cd–N(3)	2.381(2)	Cd–N(3)	2.40(2)
		Cd–N(4)	2.39(2)
N(1)–Cd–N(2)	74.0(1)	N(1)–Cd–N(2)	74.6(6)
		N(5)–Cd–N(6)	73.8(6)
N(2)–Cd–N(3)	73.8(1)	N(2)–Cd–N(3)	74.3(6)
		N(4)–Cd–N(5)	74.4(6)
N(3)–Cd–N(3')	74.3(1)	N(3)–Cd–N(4)	74.1(6)
N(1)–Cd–N(1')	107.2(1)	N(1)–Cd–N(6)	116.8(7)
N(1)–Cd–N(2')	94.6(1)	N(1)–Cd–N(5)	93.8(6)
		N(2)–Cd–N(6)	95.4(6)
N(1)–Cd–N(3')	101.8(1)	N(1)–Cd–N(4)	95.5(7)
		N(3)–Cd–N(6)	100.3(6)
N(1)–Cd–N(3)	137.9(1)	N(1)–Cd–N(3)	133.1(6)
		N(4)–Cd–N(6)	135.5(7)
N(2)–Cd–N(2')	161.0(1)	N(2)–Cd–N(5)	158.9(6)
N(2)–Cd–N(3')	122.8(1)	N(2)–Cd–N(4)	123.5(7)
		N(3)–Cd–N(5)	124.9(6)

^a The data for **3** are grouped under the assumption of C_2 symmetry.

Fig. 1. Structures and atomic labelling schemes of the $[\text{Cd}(\text{linpen})]^{2+}$ complexes in **2** (top) and **3** (bottom). Hydrogen atoms are omitted for clarity.

Relevance to metal-PEI complexes

Metal complexes of PEI are usually water-soluble. This indicates that no extensive crosslinking of the macromolecules by metal ions occurs. Probably most metal ions are attached to a single PEI molecule. This model gains support from the existence of the 1:1 complex $[\text{Cd}(\text{linpen})]^{2+}$ which is formed in spite of the strong distortion of its coordination polyhedron. A conceivable species with smaller angular distortions would be the hypothetical dimer $[\text{Cd}_2(\text{linpen})]^{4+}$ having a double helical structure analogous to that recently found in a sexipyridine complex of cadmium [32].

Based on the structure of $[\text{Cd}(\text{linpen})]^{2+}$, models of MN_6 centers in metal-PEI complexes are proposed (see Fig. 3). Perhaps the most intriguing structural features are loops induced by metal ions in linear PEI. Proving or disproving their existence may be difficult. Here, metal nucleus NMR spectroscopy seems to be one of the most promising physical methods.

Fig. 3. Schematic drawings of structures proposed for MN_6 centers in polyethyleneimine (PEI) complexes. Top: Loop in a molecule of linear PEI at the metal site. Bottom: One of several possible MN_6 arrangements in branched PEI. Coordinated N atoms are shown as dots.

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