Substanzen werden mit THF extrahiert und aus CH_2Cl_2/Hexan kristallisiert und i. HV. getrocknet.

1: Gelbe Nadeln; Ausbeute 102 mg (90%). Anal. ber. für $C_{15}H_8N_2O_{11}Ru_3S$: C 24.67, H 1.10, N 3.84; gef.: C 25.05, H 1.15, N 3.73.

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Röntgenstrukturanalyse von **1**.
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Antonia Neels and Helen Stoeckli-Evans*

Abstract. The symmetrical ligand 2,5-bis(2'-pyridyl)pyrazine (BPPZ) exists in the extended form with a dihedral angle between the pyrazine and the pyridine rings of 7.88°. BPPZ forms symmetrical bis(bidenate) complexes with Mn^{II}, Fe^{II}, and Cu^{II}. The dihedral angles between the best planes through the planar pyrazine ring and the pyridine ring are 2.6° in the Mn^{II} complex, 4° in the Fe^{II} complex, and 8.5° in the Cu^{II} complex. The metal–N_{py} bond distances are shorter than standard values and similar in length to the metal–N_{pz} distances.

Introduction

Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have received considerable attention in recent years. Binuclear and multinuclear metal complexes comprising two or more metal centers bridged by multidentate ligands can exhibit metal–metal interactions, such as energy or electron transfer, magnetic coupling and intervalence transfer [1][2].

Coordination complexes of BPPZ were unknown until recently when the photochemistry of some group VIB tetracarbonyl complexes were studied [3]. A little later *Balzani* and coworkers [4–6], *Denti*

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Abstract. The symmetrical ligand 2,5-bis(2'-pyridyl)pyrazine (BPPZ) exists in the extended form with a dihedral angle between the pyrazine and the pyridine rings of 7.88°. BPPZ forms symmetrical bis(bidenate) complexes with Mn^{II}, Fe^{II}, and Cu^{II}. The dihedral angles between the best planes through the planar pyrazine ring and the pyridine ring are 2.6° in the Mn^{II} complex, 4° in the Fe^{II} complex, and 8.5° in the Cu^{II} complex. The metal–N_{py} bond distances are shorter than standard values and similar in length to the metal–N_{pz} distances.

Introduction

Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have received considerable attention in recent years. Binuclear and multinuclear metal complexes comprising two or more metal centers bridged by multidentate ligands can exhibit metal–metal interactions, such as energy or electron transfer, magnetic coupling and intervalence transfer [1][2].

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et al. [7] and others [8–10] studied the photochemistry of Ru, Re and some Os complexes of BPPZ. Recently, BPPZ has been used as a bridging ligand in the construction of some interesting supra- or nanomolecular species [11][12]. We are particulaty interested in the possibility of using this ligand as a bridge in the formation of coordination polymers. In this paper we present the crystal and molecular structures of BPPZ and the Mn^{II}, Fe^{II}, and Cu^{II} complexes.

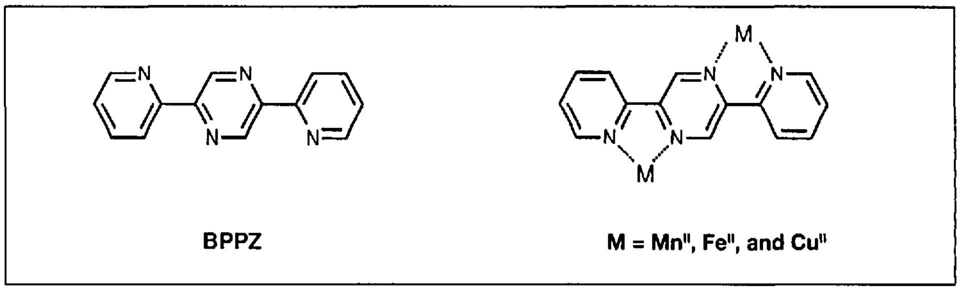
Results

Synthesis. The ligand BPPZ was synthesized in four steps according to [13–15]. To obtain crystals for X-ray analysis the transition metal complexes were best prepared using nitrate or sulphate salts. The reaction with $Zn(NO_3)_2$ gave microcrystals which from elemental and spectroscopic analyses indicates a metal to ligand ratio of 1:1. As this could indicate a polymer structure attempts are being made to grow larger crystals for X-ray analysis.

Structures. All of the structures reported (**1**–**4**) have C_i symmetry. The standard values for the metal–N_{py} and metal–N_{pz} distances were taken, if available, from [16]. The remaining distances and angles in **1**, **2**, and **4** are normal within experimental error. The crystals of **3** were twinned about the *c* axis and the structure analysis is not very satisfactory (see *Exper. Part*); hence the accuracy of the bond distances and angles is only approximate.

2,5-Bis(2'-pyridyl)pyrazine (**1**). The ligand BPPZ exists in the extended form with a dihedral angle between the best planes through the pyrazine and pyridine rings of 7.88(6)° (*Fig. 1a*). The molecules can be considered to stack up two mutally perpendicular axes, *a* and *b*, with separations of 5.56 and 6.36 Å, respectively (*Fig. 1b*).

{[2,5-Bis(2'-pyridyl)pyrazine]-$Mn_2(H_2O)_2(NO_3)_4$*}* (**2**). In this dinuclear complex the Mn-atoms are basically septacoordinate with an intramolecular metal–metal distance of 7.276 Å (*Fig. 2a*). However, in the crystal there is an intermolecular metal–metal distance of only 5.610 Å. The N_{py}–Mn–N_{pz} bite angle is 72.44(15)°. The Mn–N_{py} bond distance of 2.242(5) Å is similar to the Mn–N_{pz} bond distance, 2.274(4) Å. The molecule is almost planar with a pyrazine–pyridine dihedral angle of only 2.6(5)°. The molecules stack up the the *a* axis, separation 7.89 Å, and are linked by H-bonds involving the coordi-



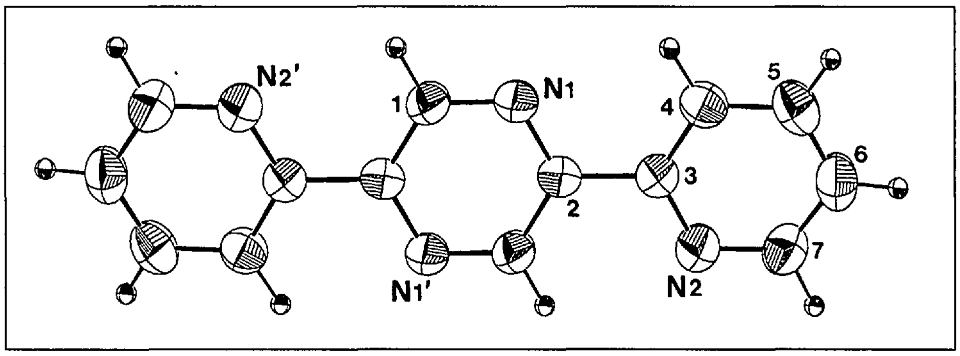


Fig. 1a. *ORTEP-II* [21] *plot of 2,5-bis(2'-pyridyl)pyrazine, BPPZ* (**1**), *illustrating the numbering scheme used in all the structures* (ellipsoids at 50% probability level)

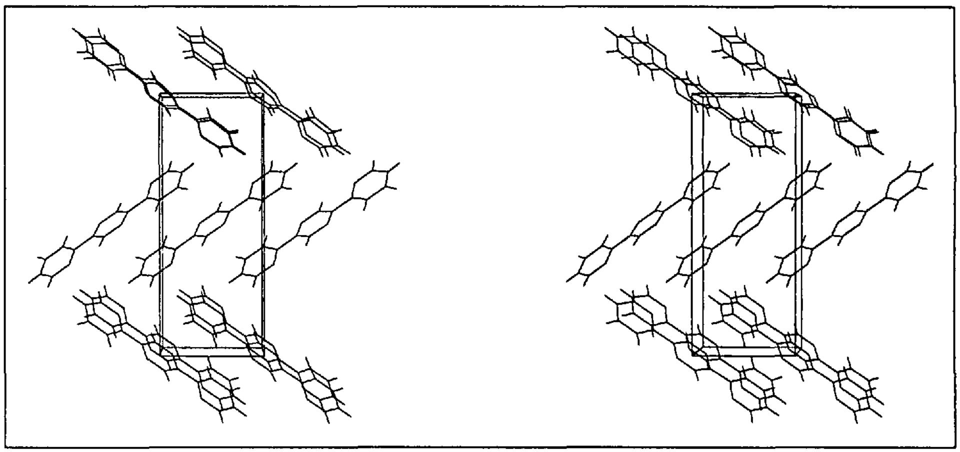


Fig. 1b. *PLUTO* [22] *plot of the crystal packing of* **1** *viewed along the* a *axis*

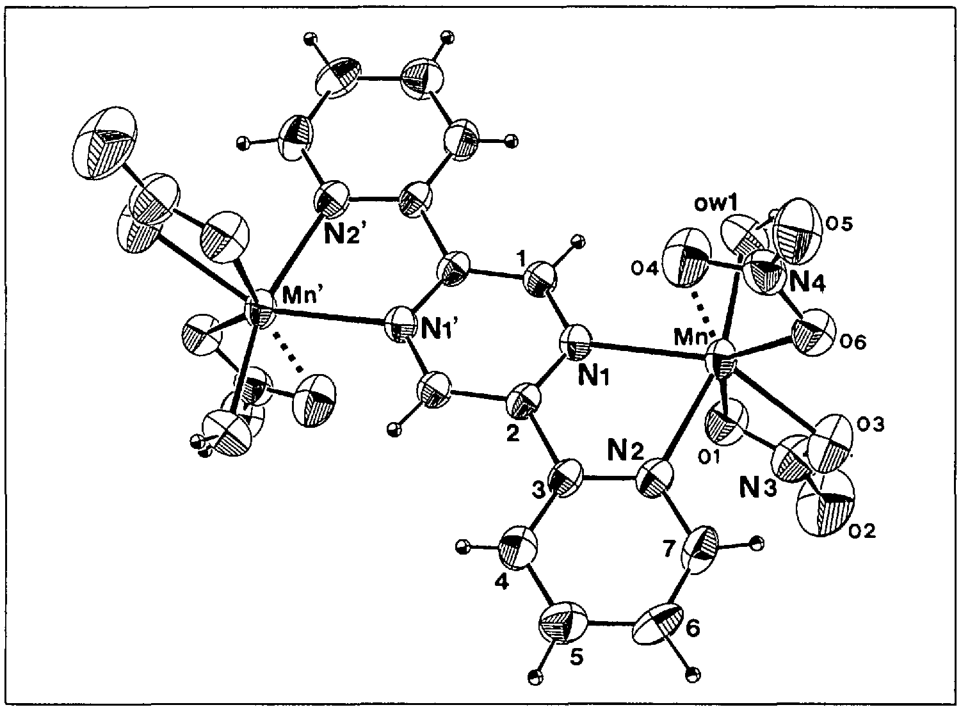


Fig. 2a. *ORTEP-II* [21] *plot of {[2,5-bis(2'-pyridyl)pyrazine]*$Mn_2(H_2O)_2(NO_3)_4$*}* (**2**) (ellipsoids at 50% probability level). Mn–N(1) 2.274(4) Å, Mn–N(2) 2.242(5) Å, N(1)–Mn–N(2) 72.44(15)°, Mn–O(W1) 2.151(5) Å, four Mn–$O_{nitrate}$ bonds varying from 2.217(4) Å to 2.433(4) Å.

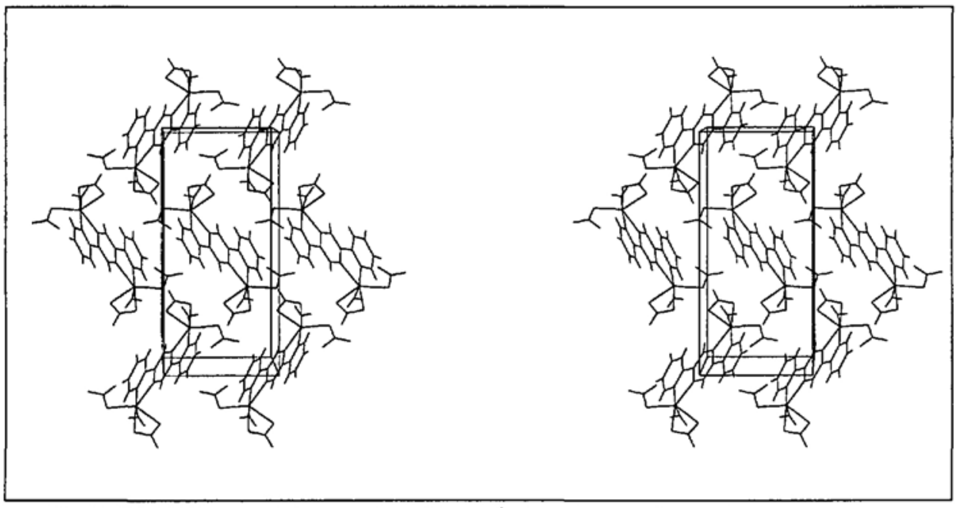


Fig. 2b. *PLUTO* [22] *plot of the crystal packing of* **2** *viewed along the* a *axis*

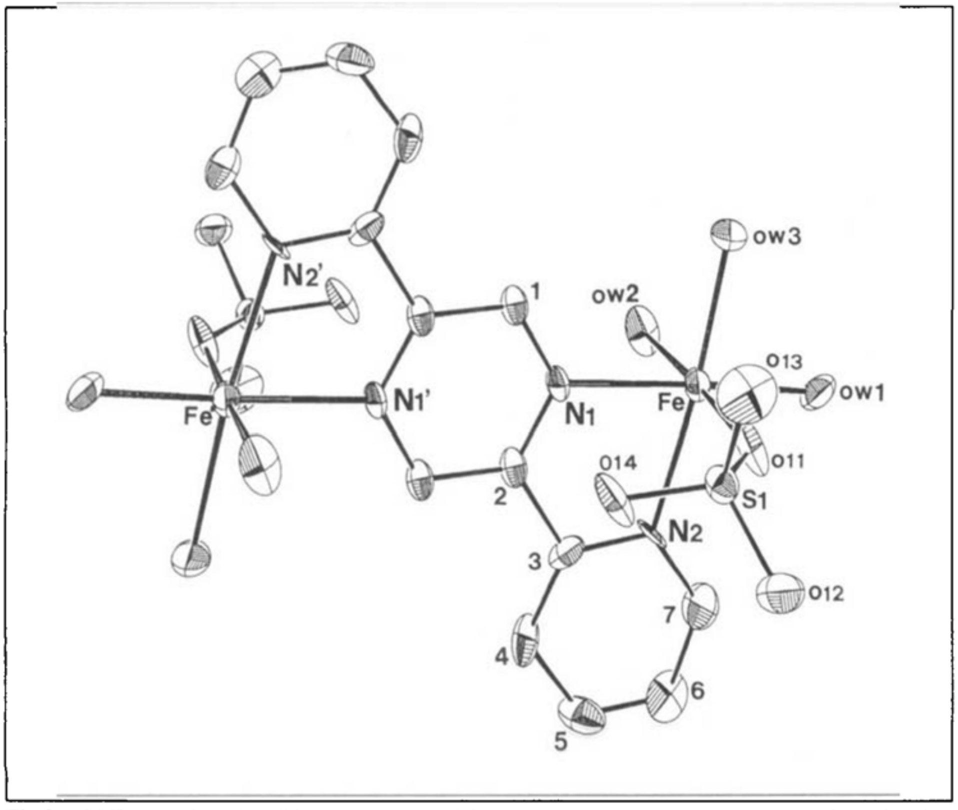


Fig 3a. *ORTEP-II* [21] *plot of {[2,5-bis(2'-pyridyl)pyrazine]*$Fe_2(H_2O)_6(SO_4)_2$*}*$(H_2O)_2$ (**3**) *(*ellipsoids at 50% probability level*)*. Fe–N(1) 2.18(2) Å, Fe–N(2) 2.18(1) Å, N(1)–Fe–N(2) 76(1)°, Fe–O(W1) 2.07(1) Å, Fe–O(W2) 2.14(1) Å, Fe–O(W3) 2.16(1) Å, Fe–O(11) 2.05(2) Å.

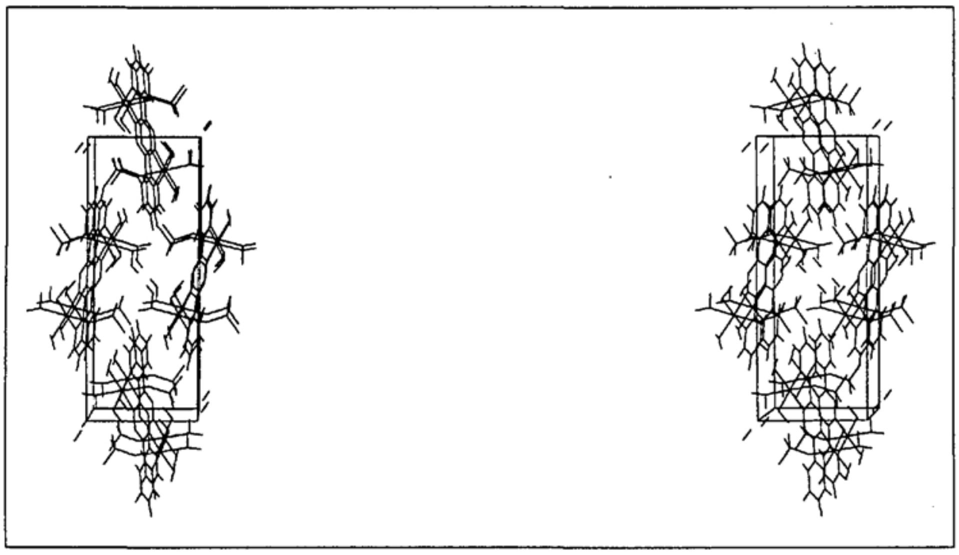


Fig. 3b. *PLUTO* [22] *plot of the crystal packing of* **3** *viewed along the* c *axis*

nated H_2O molecule, O(W1), and atoms O(1) and O(6) of the two nitrate groups (*Fig. 2b*).

{[2,5-Bis(2'-pyridyl)pyrazine]-$Fe_2(H_2O)_6(SO_4)_2$*}*$(H_2O)_2$ (**3**). The preliminary X-ray analysis of this dinuclear complex shows that the Fe-atoms are hexacoordinate with an intramolecular metal–metal distance of *ca.* 7.1 Å (*Fig. 3a*). In the crystal there are two relatively short intermolecular metal–metal distances, for example 6.4 and 6.5 Å. The N_{py}–Fe–N_{pz} bite angle is 76(1)° and the Fe–N_{py} bond distance of 2.18 Å (standard value 2.224 Å) is same as the Fe–N_{pz} distance (2.18 Å). The pyrazine–pyridine dihedral angle is 4°. The molecules stack up the *c* axis, separation 8.03 Å, and are linked by hydrogen bonds involving the H_2O molecules and the sulphate O-atoms (*Fig. 3b*).

{[2,5-Bis(2'-pyridyl)pyrazine]-$Cu_2(H_2O)_4(NO_3)_2$*}*$(NO_3)_2$ (**4**). The Cu-atom is penta-coordinate with a square pyramidal geometry. Atom Cu is displaced by 0.093(2) Å from the best plane through atoms N1, N2, OW1, and O41 [planar to within 0.048(2) Å]. The intramolecular metal–metal distance is 6.760 Å (*Fig. 4a*). In the crystal there is a short intermolecular metal–metal distance of 5.174 Å. The N_{py}–Cu–N_{pz} bite angle is 80.98(12)°. Again the Cu–N_{py} bond distance of 2.012(3) Å (standard value 2.113 Å) is similar to the Cu–N_{pz} distances of 2.021(3) Å (standard value 2.024 Å). The molecule is the least planar of the metal complexes with a pyrazine–pyridine dihedral angle of 8.5(1)°. The molecules stack up the *a* axis, separation 8.55 Å, and are linked by hydrogen bonds involving the coordinated H_2O molecules and the nitrate O-atoms (*Fig. 4b*).

Conclusion

BPPZ has been shown to form complexes with *first-row* transition metals. There is no steric hindrance to coplanarity of the hetero rings and it has relatively low lying π^* orbitals. It is a better π-acceptor than the non-planar isomer 2,3-bis(2'-pyridyl)pyrazine for which no X-ray structures of coordination complexes have been reported [17]. The largest pyrazine–pyridine dihedral angle observed here is 8.5(1)° in the Cu complex **4**, which has the shortest metal–N bonds and the largest N–metal–N bite angle. An even larger dihedral angle, 11.8°, has been found in the nitrate salt of the diprotonated form of BPPZ, $BPPZH_2^{2+}$ [18]. In the three metal complexes we were able to crystallize the metal–N(pyridine) distances are shorter

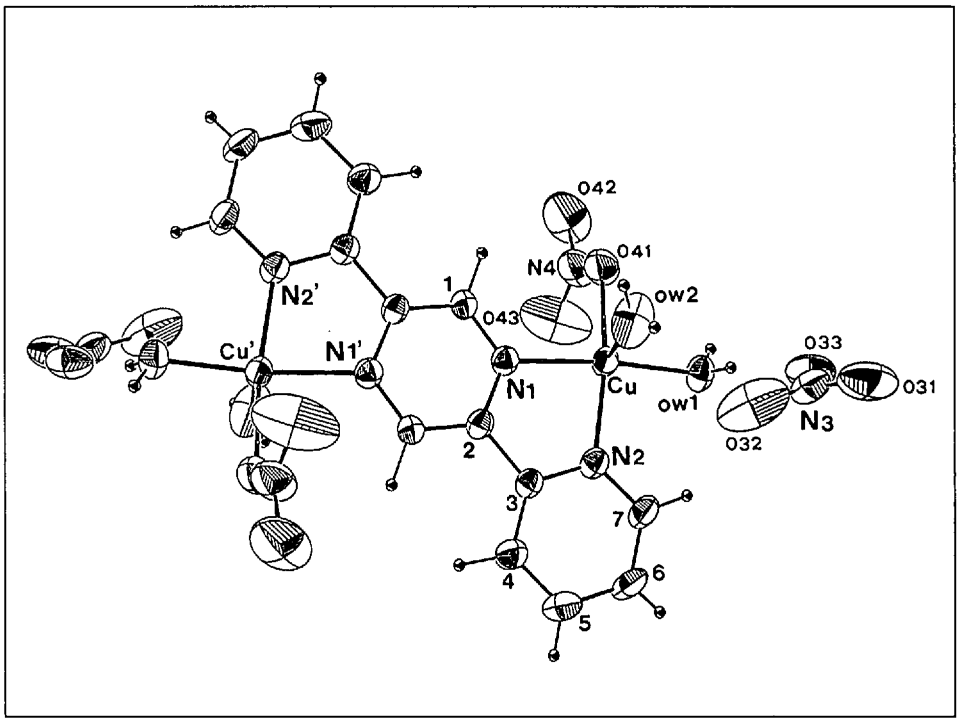


Fig. 4a. *ORTEP-II* [21] *plot of {[2,5-bis(2'-pyridyl)pyrazine]$Cu_2(H_2O)_4(NO_3)_2$}$(NO_3)_2$* (**4**) *(*ellipsoids at 50% probability level*)*. Cu–N(1) 2.021(3) Å, Cu–N(2) 2.012(3) Å, N(1)–Cu–N(2) 80.98(12)°, Cu–O(W1) 1.958(3) Å, Cu–O(W2) 2.182(3) Å, Cu–O(41) 1.990(3) Å.

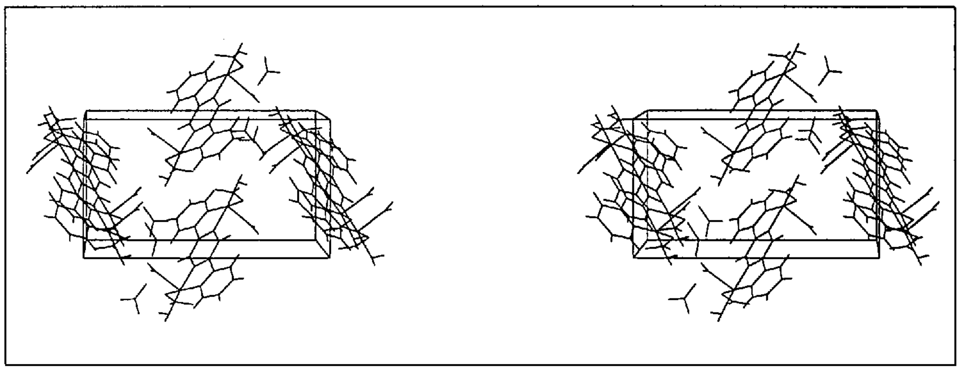


Fig 4b. *PLUTO* [22] *plot of the crystal packing of* **4** *viewed along the* a *axis*

than standard values, however, the metal-N(pyrazine) distances are close to standard values [16]. The metal coordination spheres are completed by the O-atoms of the anions and H_2O molecules. We will now look for a second bridging ligand with oxygen and/or other σ-donor atoms, in order to form coordination polymers. Efforts are being made in this direction especially with the Cu complex, as this is the only complex which does not decompose in aqueous solution.

Experimental

Instrumentation. Elemental analyses were performed by Mikroanalytisches Laboratorium, ETH, Zürich. IR Spectra: *Perkin-Elmer FTIR 1720* spectrometer using KBr pellets: in cm^{-1}. NMR Spectra: ^1H at 400 MHz using $CDCl_3$ as solvent and TMS as internal standard, were measured with a *Bruker WM400* at r.t. Chemical shift in ppm. Coupling constant *J* in Hz. UV/Vis (λ_{max} in nm, ε in $cm^{-1}M^{-1}$) spectra were obtained with a *Uvikon 8100/820*, detecter: Photomultiplier *R446* (standard).

Syntheses. 2,5-Bis(2'-pyridyl)pyrazine (**1**). The ligand was synthesized according to [13–15]. α-Acetylpyridine was first converted to methyl-α-pyridinylketoxime [13]. The *p*-tosyl-2-acetypyridineoxime was then prepared and converted to 2-α-aminoacetylpyridine according to [14]. Finally 1.932 g of 2-α-aminoacetylpyridine·HCl (11.2 mmol) were disolved in 19 ml of H_2O. A 21.1% ammoniac soln. (2.5 ml) was added and a red precipitate formed. The mixture was stirred for 3 h at r.t. and then filtered. The red solid was dried and recrystallized from $CHCl_3$. Yield: 260 mg (20%). M.p. 227° ([15]: 227.9°). UV/VIS: 250 (ε = 12124), 318 (29394). IR: 1590, 1570, 1457, 1438, 782. ^1H-NMR: 7.36 (*t*, *J* = 4.68, H–C(3), H–C(3')); 7.86 (*t*, *J* = 7.56, H–C(4), H–C(4')); 8.44 (*d*, *J* = 7.96, H–C(5), H–C(5')); 8.75 (*d*, *J* = 4.64, H–C(2), H–C(2')); 9.67 (*s*, H–C(1), H–C(1')).

{[2,5-Bis(2'-pyridyl)pyrazine]$Mn_2(H_2O)_2$-$(NO_3)_4$} (**2**). $Mn(NO_3)_2 \cdot 4\ H_2O$ (430 mg, 1.7 mmol) was added to a soln. of BPPZ (200 mg, 0.85 mmol) dissolved in THF (20 ml) and stirred. A yellow precipitate was formed which was filtered and recrystallized from MeOH. Yield: 510 mg (95%). M.p. 293° (dec.). UV/VIS: 250 (ε = 15780) 318 (37270), 435 (120). IR: 1603, 1574, 1475, 1438. Anal. calc. for $C_{14}H_{14}N_8O_{14}Mn_2$: C 26.76, H 2.25, N 17.84; found: C 27.18, H 2.34, N 17.42.

{[2,5-Bis(2'-pyridyl)pyrazine]$Fe_2(H_2O)_6$-$(SO_4)_2$}$(H_2O)_2$ (**3**). BPPZ (60 mg, 0.26 mmol) dissolved in THF (5 ml) was added to an aq. soln. of $FeSO_4 \cdot 7H_2O$ (10 ml, 145 mg, 0.52 mmol) in the absence of O_2. A blue powder precipitated, was filtered and washed with THF and dried under vacuum. Yield: 60 mg (34%). M.p. 255° (dec.). UV/VIS: 247 (ε = 93180), 320 (19240), 544 (2060). IR: 1607, 1577, 1478, 1441. Anal. calc. for $C_{14}H_{26}N_4O_{16}S_2Fe_2$: C 24.65, H 3.84, N 8.21; found: C 24.62, H 4.20, N 8.28.

{[2,5-Bis(2'-pyridyl)pyrazine]$Cu_2(H_2O)_4$-$(NO_3)_2$}$(NO_3)_2$ (**4**). BPPZ (60 mg, 0.26 mmol) dissolved in THF (10 ml) was added to a soln. of $Cu(NO_3)_2 \cdot 3H_2O$ (125 mg, 0.52 mmol) dissolved in CH_3CN (10 ml). A green precipitate was obtained which was recrystallized from DMF. Yield: 40 mg (23%). M.p. 240° (dec.) UV/VIS: 260 (ε = 40840), 280 (36730), 346 (81580), 420 (2560), 440 (2130), 706 (450). IR: 1606, 1572, 1465, 1437. Anal. calc. for $C_{14}H_{18}N_8O_{16}Cu_2$: C 24.68, H 2.66, N 16.44; found: C 24.74, H 1.92, N 16.58.

2,5-Bis(2'-pyridyl)pyrazine]$Zn(NO_3)_2 \cdot (H_2O)_4$ (**5**). BPPZ (200 mg, 0.85 mmol) dissolved in THF (20 ml) was added dropwise to a soln. of $Zn(NO_3)_2 \cdot 4(H_2O)$ (220 mg, 0.85 mmol) in DMF (10 ml). Fine white needles were obtained on slow evaporation of the solvent. Yield: 380 mg (90%). UV/VIS: 250 (ε = 15390), 320 (38940), 420 (90). IR: 1603, 1573, 1472, 1436. Anal. calc. for $Cl_4H_{18}N_6O_{10}Zn$: C 33.92, H 3.66, N 16.95; found: C 33.35, H 3.75, N 17.01.

X-Ray Crystal Structure Determinations. **1**: $[C_{14}H_{10}N_4]$, M_r = 234.3, monoclinic, $P2_1/n$, a = 5.556(1), b = 6.363(1), c = 15.995(2) Å, β = 91.69(1)°, V = 563.9(2) Å^3, Z = 2, D_x = 1.380 g·cm^{-3}, λ = 0.71073 Å, μ = 0.8 cm^{-1}, F(000) = 244. 2113 reflections measured, 993 unique, 655 observed [$I > 3\sigma(I)$], R = 0.037, R_w = 0.075, k = 0.01, S = 0.78. Max. shift/sigma ratio 0.029, residual density (e/Å^3) max. 0.12, min. –0.13.

2: $[C_{14}H_{10}N_4]Mn_2(H_2O)_2(NO_3)_4$, M_r = 628.2, monoclinic, P2_1/c, a = 7.888(2), b = 8.495(1), c = 17.434(2) Å, β = 96.19(2)°, V = 1161.4(4) Å^3, Z = 2, D_x = 1.796 g.cm^{-3}, λ = 0.71073 Å, μ = 11.2 cm^{-1}, F(000) = 592. 2048 unique reflections, 1356 observed [$I > 1.5\sigma(I)$], R = 0.055, R_w = 0.064, k = 0.002, S = 1.14. Max. shift/sigma ratio 0.017, residual density (e/Å^3) max. 0.41, min. –0.40.

3: $[C_{14}H_{10}N_4]Fe_2(H_2O)_6(SO_4)_2 \cdot (H_2O)_2$, M_r = 682.2, monoclinic, $P2_1/a$, a = 7.772(2), b = 19.919(9), c = 8.034(2) Å, β = 96.98(3)°, V = 1234.5(7) Å^3, Z = 2, D_x = 1.835 g·cm^{-3}, λ = 0.71073 Å, μ = 13.7 cm^{-1}, F(000) = 702. 2128 unique reflections, 1205 observed [$I > 3\sigma(I)$], R = 0.131, R_w = 0.190, k = 0.005, S = 2.65. Max shift/sigma ratio 0.017, residual density (e/Å^3) max. 4.79 near the sulphate, min. –1.34 (see below).

4: $[C_{14}H_{10}N_4]Cu_2(H_2O)_4(NO_3)_4$, M_r = 681.4, monoclinic, $P2_1/n$, a = 8.554(1), b = 15.768(4), c = 8.916(1) Å, β = 96.14(1)°, V = 1195.7(4) Å^3, w = 2, D_x = 1.893 g·cm^{-3}, λ = 0.71073 Å, μ = 18.7 cm^{-1}, F(000) = 688. 2116 unique reflections, 1643 observed [$I > 2.5\sigma(I)$], $R = 0.040$, $R_w = 0.056$, $k = 0.001$, $S = 1.52$. Max. shift/sigma ratio 0.003, residual density (e/Å^3) max. 0.67, min. -0.34.

Intensity data were collected at r.t. on a *Stoe AED2* 4-circle diffractometer using MoK_α graphite monochromated radiation and ω/Θ scans out to 50° in 2Θ. The structures were solved by direct methods or *Patterson* syntheses in the case of the metal complexes, using the NRCVAX [19] system, which was used for all further calculations. Neutral complex-atom scattering factors in NRCVAX [19] are from [20]. The majority of H-atoms were located from difference maps and refined isotropically. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares, where $w = 1/[\sigma^2(F_o) + k(F_o^2)]$. Crystals of the Fe complex **3** were twinned about the **c** axis. This preliminary structure analysis is rather unsatisfactory from the point of view of accuracy; the e.s.d.'s of the bond distances and angles are certainly underestimated. Further attempts will be made to improve this situation. Atomic parameters and complete tables of bond distances and angles for structures **1**, **2**, and **4** have been deposited with the *Cambridge Crystallographic Data Centre*, Union Road, Cambridge CB2 1EZ, England. The numbering schemes used are illustrated in the ORTEP-II [21] plots, *Figs. 1a*, *2a*, *3a*, and *4a*. *Figs. 1b*, *2b*, *3b*, and *4b* were drawn using PLUTO [22]. Further details may been obtained from *H. St.-E.*

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Coordination Polymers of Cu^{II} with the Ligand Pyrazine-2,3,5,6-tetracarboxylic Acid

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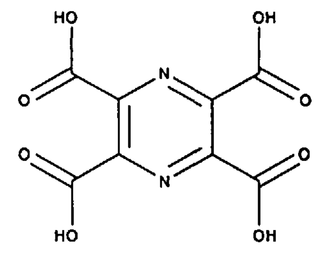
Abstract. The ligand pyrazine-2,3,5,6-tetracarboxylic acid in the presence of $CuCl_2$ and the buffers CH_3CO_2X/CH_3CO_2H, X = K^+, Rb^+, Cs^+ and $(CH_3CO_2)_2Mg/CH_3CO_2H$, forms two quite different types of coordination polymers. With the monovalent K^+, Rb^+, or Cs^+ buffer an almost right-angled dimeric unit is formed which polymerizes to form a *zig-zag* polymer $\{Cs_4[Cu_2(pztc)_2 2H_2O] \cdot 9H_2O\}_\infty$ (**1**). This 'dimerizes' about a center of symmetry to form a two-dimensional polymer sheet. With the divalent Mg^{2+} buffer a mononuclear unit polymerizes to form a *quasi-linear* polymer $\{Mg(H_2O)_6[Cu(pztc)2H_2O] \cdot 2H_2O\}_\infty$ (**2**). The X-ray crystal structures of **1** and **2** indicate that the Cu-atom exists in two quite different coordination environments (NO_3 square pyramidal for **1** and N_2O_2, square planar for **2**) and that the Cu–N(pyrazine) bond distances are much longer than normal.

Introduction

Pyrazine-2,3,5,6-tetracarboxylic acid (= H_4pztc) and its Na^+, K^+, and Ba^{2+} salts, as well as its Ag^I complex, have been known since the last century [1][2]. In the 80's the late *Werner Marty* suggested the possibility of forming *quasi-linear* coordination polymers with this potentially bis(tridentate) binucleating ligand and transition metal ions.



pyrazine-2,3,5,6-tetracarboxylic acid

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