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# Methyl groups control coordination number, stoichiometry, network and magnetism in a Cu(II)-azide-pyrazine (6,3) 2D net

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Received (in XXX, XXX) 1st January 2007, Accepted 1st January 2007

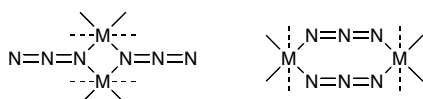
First published on the web 1st January 2007

DOI: 10.1039/b000000x

The methyl groups of  $[\text{Cu}_2(2,5\text{-dimethylpyrazine})(\text{N}_3)_4]_n$ , **1**, force penta-coordination on the Cu(II) ions, which, together with the di- $\mu_{1,1}$ -azido zigzag chains, result in a (6,3) 2D net with dominant ferromagnetic interactions.

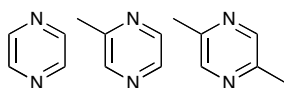
To synthesise molecule-based magnetic materials is an attractive, but difficult, goal for crystal engineers.<sup>1</sup> Many of the reported high  $T_c$  systems have been created with the help of coordination chemistry, although the complete structures of these materials remain unknown,<sup>2</sup> with the exception of the hexacyanometallate systems.<sup>3</sup>

The azide ligand, another pseudo-halide, commonly mediates strong magnetic couplings between transition metal compounds, but has not yet yielded any such materials magnetic at room temperature. In addition to this challenge, the many possible bridging modes (scheme 1)<sup>4, 5</sup> of the azide ion make the rational preparation of such structures a crystal engineering problem of some dignity. Consequently, the structure and magnetism of these compounds continue to attract attention.<sup>6</sup>



**Scheme 1** Most common bridging modes for azides ions illustrated by double bridged end-on,  $\mu_{1,1}$ -N<sub>3</sub>, EO (left) and double bridged end-to-end,  $\mu_{1,3}$ -N<sub>3</sub>, EE (right). M is commonly 4, 5 or 6 coordinated.

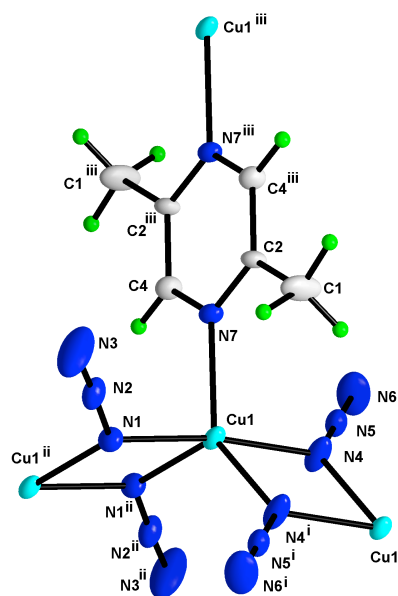
A way of increasing the dimensionality of these systems is to add a bridging co-ligand (scheme 2), and recently we have shown that  $[(\text{Cu}(\text{N}_3)_2)_2\text{Cu}(\text{N}_3)_2(\text{methylpyrazine})_2]_n$ <sup>7</sup> is a 3D coordination polymer with the unusual  $(4.10^2)_2(4^2.10^4)$ -dmd topology<sup>8</sup>, where the pyrazine transmits weak antiferromagnetic couplings, as reported in many other cases.<sup>9</sup> In this communication we report on the synthesis, and the distinctively different structure and magnetism of the compound obtained with the related 2,5-dimethylpyrazine ligand:  $[\text{Cu}_2(2,5\text{-dimethylpyrazine})(\text{N}_3)_4]_n$ , completing a triad begun by Dong et al. with the pyrazine compound.<sup>10</sup>



**Scheme 2** Bridging co-ligands pyrazine, methylpyrazine and 2,5-dimethylpyrazine used to prepare respectively 2D<sup>10</sup>, 3D<sup>7</sup> and 2D (this paper) coordination polymers with Cu(II) and azide ions.

$[\text{Cu}_2(2,5\text{-dimethylpyrazine})(\text{N}_3)_4]_n$ , **1** was obtained by

reaction of the ligand with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in an ethanol/water mixture with excess  $\text{NaN}_3$ .<sup>‡</sup> X-ray diffraction<sup>§</sup> revealed the structural unit shown in Fig. 1.



**Fig. 1** Perspective view of  $[\text{Cu}_2(2,5\text{-dimethylpyrazine})(\text{N}_3)_4]_n$ , **1**. Atomic displacement ellipsoids drawn at 50% probability level. Symmetry codes: (i):  $-x+1, -y+1, -z$  (ii):  $-x, -y+1, -z$  (iii):  $-x, -y+1, -z+1$

The 2,5-dimethylpyrazine ligand, as well as the  $\text{Cu}_2\text{N}_2$  units lie about independent inversion centres. The Cu(II) ion is penta-coordinated ( $\text{CuN}_5$ ), in a distorted trigonal bipyramidal geometry, binding four nitrogens from azido anions and one nitrogen from 2,5-dimethylpyrazine (see Fig. 1). The three equatorial Cu-N7, Cu-N1<sup>ii</sup>, Cu-N4<sup>i</sup> bond distances are 2.095(3), 2.190(4) and 2.009(3) Å, respectively, with bond angles 137.60(16), 121.88(15) and 100.00(13)°. The two apical Cu-N1 and Cu-N4 bond distances are 1.965(3) and 1.981(4) Å with a N-Cu-N angle 171.46(15)°. These data are consistent with known ( $\text{CuN}_5$ ) trigonal bipyramidal complexes.<sup>5, 11, 12</sup> The azide ions are coordinated to the Cu ions in a di-EO ( $\mu_{1,1}$ -N<sub>3</sub>) fashion giving  $\text{Cu}_2\text{N}_2$  units forming a zigzag chain along the *a*-axis. The dimethylpyrazines connect these chains along the *c*-axis giving rise to a (6,3) 2D-net in the *ac*-plane as shown in Fig. 2.

This 2D grid-like structure shows weak C-H...N hydrogen bonds between the crystallographically well defined -CH<sub>3</sub> group of the dimethylpyrazine ligand and the azido terminal N

atoms, affecting also the asymmetry of the EO bridging azido groups and the rectangular  $\text{Cu}_2\text{N}_2$  units. On the first-level of the graph-set<sup>13</sup> they form chains C(8) and C(10).

Despite the richness of metal-azide structures, (>1000 entries in the Cambridge Structural Database)<sup>14</sup> there are few structures containing a doubly bridged end-to-end coordination polymer chain.<sup>9,15, 16</sup> Moreover, double end-to-end chains are even rarer than the end-on chains found in compound **1**.<sup>16</sup> We tentatively attribute this to the spacing of  $\sim 5$  Å of the metal ions, which is too far apart to obtain  $\pi$ - $\pi$  stacking of axial aromatic ligands, but not far enough to conveniently fit in another molecule. Thus rigid objects such as polymeric rods of this type may be difficult to pack.

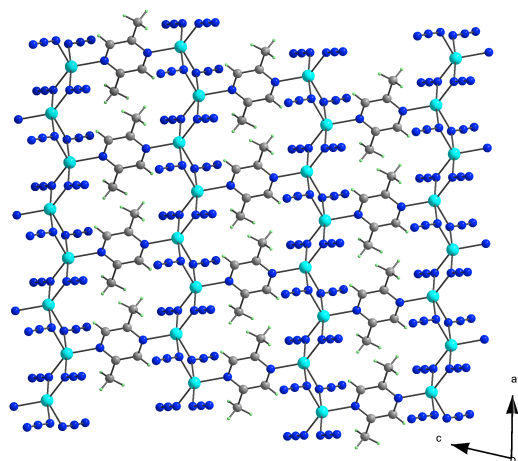


Fig.2 The (6,3) 2D-net in  $[\text{Cu}_2(2,5\text{-dimethylpyrazine})(\text{N}_3)_4]_n$ , **1**.

For end-on azide polymers, the situation is different. For example in  $[\text{Cu}_2(\text{pyrazine})_2(\text{N}_3)_4]_n$ <sup>10</sup> there is efficient  $\pi$ - $\pi$  stacking between ligands on adjacent octahedral Cu centres. Replacing the pyrazine with 2,5-dimethylpyrazine efficiently blocks the  $\pi$ - $\pi$  stacking, so an iso-structural compound is inconceivable. Efficient packing in the pyrazine compound is also manifested by the higher density (disregarding the different stoichiometry), 2.12 g/cm<sup>3</sup> vs. 1.95 g/cm<sup>3</sup> for **1**.

The stoichiometry and the coordination number of Cu(II) will determine the kind of net formed. Methyl groups *ortho* to a coordinated nitrogen will decrease the coordination number because of steric crowding, imposing 5-coordination around the metal ion. In  $[\text{Cu}_2(\text{pyrazine})_2(\text{N}_3)_4]_n$  with an octahedral Cu(II), a very regular (4,4) 2D grid was obtained.<sup>10</sup> Terminal N...H-C weak hydrogen bonds connect the 2D sheets in this compound, as in **1**, but with a more regular packing.

$[(\text{Cu}(\text{N}_3)_2)_2\text{Cu}(\text{N}_3)_2(\text{methylpyrazine})_2]_n$ <sup>7</sup> shows yet another stoichiometry, Cu/pyrazine 3:2, and has both penta- and hexa-coordinated Cu(II), resulting in a 3D  $(4.10^2)_2(4^2.10^4)$ -dmd<sup>8</sup>-net. It is not clear why this particular stoichiometry leads to a 3D net, but it may be related to the fact that the 2D, three- and four-connected net that can be constructed with a 2:1 relation between the nodes is the *Cairo tiling* of pentagons.

The molar magnetic susceptibility<sup>4</sup> data are shown in Fig. 3. At 2 K  $\chi$  is near 0 cm<sup>3</sup>/mol, reaching a maximum at 33 K and then moderately decreasing to  $\chi=0.0017$  cm<sup>3</sup>/mol at room temperature. The corresponding room-temperature value of

the effective magnetic moment,  $\mu_{\text{eff}}=2.02$  N $\beta$  ( $\mu_{\text{eff}}=2.828(\chi T)^{1/2}$ ) is considerably enhanced in comparison with the single Cu<sup>II</sup>-value (1.73 N $\beta$ ). Taking into account the temperature independent susceptibility term,  $\chi_0 = 3.0 \times 10^{-4}$  cm<sup>3</sup>/mol obtained from the  $\chi$  vs. T analysis this value decreases to the more relevant 1.84 N $\beta$ .

The maximum in the temperature dependence of  $\chi$  suggest a ferromagnetic coupling of the Cu ions, and absolute values of  $\chi$  are also typical for Cu complexes with intermediate-strength ferromagnetic coupling.

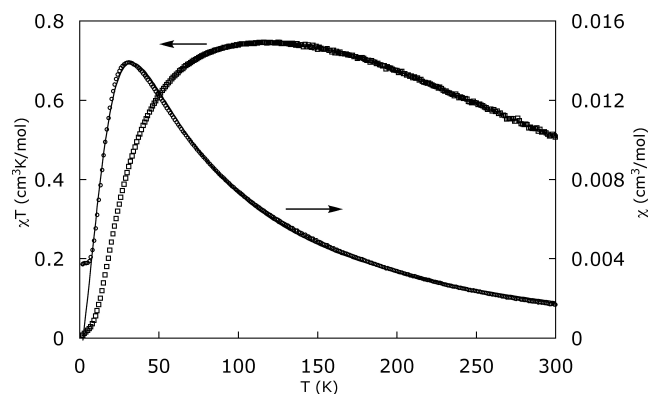


Fig.3 The magnetism for **1** presented as  $\chi T$  vs. T (squares) and as  $\chi$  vs. T (circles). The solid line represents the best fit of  $\chi$  vs. T using a 1D chain model with 2D corrections<sup>17</sup> giving  $J=24.0$  cm<sup>-1</sup> and  $J'=0.4$  cm<sup>-1</sup>.

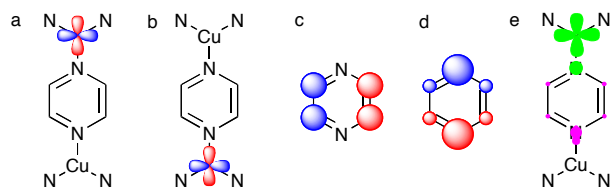
To test this, a model considering a chain of Cu-azides coupled by  $J$ , ( $\mathbf{H}=-J\mathbf{S}_i\mathbf{S}_{i+1}$ ) and additional small coupling  $J'$ ,<sup>17</sup> was fitted to the data, yielding,  $J = 24.0 \pm 0.09$  cm<sup>-1</sup> and  $J' = 0.4 \pm 0.05$  cm<sup>-1</sup>.

The ferromagnetic coupling through the azides was expected, although it has been suggested that end-on coupling should be antiferromagnetic if the Cu-N-Cu bond angle is larger than 104° (the angles in **1** are 102.95(16)° and 100.13(15)°).<sup>12, 18</sup> However, the small ferromagnetic coupling tentatively assigned to the pyrazine bridge needs accounting for, as these interactions are normally antiferromagnetic (*i.e.* in the related pyrazine and methyl-pyrazine compounds<sup>7,10</sup>).<sup>9</sup> The existing examples of ferromagnetic interactions through pyrazine bridges in Cu(II) compounds have been explained by orthogonal magnetic orbitals.<sup>19</sup> In the case of **1**, the distinctively longer equatorial bond lengths suggest that the unpaired electrons reside in a *d*-orbital in the equatorial plane, and for neighbouring Cu(II)s these orbitals are related by a centre of inversion and thus cannot be orthogonal.

However, a tentative explanation can be provided by spin-polarization.<sup>20</sup> Through the covalent part of the coordination bond, spin will be delocalized onto the Cu-N<sub>py</sub>  $\sigma$ -bond, and inducing a positive spin polarization of the N<sub>py</sub>  $p_z$ -orbital. As the total spin density is constant, this will be compensated by negative spin polarization of the other  $p_z$ -orbitals in the highest MO with a large N<sub>py</sub>  $p_z$ -component (see Scheme 3).

Now, for symmetry reasons this orbital will have a large component also on the second nitrogen, and only small components on the remaining carbon atoms. Consequently, negative spin density will build up on the nitrogen close to the second Cu atom, and this in turn will generate a ferromagnetic coupling through what has been described as "the third case of

the McConnell-I Mechanism<sup>21</sup>.



**Scheme 3** Schematic view of the interactions MO:s and spin densities in **1**; a and b: the magnetic orbitals on Cu ( $d_{z^2}$  will give the same result), c: the  $\pi$ -HOMO has no components on N, d: the  $\pi$ -HOMO-1 will be spin polarized, e: the resulting spin polarization (green positive, mauve negative) giving negative spin density on the remote nitrogen atom.

We thank the Swedish Science Council and the Swedish International Development Cooperation Agency for financial support through the Swedish Research Links program, grants 348-2004-5473 and 348-2002-6879.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Additional structural data for **1**. See DOI: 10.1039/b000000x/

‡  $[\text{Cu}_2(2,5\text{-dimethylpyrazine})(\text{N}_3)_4]_n$ , **1** was obtained by adding an ethanolic solution of 2,5-dimethylpyrazine (0.22 g, 2 mmol) in 10 mL ethanol to 15 mL of an aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.48 g, 2 mmol). Further, an aqueous solution of  $\text{NaN}_3$  (0.65 g, 10 mmol) was added dropwise with continuous stirring. The turbid greenish black solution was filtered off, and allowed to stand at room temperature for a few weeks. Deep green crystals of the compound **1**, suitable for X-ray diffraction, were collected and dried in air, yielding ~50% of product with respect to the ligand. Analytical data: Calc. C, 17.86; H, 1.99; N, 48.61; Cu, 31.50. Found: C, 18.02; H, 2.11; N, 49.30; Cu, 30.52%.

§ X-ray data were collected on a Siemens Smart CCD diffractometer at 173 K with Mo-K $\alpha$  radiation. The structure was solved by direct methods and subsequent full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms using SHELXTL. Hydrogen atoms were constrained to ideal geometry using an appropriate riding model and the individual isotropic temperature factors were freely refined. Moiety formula:  $\text{C}_3\text{H}_4\text{CuN}_7$ , Mw = 201.67, Z=2, triclinic, space group P-1, a=5.8645(4), b = 7.5587(5), c=8.1625(6) Å,  $\alpha=77.744(2)^\circ$ ,  $\beta=76.991(1)^\circ$ ,  $\gamma=83.633(1)^\circ$ ,  $V=343.75(4)$  Å<sup>3</sup>,  $\mu=3.115$  mm<sup>-1</sup>,  $\rho_{\text{calc}}=1.948$  g·cm<sup>-3</sup>, measured refl., 3937, unique refl., 1350,  $R_{\text{int}}=0.0549$ ,  $R(1>2\sigma)=0.0417$ ,  $wR_2(\text{all})=0.0804$ . CCDC 649681 contains the supplementary crystallographic data for **1**, available at [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

¶ Magnetic properties were determined with the extraction magnetometer (ACMS) and vibration magnetometer (VSM) options of the Physical Properties Measurement System (PPMS, Quantum Design (QD): [www.qdusa.com](http://www.qdusa.com)). The temperature dependence of the magnetic susceptibility was measured in the zero-field cooled regime at selected magnitudes of magnetic field in the temperature range 2–300 K. For the ACMS method the samples were placed in a gelatine capsule and fixed by PE to avoid displacement of the powder during extraction measurement; the capsule was further fixed in a PS straw attached to the sample holder. In the VSM experiment, the samples were wrapped in a PS foil and fixed to the original QD sample holder. The molar susceptibility,  $\chi$ , was determined as M/H per Cu and data were corrected with Pascal constants.

- S. J. Blundell and F. L. Pratt, *J. Phys. Cond. Mat.*, 2004, **16**, R771-R828.
- (a) R. Jain, K. Kabir, J. B. Gilroy, K. A. R. Mitchell, K. C. Wong and R. G. Hicks, *Nature*, 2007, **445**, 291-294; (b) J. S. Miller, *Inorg. Chem.*, 2000, **39**, 4392-4408; (c) J. S. Miller and K. I. Pokhodnya, *J. Mater. Chem.*, 2007, **17**, 3585-3587.
- (a) T. Mallah, S. Thiébaud, M. Verdaguer and P. Veillet, *Science*, 1993, **262**, 1554; (b) V. Gadet, T. Mallah, I. Castro, M. Verdaguer and P. Veillet, *J. Am. Chem. Soc.*, 1992, **114**, 9213-9214.
- M. M. Yu, H. Z. Kou, Z. H. Ni, C. H. Ge and A. L. Cui, *Acta Cryst. E*, 2006, **62**, M2050-M2051.
- M. Zbiri, S. Saha, C. Adhikary, S. Chaudhuri, C. Daul and S. Koner, *Inorg. Chim. Acta*, 2006, **359**, 1193-1199.
- J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama and T. Rojo, *Coord. Chem. Rev.*, 1999, **195**, 1027-1068.
- M. A. M. Abu-Youssef, A. Escuer, F. A. Mautner and L. Öhrström, *Dalton Trans.*, 2008, 3553-3558.
- M. O'Keeffe, O. M. Yaghi and S. Ramsden, Reticular Chemistry Structural Resource, <http://rcsr.anu.edu.au/>, Australian National University Supercomputer Facility, Canberra, 2008.
- (a) H. W. Richardson and W. E. Hatfield, *J. Am. Chem. Soc.*, 1976, **98**, 835-839; (b) G. W. Inman and W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 3085-3090; (c) J. L. Manson, M. M. Conner, J. A. Schluter and K. A. Hyzer, *Polyhedron*, 2007, **26**, 1912-1916; (d) J. Pasan, J. Sanchiz, F. Lloret, M. Julve and C. Ruiz-Perez, *Crystengcomm*, 2007, **9**, 478-487; (e) F. M. Woodward, P. J. Gibson, G. B. Jameson, C. P. Landee, M. M. Turnbull and R. D. Willett, *Inorg. Chem.*, 2007, **46**, 4256-4266; (f) A. Cuevas, C. Kremer, M. Hummert, H. Schumann, F. Lloret, M. Julve and J. Faus, *Dalton Trans.*, 2007, 342-350; (g) T. Liu, Y. H. Chen, Y. J. Zhang, Z. M. Wang and S. Gao, *Inorg. Chem.*, 2006, **45**, 9148-9150; (h) F. F. Awwadi, C. P. Landee, M. M. Turnbull, B. Twamley and B. M. Wells, *Polyhedron*, 2005, **24**, 2153-2159.
- W. Dong, O. Y. Yan, D. Z. Liao, S. P. Yan, P. Cheng and Z. H. Jiang, *Inorg. Chim. Acta*, 2006, **359**, 3363-3366.
- X. H. Bu, M. L. Tong, Y. B. Xie, J. R. Li, H. C. Chang, S. Kitagawa and J. Ribas, *Inorg. Chem.*, 2005, **44**, 9837-9846.
- H. Y. Shen, W. M. Bu, E. Q. Gao, D. Z. Liao, Z. H. Jiang, S. P. Yan and G. L. Wang, *Inorg. Chem.*, 2000, **39**, 396-400.
- M. C. Etter, J. C. Macdonald and J. Bernstein, *Acta Cryst. B*, 1990, **46**, 256-262; J. Bernstein, R. E. Davis, L. Shimon and N. L. Chang, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1555-1573.
- F. H. Allen, *Acta Cryst.*, 2002, **B58**, 380-388.
- (a) F. A. Mautner and M. A. S. Goher, *Polyhedron*, 1994, **13**, 2141-2147; (b) J. Cano, Y. Journaux, M. A. S. Goher, M. A. M. Abu-Youssef, F. A. Mautner, G. J. Reiss, A. Escuer and R. Vicente, *New J. Chem.*, 2005, **29**, 306-314; (c) J. Ribas, M. Monfort, C. Diaz, C. Bastos and X. Solans, *Inorg. Chem.*, 1994, **33**, 484-489; (d) M. A. M. Abu-Youssef, A. Escuer, M. A. S. Goher, F. A. Mautner, G. J. Reiss and R. Vicente, *Angew. Chem., Int. Ed.*, 2000, **39**, 1624-1626; (e) R. Cortes, M. K. Uriaga, L. Lezama, J. L. Pizarro, M. I. Arriortua and T. Rojo, *Inorg. Chem.*, 1997, **36**, 5016-5021.
- M. A. S. Goher and F. A. Mautner, *Polyhedron*, 1998, **17**, 1561.
- O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.
- (a) S. C. Manna, S. Konar, E. Zangrando, M. G. B. Drew, J. Ribas and N. R. Chaudhuri, *Euro. J. Inorg. Chem.*, 2005, 1751-1758; (b) S. Triki, C. J. Gomez-Garcia, E. Ruiz and J. Sala-Pala, *Inorg. Chem.*, 2005, **44**, 5501-5508.
- (a) W. Z. Wang, R. H. Ismayilov, G. H. Lee, H. T. Wang, R. R. Wang and S. M. Peng, *Euro. J. Inorg. Chem.*, 2008, 312-321; (b) R. H. Ismayilov, W. Z. Wang, G. H. Lee and S. M. Peng, *Dalton Trans.*, 2006, 478-491.
- (a) V. Baron, B. Gillon, O. Plantevin, A. Cousson, C. Mathoniere, O. Kahn, A. Grand, L. Öhrström and B. Delley, *J. Am. Chem. Soc.*, 1996, **118**, 11822-11830; (b) L. Öhrström, A. Grand and B. Pilawa, *Acta Chem. Scand.*, 1996, **50**, 458-461; (c) L. Öhrström, *Compt. Rend. Chimie*, 2005, **8**, 1374-1385.
- C. Hirel, J. Pécaut, D. Luneau, L. Öhrström, G. Bussière and C. Reber, *Chem. Eur. J.*, 2002, **8**, 3157-3161.
- G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.