

A Metal-directed Pyrazoline–1,5-Diazapentadiene Rearrangement of a Novel [2 + 2] Macrocycle: Crystal and Molecular Structures of L³ and [Ni₂(L²)]·5H₂O†

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The condensation of pentane-2,4-dione with pyridine-2,6-dicarbohydrazide leads to a structurally characterised [2 + 2] macrocyclic product containing two pyrazoline rings; reaction with transition metal ions leads to binuclear complexes of which the dinickel(II) complex has been structurally characterised and shown to contain two square-planar nickel ions co-ordinated to ring-opened pyrazoline groups.

The stoichiometry of template condensations may be controlled by a judicious choice of metal template ion,¹ and we have recently demonstrated that novel complexes and reactions occur when there is a mis-match in the co-ordination properties of ligands and metals.² The condensation of pyridine-2,6-dicarbohydrazide (L) with pentane-2,4-dione in the presence of [VO]²⁺ is reported to lead to complexes of L¹.³ Molecular modelling studies indicate that this small [1 + 1] macrocycle is an unlikely product, and we have only succeeded in preparing insoluble, non-homogeneous materials from these reactions. Accordingly we have investigated the non-template reaction of pyridine-2,6-dicarbohydrazide with pentane-2,4-dione.

The reaction proceeded smoothly in boiling methanol over a period of 18 h and concentration after this time yielded a white crystalline product. Its mass spectrum showed a parent ion at *m/z* 518 and a significant decomposition ion at *m/z* 259. This is consistent with the formation of the [2 + 2] macrocycle L². However, the ¹H n.m.r. spectrum of a solution of this product revealed the product to have a lower symmetry than that expected for L². The aromatic protons appeared as an ABM multiplet, and two methyl environments (δ 1.87 and δ 1.97) were observed in addition to an AB multiplet at δ 2.95.

In view of the above features we determined the single crystal structure of the product, and a view of the molecular

structure is presented in Figure 1.‡ The compound has structure L³ which is an isomer of the expected species L². The pyrazoline rings may be viewed as the products of an intramolecular nucleophilic attack by N(2) upon C(4) of L², although we have no direct mechanistic data to support this proposal. The atoms N(3), N(4), N(3a), and N(4a) define a plane, although the molecule as a whole is not planar. The two pyridine rings are coplanar and lie in the N(3)–N(4)–N(3a)–N(4a) plane; the individual pyridine rings are skewed by 10° with respect to the angle the N(3)–C(10) vector makes with

‡ *Crystal data:* C₂₄H₂₆N₁₀O₄, colourless blocks, *M* = 518.54, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 7.404(2), *b* = 17.455(3), *c* = 9.806(2) Å, β = 98.90(1)°, *Z* = 2, *U* = 1252 Å³, *D_c* = 1.375 g cm⁻³, *D_m* not measured, Cu-K α radiation (λ = 1.5418 Å), μ (Cu-K α) = 7.78 cm⁻¹, *F*(000) = 544. 1955 Reflections collected on a four-circle diffractometer to $2\theta_{\max}$ = 116°. The data were averaged and 1421 unique reflections with *F* > 3 σ (*F*) were used in structure solution and refinement. The structure was solved by direct methods, and refined (C, N, and O anisotropic; H isotropic in calculated positions) to *R* = 0.0569, *R_w* = 0.0642.

Crystal data: C₂₄H₂₂N₁₀O₄Ni₂·5H₂O, red blocks, *M* = 722.05, monoclinic, space group *P*2₁/*n*, *a* = 10.639(2), *b* = 18.881(3), *c* = 14.787(7) Å, β = 92.74(3)°, *Z* = 4, *U* = 2967 Å³, *D_c* = 1.620 g cm⁻³, *D_m* not measured, Cu-K α radiation (λ = 1.5418 Å), μ (Cu-K α) = 23.60 cm⁻¹, *F*(000) = 1656. 5055 Reflections collected on a four-circle diffractometer to $2\theta_{\max}$ = 120°. The data were averaged and 3315 unique reflections with *F* > 4 μ (*F*) were used in structure solution and refinement. The structure was solved by direct methods, and refined by blocked cascade least squares (non-hydrogen anisotropic; H isotropic in calculated positions) to *R* = 0.078, *R_w* = 0.083.

For both structures, atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

† L² = 4,6,19,21-Tetramethyl-2,3,7,8,17,18,22,23-octa-aza[9,9]-(2,6)pyridinophane-3,6,18,22-tetraene-1,9,16,24-tetraone; L³ = 5,6,20,21-tetrahydro-4,6,19,21-tetramethyl-7,8,22,23-tetra-aza[3]-(1,5)pyrazolo[1](2,6)pyridino[3](1,5)pyrazolo[1](2,6)pyridinophane-1,9,16,24-tetraone.

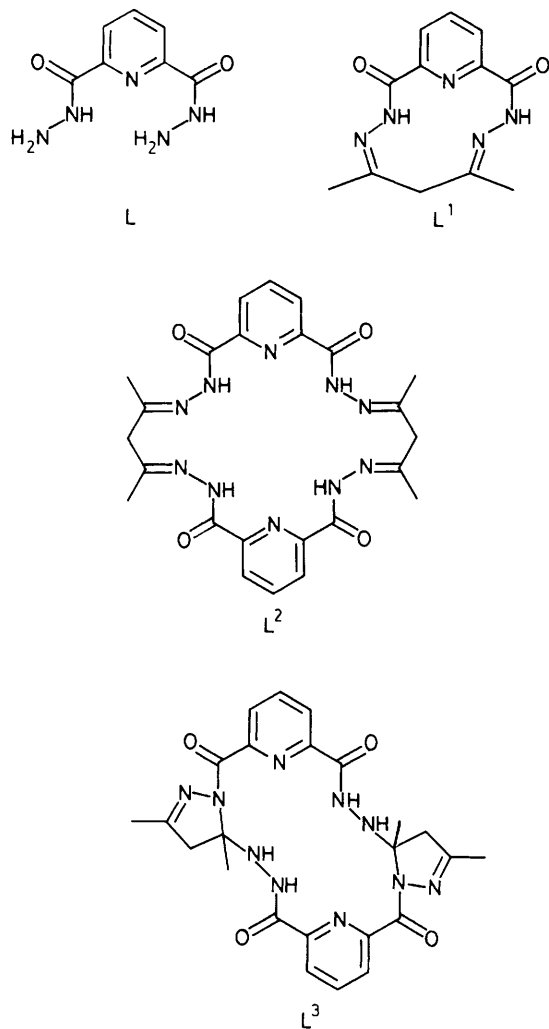


Figure 1. The molecular structure of L^3 showing the numbering scheme adopted. Selected bond lengths. (Å): N(1)–N(2) 1.401(3), C(2)–N(1) 1.284(3), C(6)–N(2) 1.344(3), C(6)–O(1) 1.224(3), N(4)–N(5) 1.404(3), N(4)–C(12) 1.335(3), C(12)–O(2) 1.223(3). Selected bond angles (°): C(4)–N(2)–N(1) 112.7(2), C(2)–N(1)–N(2) 107.3(2).

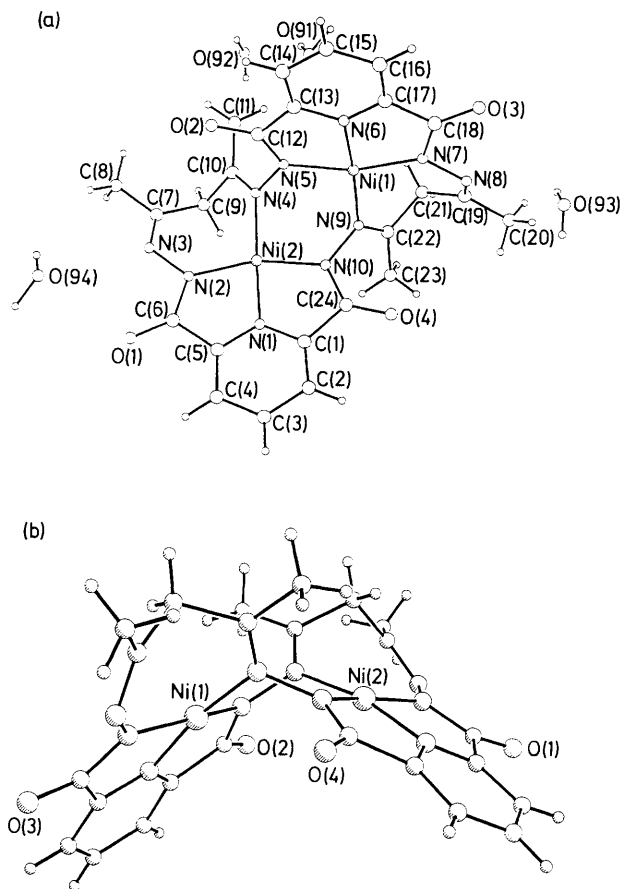


Figure 2. (a) The molecular structure of $[Ni_2(L^2)] \cdot 5H_2O$ showing the numbering scheme adopted. Selected bond lengths (Å): Ni(1)–N(5) 1.893(5), Ni(1)–N(6) 1.823(5), Ni(1)–N(7) 1.886(5), Ni(1)–N(9) 1.866(5), Ni(2)–N(1) 1.825(5), Ni(2)–N(2) 1.906(5), Ni(2)–N(4) 1.877(5), Ni(2)–N(10) 1.885(5). Selected bond angles (°): N(5)–Ni(1)–N(6) 82.8(2), N(5)–Ni(1)–N(7) 164.5(2), N(6)–Ni(1)–N(7) 83.2(2), N(5)–Ni(1)–N(9) 95.3(2), N(6)–Ni(1)–N(9) 170.3(2), N(7)–Ni(1)–N(9) 99.6(2), N(1)–Ni(2)–N(2) 83.0(2), N(1)–Ni(2)–N(4) 168.0(2), N(2)–Ni(2)–N(4) 100.6(2), N(1)–Ni(2)–N(10) 81.7(2), N(2)–Ni(2)–N(10) 163.7(2), N(4)–Ni(2)–N(10) 95.5(2). (b) An alternative view showing the shape of the molecule.

the N(3)–N(3a) axis. The pyrazoline rings adopt a flattened envelope configuration and lie above and below the mean N_4 plane; the mean planes through the two pyrazolines are parallel and at 73° with respect to the mean N_4 plane. All bond angles and distances within the macrocycle are normal. The amide bonds are short [1.344(3) and 1.335(3) Å], consistent with a considerable degree of π -overlap with the nitrogen lone-pair; a necessary consequence of the out-of-plane pyrazoline is an interplanar angle of 75.3° between the pyridine ring and the N(2)–C(6)–O(1) plane. The shortest N–N contact within the N_4 plane is 4.9 Å, indicating that the bonding cavity is too large for a first-row transition metal ion.

The reaction of L^3 with nickel(II) acetate in methanol results in the formation of a dark brown solution, from which a red crystalline solid may be obtained. The fast atom bombardment mass spectrum of the brown complex showed a parent ion at m/z 631 showing the expected pattern for an Ni_2 complex, and the elemental analysis was in accord with a 2 : 1 ratio of metal to L^3 . The complex is diamagnetic and the 1H n.m.r. spectrum indicates that the gross structure of the ligand has not altered.

The molecular structure of the complex is shown in Figure 2a.‡ It is evident that reaction of L³ with nickel(II) has resulted in a rearrangement and the formation of a binuclear complex of L². Each metal is in an approximately square-planar N₄ environment and is co-ordinated to a pyridine and its associated amide N atoms and to the remote imine from the far end of the molecule. The two nickel atoms are in similar but non-identical environments. Two of the four imine nitrogen atoms are not co-ordinated. The binuclear complex is not planar but describes a V shape, with the two square planes about the nickel atoms tilted and skewed with respect to each other as shown in Figure 2b. The distance between the two nickel atoms is 3.64 Å. The complex is neutral and the ligand is quadruply deprotonated at the amido groups. A consequence of this is an extensive hydrogen bonding network in which water molecules link adjacent molecules of the complex. The metal-directed rearrangement results in the formation of a binuclear binding site with four donor atoms arranged in an approximate square plane about the metals. The rearrangement is reminiscent of those observed by Nelson and co-workers, although these commonly involve nucleophilic attack at an imine rather than the formation of imines.⁴

Other first row transition metal ions react with the ligand L³ to give related complexes. We are currently investigating the electrochemistry and the reactivity of small molecules with these new binuclear sites.

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References

- 1 L. F. Lindoy, *Chem. Soc. Rev.*, 1975, **4**, 421; G. A. Melson, 'Coordination Chemistry of Macrocyclic Compounds,' Plenum, New York, 1979; M. de Sousa Healy and A. J. Rest, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 1; S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461.
- 2 E. C. Constable, J. Lewis, M. C. Liptrot, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1984, 2177; L.-Y. Chung, E. C. Constable, J. Lewis, P. R. Raithby, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1984, 1425; E. C. Constable, F. K. Khan, J. Lewis, M. C. Liptrot, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1985, 333; E. C. Constable, J. Lewis, V. E. Marquez, and P. R. Raithby, *ibid.*, 1986, 1747; E. C. Constable, J. M. Holmes, and R. C. S. McQueen, *ibid.*, 1987, 5; E. C. Constable, S. Corr, and M. D. Ward, *Inorg. Chim. Acta*, 1988, **141**, 201; E. C. Constable and J. M. Holmes, *Polyhedron*, 1988, **7**, 2531.
- 3 V. B. Rana, S. K. Sahni, and S. K. Sangal, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1498; S. Kher, S. K. Sahni, V. Kumari, and R. N. Kapoor, *Inorg. Chim. Acta*, 1979, **37**, 121; S. K. Sahni, S. K. Sangal, S. P. Gupta, and V. B. Rana, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1098.
- 4 J. de O. Cabral, M. F. Cabral, M. G. B. Drew, F. S. Esho, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 1068; J. de O. Cabral, M. F. Cabral, M. G. B. Drew, F. S. Esho, O. Haas, and S. M. Nelson, *ibid.*, 1982, 1066; M. G. B. Drew, S. M. Nelson, and F. S. Esho, *J. Chem. Soc., Dalton Trans.*, 1982, 407; M. G. B. Drew, J. Nelson, F. S. Esho, V. McKee, and S. M. Nelson, *ibid.*, 1982, 1837; J. Nelson, B. P. Murphy, M. G. B. Drew, P. C. Yates, and S. M. Nelson, *ibid.*, 1988, 1001; S. M. Nelson, J. A. Knox, H. McCann, and M. G. B. Drew, *ibid.*, 1981, 1669; M. G. B. Drew, S. McFall, S. M. Nelson, and C. P. Waters, *J. Chem. Res., (S)*, 1979, 16; M. G. B. Drew, J. Nelson, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1691; S. M. Nelson, F. S. Esho, J. de O. Cabral, M. F. Cabral, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 1979, 1935.