Sawhorse connections in a Ag(I)-nitrite coordination network: $\{[Ag(pyrazine)]NO_2\}_\infty$

Alexander J. Blake,[a] Neil R. Champness,*[a] Marcello Crew[a] and Simon Parsons[b]

[a] *School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD. E-mail: pcznc@unix.ccc.nottingham.ac.uk*
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

Received (in Cambridge, UK) 15th October 1998, Accepted 5th November 1998

The Ag(8) coordination networks, $\{[Ag(pyrazine)]NO_2\}_\infty$ and $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$ have been constructed in order to investigate the effect of anion upon network topology; an unusual sawhorse connection is observed in the structure of $\{[Ag(pyrazine)]NO_2\}_\infty$ with the nitrite anion acting to 'block' *cis* coordination sites.

The preparation of extended networks using inorganic coordination polymers has become an area of increasing study in recent years.[1] One of the reasons that this interest has arisen is because the synthetic procedure used to construct these materials allows a high degree of design. Ultimately this may lead to the development of materials with tuneable properties including structures with host–guest properties similar to those observed with zeolites,[2] and compounds with interesting electronic or magnetic properties. The high degree of design arises from the coupling of the well understood coordination properties of individual metal ions and highly-developed ligand syntheses with the newer areas of supramolecular chemistry and crystal engineering.[3] We have been studying the effect of individual building-blocks upon network structure. This has included the control of network topology and interpenetration in adamantoid networks *via* ligand design[4] and studies on the effect of variation of solvent of crystallisation upon network structure.[5] The nature of the counter-anion has also been shown to have a dramatic effect upon network topology and this is particularly noticeable in Ag(I) chemistry.[6,7] Recently we have demonstrated that replacement of $AgBF_4$ or $AgPF_6$ with $AgNO_3$ results in a fundamental change of the extended structure of a coordination polymer with the ligand 3,6-di-4-pyridyl-1,2,4,5-tetrazine due to interactions between the Ag(I) centre and the NO_3^- anion to give a 'helical staircase' structure.[6] We now report the extension of these investigations to the use of $AgNO_2$, and report an unusual example of a sawhorse connection within an extended network.

$\{[Ag(pyz)]NO_2\}_\infty$ (pyz = pyrazine) and $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$ (4,4′-bipy = 4,4′-bipyridyl) were prepared as colourless microcrystalline samples by adding a solution of the appropriate ligand in EtOH to a solution of $AgNO_2$ in H_2O.† In order to assess the effect of the nitrite counter-anion upon network topology single crystals of both complexes were grown by slow diffusion between an aqueous solution of $AgNO_2$ and an ethanolic solution of the ligand. $\{[Ag(pyz)]NO_2\}_\infty$‡ exists as a three-dimensional network in which each Ag(I) ion adopts a distorted octahedral environment (Fig. 1): each Ag(I) centre is coordinated by two pyrazine ligands, Ag–N 2.277(5) Å, which bridge adjacent Ag(I) ions, and by the chelating nitrite counter-anion, Ag–O 2.487(6) Å, in the equatorial sites. The two remaining axial coordination sites are occupied by weak Ag···Ag interactions (Fig. 1). The Ag···Ag separation of 3.2168(3) Å is a typical value for Ag···Ag interactions unsupported by ligands.[8] Ag···Ag interactions have been found to be significant in the extended structures of inorganic supramolecular networks. This is perhaps best illustrated by the formation of short interactions [Ag···Ag 2.970(2) Å] in the extended three-dimensional network formed by $\{[Ag(4,4'\text{-bipy})]NO_3\}_\infty$,[9] in which each Ag(I) centre is coordinated by one N-donor from each of two 4,4′-bipy ligands and participates in one Ag···Ag interaction to give a T-shaped motif.[9]

It can be seen that in $\{[Ag(pyz)]NO_2\}_\infty$ each Ag(I) ion acts as a sawhorse junction in the network, with the nitrite blocking two *cis* sites of the junction (Fig. 2). To our knowledge this represents the first example of such a junction within a coordination polymer array. Sawhorse junctions are extremely rare in inorganic framework structures with the most notable examples being IrF_4, RhF_4 and PtF_4.[10] Therefore the overall network topology (Fig. 2) can be thought of as being related to the solid-state structure of IrF_4 which has been described as '$\{IrF_6\}$ octahedra which share 4 F atoms, each with one other $\{IrF_6\}$ group leaving a pair of *cis* vertices

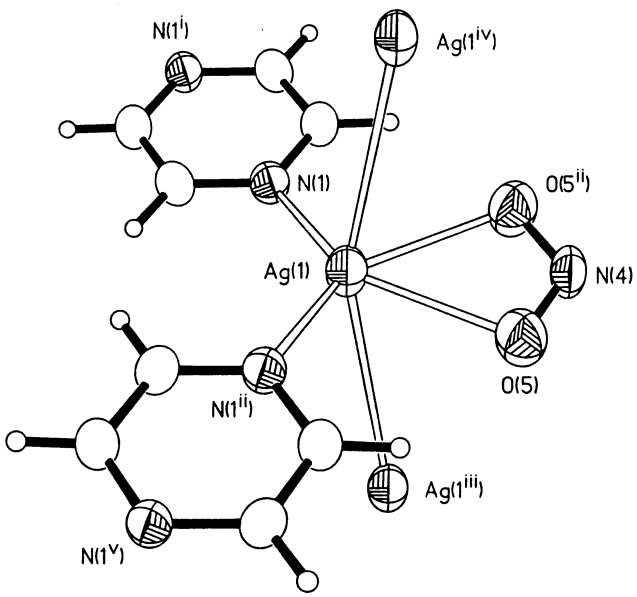

Fig. 1 View of the Ag(I) coordination environment in $\{[Ag(pyz)]NO_2\}_\infty$. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.277(5), Ag(1)–O(5) 2.487(6), Ag(1)···Ag(1^{iii}), Ag(1)···Ag(1^{iv}) 3.2168(3), Ag(1^{iii})–Ag(1)–Ag(1^{iv}) 158.59(5), Ag(1^{iv})–Ag(1)–N(1) 110.1(1), Ag(1^{iii})–Ag(1)–N(1) 79.9(1), Ag(1^{iv})–Ag(1)–O(5^{ii}) 66.5(1), Ag(1^{iii})–Ag(1)–O(5^{ii}) 93.5(1), N(1)–Ag(1)–O(5^{ii}) 140.7(2), N(1^{ii})–Ag(1)–O(5) 92.8(2), O(5)–Ag(1)–O(5^{ii}) 50.1(2), N(1)–Ag(1)–N(1^{ii}) 126.0(3) (symmetry codes: i = $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$; ii = $-x$, y, $\frac{1}{2}-z$; iii = $-x$ $-y$, $-z$; iv = $-x$, $-y$, $1-z$; v = $x-\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$).

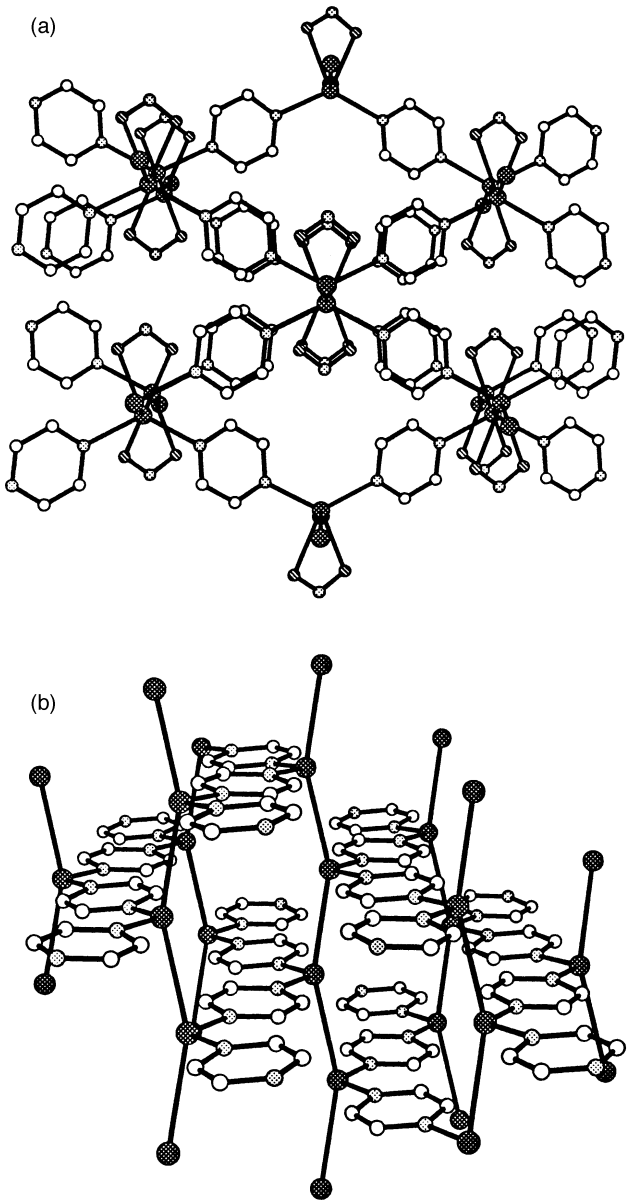

Fig. 2 The overall network structure of $\{[Ag(pyz)]NO_2\}_\infty$: (a) view down the *c*-axis, (b) view illustrating the development of the three-dimensional lattice through Ag···Ag contacts and showing the saw-horse connections (nitrite anions are removed for clarity) (Ag, cross-hatched; O, hatched; N, dotted, C, plain).

unshared'.[10,11] Similarly the network of $\{[Ag(pyz)]NO_2\}_\infty$ is built from octahedra with *cis* vertices unshared.

The structure of $\{[Ag(pyz)]NO_2\}_\infty$ contrasts with that observed in the corresponding NO_3^- salt, $\{[Ag(pyz)]NO_3\}_\infty$.[12] Extended chains of alternating Ag(I) ions and pyrazine ligands are observed in $\{[Ag(pyz)]NO_3\}_\infty$[12] and significantly the nitrate anion is non-coordinating, in contrast to the behaviour of the nitrite anion observed in $\{[Ag(pyz)]NO_2\}_\infty$.

Single crystal X-ray studies of $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$‡ reveal that a different network structure is adopted to that observed for $\{[Ag(pyz)]NO_2\}_\infty$. The structure consists of slightly distorted linear chains of alternating Ag(I) ions and 4,4′-bipy ligands, N–Ag–N 171.98(10)° (Fig. 3) with the NO_2^- anions sitting between adjacent $\{[Ag(4,4'\text{-bipy})]^+\}_\infty$ chains so that each Ag(I) centre forms two weak Ag···O interactions of 2.667(2) Å and one weak Ag···N interaction of 2.978(3) Å. Significantly, no Ag···Ag interactions are observed in $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$, in contrast to $\{[Ag(pyz)]NO_2\}_\infty$. The bridging 4,4′-bipy ligands in $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$ adopt a very twisted arrangement, with a dihedral angle between the

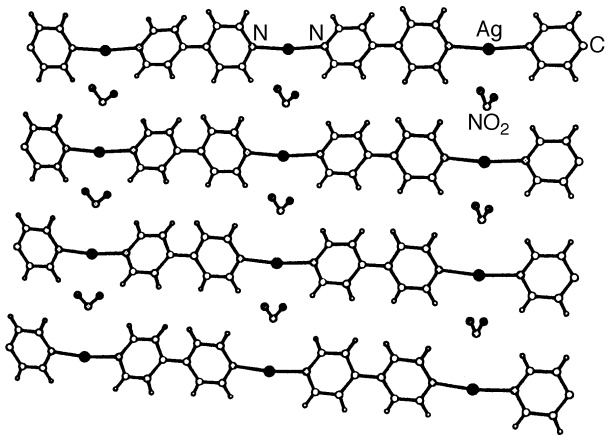

Fig. 3 View of the structure of $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$ showing the linear chains of alternating Ag(I) ions and 4,4′-bipy ligands. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.208(3); N(1)–Ag(1)–N(1^i) 171.98(10) (symmetry codes: i = $-x+\frac{1}{2}, y, -z+\frac{1}{2}$).

pyridyl rings of 41.3°. This value compares with observed values of 4.3° in $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-bipy})][BF_4]_2$[13] (cnge = 2-cyanoguanidine), and 28.0, 30.0° observed in [Cu(4,4′-bipy)$(MeCN)_2$]BF_4.[13] Both twisted and flat 4,4′-bipy molecules are incorporated in $[Cu(\mu\text{-}4,4'\text{-bipy})(H_2O)_2(FBF_3)_2]\cdot 4,4'\text{-bipy}$, with a dihedral angle of 9.29° being observed for the coordinated 4,4′bipy ligands. In contrast the non-coordinated 4,4′-bipy ligands are constrained to be ideally planar by crystallographic symmetry.[14]

The IR spectra of the two complexes $\{[Ag(pyz)]NO_2\}_\infty$ and $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$ are consistent with the non-coordinating nitrite anion in $\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$ [$\nu_{sym}(NO_2) = 1243$ cm^{-1}] and the chelating mode of coordination for the anion in $\{[Ag(pyz)]NO_2\}_\infty$ [$\nu_{sym}(NO_2) = 1269$ cm^{-1}].[17] IR spectra of both the precipitated (microcrystalline) products and single crystals were found to be identical confirming the crystal structures to be representative of the bulk.

Of the few previously reported examples of structurally characterised $AgNO_2$ complexes both strongly coordinated[15] and uncoordinated/weakly interacting[16] NO_2^- have been reported. In the former Ag–O bond lengths are comparable to those observed here.[15]

Current work is aimed at studying the wider application of the nitrite anion as a fundamental building-block of extended coordination polymers and investigating the use of anions as a controlling factor in Ag(I) supramolecular networks.

Acknowledgements

We thank the EPSRC, Nuffield Foundation and the University of Nottingham for support.

Notes and references

† $\{[Ag(pyz)]NO_2\}_\infty$: to a solution of $AgNO_2$ (100 mg, 0.65 mmol) in water (10 cm^3) heated to 50 °C was added a solution of pyrazine (52 mg, 0.65 mmol) in EtOH (10 cm^3). A colourless crystalline precipitate formed over the period of 5 minutes and the suspension was then stirred for a further 5 min. The product was filtered off and washed with diethyl ether and then dried *in vacuo*. Yield 99 mg, 65%. (Found: C, 20.26; H, 1.59; N, 17.39. Calc. for $C_4H_4Ag_1N_3O_2$: C, 20.51; H, 1.71; N, 17.95%). IR (KBr)/cm^{-1}: 2928w, 2857w, 1507w, 1411w, 1269s, 1143w, 1095w, 1024w, 800s.

$\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$ was prepared similarly as a colourless precipitate in 75% yield. (Found: C, 38.32; H, 2.37; N, 13.38. Calc. for $C_{10}H_8Ag_1N_3O_2$: C, 38.71; H, 2.58; N, 13.55%). IR (KBr)/cm^{-1}: 3051w, 3027w, 1599s, 1526s, 1487m, 1410m, 1314m, 1243s, 1222s, 1091w, 1070m, 1039w, 1000m, 992m, 963w, 880w, 846m, 804s, 732w, 667w, 621s, 565m, 510s.

‡ *Crystal data*: $\{[Ag(pyz)]NO_2\}_\infty$: $C_4H_4AgN_3O_2$, $M = 233.96$, monoclinic, space group *C*2/*c* (no. 15), $a = 12.378(5)$, $b = 7.934(3)$, $c = 6.322(3)$ Å, $\beta = 99.07(3)°$, $U = 613.04$ Å^3, $Z = 4$, $D_c = 2.53$ g cm^{-3},

μ(Cu-Kα) = 26.42 mm^{-1}. A colourless plate (0.31 × 0.21 × 0.06 mm) was used for data collection on a Stoe Stadi-4 four-circle diffractometer (graphite monochromated Cu-Kα radiation, ω–θ scans, θ_{max} = 70°) equipped with an Oxford Cryosystems low-temperature device operating at 220(2) K.[18] Absorption corrections utilised ψ-scan data (lamina procedure, T_{min} = 0.203, T_{max} = 0.785). Of 554 unique reflections (R_{int} = 0.10) 480 with $I \geqslant 2\sigma(I)$ were used in all calculations. The structure was solved using Patterson methods[19] and all non-H atoms were located in a subsequent difference-Fourier map.[20] The structure was refined against F with all non-H atoms modelled with anisotropic displacement parameters and H-atoms placed in calculated positions. At final convergence[20] R_1 [$I > 2\sigma(I)$] = 0.0443, R_w = 0.0459 for 48 parameters, S = 1.05, $(\Delta/\sigma)_{max}$ = 0.02, $\Delta\rho_{max}$ = 1.65 e Å^{-3} [located 0.9 Å from Ag(1)], $\Delta\rho_{min}$ = −1.28 e Å^{-3}.

$\{[Ag(4,4'\text{-bipy})]NO_2\}_\infty$: $C_{10}H_8AgN_3O_2$, M = 310.06, monoclinic, space group $P2/n$ (no. 13, alt. 2), a = 7.2931(12), b = 6.08(2), c = 11.481(3) Å, β = 102.817(17)°, U = 496.8 Å^3, Z = 2, D_c = 2.073 g cm^{-3}, μ(Cu-Kα) = 16.195 mm^{-1}. A colourless needle (0.44 × 0.07 × 0.02 mm) was used. Data were collected as for $\{[Ag(pyz)]NO_2\}_\infty$. Absorption corrections were carried out by Gaussian integration following refinement of the crystal size and morphology against a set of ψ-scans,[21] (T_{min} = 0.198, T_{max} = 0.720), 880 unique reflections (R_{int} = 0.014), of which 838 had $I \geqslant 2\sigma(I)$, were used in all calculations. The structure was solved using direct methods[22] and all non-H atoms were located in a subsequent difference-Fourier map.[23] The structure was refined against F^2 with all non-H atoms modelled with anisotropic displacement parameters; H-atoms were placed in calculated positions and were allowed to ride on their parent atoms. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.0335P)^2 + 0.0485P]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$ was adopted and the extinction coefficient refined to 0.0010(2). At final convergence[23] R_1 [$I > 2\sigma(I)$] = 0.0198, wR_2 (all data) = 0.0503 for 75 parameters, S = 1.081, $(\Delta/\sigma)_{max}$ in final cycle = <0.001, $\Delta\rho_{max}$ = 0.50 e Å^{-3}, $\Delta\rho_{max}$ = −0.42 e Å^{-3}.

CCDC reference number 440/081. See http://www.rsc.org/suppdata/njc/1998/13/ for crystallographic files in cif format.

1 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1460; A. J. Blake, N. R. Champness, P. Hubberstey, W-S. Li, M. Schröder and M. A. Withersby, *Coord. Chem. Rev.*, 1998, in press; N. R. Champness and M. Schröder, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 419. M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1727.

2 C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431.

3 G. R. Desiraju in *Crystal Engineering: Design of Organic Solids*, Elsevier, Amsterdam, 1989; *The Crystal as a Supramolecular Entity*, ed. G. R. Desiraju, Wiley, 1995; G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; C. B. Aakeroy, *Acta Crystallogr., Sect. B*, 1997, **53**, 569.

4 A. J. Blake, N. R. Champness, S. S. M. Chung, W-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005; A. J. Blake, N. R. Champness, A. N. Khlobystov, D. A. Lemenovski, W-S. Li and M. Schro¨der, *Chem. Commun.*, 1997, 1339.

5 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W-S. Li and M. Schröder, *Inorg. Chem.*, submitted.

6 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W-S. Li and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327.

7 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562; D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030; K. A. Hirsch, S. R. Wilson and J. S. Moore, *Inorg. Chem.*, 1997, **36**, 2960.

8 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; A. D. Burrows, M. F. Mahon and M. T. Palmer, *J. Chem. Soc., Dalton Trans.*, 1998, 1941; M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle and H. H. Patterson, *Inorg. Chem.*, 1998, **37**, 1380.

9 F. Robinson and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1995, 2413; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295.

10 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, 5th edn., 1983.

11 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, 1984; N. Bartlett and A. Tressaud, *Compt. Rend.*, 1974, **C278**, 1501.

12 R. G. Vranka and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1020.

13 A. S. Batsanov, M. J. Begley, P. Hubberstey and J. Stroud, *J. Chem. Soc., Dalton Trans.*, 1996, 1947.

14 A. J. Blake, S. J. Hill, P. Hubberstey and W-S. Li, *J. Chem. Soc., Dalton Trans.*, 1997, 913.

15 H. Lang, M. Herres and L. Zsolnai, *Organometallics*, 1993, **12**, 5008.

16 R. H. Benno and C. J. Fritchie, Jr., *Acta Crystallogr., Sect. B*, 1973, **29**, 2493.

17 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 4th edn., 1986.

18 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

19 P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits. The DIRDIF-96 program system. Crystallography Laboratory, University of Nijmegen, The Netherlands, 1996.

20 D. J. Watkin, C. K. Prout, R. J. Carruthers and P. Betteridge, CRYSTALS Issue 10, Chemical Crystallography Laboratory, Oxford, UK, 1996.

21 X-SHAPE—crystal optimisation for absorption correction, Stoe and Cie, Darmstadt, Germany, 1996.

22 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli. SIR-92, *J. Appl. Crystallogr.*, 1994, **27**, 435.

23 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

Letter 8/08025I