Inorg. Chem. **1999,** *38,* 6164−6170

Trinuclear Zinc(II) Complexes and Polymeric Cadmium(II) Complexes with the Ligand 2,5-Bis(2-pyridyl)pyrazine: Synthesis, Spectral Analysis, and Single-Crystal and Powder X-ray Analyses

Antonia Neels and Helen Stoeckli-Evans*

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

Received July 16, 1999

Three zinc compounds, $[ZnCl_2(bppz)(dmf)]$ (**1**), $[Zn_3(OAc)_6(bppz)_2](H_2O)$ (**2**), and $[Zn_3(Cl)_6(bppz)_3](H_2O)$ (**3**), and two cadmium complexes, $\{[Cd(OAc)_2(bppz)](H_2O)_5\}_n$ (**4**) and $[Cd(NO_3)_2(bppz)]_n$ (**5**), where bppz is 2,5-bis(2-pyridyl)pyrazine, have been synthesized and characterized spectroscopically and crystallographically. The mononuclear complex **1**, $C_{17}H_{17}Cl_2N_5OZn$, crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.654(1)$ Å, $b = 9.500(1)$ Å, $c = 22.997(1)$ Å, $\beta = 97.99(1)°$, and $Z = 4$; R1 for 2356 observed reflections $[I > 2\sigma(I)]$ was 0.058. The zinc atom has a distorted square planar coordination sphere with the ligand bppz connected in a mono-bidentate manner. The remaining coordination sites are occupied by the chloride counterions and by an oxygen atom of a solvent molecule. The trinuclear zinc compound **2**, $C_{40}H_{38}N_8O_{12}Zn_3\cdot H_2O$, crystallizes in the triclinic space group $P\bar{1}$, with $a = 12.238(4)$ Å, $b = 12.986(3)$ Å, $c = 15.470(4)$ Å, $\alpha = 75.65(1)°$, $\beta = 97.99(1)°$, $\gamma = 65.98(1)°$, and $Z = 2$; R1 for 4511 observed reflections $[I > 2\sigma(I)]$ was 0.07. This complex consists of a linear arrangement of three zinc atoms. The central zinc atom, located on a crystallographic inversion center, is connected by six bridging acetate groups to two symmetry-related zinc atoms. It has an almost perfect octahedral coordination environment. The outer symmetry-related zinc atoms are in a square pyramidal environment, and they coordinate to three acetate groups and to one bppz molecule in a mono-bidentate manner. Compound **3**, $C_{42}H_{30}Cl_6N_{12}Zn_3\cdot 1.25H_2O$, a cyclic zinc(II) trimer, crystallizes in the cubic space group $Ia\bar{3}d$, with $a = 26.311(1)$ Å and $Z = 16$; R1 for 692 observed reflections $[I > 2\sigma(I)]$ was 0.038. This trinuclear complex has a perfect triangular arrangement of the zinc atoms. Each zinc atom is connected to the other two by a bppz molecule. The coordination about the metal is best described as a distorted octahedral with four long distances in the basal plane, to two chlorines and to two nitrogen atoms, and two short distances in the axial direction, to two nitrogen atoms. With Cd^{II} two polymeric complexes, **4** and **5** were obtained. Compound **4**, $C_{18}H_{16}N_4O_4Cd\cdot 5H_2O$, crystallizes in the triclinic space group $P\bar{1}$, $a = 9.045(1)$ Å, $b = 10.438(1)$ Å, $c = 12.719(1)$ Å, $\alpha = 100.48(1)°$, $\beta = 95.05(1)°$, $\gamma = 95.86(1)°$, and $Z = 2$; R1 for 3694 observed reflections $[I > 2\sigma(I)]$ was 0.029. The analogous $Cd(NO_3)_2$ complex with bppz, **5**, could only be obtained in microcrystalline form, and its structure was solved by the use of X-ray powder diffraction methods. Compound **5**, $C_{14}H_{10}N_6O_6Cd$, crystallizes in the monoclinic space group $C2/c$, with $a = 11.6601(3)$ Å, $b = 11.9870(3)$ Å, $c = 12.1453(3)$ Å, $\beta = 103.348(2)°$, and $Z = 4$. In both **4** and **5** the cadmium atoms are bridged by the ligand bppz, so forming uniform one-dimensional coordination polymers. The cadmium ions exhibit the rare coordination number of 8, with two coordinated ligand molecules and two chelating acetate (**4**) or nitrate (**5**) groups.

Introduction

The pyrazine derivative 2,5-bis(2-pyridyl)pyrazine (bppz) has been used in the formation of one- and two-dimensional copper(II) coordination polymers, and their structural and magnetic properties have been described previously.[1−3] Using acetate, benzoate, or chloride ions, the metal centers are linked by the ligand bppz and the anions, which results in the formation of alternating polymeric chains. Binuclear complexes with first-row transition metals, such as Mn^{II}, Cu^{II}, and Fe^{II}, and oxygen-rich anions, such as SO_4^{2-}, NO_3^-, etc., are also known.[4] This electron-rich ligand has also been shown to form supra- or nanomolecular species with ruthenium and osmium.[5,6]

Here we present some zinc(II) and cadmium(II) chemistry with the ligand 2,5-bis(2-pyridyl)pyrazine (bppz). Our interest in the coordination chemistry of bppz with zinc(II) stems from the fact that several linear trinuclear zinc compounds have been reported as part of an investigation into zinc(II) carboxylate complexes with different organic ligands.[7] A number of polymeric zinc compounds were also prepared, and the carboxylate anions were found to coordinate in a *syn*−*syn* or a *syn*−*anti* manner.[8]

For cadmium(II), much attention has been given to one-, two-, and three-dimensional extended coordination compounds involving cadmium in the search for molecular-based materials

---

(1) Neels, A.; Stoeckli-Evans, H.; Escuer, A.; Vicente, R. *Inorg. Chem.* **1995**, *34*, 1946.

(2) Neels, A.; Stoeckli-Evans, H.; Escuer, A.; Vicente, R. *Inorg. Chim. Acta* **1997**, *260*, 189.

(3) Neels, A.; Mathez Neels, B.; Stoeckli-Evans, H.; Clearfield, A.; Poojary, D. *Inorg. Chem.* **1997**, *36*, 3402.

(4) Neels, A.; Stoeckli-Evans, H. *Chimia* **1993**, *47*, 198.

(5) Serroni, S.; Denti, G. *Inorg. Chem.* **1992**, *31*, 4251.

(6) Denti, G.; Serroni, S.; Campagna, S.; Ricevuto, V.; Juris, A.; Ciano, M.; Balzani, V. *Inorg. Chim. Acta* **1993**, *47*, 198.

(7) Clegg, W.; Little, I. R.; Straughan, B. P. *Inorg. Chem.* **1988**, *27*, 1916.

(8) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic: New York, 1993.

10.1021/ic990843v CCC: $18.00

with interesting physical properties.[9,10] The d^{10} configuration permits a wide variety of geometries and coordination numbers; however, the high coordination numbers of 7[11] and 8[12] are rare. While the use of cadmium(II) halides[10] and pseudohalides[13] in the reaction with pyrazine resulted in an octahedral coordination of the cadmium(II) ion and the formation of three-dimensional polymers, the use of cadmium(II) acetate, in a similar reaction, gave the coordination number of 7 for cadmium in a binuclear complex.[14]

Experimental Section

Materials and Methods. All chemicals were used as received without further purification. The synthesis and analytical and spectroscopic data for bppz have been reported elsewhere.[4] Infrared spectra were recorded on a Perkin-Elmer FT 1720X spectrometer using KBr pellets (abbreviations: vs = very strong, s = strong, m = middle, w = weak, b = broad). ^{1}H NMR measurements were carried out on a Bruker AMX 400 FTP spectrometer in CD_3OD (abbreviations: s = singlet, d = doublet, t = triplet). C, H, and N microanalysis were carried out by the Mikroelementaranalytische Laboratorium of the ETH in Zürich for compounds **1**, **2**, **4**, and **5** and by the Galbraith Laboratories, Knoxville, TN, for compound **3**. FAB mass-spectroscopy was carried out using a Bruker FTMS 4.7T BioAPEX II at the Institute of Organic Chemistry, University of Fribourg.

Preparation of [$ZnCl_2$(bppz)(dmf)] (1). 2,5-Bis(2-pyridyl)pyrazine (200 mg, 0.85 mmol) was added to an aqueous solution of $ZnCl_2$ (700 mg, 5.1 mmol, 50 mL). After stirring of the mixture for 2 days at room temperature, a light yellow powder was obtained. It was filtered off and recrystallized from dimethylformamide giving yellow crystals (yield 130 mg, 35%). Anal. Calcd for $C_{14}H_{10}N_4Cl_2Zn$: C, 45.38; H, 2.72; N, 15.12. Found: C, 45.61; H, 3.67; N, 15.29.

Preparation of [$Zn_3(OAc)_6(bppz)_2$](H_2O) (2). 2,5-Bis(2-pyridyl)pyrazine (200 mg, 0.85 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (168 mg, 0.85 mmol) were dissolved in acetic acid (20 mL) and refluxed for 4 h. After evaporation of the solvent, the residue was dissolved in acetonitrile (40 mL). After several days, yellow crystals were obtained (yield: 200 mg, 46%). Anal. Calcd for $C_{40}H_{38}N_8O_{12}Zn_3\cdot 0.5H_2O$: C, 46.69; H, 3.79; N, 10.89. Found: C, 46.48; H, 3.94; N, 10.72.

Preparation of [$Zn_3(Cl)_6(bppz)_3$](H_2O) (3). 2,5-Bis(2-pyridyl)pyrazine (50 mg, 0.21 mmol) was added to a solution of $ZnCl_2$ (29 mg, 0.21 mmol) in acetonitrile/water (10 mL/1 mL). After a few days the complex crystallized in the form of small orange crystals (yield: 85%). Anal. Calcd for $C_{14}H_{10}Cl_2N_4Zn$: C; 45.34; H, 2.70; N, 15.11. Found: C, 44.76; H, 2.71; N, 14.67.

Preparation of {[$Cd(OAc)_2$(bppz)]$(H_2O)_5$}$_n$ (4). 2,5-Bis(2-pyridyl)pyrazine (50 mg, 0.21 mmol) was added to a solution of $Cd(OAc)_2\cdot 2H_2O$ (56 mg, 0.21 mmol) in acetronitrile/water (20 mL/5 mL). By slow evaporation of the solution, yellow crystals were obtained after a few days (yield: 80 mg, 69%). Anal. Calcd for $C_{18}H_{20}CdN_4O_6$: C, 43.17; H, 4.03; N, 11.19; O, 19.17. Found: C, 42.70; H, 3.72; N, 11.03; O, 19.71.

Preparation of [$Cd(NO_3)_2$(bppz)]$_n$ (5). 2,5-Bis(2-pyridyl)pyrazine (100 mg, 0.42 mmol) was added to a solution of $Cd(NO_3)_2\cdot 4H_2O$ (130 mg, 0.42 mmol) in acetronitrile/water (20 mL/5 mL). By slow evaporation of the solution, a yellow microcrystalline powder was obtained within 3 days (yield: 142 mg, 70%). Anal. Calcd for $C_{14}H_{10}CdN_6O_6$: C, 35.69; H, 2.12; N, 17.84. Found: C, 35.62; H, 2.31; N, 17.62.

X-ray Data Collection and Structure Solution. Yellow crystals of compounds **1**, **2**, and **4**, having approximate dimensions of 0.49 × 0.23 × 0.11 mm (**1**), 0.34 × 0.15 × 0.15 (**2**), and 0.49 × 0.38 × 0.27 mm (**4**), were mounted on a Stoe-Siemens AED2 four-circle diffractometer. Intensity data were measured at room temperature using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The $\omega/2\theta$ scan technique was used to a maximum 2θ value of 50.0°. The cell parameters were determined from a least-squares treatment of the setting angles of 22 reflections with $13.0° < \theta < 18.5°$ (**1**), 23 reflections with $11.0° < \theta < 16.0°$ (**2**), and 24 reflections with $14.0° < \theta < 19.0°$ (**4**). For each data collection the intensities of the two standard reflections were measured every 60 min and were shown to decrease by less than 3% for all three compounds. For compound **3** a very small yellow crystal (ca. 0.05 × 0.05 × 0.05 mm) was mounted on a Stoe Imaging Plate diffractometer system (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite monochromator. Data collection was performed at room temperature using Mo Kα radiation ($\lambda = 0.710\,73$ Å). A total of 120 exposures (5 min/exposure) were obtained at an image plate distance of 80 mm (resolution $D_{\min}-D_{\max} = 14.23-0.87$ Å) with $0 < \varphi < 120°$ and the crystal oscillating through 1° in φ. The structures were solved by direct methods using the program SHELXS-97[15] and refined by full-matrix least-squares on F^2 with SHELXL-97.[16] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. One water molecule per molecule of complex was found in the crystal structure of compound **1**, and one highly disordered water molecule was found per asymmetric unit for complex **3**. For compound **4,** five water molecules were located in the asymmetric unit. No absorption corrections were applied. Crystallographic data for compounds **1**−**4** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2 for **1**−**3**, and in Table 3 for **4**.

X-ray Data Collection and Structure Solution for Compound 5. Compound **5** could only be obtained in microcrystalline form. Therefore, X-ray powder diffraction data were measured in transmission mode (0.3 mm rotating capillary) on a high-resolution laboratory powder diffractometer (Stoe STADIP) using copper Kα_1 radiation (1.5406 Å) and a curved germanium monochromator. Eight equivalent data sets were collected, each from 8 to 90° in 2θ with steps of 0.1° and a counting time of 28 s per step using a linear position sensitive detector (PSD). The latter is capable of measuring ca. 5° in 2θ for each step. No decomposition was observed during the measurement. A total of 668 peaks were extracted from the profile using the program EXPO.[17] With this data set a Patterson map was computed using SHELXS-97.[15] The position of the cadmium atom (special position 0.50, 0.32, 0.25) could be located. The approximate atomic positions of the nitrate anion and the ligand bppz were located from difference Fourier maps using the program SHELXL-97.[16] The ligand bppz was found to possess C_i symmetry. This structural model was refined in GSAS[18] using the profile over the range $8° < 2\theta < 90°$. After the initial refinement of the scale, background, and unit cell constants, the atomic positions were refined using soft constraints consisting of C−C and C−N bond distances and bond angles for the ligand bppz and the N−O bond distances and bond angles for the nitrate anion. Hydrogen atoms were included in calculated positions. Final refinement was carried out with low-weighted soft constraints for all atoms except for the cadmium atom and its coordination geometry which were refined freely. The constraints could not be removed completely without reducing the stability of the refinement. The cadmium atom was refined anisotropically while the remainder of the non-hydrogen atoms were refined isotropically. In the final cycles of refinement the shifts in all parameters were less than their estimated standard deviations. Neutral scattering factors were used for all atoms. No corrections were made for absorption or preferred orientation effects. The final Rietveld plot is given in Figure 1, and selected bond distances and angles are in Table 3.

---

(9) Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1665.

(10) Bailey, R. D.; Pennington, W. T. *Polyhedron* **1997**, *16*, 417.

(11) Fujita, M.; Yoon Jung Kwon; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.

(12) Jackson, A.; Turner, R. *Am. Crystallogr. Assoc., Ser. 2* **1983**, *11*, 33.

(13) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robsen, R.; Sutherland, E. E. *J. Chem. Soc., Chem. Commun.* **1994**, 1049.

(14) Wagner, C. E., Dissertation, University of Ulm, Ulm, Germany, 1992.

(15) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(16) Sheldrick, G. M. *SHELXL-93, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

(17) Altomare, A.; Burla, M. C.; Cascarano, G.; Giaccovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G. *EXPO, Program for Extracting Structure-Factor Amplitudes and Structure Solution from Powder Diffraction Data*, Bari, Italy, 1997.

(18) Larson, A.; Von Dreele, R. B. *GSAS, Generalized Structure Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 1994.

Table 1. Crystallographic Data for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**[a]
empirical formula	$C_{17}H_{17}Cl_2N_5OZn$	$C_{40}H_{38}N_8O_{12}Zn_3{\cdot}H_2O$	$C_{42}H_{30}Cl_6N_{12}Zn_3{\cdot}1.25H_2O$	$C_{18}H_{16}N_4O_4Cd{\cdot}5H_2O$	$C_{14}H_{10}N_6O_6Cd$
fw	443.63	1036.91	1134.11	554.83	470.67
a, Å	8.654(1)	12.238(4)	26.311(1)	9.045(1)	11.6601(3)
b, Å	9.500(1)	12.986(3)	26.311(1)	10.438(1)	11.9870(3)
c, Å	22.997(1)	15.470(4)	26.311(1)	12.719(1)	12.1453(3)
α, deg	90	75.65(1)	90	100.48(1)	90
β, deg	97.99(1)	77.01(2)	90	95.05(1)	103.348(2)
γ, deg	90	65.98(1)	90	95.86(1)	90
V, $Å^3$	1872.3(3)	2154(1)	18215(1)	1167.6(2)	1651.69(4)
Z	4	2	16	2	4
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$Ia\bar{3}d$ (No. 230)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
T, °C	20(2)	20(2)	20(2)	−60(2)	20(2)
ρ_{calc}, g cm^{-1}	1.574	1.599	1.654	1.578	1.893
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	1.5406
μ, cm^{-1}	16.14	17.31	19.70	9.89	110.87
R1[b]	0.058	0.070	0.038	0.029	0.026[d]
wR2[c]	0.118	0.115	0.076	0.072	0.084[e]

[a] Powder structure. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum wF_o^4]^{1/2}$. [d] $Rp = \sum|I_o - I_c|/\sum I_o$. [e] $R_F = \langle|F_o| - |F_c|\rangle/\langle|F_o|\rangle$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **1**−**3**[a]

	Complex 1		
Zn1−Cl1	2.282(2)	Cl1−Zn1−N1	142.8(1)
Zn1−Cl2	2.262(2)	Cl1−Zn1−N3	91.7(1)
Zn1−O1	2.110(4)	Cl2−Zn1−O1	100.7(1)
Zn1−N1	2.187(4)	Cl2−Zn1−N1	99.3(1)
Zn1−N3	2.182(4)	Cl2−Zn1−N3	103.4(1)
		O1−Zn1−N1	83.7(2)
Cl1−Zn1−Cl2	117.58(7)	O1−Zn1−N3	149.3(2)
Cl1−Zn1−O1	93.8(1)	N1−Zn1−N3	74.0(2)
	Complex 2		
Zn1−O1	2.014(5)	O5−Zn1−N1	166.2(2)
Zn1−O3	1.988(5)	O1−Zn1−N3	142.4(2)
Zn1−O5	2.005(5)	O3−Zn1−N3	103.3(2)
Zn1−N1	2.227(6)	O5−Zn1−N3	92.6(2)
Zn1−N3	2.126(6)	N1−Zn1−N3	74.5(2)
Zn2−O1, O1[a]	2.134(5)	O1−Zn2−O4	90.4(2)
Zn2−O4, O4[a]	2.079(5)	O1−Zn2−O6	89.8(2)
Zn2−O6, O6[a]	2.067(5)	O1−Zn2−O1[a]	180.0
		O1−Zn2−O4[a]	89.6(2)
O1−Zn1−O3	108.9(2)	O1−Zn2−O6[a]	90.2(2)
O1−Zn1−O5	100.4(2)	O4−Zn2−O6[a]	86.8(2)
O3−Zn1−O5	99.5(2)	O6−Zn2−O6[a]	180.0
O1−Zn1−N1	87.4(2)	O6−Zn2−O4	93.2(2)
O3−Zn1−N1	88.5(2)	O4−Zn2−O4[a]	180.0
	Complex 3		
Zn1−Cl1, Cl1[b]	2.342(1)	Cl1−Zn1−N2	98.0(1)
Zn1−N2, N2[b]	2.154(4)	Cl1−Zn1−N2[b]	98.3(1)
Zn1−N1, N1[b]	2.361(4)	N1−Zn1−N1[b]	81.6(2)
		N1−Zn1−N2	72.9(2)
Cl1−Zn1−Cl1[b]	100.93(8)	N1−Zn1−N2[b]	87.4(2)
Cl1−Zn1−N1	167.4(1)	N2−Zn1−N2[b]	154.2(2)
Cl1−Zn1−N1[b]	89.3(1)		

[a] Symmetry codes: (a) $-x, -y + 1, -z + 1$; (b) $-y + {}^5/_4, -x + {}^5/_4, -z + {}^1/_4$.

Results

Spectral Characterization. The infrared spectra for compounds **1**−**5** contain characteristic C−N and C−C vibrational frequencies for the heteroaromatic rings of the ligand bppz (Table 4). Evidence for the coordination of bppz is provided by the shift of ca. 20 cm^{-1} of these absorption bands to higher frequencies (1450−1650 cm^{-1}) compared with the corresponding frequencies for bppz itself (1585, 1566, 1455, 1435 cm^{-1}). The absence of a center of symmetry in bppz of compounds **1** and **2** gives rise to supplementary bands in the same region (1400−1650 cm^{-1}) due to the valence vibrations of the pyridine and pyrazine ring. This can best be observed for complex **1** as there is no superposition with the vibrational bands of the acetate anions as found in compound **2**. Two strong absorption bands are found for the acetates in complexes **2** (1602, 1421 cm^{-1}) and **4** (1559, 1435 cm^{-1}). The strong coordination of the acetates to the zinc(II) ions in **2** results in a shift of these absorption bands to higher frequencies compared to the corresponding frequencies of the more loosely coordinated acetates ions in the cadmium(II) complex **4**. Broad O−H stretching bands for the water molecules in complexes **2**−**4** can be seen between 2170 and 3300 cm^{-1}. The coordinated dimethylformamide molecule in **1** is confirmed by the presence of a supplementary absorption band at 1651 cm^{-1}. The ^1H NMR spectrum was recorded for compound **4** and compared with the corresponding spectrum of the free ligand (Table 5). The ^1H NMR spectrum of **4** shows five signals for the symmetrically coordinated ligand bppz. One singlet with the highest chemical shift at 9.67 ppm was observed for the hydrogen atom on the pyrazine ring (bppz: 8.66 ppm), and multiplets (doublets or triplets depending on the coupling with neighboring hydrogen atoms) were observed for the hydrogen atoms connected to the pyridine rings. All signals are displaced to higher chemical shifts. Compound **5** was found to be extremely insoluble in all common organic solvents.

Using FAB mass spectroscopy for the polymeric compound **4**, it was possible to show that fragments of the one-dimensional polymer, containing two or three mononuclear complex units, can be found in solution. It was possible to identify the peaks for the following fragments: $[Cd_2(OAc)_3(bppz)_2]^+$ ($M^+ = 869$), $[Cd_3(OAc)_5(bppz)_2]^+$ ($M^+ = 1099$), $[Cd_2(OAc)_3(bppz)_3]^+$ ($M^+ = 1103$), and $[Cd_3(OAc)_5(bppz)_3]^+$ ($M^+ = 1333$).

Structure of [ZnCl$_2$(bppz)(dmf)] (1). The reaction of bppz with an excess of $ZnCl_2$ lead to the formation, on recrystallization, of this mononuclear complex. The zinc atom is five coordinate with a square-pyramidal coordination geometry (Figure 2) and is coordinated to two nitrogen atoms of the bppz ligand, two chloride anions, and an oxygen atom of a dimethylformamide molecule. The latter comes from the solvent used for recrystallization. The metal is displaced by 0.623(2) Å from the best plane formed by atoms N1, N3, Cl1, and O1. The chlorine atom Cl2 is situated at a distance of 2.839(3) Å from this plane. Important bond lengths and bond angles are given in Table 2. The axial Zn1−Cl1 distance [2.262(2) Å] is slightly shorter than the equatorial Zn1−Cl2 distance [2.282(2) Å].

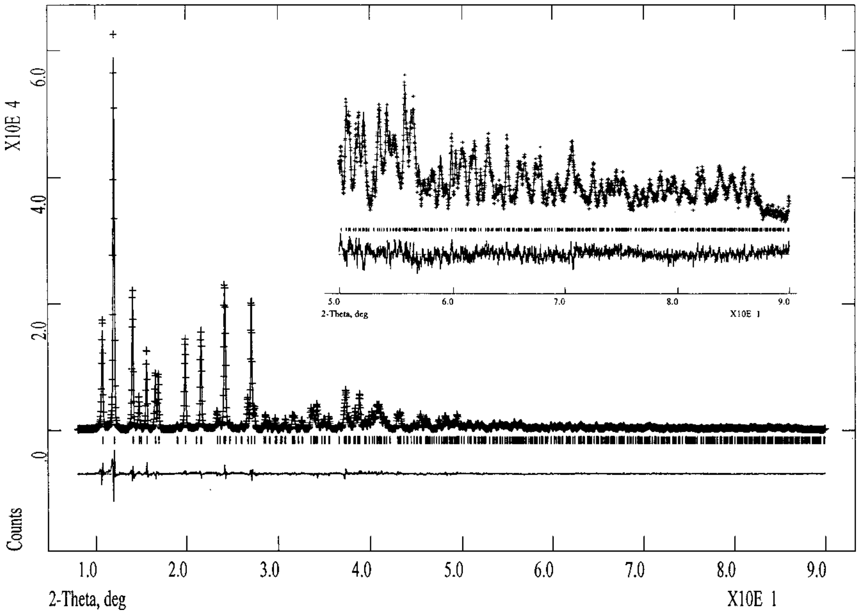


Figure 1. Observed (+) and calculated (−) profiles for the Rietveld refinement for $[Cd(NO_3)_2(bppz)]_n$ **(5)**. The bottom curve is the difference plot on the same intensity scale. Inset: 2θ range 50−90° magnified by a factor of 20.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **4** and **5**[a]

	4	5		4	5
Cd1−N1	2.478(2)	2.400(6)	O2−Cd1−N2	82.91(8)	148.8(5)
Cd1−N2	2.432(3)	2.407(7)	O2−Cd1−N3(N1)[a]	78.86(8)	114.5(5)
Cd1−N3	2.453(2)		O2−Cd1−N4(N2)[a]	141.93(8)	81.0(3)
Cd1−N4	2.406(3)		O3−Cd1−O4	51.79(8)	
Cd1−O1	2.377(2)	2.448(9)	O3(O1)[a]−Cd1−N1	83.91(8)	114.5(3)
Cd1−O2	2.455(2)	2.575(9)	O3(O1)[a]−Cd1−N2	143.95(8)	81.0(3)
Cd1−O3	2.401(2)		O3−Cd1−N3	113.23(8)	
Cd1−O4	2.594(3)		O3−Cd1−N4	83.91(8)	
O1−Cd1−O2	53.67(8)	50.1(2)	O4(O2)[a]−Cd1−N1	129.67(8)	114.5(5)
O1−Cd1−O3(O1)[a]	88.97(8)	114.1(4)	O4(O1)[a]−Cd1−N2	163.16(8)	81.0(3)
O1−Cd1−O4(O2)[a]	89.02(8)	114.1(5)	O4−Cd1−N3	74.47(8)	
O1−Cd1−N1	73.57(8)	79.9(3)	O4−Cd1−N4	99.32(9)	
O1−Cd1−N2	96.24(8)	148.8(3)	N1−Cd1−N2	67.14(8)	68.9(3)
O1−Cd1−N3(N1)[a]	130.56(8)	114.5(3)	N1−Cd1−N3(N1)[a]	150.01(8)	154.6(5)
O1−Cd1−N4(N2)[a]	162.06(8)	81.0(3)	N1−Cd1−N4(N2)[a]	88.98(8)	94.5(3)
O2−Cd1−O3(O1)[a]	126.89(8)	114.1(5)	N2−Cd1−N3(N1)[a]	90.10(8)	94.5(3)
O2−Cd1−O4(O2)[a]	87.42(8)	67.9(4)	N2−Cd1−N4(N2)[a]	80.33(9)	100.1(5)
O2−Cd1−N1	115.31(8)	79.9(3)	N3−Cd1−N4	67.29(8)	

[a] Symmetry code: (a) $-x + 1, y, -z + {}^1/_2$.

Table 4. Selected IR Data for Compounds **1**−**5**

compd	IR, ν (cm^{-1})
$[ZnCl_2(bppz)(dmf)]$ (**1**)	3061 (w), 1651 (vs, dmf), 1601 (m), 1580 (m), 1525 (w), 1497 (w), 1475 (m), 1457 (s), 1442 (s), 1434 (s)
$[Zn_3(OAc)_6(bppz)_2](H_2O)$ (**2**)	3433 (b), 3061 (w), 1602 (b, vs, OAc^-), 1478 (w), 1462 (m), 1421 (b, s, OAc^-)
$[Zn_3(Cl)_6(bppz)_3](H_2O)$ (**3**)	3442 (b), 3057 (w), 1600 (m), 1568 (m), 1504 (w), 1472 (s), 1427 (m)
$\{[Cd(OAc)_2(bppz)](H_2O)_5\}_n$ (**4**)	3388 (b), 3070 (w), 1634 (m), 1598 (s), 1577 (vs), 1559 (b, vs, OAc^-), 1471 (s), 1435 (b, vs, OAc^-)
$[Cd(NO_3)_2(bppz)]_n$ (**5**)	3072 (w), 1598 (m), 1572 (w), 1510 (w), 1456 (s), 1439 (vs, NO_3^-), 1303 (vs, NO_3^-)

Equivalent bond lengths are found for Zn1−N1(pyrazine) and Zn1−N3(pyridine). The ligand bppz, which is coordinated to the metal in a mono-bidentate fashion, is almost planar with dihedral angles of 4.5(2)° (pyz∧py1) and 3.6(2)° (pyz∧py2). In the crystal the molecules stack in pairs related by a center of symmetry. The overlap of the bppz ligands is considerable with the shortest C···C nonbonded distance being C2···C5′ at 3.32(1) Å.

Structure of $[Zn_3(OAc)_6(bppz)_2](H_2O)$ (2). Reacting bppz with 1 equiv of zinc acetate gave the trinuclear complex **2**, with a linear arrangement of the three zinc atoms (Figure 3). The central zinc atom Zn2, which is located on an inversion center, is bridged to the symmetry-related Zn1 atoms by six acetate anions, two of which bridge in a *syn*−*syn* manner and one in a monodentate manner. The coordination sphere of the square pyramidal Zn1 atoms is completed by two nitrogen atoms of the ligand bppz, the latter acting in a mono-bidentate coordination mode. Atom Zn1 is displaced by 0.217(4) Å from the best plane formed by atoms N1, N3, O1, and O5. Atom O3 is situated at a distance of 2.150(7) Å from the same plane. The ligand bppz is again almost planar with dihedral angles of 4.1(4)° (pyz∧py1) and 5.4(5)° (pyz∧py2). Atom Zn2 is at a distance of 3.347(1) Å to atoms Zn1 and Zn1[a]. In the symmetrical acetate bridges, the distances C−O (1.25 Å) are practically equivalent caused by the delocalization of electrons in the $Me-COO^-$ system. The third acetate bridge links two zinc atoms by only

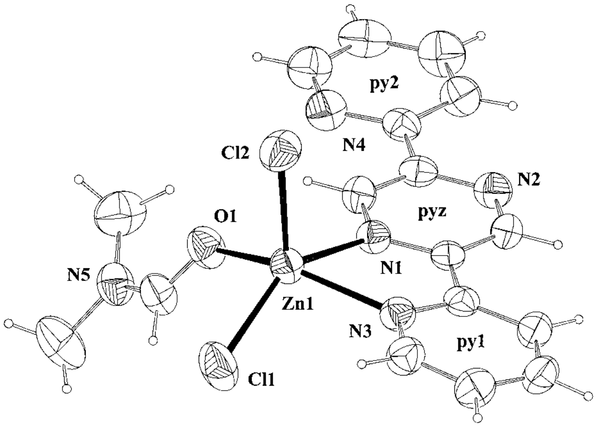
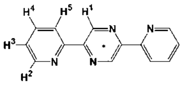


Figure 2. PLATON[25] drawing of the mononuclear complex $[ZnCl_2(bppz)(dmf)]$ **(1)**, showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

Table 5. Comparison of ^1H NMR Data for the Ligand bppz and Compound **4**

	Chemical Shifts (δ, ppm)	
	bppz	**4**
H^1	9.67 (s, 2H)	10.53 (s, 2H)
H^2	8.75 [d, $^3J(2,3) = 4.3$, 2H]	9.69 [ddd, $^3J(2,3) = 4.7$, $^4J(2,4) = 1.8$, $^5J(2,5) = 0.9$, 2H)
H^3	7.36 [t, $^3J(3,2) = {}^3J(3,4) = 4.9$, 2H]	8.46 [ddd, $^3J(3,4) = 7.6$, $^3J(3,2) = 4.8$, $^4J(3,5) = 1.2$, 2H]
H^4	7.88 [dt, $^4J(4,2) = 1.6$, $^3J(4,3) = {}^3J(4,5) = 7.8$, 2H]	8.94 [dt, $^4J(4,2) = 1.8$, $^3J(4,3) = {}^3J(4,5) = 7.7$, 2H]
H^5	8.45 [d, $^3J(5,4) = 8.0$, 2H]	9.32 [dt, $^3J(5,4) = 7.9$, $^4J(5,3) = {}^5J(5,2) = 1.1$, 2H]

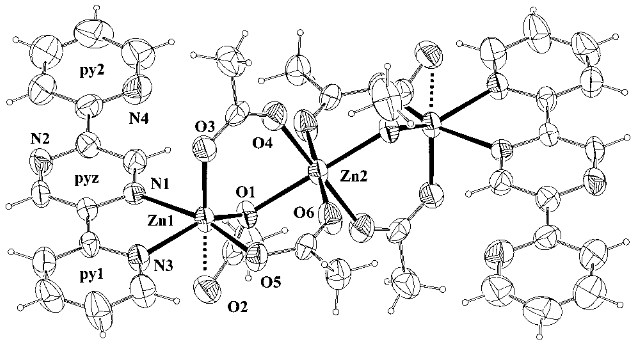


Figure 3. Crystal structure of the trinuclear complex $[Zn_3(OAc)_6(bppz)_2](H_2O)$ **(2)**, showing the numbering scheme and the thermal ellipsoids at the 50% probability level (dashed lines indicate weak intramolecular contacts; water molecules of crystallization omitted for clarity).

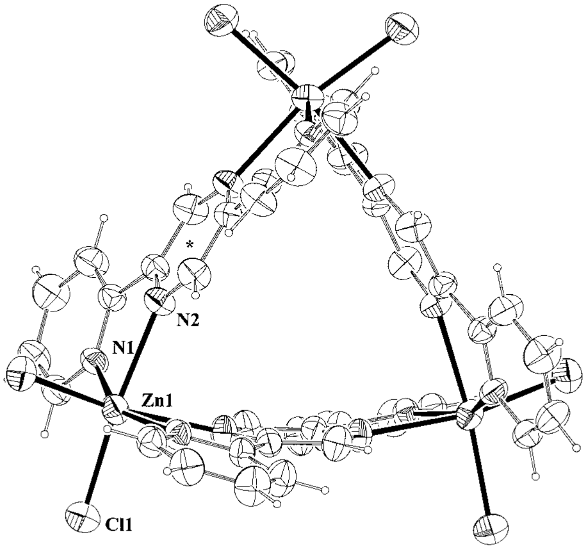


Figure 4. PLATON[25] drawing of the cyclic trimer $[Zn_3(Cl)_6(bppz)_3](H_2O)$ **(3)**, showing the numbering scheme and the thermal ellipsoids at 50% probability level (water molecules of crystallization omitted for clarity).

one oxygen atom (O1). The C−O1 and C−O2 distances [1.22(1), 1.28(1) Å, respectively] are characteristic for double and single bonds.[19] There is a weak interaction between the oxygen atom O2 of the monoatomic acetate bridge and zinc atom Zn1 [2.791(8) Å], which has a distorted square pyramidal coordination sphere. Here distance Zn1−N1(pyrazine) [2.227(6) Å] is slightly longer than distance Zn1−N3(pyridine) [2.126(6) Å]. The centrosymmetric zinc atom Zn2 is octahedrally coordinated to six oxygen atoms with Zn−O distances of 2.07 Å (O4, O6, O4^a, O6^a) and 2.14 Å (O1, O1^a) (see Table 2). The O−Zn−O bond angles are close to 90 or 180°. In the asymmetric unit there are two independent neutral molecules of $[Zn_3(OAc)_6(bppz)_2]$, with small differences in bond distances and angles, and one water molecule of crystallization. The hydrogen atoms of water O1W were not located, but it is found at a distance of 3.03(1) Å from atoms O4 and N4.

Structure of $[Zn_3(Cl)_6(bppz)_3](H_2O)$ (3). Complex **3** was obtained by reacting bppz with 1 equiv of $ZnCl_2$. A most interesting neutral triangular structure was obtained consisting of three $[Zn(bppz)Cl_2]$ units (Figure 4). The molecule possesses crystallographic C_{3i} symmetry with each zinc atom linked to the other two by the ligand bppz, coordinating in a bis-bidentate manner. Each zinc(II) ion is octahedrally coordinated to four nitrogen atoms from the bridging bppz ligands and to two chlorine atoms. Four long bonds are found in the basal plane, to the chlorine atoms [Zn1−Cl1, Cl1^a = 2.342(1) Å] and the nitrogen atoms of the pyrazine rings [Zn1−N1, N1^a = 2.361(4) Å]. The axial bonds to the nitrogen atoms of the pyridine rings are significantly shorter [Zn1−N2, N2^b = 2.154(4) Å]. The zinc atoms are located on crystallographic 2-fold axes while the ligand bppz possesses C_i symmetry. The ligand bppz is twisted with a dihedral angle between the pyrazine and pyridine rings of 15.2(7)°. The intramolecular Zn1···Zn1^c distance is 7.390(1) Å (c indicates the symmetry $-x + {}^7/_4$, $z + {}^1/_4$, $y - {}^1/_4$). In the crystal highly disordered water molecules were found to occupy the center of the entrance to the $[Zn_3(bppz)_3]$ triangle and lie on the 3-fold inversion axis.

Structure of $\{[Cd(OAc)_2(bppz)](H_2O)_5\}_n$ (4). Complex **4**, a zigzag one-dimensional coordination polymer (Figure 5), was obtained by reacting bppz with 1 equiv of $Cd(OAc)_2$. The cadmium(II) ions are linked by two independent ligand molecules, each possessing C_i symmetry. The metal atom is 8-fold coordinate, with four bonds to the nitrogen atoms of the two ligand molecules and four bonds to the oxygen atoms of two chelating acetate anions. The bppz ligands, which both possess C_i symmetry, are weakly coordinated with an average Cd−N distance of 2.44 Å. The Cd1−N(pyrazine) bond distances (average value 2.466 Å) are slightly longer than the Cd1−N(pyridine) bond distances (average value 2.419 Å). One bppz

---

[19] *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C.

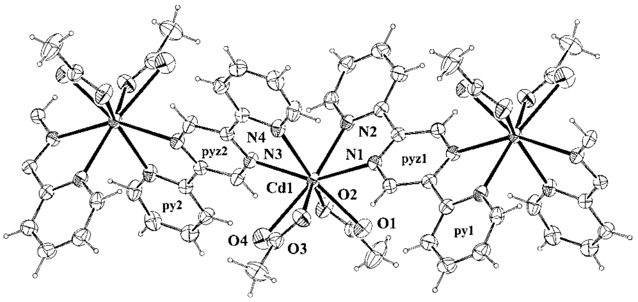


Figure 5. Structure of polymer $\{[Cd(OAc)_2(bppz)](H_2O)_5\}_n$ **(4)**, showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

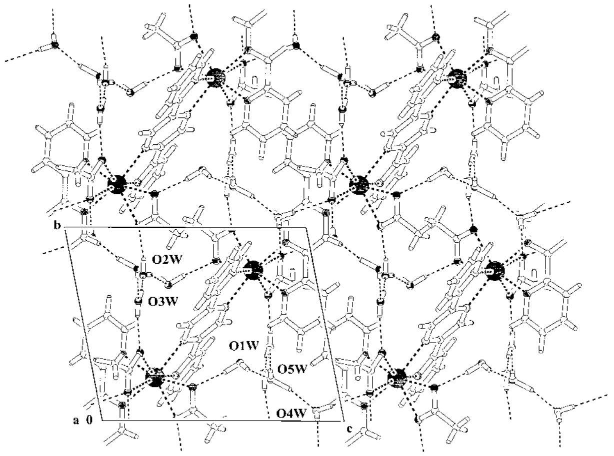


Figure 6. Crystal packing of the polymer $\{[Cd(OAc)_2(bppz)](H_2O)_5\}_n$ **(4)**, viewed down the *a* axis. A portion of the hydrogen-bonding network is shown as dashed lines.

Table 6. Strong Hydrogen Bonds for Complex **4**[a]

bond	D−H⋯A (Å)	D−H (Å)	H⋯A (Å)	D−H⋯A (deg)
O1W−H1⋯O1	2.811(4)	0.90(5)	1.92(5)	172(4)
O2W−H3⋯O2	2.737(4)	0.83(4)	1.92(4)	168(4)
O3W−H5⋯O3	2.851(4)	0.76(4)	2.10(4)	168(4)
O4W−H7⋯O4	2.951(5)	0.80(6)	2.15(6)	174(6)
O4W−H8⋯O4[a]	2.902(5)	0.87(10)	2.05(10)	165(9)

[a] Symmetry code: (a) $-x$, $-y$, $-z$.

ligand is less planar than the other with a dihedral angle of 16.4(3)° for pyz1∧py1 compared to 4.7(3)° for pyz2∧py2. The symmetrical acetate groups [average C−O distance 1.253(1) Å] are connected in an asymmetric manner to the metal. One of the Cd−O bonds is longer than the other with distances Cd1−O1, −O2 being 2.377(2) and 2.455(2) Å, respectively, and distances Cd1−O3, −O4 being 2.401(2) and 2.594(3) Å, respectively (see Table 3). The intramolecular Cd−Cd distances are 7.650(1) [Cd1⋯Cd1^a, (a) $-x + 1$, $-y + 1$, $-z + 1$] and 7.670(1) Å [Cd1⋯Cd1^b, (b) $-x + 1$, $-y$, $-z$]. In the crystal the polymeric chains, $\{[Cd(OAc)_2(bppz)]_n$, run parallel to the [011] direction and stack up the *a* axis. The bppz ligand molecules within the chain are almost perpendicular to one another, Figure 6. The polymer chains are connected by hydrogen bonds involving the five water molecules of crystallization and the acetate O-atoms, so forming a dense three-dimensional network. Further details of the hydrogen bonding for complex **4** are given in Table 6.

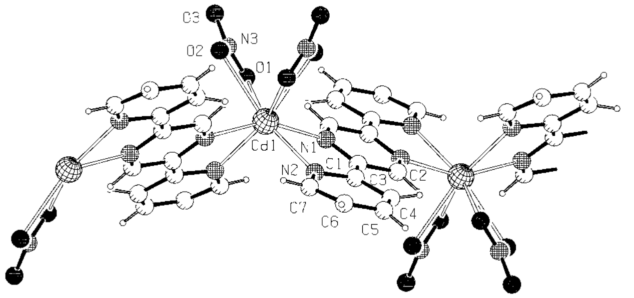


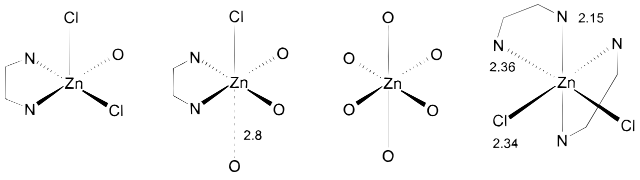
Figure 7. PLATON[25] drawing of polymer $[Cd(NO_3)_2(bppz)]_n$ **(5)**, showing the numbering scheme (only the cadmium atom refined anisotropically).

Structure of $[Cd(NO_3)_2(bppz)]_n$ (5). Complex **5**, like complex **4,** is a zigzag one-dimensional coordination polymer (Figure 7) obtained by reacting bppz with 1 equiv of $Cd(NO_3)_2$. The cadmium(II) ions are linked by the ligand bppz, which again coordinates in a bis-bidentate manner, and the metal is also similarly coordinated to the anions. Bond distances and angles are compared in Table 3. In **5**, however, the Cd atom is located on a crystallographic 2-fold axis resulting in equivalent ligand and anion coordination. The ligand molecule bppz possesses C_i symmetry and is twisted with dihedral angles (pyz∧py) of 13°. The ligand is weakly coordinated to the Cd atom with an average Cd−N distance of 2.40 Å. However, compared to **4**, bppz is more strongly coordinated to the cadmium [$(Cd-N)_{av}$ = 2.44 Å (**4**), 2.40 Å (**5**)], while the anion is more weakly coordinated [$(Cd-O)_{av}$ = 2.46 Å (**4**, acetate), 2.51 Å (**5**, nitrate)]. The intramolecular Cd⋯Cd distance is 7.556(1) Å which is significantly shorter than the same distances in complex **4** [7.65 and 7.67 Å]. In the crystal the polymer chains run parallel to the [101] direction and stack up the *b* axis with the shortest interchain Cd⋯Cd distance being 7.491(2) Å.

Discussion

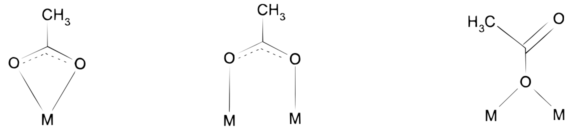
Pyrazine and its derivatives are often used to bridge metal atoms with the objective of constructing one-, two-, or three-dimensional molecular frameworks. The ligand 2,5-bis(2-pyridyl)pyrazine has previously been used to prepare a series of 3d transition metal compounds. It was found that the type of complex formed depended strongly on the counterion used for such reactions. Oxygen-rich anions such as nitrate or sulfate favor the formation of binuclear complexes.[4] Using chloride, acetate, and benzoate it was found that binuclear [M(bppz)M] units can be linked to form one-[2,3] and two-dimensional polymeric complexes.[1,3] Using the d^{10} metals zinc(II) and cadmium(II), three new zinc and two new cadmium compounds were synthesized. It is seen that zinc is capable of coordinating bppz in a mono- or a bis-bidentate manner, while cadmium coordinates bppz in a bis-bidentate manner only. In contrast to the copper(II) and nickel(II) complexes,[4] where the chlorine atoms bridge the metal centers resulting in polymeric structures, the zinc(II) ion in **1** and **3** coordinates only to terminal chlorine atoms, Chart 1. In complex **1**, bppz is connected to only one zinc atom forming a mononuclear compound with a square pyramidal coordination sphere, while in **3** the zinc atom is octahedrally coordinated. Here, the rare case of the tetragonal distortion resulting in short axial bonds and longer equatorial bonds is observed. The Zn−N(pyrazine) bond distance is much longer in **3** [2.361(4) Å] than in **1** [2.187(4) Å], probably due to the bridging mode of the ligand. To our knowledge it is the first complex containing three zinc atoms bridged by a pyrazine derivative forming this special triangular arrangement. Disordered water molecules are found to occupy the entrance to the $[Zn_3(bppz)_3]$ triangle. Using acetate anions a second trinuclear

Chart 1. Coordination Geometry Found in Complexes **1**−**3** [Normal Bond Lengths (Å) in Parentheses]



(1) (2) (2) (3)

Chart 2. Coordination Modes of Acetate Anions Found in Compounds **2** and **4** (I, Chelating Ligand; II, Symmetric Bridging Ligand; III, Monoatomic Bridging Ligand)



I. chelate II. bidentate metal bridge III. mono-atomic bridge

complex could be obtained, **2**. Here a linear disposition of the three zinc atoms linked by the acetate groups was found. This arrangement of the zinc atoms, which are coordinated in two different modes (Chart 1), has also been found in the complex $[Zn_3(crotonate)_6(quinoline)_2]$.[20] There, however, the intramolecular metal−metal distance of 3.54 Å is much longer than the corresponding distance in **3** (3.35 Å). For the binuclear cation $[Zn_2(OAc)_3(bipyridine)_2]^+$, where the two metal centers are linked in a similar manner, the intramolecular distance is shorter (3.29 Å) than in **3**.[21] Acetates are flexible anions concerning their complexation capabilities as is shown in Chart 2. While in zinc complex **3** the acetates bridge the metal centers (types II and III), in the cadmium compound **4** they act as chelating ligands (type I). In addition to the coordination of two acetates, two bppz molecules are connected to one cadmium ion. This situation is similar to that observed for complex **5** where the acetates are now replaced by chelating nitrate anions. In both **4** and **5** the cadmium(II) ion has the rare coordination number of 8 resulting in longer Cd−N bond distances compared to hexa- or heptacoordinated cadmium complexes (Table 7). In both **4** and **5** there are two ligand molecules connected to the metal, so forming uniform polymeric chains. Previously, with first-row transition metals one- or two-dimensional alternating polymers were always obtained with bppz, containing in addition anions in bridging positions. It was not possible to obtain single crystals suitable for a single-crystal X-ray structure analysis for compound **5**. However, as the structure of **5** was found to be very similar to that of **4,** and as there are only a small number of atoms per asymmetric unit, this favored the structure determination from X-ray powder diffraction data.

Table 7. Comparison of Selected Bond Distances (Å) in Cadmium Complexes

compd	CN[a]	Cd1−O1, O2	Cd1−O3, O4	Cd1−N_{pyz}	Cd1−N_{py}
4	8	2.38, 2.46	2.40, 2.59	2.48, 2.45	.43, 2.41
5	8	2.45, 2.58		2.40	2.41
$[Cd_2(OAc)_4(pyz)]$[15]	7	2.51, 2.33	2.51, 2.33	2.33	
$[Cd(CN)_2(pyz)]_n$[13]	6			2.45	
$[Cd(SCN)_2(bpy)_2]$[22]	6				2.39

[a] Coordination number.

As expected, the ligand bppz itself is reasonably flexible. This can be seen when comparing the dihedral angles between the plane of the pyrazine ring and the plane of the pyridine rings. In **1,** for example, dihedral angle pyz∧py1 involving the coordinated N-atoms is 4.5(2)° compared to angle pyz∧py2 of 3.6(2)° for the noncoordinated N-atoms. This situation is similar to that observed in **2** where the same angles are 4.1(4) and 5.4(5)°, respectively. In the more strained triangular complex **3** dihedral angle pyz∧py is 15.2(7)°. An even larger angle of 16.4(3)° [pyz1∧py1] was observed for one of the bppz ligands in polymer **4**, while for the second bppz ligand the same angle is only 4.7(3)°. Finally in polymer **5** a dihedral angle of ca. 13° was found. The variation in the metal to nitrogen bond lengths, at least for the zinc complexes, is also indicative of the strain in the ligand, being longer when the pyz∧py dihedral angle is larger. For example in **1,** where the ligand is reasonably flat, the Zn−Npyz and Zn−Npy distances are 2.182 and 2.187 Å, respectively, compared to 2.154 and 2.361 Å in **3** where the dihedral angle is 15.2(7)°. Similar large dihedral angles and long metal to nitrogen bond distances have been observed previously in some zinc and cadmium bis(2,2′-bipyridine) complexes.[23,24]

Acknowledgment. Financial support from the Swiss National Science Foundation is gratefully acknowledged. We also wish to thank H. Bursian for carrying out the ^1H NMR experiments and Prof. T. Jenny and his group from the Institute of Organic Chemistry, University of Fribourg, for the FAB mass-spectrometry experiments.

Supporting Information Available: Five X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990843V

---

(20) Clegg, W.; Little, I. R.; Straughan, B. P. *J. Chem. Soc., Chem. Commun.* **1985**, 73.

(21) Chen, X.-M.; Tong, Y.-X. *Inorg. Chem.* **1994**, *33*, 4586.

(22) Rodesiler, P. F.; Turner, R. W.; Charles, N. G.; Griffith, E. A. G.; Amma, E. L. *Inorg. Chem.* **1984**, *23*, 999.

(23) Zhang, Y.; DeBord, J. R. D.; O'Connor, C. J.; Haushalter, R. C.; Clearfield, C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 989.

(24) Turner, R. W.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem. Acta* **1982**, *66*, L13.

(25) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.