# Notes

## A Planar, Binucleating, Pyrazole Derivative Ligand. Crystal Structure of Bis[$\mu$-3,5-bis(2′-pyridyl)pyrazolato-$N^1N'$:$N^2N''$]-bis[dimethanolnickel(II)] Dichloride Dihydrate†

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The co-ordinating properties of the ligand 3,5-bis(2-pyridyl)pyrazole (Hbpypz) are reported and complexes of general formulae [M(bpypz)]$NO_3\cdot xH_2O$ (M = Co$^{II}$, Ni$^{II}$, Cu$^{II}$, Zn$^{II}$, or Cd$^{II}$), [M(bpypz)]Cl$\cdot xH_2O$ (M = Mn$^{II}$, Co$^{II}$, Ni$^{II}$, or Zn$^{II}$), and [M(bpypz)]Br$\cdot xH_2O$ (M = Co$^{II}$, Ni$^{II}$ or Zn$^{II}$) are described. The crystal and molecular structure of $[Ni_2(bpypz)_2(MeOH)_4]Cl_2\cdot 2H_2O$ is also reported. The crystals are triclinic, space group $P\bar{1}$ with $a$ = 8.934(3), $b$ = 8.958(6), $c$ = 12.040(5) Å, $\alpha$ = 72.02(3), $\beta$ = 77.66(3), and $\gamma$ = 68.58(3)°.

As part of our research programme investigating polynuclear complexes we have focused attention on polynucleating ligands in order to synthesize homo- or hetero-trinuclear complexes.

In the past, we have reported the synthesis of the compound 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($H_3$bhpp),[1] a planar and potentially trinucleating molecule. With this ligand we were able to synthesize pure monomeric complexes,[2,3] and also some heterotrinuclear complexes of the type $UO_2$–M–$UO_2$(M = Co$^{II}$ or Ni$^{II}$).[4] Similarly we have synthesized the 1,3-bis(2-pyridyl)-1,3-propanedione ligand and characterized some of its complexes.[5]

By reaction of 1,3-bis(2-pyridyl)-1,3-propanedione with hydrazine the title compound 3,5-bis(2-pyridyl)pyrazole (Hbpypz) is synthesized, which is a planar, binucleating ligand. An early report of this same ligand was made by Ball and Blake[6] in 1969. These authors synthesized the organic molecule and nickel(II) complexes using the nitrate anion. On the basis of spectrophotometric and magnetic measurements they assigned a tentative binuclear structure to these compounds. Our results are in agreement with theirs.

### Experimental

Microanalyses (C, H, and N) were performed in our analytical laboratory on a Perkin-Elmer 240-B microanalyzer. Proton and $^{13}$C n.m.r. spectra were run on a Bruker WP 80SY spectrometer in $CDCl_3$ solution, i.r. spectra on a Perkin-Elmer 240 FT spectrophotometer.

*3,5-Bis(2-pyridyl)pyrazole (Hbpypz).*—This compound was synthesized as previously reported.[6] I.r. (most characteristic bands): ν(N–H) 3 200; ν(C–H, aromatic) 3 062; ν(C–C, pz) 1 595, 1 570 cm$^{-1}$. Mass spectrum: $m/z$ 222 (99.2), $M$ (molecular peak); 193 (100) $M - N_2H$. (The values in parentheses represent the intensities referred to the base peak in the mass spectrum; $M = {}^{12}C_{13}H_{10}{}^{14}N_4$.) N.m.r.: $^1$H, 8.6 (d, 2, pyridyl H$^6$), 7.85 (d, 2, pyridyl H$^3$), 7.66 (t, 2, pyridyl H$^4$), 7.34 (s, 1, pyrazole H$^4$), and 7.14 (t, 2, pyridyl H$^5$). $^{13}$C, 149.5 (py C$^2$ or pz C$^3$), 148.7 (py C$^6$), 148.1 (pz C$^3$, py C$^2$), 137.5 (py C$^4$), 122.7 and 120.2 (py C$^{3,5}$), and 101.8 p.p.m. (pz C$^4$) (Found: C, 70.2; H, 4.4; N, 25.0. Calc. for $C_{13}H_{10}N_4$: C, 70.25; H, 4.50; N, 25.20%).

*Complexes* [M(bpypz)]$NO_3\cdot xH_2O$ (M = Co, Cd, Ni, Zn, *or* Cu).—The reactions were carried on under aerobic conditions. To the appropriate hydrated metal nitrate salt (0.9 mmol) in methanol (10 cm$^3$) was added 3,5-bis(2-pyridyl)pyrazole (Hbpypz) (0.1 g, 0.44 mmol) in the same solvent (10 cm$^3$). Upon addition no appreciable change in colour was observed, but after 24 h crystalline solids were obtained, which were filtered off and dried *in vacuo*.

Table 1 reports the analysis, colour, and yields of all the different complexes synthesized.

*Complexes* [M(bpypz)]Cl$\cdot xH_2O$ (M = Zn, Ni, Co, *or* Mn).—The reactions were carried out under a dinitrogen atmosphere. To a Schlenk flask containing deoxygenated warm ethanol (20 cm$^3$) was added, in this order, 3,5-bis(2-pyridyl)pyrazole (100 mg, 0.45 mmol) and $MCl_2\cdot xH_2O$ (0.9 mmol). The resulting solution was stirred at room temperature for 2 h and concentrated on a vacuum line to one-fifth of the initial volume. After standing at room temperature for a few hours, crystalline solids were obtained, which were filtered off and dried *in vacuo*. In the case of $MnCl_2\cdot 4H_2O$ immediate precipitation takes place after mixing of the reagents.

*Complexes* [M(bpypz)]Br$\cdot xH_2O$ (M = Ni, Co, *or* Zn).—The procedure was the same as given above (using bromide salts instead of chloride) but concentrating of the reagent mixture almost to dryness was necessary in order to obtain crystalline solids in all cases. The solids were filtered off, washed with ethanol, and dried *in vacuo*.

*Crystal-structure Determination of* $[Ni_2(bpypz)_2(MeOH)_4]$-$Cl_2\cdot 2H_2O$.—*Crystal data.* $C_{26}H_{20}Cl_2N_8Ni_2\cdot 4MeOH\cdot 2H_2O$, $M$ = 796.4, triclinic, space group $P\bar{1}$, $a$ = 8.934(3), $b$ = 8.958(6), $c$ = 12.040(5) Å, $\alpha$ = 72.02(3), $\beta$ = 77.66(3), $\gamma$ = 68.58(3)°, $U$ = 847.5 Å$^3$, $\lambda$(Mo-$K_\alpha$) = 0.710 60 Å, $\mu$ = 13.0 cm$^{-1}$, $D_c$ = 1.24 mg m$^{-3}$, $F$(000) = 410. A violet crystal of dimensions 0.22 × 1.10 × 0.11 mm was covered with commercial glue to

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

**Table 1.** Analytical and physical data for the complexes. L = bpypz

| | Analysis (%) | | | | |
|---|---|---|---|---|---|
| Compound | C | H | N | Colour | Yield (%) |
| $[CoL]NO_3 \cdot H_2O$ | 43.30 (43.20) | 3.15 (3.30) | 19.75 (19.40) | Orange | 58.0 |
| $[CdL]NO_3 \cdot H_2O$ | 37.40 (37.65) | 2.80 (2.65) | 17.25 (16.90) | Colourless | 42.0 |
| $[NiL]NO_3 \cdot H_2O$ | 43.05 (43.35) | 3.10 (3.05) | 19.00 (19.45) | Violet | 63.0 |
| $[ZnL]NO_3 \cdot 2H_2O$ | 40.30 (40.60) | 3.25 (3.40) | 17.95 (18.20) | Colourless | 45.0 |
| $[CuL]NO_3 \cdot H_2O$ | 42.90 (42.80) | 2.95 (3.00) | 19.15 (19.20) | Dark green | 48.0 |
| $[MnL]Cl \cdot H_2O$ | 47.75 (47.35) | 3.60 (3.35) | 16.55 (17.00) | Colourless | 55.0 |
| $[NiL]Cl \cdot 2H_2O$ | 44.30 (44.40) | 3.60 (3.70) | 15.75 (15.95) | Green-yellow | 52.0 |
| $[CoL]Cl \cdot 2H_2O$ | 44.05 (44.40) | 3.65 (3.70) | 15.80 (15.95) | Dark green | 39.0 |
| $[ZnL]Cl \cdot H_2O$ | 45.75 (45.90) | 3.20 (3.25) | 16.05 (16.50) | Colourless | 48.0 |
| $[NiL]Br \cdot 2H_2O$ | 39.25 (39.40) | 3.30 (3.30) | 13.90 (14.15) | Violet | 42.0 |
| $[CoL]Br \cdot 2H_2O$ | 39.15 (39.40) | 3.05 (3.30) | 14.10 (14.15) | Dark green | 35.0 |
| $[ZnL]Br \cdot H_2O$ | 40.60 (40.60) | 2.75 (2.85) | 14.30 (14.55) | Colourless | 56.0 |

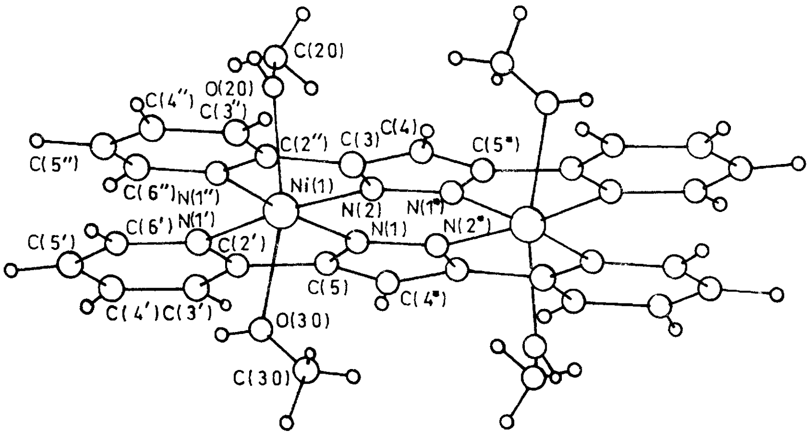

**Figure 1.** The molecular structure of $[Ni_2(bpypz)_2(MeOH)_4]Cl_2 \cdot 2H_2O$

avoid dehydration. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer using ω—2θ scan mode up to $2\theta_{max.} = 50°$ $(-10 < h < 10, -10 < k < 10, 0 < l < 14)$ giving 2 962 unique reflections. Standard reflection decay during the data collection process was 1.03%.

A straightforward run of the program MULTAN 11/84[7] failed to show the structure. A subsequent run considering the non-centrosymmetric $P\bar{1}$ space group gave a correct solution. Taking the centre of two Ni positions as a new origin in the space group $P\bar{1}$, the structure could be correctly refined. After several cycles of refinement using anisotropic, full-matrix least-squares methods (SHELX 76),[8] the value of $R = 0.031$ $\{R' = 0.036, w = 1/[\sigma^2(F) + 0.001\,64F^2]\}$ was achieved over 2 714 observed reflections $[F > 5\sigma(F)]$. All hydrogen atoms were located by Fourier difference synthesis and refined with a global thermal parameter (275 free parameters). The maximum and minimum peaks in the final Fourier difference map were 0.40 and $-0.30$ e Å$^{-3}$ respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

*Magnetic Measurements.*—Susceptibility measurements were made on polycrystalline samples at temperatures between 77 K and room temperature (298 K), with a Faraday-type balance. Diamagnetic corrections were calculated from Pascal's constants, but no t.i.p. (temperature independent paramagnetism) corrections were introduced in the experimental values.

## Results and Discussion

Reaction of Hbpypz with metal nitrates, chlorides, and bromides in methanol yields compounds with the general formulae $[M(bpypz)]X \cdot xH_2O$ ($X = NO_3$, M = Co, Cd, Ni, Zn, or Cu; X = Cl, M = Mn, Ni, Co, or Zn; X = Br, M = Ni, Co, or Zn).

Even though it has not been explicitly indicated it is important to mention that reaction of Hbpypz with bis(triphenylphosphine)cobalt(II) chloride yields a compound with the same stoicheiometry, which implies that the phosphine ligands have been totally replaced by the pyrazole derivative.

*Molecular Structure of the Nickel*(II) *Compound.*—Figure 1 shows the geometry of the molecule with the atomic numbering scheme, Table 2 the atomic co-ordinates of the non-hydrogen atoms, and Table 3 selected bond distances and angles. The two ligands and two nickel(II) ions are coplanar. Each of the nickel(II) ions is six-co-ordinated by two pyridine nitrogens, two pyrazole nitrogens at the equatorial positions, and two methanol molecules at the axial positions. The two co-ordination polyhedra about the nickel(II) ions are distorted octahedra sharing an edge. Figure 2 shows a view of the molecular packing in the crystal. The molecules are arranged in a parallel form, but due to the axial methanol molecules there is no interaction between them. Perhaps a strongly directed square-planar transition-metal ion would force the planar molecules to stack with significant metal–metal interactions,

Table 2. Atomic co-ordinates of non-hydrogen atoms with estimated standard deviations (e.s.d.s) in parentheses

| Atom | X/a | Y/b | Z/c |
|---|---|---|---|
| Ni(1) | 4 314.3(0.3) | 292.5(0.3) | 3 402.3(0.2) |
| O(20) | 3 973(2) | 1 973(2) | 6 926(2) |
| C(20) | 4 074(5) | 3 589(4) | 6 486(3) |
| O(30) | 7 580(2) | −2 565(2) | 6 605(2) |
| C(30) | 7 473(6) | −3 897(5) | 6 290(5) |
| N(1) | 3 601(2) | −763(2) | 5 054(2) |
| N(2) | 4 036(2) | −962(2) | 6 095(2) |
| C(3) | 3 188(3) | −1 785(3) | 6 931(2) |
| C(4) | 2 124(3) | −2 134(3) | 6 433(2) |
| C(5) | 2 438(3) | −1 450(3) | 5 238(2) |
| N(1′) | 2 422(2) | −521(3) | 3 169(2) |
| C(2′) | 1 759(3) | −1 305(3) | 4 190(2) |
| C(3′) | 530(3) | −1 924(3) | 4 239(2) |
| C(4′) | −56(3) | −1 733(3) | 3 211(3) |
| C(5′) | 602(3) | −938(4) | 2 170(3) |
| C(6′) | 1 822(3) | −346(3) | 2 183(2) |
| N(1″) | 4 648(2) | −1 511(2) | 8 243(2) |
| C(2″) | 3 523(3) | −2 116(3) | 8 136(2) |
| C(3″) | 2 755(4) | −2 975(4) | 9 092(2) |
| C(4″) | 3 135(4) | −3 259(4) | 10 201(3) |
| C(5″) | 4 324(4) | −2 669(4) | 10 312(3) |
| C(6″) | 5 034(3) | −1 796(3) | 9 324(2) |
| Cl | 8 358(1) | 7 444(1) | 825(1) |
| O | 9 159(3) | −3 889(3) | 8 511(2) |

Table 3. Selected interatomic distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| N(1)–Ni(1) | 1.998(2) | C(6′)–N(1′) | 1.347(4) |
| N(1′)–Ni(1) | 2.168(2) | C(3′)–C(2′) | 1.384(4) |
| C(20)–O(20) | 1.410(4) | C(4′)–C(3′) | 1.384(4) |
| C(30)–O(30) | 1.397(4) | C(5′)–C(4′) | 1.365(5) |
| N(2)–N(1) | 1.342(3) | C(6′)–C(5′) | 1.380(4) |
| C(5)–N(1) | 1.339(3) | C(2″)–N(1″) | 1.348(3) |
| C(3)–N(2) | 1.340(3) | C(6″)–N(1″) | 1.342(3) |
| C(4)–C(3) | 1.391(4) | C(3″)–C(2″) | 1.374(4) |
| C(2″)–C(3) | 1.462(4) | C(4″)–C(3″) | 1.387(4) |
| C(5)–C(4) | 1.390(4) | C(5″)–C(4″) | 1.360(5) |
| C(2′)–C(5) | 1.465(3) | C(6″)–C(5″) | 1.377(4) |
| C(2′)–N(1′) | 1.347(3) | | |
| | | | |
| N(1′)–Ni(1)–N(1) | 77.8(1) | N(1′)–C(2′)–C(5) | 115.0(2) |
| N(2)–N(1)–Ni(1) | 132.8(2) | C(3′)–C(2′)–C(5) | 122.8(2) |
| C(5)–N(1)–Ni(1) | 118.4(2) | C(3′)–C(2′)–N(1′) | 122.2(2) |
| C(5)–N(1)–N(2) | 108.7(2) | C(4′)–C(3′)–C(2′) | 119.5(3) |
| C(3)–N(2)–N(1) | 107.8(2) | C(5′)–C(4′)–C(3′) | 118.9(3) |
| C(4)–C(3)–N(2) | 110.4(2) | C(6′)–C(5′)–C(4′) | 118.7(3) |
| C(2″)–C(3)–N(2) | 115.7(2) | C(5′)–C(6′)–N(1′) | 123.7(3) |
| C(2″)–C(3)–C(4) | 133.9(2) | C(6″)–N(1″)–C(2″) | 117.9(2) |
| C(5)–C(4)–C(3) | 103.2(2) | N(1″)–C(2″)–C(3) | 114.8(2) |
| C(4)–C(5)–N(1) | 109.9(2) | C(3″)–C(2″)–C(3) | 123.0(2) |
| C(2′)–C(5)–N(1) | 115.9(2) | C(3″)–C(2″)–N(1″) | 122.2(2) |
| C(2′)–C(5)–C(4) | 134.1(2) | C(4″)–C(3″)–C(2″) | 119.0(3) |
| C(2′)–N(1′)–Ni(1) | 112.8(2) | C(5″)–C(4″)–C(3″) | 119.1(3) |
| C(6′)–N(1′)–Ni(1) | 130.2(2) | C(6″)–C(5″)–C(4″) | 119.3(3) |
| C(6′)–N(1′)–C(2′) | 117.0(2) | C(5″)–C(6″)–N(1″) | 122.6(3) |

giving materials with interesting electric properties. Further work is in progress to investigate this.

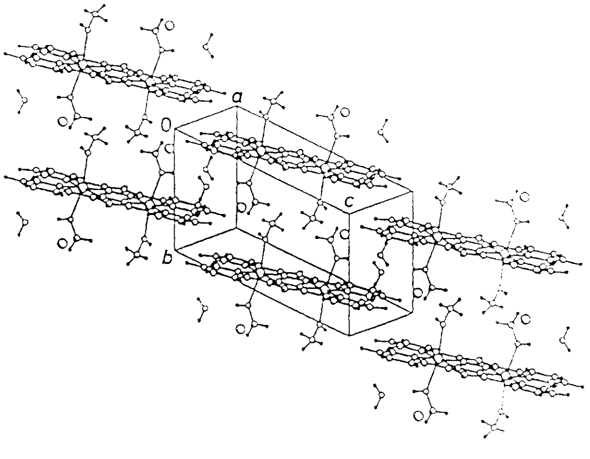

**Figure 2.** The unit-cell packing diagram of $[Ni_2(bpypz)_2(MeOH)_4]Cl_2 \cdot 2H_2O$

*Infrared Spectra of the Nitrate Complexes.*—The complexes of $Co^{II}$, $Cu^{II}$, and $Zn^{II}$ exhibit one single band in the $\nu_1 + \nu_4$ ($E'$, $D_{3h}$) combination band region (at 1 768, 1 764, and 1 767 $cm^{-1}$, respectively), indicating ionic behaviour for the nitrate group.[9] The nickel(II) complex exhibits two bands in the same region at 1 766 and 1 753 $cm^{-1}$. This splitting is typical for a unidentate nitrate group.[9] According to the stoicheiometry of this compound, an octahedral co-ordination for the $Ni^{II}$ is proposed, which is in agreement with the magnetic measurements. The cadmium(II) compound exhibits a more complex behaviour. Four bands at 1 733, 1 743, 1 760, and 1 767 $cm^{-1}$ appear in this region, indicating a mixture of uni- and bi-dentate nitrate groups.[9]

*Magnetic Measurements.*—The nickel and copper nitrate compounds behave as typical exchange-coupled binuclear complexes with antiferromagnetic interactions between both metal centres. At room temperature a $\mu_{eff.}$ value of 3.0 or 1.4 respectively, is found. These values decrease when the temperature is lowered, reaching a value of 2.4 at 78.4 K for the nickel compound, and 0.4 at 99.5 K for the copper complex.

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