[5] B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.* **1997**, *119*, 10956.

[6] O. Mamula, A. von Zelewsky, G. Bernardinelli, *Angew. Chem.* **1998** *110*, 301; *Angew. Chem. Int. Ed.* **1998**, *37*, 289; C. Provent, S. Hewage, G. Brand, G. Bernardinelli, L. J. Charbonnière, A. F. Williams, *Angew. Chem.* **1997**, *109*, 1346; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1287.

[7] R. Krämer, J.-M. Lehn, A. De Cian, J. Fischer, *Angew. Chem.* **1993**, *105*, 764; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 703.

[8] $[n]^m$**H** is used as a short notation for helicates (**H**) and circular helicates (**cH**). $[n]$ indicates the number of metal ions, and m the helicity ($m = 2$ for a double helix, $m = 3$ for a triple helix).

[9] F. W. Cagle, Jr., G. F. Smith, *J. Am. Chem. Soc.* **1947**, *69*, 1860.

[10] J. H. Baxendale, P. George, *Trans. Faraday Soc.* **1950**, *46*, 736.

[11] F. Basolo, J. C. Hayes, H. M. Neumann, *J. Am. Chem. Soc.* **1953**, *75*, 5102.

[12] The interconversion of glucan polymers between linear triple helix and macrocycle forms was recently reported: T. M. McIntire, D. A. Brant, *J. Am. Chem. Soc.* **1998**, *120*, 6909.

[13] *Self-Organization. The Emergence of Order* (Ed.: F. E. Yates), Plenum, New York, **1987**.

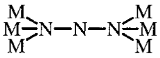
A μ-1,1,1,3,3,3 Azide Anion inside a Trigonal Prism of Silver Centers**

Guo-Cong Guo and Thomas C. W. Mak*

Dedicated to Professor George A. Jeffrey
on the occasion of his 83rd birthday

Azide compounds have been known for more than a century and continue to attract much current interest.[1] The field has undergone quite spectacular advances in the last decade for three main reasons: 1) covalent inorganic azides are potentially better explosives than lead azide, which is used as a detonator;[2] 2) the μ-azido bridging ligand is undoubtedly one of the most versatile ingredients for the creation of new materials with different magnetic properties, leading to an intensive study of magnetostructural correlations in discrete complexes as well as in polymeric one-, two-, and three-dimensional systems;[3] 3) azido complexes can serve as precursors in preparative materials chemistry as a source of atomic nitrogen.[4] As a sequel to our study on the bonding interaction between silver(I) atoms and the acetylenediide anion, C_2^{2-},[5] we have turned our attention to the isoelectronic cyanide ion CN^-,[6] as well as the azide ion N_3^-, as these species have been well studied together with N_2 in comparative substrate binding to the FeMo cofactor of nitrogenase.[7]

Up to now the known coordination modes of the azido ligand in transition metal complexes are terminal monodentate or bridging bidentate (μ-1,1; μ-1,3), tridentate (μ-1,1,1; μ-1,1,3), and tetradentate (μ-1,1,3,3; μ-1,1,1,3).[8] Herein we report a novel compound $AgN_3 \cdot 2AgNO_3$ in which the azide unit exhibits an unprecedented bridging hexadentate (μ-1,1,1,3,3,3) coordination mode as an encapsulated species inside a trigonal prism (Scheme 1).



Scheme 1. Schematic representation of the μ-1,1,1,3,3,3 coordination mode of the azido ligand in the Ag_6 prisms of $AgN_3 \cdot 2AgNO_3$.

The layer-type framework in $AgN_3 \cdot 2AgNO_3$ can be regarded as constructed from a stacking of slant trigonal prisms each composed of silver atoms at its vertices with azide units imprisoned within half of them (Figure 1). The filled and hollow prisms are stacked on their trigonal faces to form a zigzag column extending along the c direction. Such prismatic columns share rectangular faces and edges alternately along the a direction to generate a grooved slab, with pendant η^1-nitrate anions attached to Ag1 atoms on both sides (Figure 2). In any filled trigonal prism, the Ag2 atoms and the encapsulated azide unit all lie on the same mirror plane. The azide unit in $AgN_3 \cdot 2AgNO_3$ is linear and asymmetrical (N1–N2 1.239(2), N2–N3 1.174(2) Å), which is consistent with its Raman spectrum. The terminal N atoms of the azide ligand are each asymmetrically bound to two Ag1 and one Ag2 atoms (Ag1–N1 2.503(1), Ag2–N1 2.278(2), Ag1–N3 2.409(1), Ag2–N3 2.351(2) Å), and the bond angles Ag-N1-N2 and Ag-N3-N2 lie in the range of 118.2 to 122.1°. It is

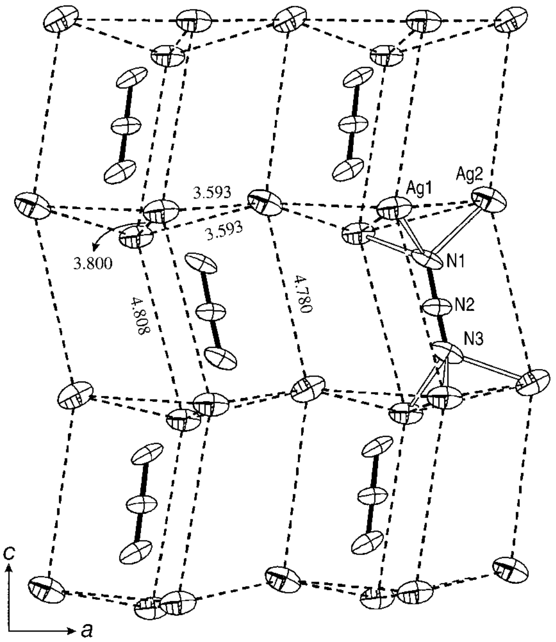


Figure 1. Layer-type framework in $AgN_3 \cdot 2AgNO_3$ built of filled and empty trigonal prisms viewed along the b direction. The lengths [Å] of the edges of a prism are shown. For clarity, the nitrate anions have been omitted, and Ag–N bonds are shown only for one of the encapsulated azide ions. Selected bond lengths [Å] and angles [°]: Ag1–N3^{i} 2.409(1), Ag1–N1 2.503(1), Ag2–N1 2.278(2), Ag2–N3^{ii} 2.351(2), N1–N2 1.239(2), N2–N3 1.174(2); N2-N1-Ag(2) 122.09(15), N2-N1-Ag1 118.21(8), N3-N2-N1 179.4(2), N2-N3-Ag2^{iii} 120.0(2), N2-N3-Ag1^{iv} 119.80(7). Symmetry codes: i: $-x, -y, z+1/2$; ii: $-x-1, -y, z+1/2$; iii: $-x-1, -y, z-1/2$; iv: $-x, y, z-1/2$.

---

[*] Prof. T. C. W. Mak, G.-C. Guo
Department of Chemistry, The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong (China)
Fax: (+86) 852-260-35057
E-mail: tcwmak§cuhk.edu.hk

[**] This work was supported by Hong Kong Research Grants Council Earmarked Grant CUHK 4179/97P and Direct Grant A/C 2060129 of The Chinese University of Hong Kong.

1433-7851/98/3723-3268 $ 17.50+.50/0

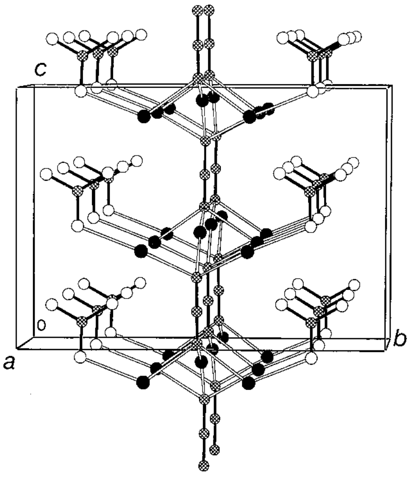


Figure 2. Crystal structure of $AgN_3 \cdot 2\,AgNO_3$ viewed along the *a* direction. The solid, cross-hatched and open circles represent Ag, N, and O atoms, respectively.

worthy of note that the Ag–N distances, especially those involving the Ag2 atom, are significantly shorter than that found in an early study of AgN_3 (2.56 Å).[9] The complete encapsulation of the azide species inside an Ag_6 polyhedron may be denoted as $N_3^-@Ag_6$, by analogy to $C_2^{2-}@Ag_6$,[5a] $C_2^{2-}@Ag_7$,[5c] $C_2^{2-}@Ag_8$,[10] and $C_2^{2-}@Ag_9$[5b] that are found in a series of complexes of silver acetylide with soluble silver salts. The coordination mode of the present N_3^- ion differs from those of other isoelectronic three-atom groups such as CN_2^{2-}, C_3^{4-}, BN_2^{3-}, and CBN^{4-}, which were found to exist in solid-state alkali and alkaline-earth compounds.[11]

It is interesting to compare the Raman spectra of NaN_3, AgN_3, and $AgN_3 \cdot 2\,AgNO_3$.[12] The azide unit of $AgN_3 \cdot 2\,AgNO_3$ exhibits both υ_s and υ_{as} stretching vibrations that are characteristic of a linear and asymmetrical structure. As expected, $\upsilon_{as}(N_3)$ in $AgN_3 \cdot 2\,AgNO_3$ shifts to a higher wavenumber in comparison with that in AgN_3, whereas a decrease of $\upsilon_s(N_3)$ in the sequence $NaN_3 > AgN_3 > AgN_3 \cdot 2\,AgNO_3$ may be reasonably rationalized in terms of increasing metal → ligand π-back bonding.

Two structural models have been considered for binding of dinitrogen to the FeMo cofactor of nitrogenase:[13] the substrate either binds externally to a Fe_4 rhombus face of a twisted form of the central Fe_6 trigonal prism,[14] or lies completely within the cavity.[15] The μ_6 coordination mode of dinitrogen in the latter model, denoted as $N_2@Fe_6$, is structurally analogous to the $N_3^-@Ag_6$ unit in $AgN_3 \cdot 2\,AgNO_3$, and also somewhat resembles the $[C_2^{2-}@Ag_n, n = 6-9]$ systems that exist in double salts of silver acetylide with soluble silver salts.[5, 10] The fact that acetylene is one of the longest established nitrogenase substrates and that C_2^{2-}, which has the same set of molecular orbitals as N_2, exhibits a strong tendency of being encaged inside an assembled silver polyhedron may be of relevance in understanding the binding and weakening of N_2 in the FeMo cofactor cavity.

Experimental Section

AgN_3 was prepared by mixing aqueous solutions of sodium azide and silver nitrate at room temperature.[16] The white precipitate was filtered, washed several times with de-ionized water, and temporarily stored in wet form in the dark. **Caution**: AgN_3 should never be dried or kept for a prolonged period, and only a small quantity should be used in any chemical reaction.

$AgN_3 \cdot 2\,AgNO_3$: Wet AgN_3 was added to a concentrated aqueous solution of $AgNO_3$ (2 mL; about 40 %) under stirring until saturated. The excess amount of AgN_3 was filtered off, and the solution was put into a desiccator charged with P_2O_5. In the course of two days colorless crystals of $AgN_3 \cdot 2\,AgNO_3$ were obtained in nearly quantitative yield. The compound is stable when immersed in its mother liquor; it is hygroscopic and slowly decomposes in air, and explodes violently when heated.

Crystal structure analysis: A colorless crystal of dimensions $0.15 \times 0.20 \times 0.10\ mm^3$ mounted inside a 0.3 mm Lindemann glass capillary was used for data collection on a Rigaku RAXIS IIC imaging plate diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, rotating-anode, 50 kV, 90 mA). Thirty-one oscillation frames were taken in the range of $\phi = 0-180°$ with $\Delta\phi = 5.0°$ and 8 min exposure per frame. Crystal data for $AgN_3 \cdot 2\,AgNO_3$: $M_r = 489.66$, orthorhombic, space group $Ccm2_1$ (No. 36), $a = 5.871(1)$, $b = 13.351(3)$, $c = 9.397(2)$ Å, $V = 736.6(3)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{calcd} = 4.416\ g\,cm^{-3}$, $F(000) = 896$, $\mu(Mo_{K\alpha}) = 79.14\ cm^{-1}$, absorption corrections applied using ABSCOR, relative transmission factors in the range 0.445–1.0. A total of 1178 reflections were collected in the 2θ range 4.0–52.0° ($0 \leq h \leq 6$, $-15 \leq k \leq 16$, $-11 \leq l \leq 11$), yielding 653 unique reflections ($R_{int} = 0.0911$), 570 of which with $I > 2\sigma(I)$ were considered as observed, 71 parameters, $R(F^2) = 0.0733$, $R_w(F^2) = 0.1908$, and $GOF(F^2) = 1.155$. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix anisotropic least squares on F^2 using the Siemens SHELXTL-93 (PC Version) package of crystallographic software. Data collected on another selected crystal did not lead to significantly improved precision of the crystal structure determination. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408802.

Received: June 15, 1998 [Z11988IE]
German version: *Angew. Chem.* **1998**, *110*, 3460–3462

Keywords: azides · clusters · coordination modes · N ligands · silver

---

[1] A. M. Golub, H. Kohler, V. V. Skopenko in *Chemistry of Pseudohalides* (Ed.: R. J. H. Clark), Elsevier, New York, **1986**, pp. 28–64, and references therein.

[2] a) I. C. Tornieporth-Oetting, T. M. Klapötke, *Angew. Chem.* **1995**, *107*, 559–568; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 511–520, and references therein; b) K. O. Christe, W. W. Wilson, R. Bau, S. W. Bunte, *J. Am. Chem. Soc.* **1992**, *114*, 3411–3416; c) T. M. Klapötke, *Chem. Ber.* **1997**, *130*, 443–451; d) V. V. Zhdankin, A. P. Krasutsky, C. J. Kuehl, A. J. Simonsen, J. K. Woodward, B. Mismash, J. T. Bolz, *J. Am. Chem. Soc.* **1996**, *118*, 5192–5197

[3] a) J. Ribas, M. Monfort, I. Resino, X. Solans, P. Rabu, F. Maingot, M. Drillon, *Angew. Chem.* **1996**, *108*, 2671–2673; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2520–2522; b) A. Escuer, R. Vicente, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1998**, *37*, 782–787; c) G. Viau, M. G. Lombardi, G. De Munno, M. Julve, F. Lloret, J. Faus, A. Caneschi, J. M. Clemente-Juan, *Chem. Commun.* **1997**, 1195–1196; d) F. A. Mautner, R. Cortés, L. Lezama, T. Rojo, *Angew. Chem.* **1996**, *108*, 96–98; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 78–80; e) R. Cortés, L. Lezama, F. A. Mautner, T. Rojo in *Molecule-Based Materials: Theory, Techniques, and Applications* (Eds.: M. M. Turnbull, T. Sugimoto, L. K. Thompson), American Chemical Society, Washington, DC, **1996**, pp. 187–200; f) P. D. Beer, M. G. B. Drew, P. B. Lesson, K. Lyssenko, M. I. Ogden, *J. Chem. Soc. Chem. Commun.* **1995**, 929–930; g) M. A. Halcrow, J. S. Sun, J. C. Huffman, G. Christou, *Inorg. Chem.* **1995**, *34*, 4167–4177.

[4] a) D. Sellman, T. Gottschalk-Gaudig, F. W. Heinemann, *Inorg. Chim. Acta* **1998**, *269*, 63–72; b) D. A. Neumayer, A. H. Cowley, A. Decken, R. A. Jones, V. Lakhotia, J. G. Ekerdt, *J. Am. Chem. Soc.* **1995**, *117*, 5893–5894; c) R. A. Fischer, H. Sussek, A. Miehr, H. Pritzkow, E.

Herdtweck, *J. Organomet. Chem.* **1997**, *548*, 73–82; d) J. Kouvetakis, J. McMurran, P. Matsunaga, M. O'Keefe, J. L. Hubbard, *Inorg. Chem.* **1997**, *36*, 1792–1797.

[5] a) G.-C. Guo, Q.-G. Wang, G.-D. Zhou, T. C. W. Mak, *Chem. Commun.* **1998**, 339–340; b) G.-C. Guo, Q.-G. Wang, G.-D. Zhou, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 652–654; *Angew. Chem. Int. Ed.* **1998**, *37*, 630–632; c) G.-C. Guo, Q.-G. Wang, G.-D. Zhou, T. C. W. Mak, unpublished results.

[6] G.-C. Guo, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 3296–3299; *Angew. Chem. Int. Ed.* **1998**, *37*, 3183–3186.

[7] a) B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983–3011; b) G. N. Schrauzer, G. W. Kiefer, P. A. Doemeny, H. Kirsh, *J. Am. Chem. Soc.* **1973**, *95*, 5582–5592.

[8] M. A. S. Goher, F. A. Nautner, *Polyhedron*, **1995**, *14*, 1439–1446, and references therein.

[9] a) J. I. Bryant, R. L. Brooks, *J. Chem. Phys.* **1971**, *54*, 5315–5323; b) C. D. West, *Z. Kristallogr.* **1936**, *85*, 421–425.

[10] a) G.-D. Zhou, *Acta Sinica Peking Univ.* **1963**, *9*, 389. [In Chinese]; b) X.-L. Jin, G.-D. Zhou, N.-Z. Wu, Y.-Q. Tang, H.-C. Huang, *Acta Chemica Sinica* **1990**, *48*, 232–236. [In Chinese].

[11] H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1991**, *594*, 113–118, and references therein.

[12] Raman spectra of solid samples were measured on a Renishaw Raman Image Microscope System 2000: NaN_3: $\tilde{\nu}_s(N_3)$ 1361 cm^{-1}, $\tilde{\nu}_{as}(N_3)$ inactive; AgN_3: $\tilde{\nu}_s(N_3)$ 1338, $\tilde{\nu}_{as}(N_3)$ 2070 cm^{-1}; $AgN_3 \cdot 2\,AgNO_3$: $\nu_{as}(N_3)$ 2079, $\nu_s(N_3)$ 1330 cm^{-1}. The Raman spectrum of NaN_3 is consistent with $D_{\infty h}$ symmetry of the azide unit. However, the literature assignment of a linear and symmetrical structure for the azide unit in AgN_3[9] is at variance with the present data, which clearly indicate a linear and asymmetrical structure in both AgN_3 and $AgN_3 \cdot 2\,AgNO_3$.

[13] J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965–2982.

[14] a) I. G. Dance, *Aust. J. Chem.* **1994**, *47*, 979–990; b) I. G. Dance, *Chem. Commun.* **1998**, 523–530.

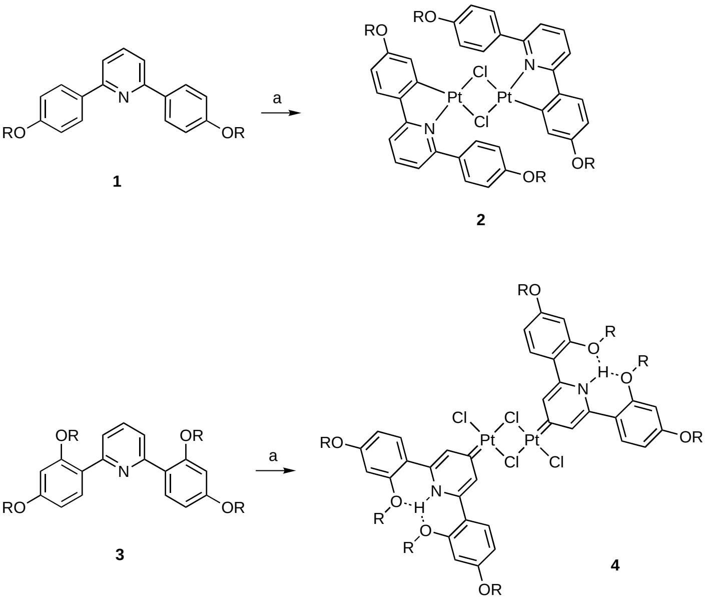
[15] a) M. K. Chan, J. Kim, D. C. Rees, *Science (Washington)* **1993**, *260*, 792–794; b) K. K. Stavrev, M. C. Zerner, *Chem Eur. J.* **1996**, *2*, 83–87.

[16] N. R. Thompson in *Comprehensive Inorganic Chemistry Vol. 3* (Eds.: J. C. Bailar, H. J. Emeléus, R. Nyholm, A. F. Trotman-Dickenson), Pergamon, Oxford, **1973**, Chap. 2, Section 2.10, p. 101.

Inter- versus Intramolecular C–H Activation: Synthesis and Characterization of a Novel Platinum–Carbene Complex**

Gareth W. V. Cave, Andrew J. Hallett, William Errington, and Jonathan P. Rourke*

Cyclometalation is a reaction that has been both widely used[1, 2] and widely studied.[3, 4] Typically, the coordinating moiety within a ligand forms a bond to a metal center, and then intramolecular C–H activation takes place to yield a five- or six-membered chelate ring. In the course of our studies, we sought to synthesize a number of cycloplatinated species that would show novel mesogenic behavior. To this end, we have prepared a number of 2,6-disubstituted pyridines, such as **1** and **3** (Scheme 1), and allowed them to react with potassium tetrachloroplatinate under normal cycloplatination conditions.[5] When we used pyridine **1** we isolated the expected cycloplatinated product **2**, formed by coordination of the pyridine followed by intramolecular C–H activation, in high yield. However, when we used pyridine **3** we isolated a very different product. The only product isolated (indeed, the only product observed in the crude reaction mixture) was that which forms from the intermolecular activation of a C–H bond, that is, **4**. Complex **4** was isolated in reasonable yield and analyzed by ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction.



Scheme 1. Synthesis of **2** and **4**. a) $K_2[PtCl_4]$, acetic acid. R = n-C_6H_{13}.

The X-ray crystal structure of **4** shows a number of interesting features (Figure 1). A crystallographically imposed center of symmetry exists between the two platinum and two chlorine atoms (Cl1) to give a flat rectangle, with the other two chlorine atoms (Cl2) only 0.082(4) Å out of this plane. The nitrogen-containing ring is at an angle of 38.62(24)° to the plane defined by the Pt_2Cl_2 rectangle. Two extremes for the bonding of this organic fragment to this rectangle are illustrated in Scheme 2. The Pt–C bond length of 1.951(9) Å is very similar to the values observed for the Pt^0–carbene complex derived from 1,3-dimesitylimidazol-2-ylidene (1.959(8) and 1.942(8) Å).[6] It is also similar to the length of 1.973(11) Å for the cationic Pt^{IV}–carbene complex $[PtCl_2\{C(NHMe)(NHC_6H_4Cl)\}(PEt_3)_2]ClO_4$,[7] and significantly shorter than that in the non-carbene cycloplatinated species $[\{PtCl(t\mathrm{Bu}_2PCMe_2CH_2)\}_2]$ (2.062(6) Å)[8] or Pt^{II}–C_{aryl} single bond lengths of 1.98–2.02 Å in arylplatinum complexes.[9, 10] Two shorter Pt–C bonds have been reported: a bond length of 1.82(6) Å for the platinum–carbene complex $[\{PtCl(t\mathrm{Bu}CH_2CO\,i\mathrm{Pr})\}_2]$[11] (though given the relatively large estimated standard deviations associated with this measurement, this value is not significantly different from ours), and a

---

[*] Dr. J. P. Rourke, G. W. V. Cave, A. J. Hallett, Dr. W. Errington
Department of Chemistry
Warwick University
Coventry CV47AL (UK)
Fax: (+44) 1203-524-112
E-mail: j.rourke@warwick.ac.uk

[**] This work was supported by the Engineering and Physical Sciences Research Council (UK). We thank Johnson Matthey for the loan of platinum salts.