

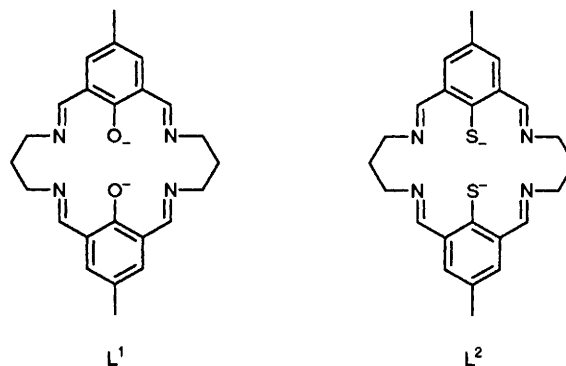
Polynuclear Nickel(II) Complexes of N_4O_2 - and N_4S_2 -Compartmental Macrocycles: The Structures of a Ni_4O_4 Cubane Cluster and the Binuclear Nickel(II) Complex of a Benzenethiolate Macrocycle

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The tetranuclear cluster $[\{Ni_2(L^1)(MeCO_2)\}_2]^{2+}$ (L^1 = the dianion of the condensation product of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol) shows a distorted Ni_4O_4 cubane structure consisting of octahedral nickel(II) centres; the structure of the dithiolate analogue $[Ni_2(L^2)](PF_6)_2 \cdot 2dmf$ (L^2 = the dianion of the condensation product of 1,3-diaminopropane and 2,6-diformyl-4-methylbenzenethiol; dmf = dimethylformamide) shows square-planar coordination at nickel(II).

Complexes of binucleating compartmental ligands have been reported with a wide range of transition metal and main group metal ions.¹⁻⁵ The major synthetic route to these complexes is *via* template condensation of the appropriate dialdehyde and diamine precursors around the metal centres.¹⁻⁴ We have recently reported the isolation and structural characterisation of the protonated metal-free macrocycle $[L^1H_4](PF_6)_2$ and complexation reactions with L^1 and the platinum group metals by metal insertion into the preformed macrocycle.⁴ Robson and Pilkington¹ have reported the synthesis of $[Ni_2(L^1)Cl_2]$ and proposed that the paramagnetic Ni^{II} centres were square-pyramidal with *trans*-diaxial coordination to two apical Cl^- ligands. Gagné and coworkers² have also reported the paramagnetic, octahedral complex $[Ni_2(L^1)(pyri-$



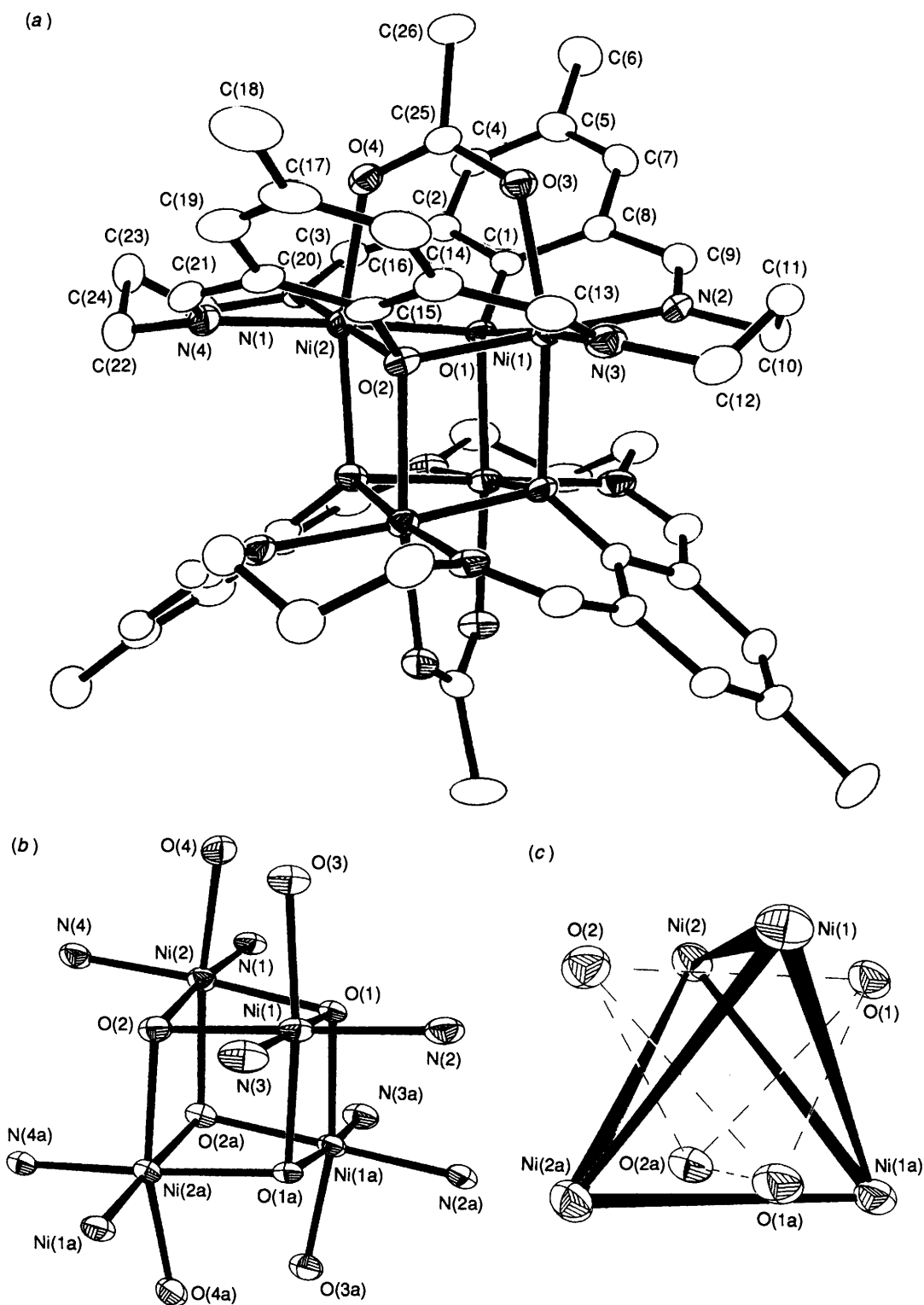


Fig. 1 (a) View of $[\{\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)_2\}]^{2+}$ with numbering scheme adopted. (b, c). Two views of the Ni_4O_4 cube in $[\{\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)_2\}]^{2+}$ with numbering scheme adopted.

dine)₄](BF₄)₂. We report herein the synthesis and structures of polynuclear Ni^{II} complexes of L¹ and of an Ni^{II} complex of the previously unknown thiolate macrocycle, L².

The reaction of two equivalents of Ni(MeCO₂)₂ with [L¹H₄](PF₆)₂ in the presence of an excess of Et₃N in MeCN gives a green product, which was formulated as [Ni₂(L¹-

(MeCO₂)](PF₆).† Crystals of the complex were grown from MeNO₂-Et₂O and a single crystal X-ray structure determina-

† All products have been characterised by elemental analyses, and by IR, electronic and FAB (fast atom bombardment) mass spectroscopy.

tion was undertaken. The structure of $[\{\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)\}_2](\text{PF}_6)_2$ shows \ddagger § the complex to be tetranuclear [Fig. 1(a)] with $[\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)]^+$ units having dimerised to give an Ni_4O_4 cubane-type structure. Fig. 1(b) shows the central $\text{Ni}_4\text{N}_8\text{O}_8$ unit with a crystallographic two-fold axis passing through the centres of the open faces of the cube. Each Ni^{II} centre is in a distorted octahedral environment, being equatorially bound to the N_2O_2 donor set of one L^1 macrocycle [Ni–N 2.014(4), 2.027(4), 2.027(4), 2.028(4); Ni–O 2.080(3), 2.095(3), 2.099(3), 2.081(3) Å] and with axial interactions to a carboxylic O-donor of a bridging MeCO_2^- group [Ni–O 2.031(3), 2.035(3) Å] and a phenoxy O-donor from a L^1 macrocycle from the other half of the dimer [Ni–O 2.152(3), 2.168(3) Å]. The Ni–Ni distance within the macrocycle L^1 is 3.0240(9) Å. The four Ni–Ni vectors describe a distorted tetrahedron with two sides *ca.* 3.02 Å long and four sides *ca.* 3.22 Å long [Fig. 1(c)], with the superimposed O_4 tetrahedron of the phenoxy O-donors having sides of *ca.* 2.70, 2.78 or 2.84 Å.

The macrocycle L^1 in $[\{\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)\}_2]^{2+}$ is non-planar and the angle between the planes defined by the two phenolic groups is 105° . There are probably two reasons for this bowed conformation of the compartmental ligands. Firstly, the bending avoids steric interactions with the macrocycle in the other half of the molecule. Secondly, from the dimensions of the O_4 tetrahedron in Fig. 1(c), it can be seen that the phenoxy O-donors are closer to the centre of the Ni_4O_4 cube than the Ni^{II} ions. To achieve this geometry the macrocycle L^1 must fold. The two MeCO_2^- and L^1 groups in $[\{\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)\}_2]^{2+}$ are orthogonal to each other, so there is no possibility for intramolecular π – π interactions between neighbouring macrocycles within the same molecule.

There have been a number of Ni_4O_4 cubane-type structures with non-macrocylic ligands reported in the literature.⁶ We tentatively propose that the cubane structure is maintained in solution since no colour change is observed on dissolution of $[\{\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)\}_2]^{2+}$ in coordinating solvents. The driving force for the dimerisation is probably the requirement of the Ni^{II} centres for octahedral coordination, since the ligand field strength of L^1 is insufficient to give diamagnetic, square-planar Ni^{II} complexes.⁵ Modification of the macrocyclic donor set from N_4O_2 to N_4S_2 would be expected to increase the

ligand field strength of the macrocycle, and so we undertook the preparation of complexes of L^2 .

Reaction of $\text{Ni}(\text{MeCO}_2)_2$ with 2,6-diformyl-4-methylbenzenethiol and 1,3-diaminopropane in MeCN in the presence of NH_4PF_6 gives $[\text{Ni}_2(\text{L}^2)](\text{PF}_6)_2$ as a red product. Crystals of $[\text{Ni}_2(\text{L}^2)](\text{PF}_6)_2 \cdot 2\text{dmf}$ (dmf = dimethylformamide) were grown from dmf–MeCN–Et₂O and a single crystal X-ray structure determination was undertaken. \S ¶ This crystal structure shows (Fig. 2) the complex disposed about a crystallographic inversion centre with two equivalent Ni^{II} positions within the complex. Each Ni^{II} ion is bonded directly to two bridging benzenethiolate S-donors [Ni–S 2.181(6), 2.171(6) Å] and two imine N-donors [Ni–N(1) 1.927(15), 1.906(15) Å]; additional interactions with O-donors from two dmf molecules [Ni–O 2.644(15) Å] are observed. The coordination geometries at the Ni^{II} centres are therefore distorted square-planar with the Ni^{II} ions displaced by *ca.* 0.1 Å out of the least-squares plane defined by the N_2S_2 donor set. The angle between the two square planes defined by the N_2S_2 arrays

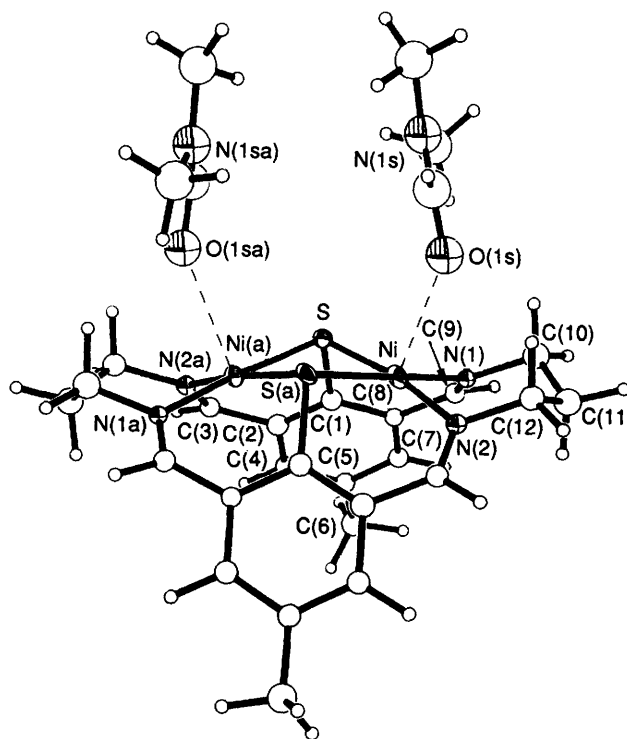


Fig. 2 View of $[\text{Ni}_2(\text{L}^2)]^{2+} \cdot 2\text{dmf}$ with numbering scheme adopted

\ddagger Crystal data for $\text{C}_{52}\text{H}_{58}\text{N}_8\text{O}_8\text{Ni}_4^{2+} \cdot 2\text{PF}_6^- \cdot 2\text{CH}_3\text{CN} \cdot \text{CH}_3\text{NO}_2$, $M = 1590.92$, monoclinic, space group $C2/c$, $a = 22.540(7)$, $b = 19.983(8)$, $c = 15.418(5)$ Å, $\beta = 109.74(3)^\circ$, $V = 6535$ Å³ (from 2 θ values of 25 reflections measured at $\pm\omega$ [$30 \leq 2\theta \leq 32^\circ$, $\lambda = 0.71073$ Å]), $Z = 4$, $D_c = 1.616$ g cm⁻³, $T = 150$ K, $\mu(\text{Mo-K}\alpha) = 1.284$ mm⁻¹. A green lath ($0.90 \times 0.50 \times 0.30$ mm³) was mounted on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.⁸ Data collection using Mo-K α X-radiation ($\lambda = 0.71073$ Å), ω -2 θ scans and the learnt-profile method⁹ gave 4422 reflections ($2\theta_{\text{max}}$, 45°) of which 3444 with $F > 4\sigma(F)$ were used in all calculations. Following identification of the Ni position from a Patterson synthesis, iterative cycles of least-squares refinement and difference Fourier synthesis located the positions of all other atoms.¹⁰ During refinement disorder of the PF_6^- was observed and thirteen F positions were found with a variety of occupancies: these were fixed in proportion to the refined occupancies (66% \rightarrow 24%). Modelling of the PF_6^- group as idealised octahedra was unsuccessful. Two molecules of CH_3CN and one of CH_3NO_2 per Ni_4 unit were located. The structure was refined by full-matrix least-squares (on F) with anisotropic thermal parameters for all non-H atoms except the F atoms with occupancies $< 50\%$. H atoms were located from a difference map and included in fixed, calculated positions. At final convergence, $R = 0.0417$, $R_w = 0.0528$, $S = 1.297$ for 464 parameters, and the final ΔF synthesis showed no feature above $+0.78$ e Å⁻³.

\S Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$\¶$ Crystal data for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{S}_2\text{Ni}_2^{2+} \cdot 2\text{PF}_6^- \cdot 2(\text{CH}_3)_2\text{NCHO}$: $M = 988.02$, monoclinic, space group $C2/c$, $a = 24.50(3)$, $b = 10.004(12)$, $c = 18.218(24)$ Å, $\beta = 120.23(5)^\circ$, $V = 3858$ Å³ [from 2 θ values of 27 reflections measured at $\pm\omega$ [$20 \leq 2\theta \leq 26^\circ$, $\lambda = 0.71073$ Å]), $Z = 4$, $D_c = 1.701$ g cm⁻³, $T = 150$ K, $\mu(\text{Mo-K}\alpha) = 1.261$ mm⁻¹. A red tablet ($0.35 \times 0.23 \times 0.08$ mm³) was mounted on a Stoë STADI-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.⁸ Data collection using Mo-K α X-radiation ($\lambda = 0.71073$ Å), ω -2 θ scans and the learnt-profile method⁹ gave 2790 reflections ($2\theta_{\text{max}}$, 45°), 2127 unique (R_{int} 0.15), of which 1543 with $F > 4\sigma(F)$ were used in all calculations. Following identification of the Ni position from a Patterson synthesis, iterative cycles of least-squares refinement and difference Fourier synthesis located the positions of all other atoms.¹⁰ At isotropic convergence, final corrections (min. 0.595, max. 1.246) for absorption were made using DIFABS.¹¹ Anisotropic thermal parameters were refined for Ni, S, P and F but the C and N atoms could only be refined isotropically owing to limitations in the quality of the data imposed by the quality of the best available crystal. H atoms were located from a difference map and included in fixed, calculated positions. At final convergence, $R = 0.1263$, $R_w = 0.1676$, $S = 1.195$ for 167 independent parameters, and the final ΔF synthesis showed no feature above $+1.39$ or below -1.72 e Å⁻³.

about Ni and Ni(a) is 144.4° . The metal-metal distance in $[\text{Ni}_2(\text{L}^2)]^{2+}$ [Ni-Ni(a) $3.163(4)$ Å] is similar to those observed in the macrocyclic complexes of L^1 ,²⁻⁴ which suggests that there is a well defined metal-metal distance that can be accommodated by two bridging phenolate or benzenethiolate donors within the Schiff-base macrocyclic framework.

In order to accommodate the coordination geometries about the Ni^{II} ions in $[\text{Ni}_2(\text{L}^2)]^{2+}$, the macrocycle L^2 adopts a folded conformation. This folding allows the bridging benzenethiolate S-donors to form a *syn-endo* Ni_2S_2 ring, and the geometries about the S-atoms are pyramidal [$\angle\text{Ni-S-C}(1)$ $99.3(7)$, Ni(a)-S-C(1) $101.6(7)^\circ$]. The folded conformation of ligand L^2 also permits a lengthening of the S...S distance within the macrocycle [S...S(a) $2.872(20)$ Å], thus minimising repulsive S...S interactions. If L^2 were to adopt a planar conformation, the S...S distance would become prohibitively short. Although complexes of open-chain analogues of L^2 have been reported,⁷ this is, to our knowledge, the first structural report of the cyclised system.

The complexes $[\{\text{Ni}_2(\text{L}^1)(\text{MeCO}_2)\}_2]^{2+}$ and $[\text{Ni}_2(\text{L}^2)]^{2+}$ reveal some interesting differences between the donor properties of bridging phenolate and benzenethiolate ligands. Current work is aimed at an investigation of the redox properties of these and related complexes.

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References

- 1 R. Robson and N. H. Pilkington, *Aust. J. Chem.*, 1970, **23**, 2225.
- 2 C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagné and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229.
- 3 For example see: B. F. Hoskins and G. A. Williams, *Aust. J. Chem.*, 1975, **28**, 2607; 1975, **28**, 2593; R. R. Gagné, L. M. Henling and T. J. Kistenmacher, *Inorg. Chem.*, 1980, **19**, 1226; R. R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073; R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105**, 1513; S. K. Mandal, L. K. Thompson, K. Nag, J.-P. Charland and E. Gabe, *Inorg. Chem.*, 1987, **26**, 1391; D. Luneau, J.-M. Savariault, P. Cassoux and J.-P. Tuchagues, *J. Chem. Soc., Dalton Trans.*, 1988, 1225; V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 385; M. Tadokoro, H. Sakiyama, N. Matsumoto, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3337; M. Tadokoro, H. Okawa, N. Matsumoto, M. Koikawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1991, 1657; M. Tadokoro, H. Sakiyama, N. Matsumoto, M. Koderu, H. Okawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1992, 313; K. K. Nanda, R. Das, M. J. Newlands, R. Hynes, E. J. Gabe and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1992, 897 and references therein.
- 4 A. J. Atkins, A. J. Blake and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1993, 353.
- 5 H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1759.
- 6 J. A. Bertrand and D. G. Caine, *J. Am. Chem. Soc.*, 1964, **86**, 2298; G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 1964, **97**, 1727; J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1969, 1456; A. G. Krüger and G. Winter, *Aust. J. Chem.*, 1970, **23**, 1; J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin and R. C. Sherwood, *Inorg. Chem.*, 1971, **10**, 240; A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45; J. A. Barnes and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 2355; B. W. Clare and D. L. Kepert, *Aust. J. Chem.*, 1975, **28**, 1489; B. Aurivillius, *Acta Chem. Scand., Ser. A*, 1977, 501; J. A. Bertrand, C. Marabella and D. G. Van Derveer, *Inorg. Chim. Acta*, 1978, **26**, 113; W. L. Gladfelter, M. W. Lynch, W. P. Schaefer, D. N. Hendrickson and H. B. Gray, *Inorg. Chem.*, 1981, **20**, 2390; F. Paap, E. Bouwman, W. L. Driessen, R. A. G. de Graaff and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1985, 737; K. Bizilj, S. G. Hardin, B. F. Hoskins, P. J. Oliver, E. R. T. Kiekink and G. Winter, *Aust. J. Chem.*, 1986, **39**, 1035.
- 7 J. G. Hughes and R. Robson, *Inorg. Chim. Acta*, 1979, **35**, 87; P. Iliopoulos, K. S. Murray, R. Robson, J. C. Wilson and G. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1987, 1585; A. M. Bond, M. Haga, I. S. Crece, R. Robson and J. C. Wilson, *Inorg. Chem.*, 1989, **28**, 559; B. F. Hoskins, R. Robson, G. A. Williams and J. C. Williams, *Inorg. Chem.*, 1991, **30**, 4160; B. F. Hoskins, C. J. MacKenzie, R. Robson and L. Zhenrong, *J. Chem. Soc., Dalton Trans.*, 1990, 2637.
- 8 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
- 9 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
- 10 SHELX-76, program for crystal structure refinement, G. M. Sheldrick, University of Cambridge, 1976.
- 11 DIFABS, program for empirical absorption correction, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.