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Reduction of rhenium decacarbonyl by samarium(II): synthesis and structure of the spiked triangular anion $[HRe_4(CO)_{17}]^-$

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Abstract

The reaction of $[Sm(Tp_2^{Me,Me})]$ with $[Re_2(CO)_{10}]$ gives $[Sm(Tp_2^{Me,Me})]Re(CO)_5$, which on further heating gives moderate yields of $[Sm(Tp^{Me,Me})_2]_2[Re_4(CO)_{17}]$. Crystallization from toluene yields $[Sm(Tp^{Me,Me})_2][HRe_4(CO)_{17}]$, which has been crystallographically characterized. It consists of a 64-electron cluster that adopts a spiked triangular structure with the hydride bridging two metal atoms in the equatorial plane of the cluster. A mechanism for the formation of these tetranuclear clusters is proposed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium; Carbonyl; Samarium; Cluster; Hydride

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1. Introduction

The synthesis of transition metal cluster compounds is an area of wide interest to inorganic and materials chemists. A number of methods have been developed for the synthesis of large clusters. These include ligand dissociation via photolysis, thermolysis, or chemically induced ligand elimination using reagents such as trimethylamine-*N*-oxide, or by displacement of anionic and weakly coordinated ligands. Oligomerization of unsaturated/multiply bonded systems provides another approach to the creation of larger clusters. In some cases the use of potentially bridging ligands encourages the formation of M–M bonds [1]. Redox condensation reactions initiated by electron transfer have been used to synthesize clusters either by conproportionation or through carbonyl labilization. Sodium benzophenone ketyl has been widely used for such reactions. The reaction of sodium with $M_3(CO)_{12}$ (M = Ru, Os) at reflux in THF gives good yields of $[M_6(CO)_{18}]^{2-}$ [2]. The reduction of $Re_2(CO)_{10}$ with sodium in glyme-like solvents results in the efficient formation of $[Re_4(CO)_{16}]^{2-}$ [3] and, at higher temperatures, of the carbido clusters $[HRe_6C(CO)_{18}]^{3-}$ and $[HRe_5C(CO)_{16}]^{2-}$ [4].

The wide use of samarium(II) as a mild one-electron reducing agent in organic chemistry suggests that it might have a useful role as an alternative reductant in cluster synthesis. We have recently become interested in the reactivity of pyrazolylborate complexes of samarium and ytterbium(II) with transition metal carbonyls because of the range of reactivity observed with the carbonyl groups themselves. This ranges from the formation of isocarbonyls [5], the conversion of CO to formate by adventitious water [6] and the formation of salts. In this paper we report the reaction of $[Sm(Tp^{Me,Me})_2]$ with $Re_2(CO)_{10}$, in which the samarium(II) reagent acts as a mild redox agent capable of producing a previously unknown tetranuclear cluster.

2. Results and discussion

In contrast to the reactions of $Sm(Tp^{Me,Me})_2$, **1**, with other transition metal carbonyl such as $Co_2(CO)_8$ and $[CpM(CO)_3]_2$ (M = Cr, Mo, W), which occur at room temperature, no change was observed after 2 days when a 2:1 ratio of **1** was stirred with $Re_2(CO)_{10}$. When heated to 80°C a slow reaction ensued, in which ap-

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proximately half of the lanthanide starting material dissolved giving an orange solution. After filtration and cooling overnight a reddish–pink microcrystalline material, **2**, was obtained. Elemental microanalysis on **2** was consistent with the formulation $[Sm(Tp^{Me,Me})_2]_2[Re_4(CO)_{17}]$, **2**. The infrared spectra show a large number of overlapping peaks in the range 2028–1881 cm^{-1} consistent with terminal carbonyl groups on an anionic multimetallic cluster, rather than with the presence of isocarbonyl groups between the d- and f-block elements as seen previously for a number of products of the electron transfer reactions of divalent lanthanides with metal–metal bonded transition metal carbonyls [7,5]. The ^1H-NMR spectrum showed the three peaks expected for the $[Sm(Tp^{Me,Me})_2]^+$ unit, suggesting a salt-like formulation with an anionic cluster. In addition a high field peak assigned to a hydride was also observed. The integration of this peak varied markedly from sample to sample and was therefore assigned to an impurity (*vide infra)*. The solubility of **2** was insufficient for ^{13}C-NMR spectra to be recorded.

On repeating the reaction between **1** and $Re_2(CO)_{10}$ at lower temperature and for shorter periods it was possible to isolate varying amounts of yellow crystals, **3**, in addition to the pink material. The elemental analysis was consistent with the formulation $[Sm(Tp^{Me,Me})_2][Re(CO)_5]$, consistent with reductive cleavage of the Re–Re bond with concomitant oxidation of the samarium to the trivalent state. The infrared spectrum showed two broad bands at 1912 and 1868 similar to those observed by Kaesz [8]. The ^1H-NMR spectrum consisted of three peaks in the ratio of 3:3:1 with chemical shifts similar to those observed for the salt $[Sm(Tp^{Me,Me})_2]I$. Attempts to collect X-ray data on these crystals were unsuccessful but we presume the structure to be broadly similar to that of $[Sm(Tp^{Me,Me})_2][Mn(CO)_5]$, which shows clearly separated and independent cations and anions [6].

In order to establish the structure of the rhenium cluster in **2**, the material was recrystallized from toluene at low temperature. The crystalline orange material grown in this manner gave an elemental microanalysis similar to that obtained for the unrecrystallized material. A low-temperature X-ray dataset was collected yielding a structure with a markedly different stoichiometry from that expected on the basis of microanalytical data for **2**. The formulation of **4** is $[Sm(Tp^{Me,Me})_2][HRe_4(CO)_{17}]$, with discrete $[HRe_4(CO)_{17}]^-$ anions with $[Sm(Tp^{Me,Me})_2]^+$ cations and a toluene of solvation. No short interionic contacts were noted. The cations lie on crystallographic inversion centres and are essentially identical to those observed previously in the structures of $[Sm(Tp^{Me,Me})_2]I$, $[Sm(Tp^{Me,Me})_2]BPh_4$ (J. Takats, personal communication), and $[Sm(Tp^{Me,Me})_2](Te_3Ph_3)$ [9]. The average metal–nitrogen distance, 2.443(9) Å, is consistent with the trivalent oxidation state of the samarium.

The structure of the anion of **4** is shown in Fig. 1 and consists of a spiked triangular array of metal atoms, consistent with a 64-electron count, but unusual in rhenium chemistry. The carbonyl groups are all terminal consistent with the typically long Re–Re bonds [10], and those on the spike lies in an equatorial position, almost coplanar with the Re_3 triangle (0.086 Å above the plane) in a manner reminiscent of tetraosmium and other clusters [11]. The carbonyl groups on the spike are staggered with respect to those on the adjacent rhenium atom. Although the hydride was not located in the X-ray structure and the Re–Re bonds are all much the same length, the disposition of the carbonyl groups within the cluster indicates that the most probable location is bridging between the two rhenium atoms

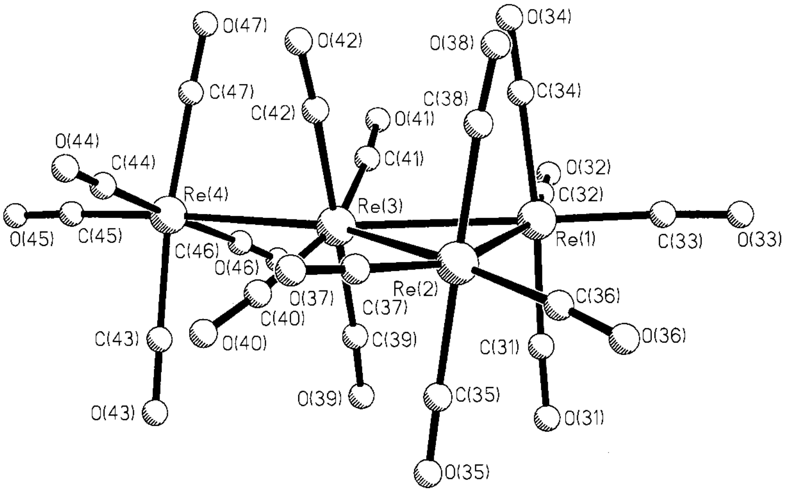
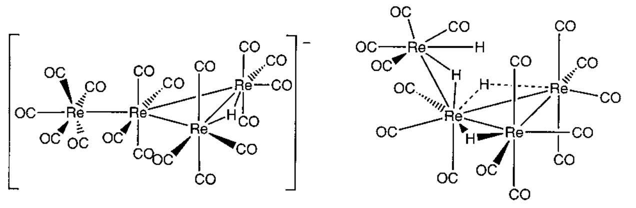


Fig. 1. The molecular structure of the anion of **4**. Selected bond angles and distances: Re(1)–Re(3) 3.0610(6) Å, Re(1–Re(2) 3.0659(6) Å, Re(2)–Re(3) 3.0776(6) Å and Re(3)–Re(4) 3.0392(6) Å. Re(3)–Re(1)–Re(2) 60.307(14)°, Re(4)–Re(3)–Re(1) 148.098(19)°, Re(1)–Re(3)–Re(2) 59.926(14)°, Re(1)–Re(2)–Re(3) 59.767(4)°, Re(4)–Re(3)–Re(2) 151.897(19)°.



Scheme 1.

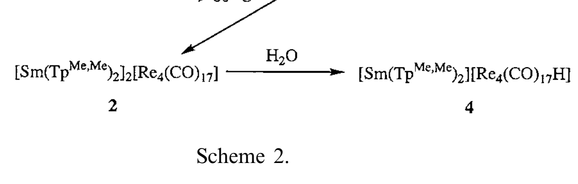
opposing the spike, Re(1) and Re(2). The symmetrical nature of the Re(4)$(CO)_5$ unit with respect to the Re(1)Re(2)Re(3) triangle suggests that there is no μ-H along Re(3)–Re(4), Re(1)–Re(3) or Re(2)–Re(3). The 'top' and the 'bottom' of the triangle Re(1)Re(2)Re(3) appear much the same, which tends to rule out a triply bridging μ^3-H since this would open up the face on which it was bridged. The Re–Re–CO angles for the equatorial carbonyls are larger for Re(1)–Re(2) than for Re(1)–Re(3) and Re(2)–Re(3) (110.3° and 110.6° compared with 97.7° and 100.8°). This extra 10° suggests that it is the Re(1)–Re(2) edge which is bridged.

The Re(1)–Re(2) bond, at 3.0659(6) Å, is not significantly longer than the other, non-hydride bridged, Re–Re distances in the triangle as might be expected on the evidence of the previously X-ray characterised ReH(CO) spiked triangular clusters. It is also considerably shorter than the hydride-bridged Re–Re bonds on the triangle in $[Re_4H_4(CO)_{15}]^{2-}$, (3.192(8) and 3.211(8) Å) [12]. In **2** the average rhenium–rhenium bond distance in the triangle is 3.068 Å, somewhat longer than in $Re_2(CO)_{10}$ (3.02 Å) [13] and $[Re_4(CO)_{16}]^{2-}$ (2.98–3.02 Å) [14] and for the non-hydride-bridged Re–Re bond in $[Re_4H_4(CO)_{15}]^{2-}$ (3.032(8) Å) [12] (Scheme 1).

The chemistry of 64-electron M_4 clusters has attracted considerable interest because of the different topologies possible when linking four metal centres through four bonds [1]. Puckered square and spiked-triangular clusters have been identified for a range of transition metals. In the case of rhenium only a relatively small number of tetranuclear clusters have been identified [15,16]. Pomeroy and co-workers have argued convincingly that in a spiked triangle, the spike acts as a two-electron donor to the remaining triangular framework [17] and that the electron-richness of the cluster determines the structure adopted. Thus in osmium chemistry the structure can be tuned simply by altering the equatorial substituents on the spike [11]. With good σ donors, such as trialkylphosphines and isonitriles, a spiked triangle is isolated, while with better π-acceptors such as CO and PF_3 a closed square structure results. Thus in **4** the 18-electron $Re(CO)_5^-$ unit of the spike may be viewed as acting as a two-electron donor at the unsaturated triangular $HRe_3(CO)_{12}$ species, with an unsupported dative bond to the triangle. The structure is, therefore, in contrast to the only other spiked triangular tetrarhenium clusters, $[Re_4H_4(CO)_{15}]^{2-}$ and $[Re_4H_4(CO)_{15}I]^-$ in which the spiked rhenium atom is bridged by a hydride to the metal triangle and is in an axial rather than equatorial position [12]. In $[Re_4H_4(CO)_{15}I]^-$ [18], prepared from $[Re_4H_4(CO)_{15}]^{2-}$, the iodide occupies a formerly CO site on the apical rhenium atom and the terminal hydride migrates to bridge the previously unbridged (in $[Re_4H_4(CO)_{15}]^{2-}$) Re–Re bond [19].

Repeated attempts to crystallize **2** were not successful, nor were attempts to obtain bulk samples of **4**. On the other hand, ^{1}H-NMR spectra of samples having elemental microanalyses consistent with **2** nevertheless showed a sharp peak at δ −17.22 ppm consistent with the hydride ligand of **4**. Thus we believe the crystal chosen for the X-ray study to be unrepresentative of the bulk and simply a minor contaminant which is visible in the ^{1}H-NMR spectrum. We presume that **4** results from the protonation of the dianion in **2** by adventitious water present in the crystallization flask.

In considering a mechanism for the formation of **2** several points must be borne in mind. As noted by several authors previously, although the reduction of both rhenium and technetium carbonyls leads to the pentacarbonyl anion, such reactions are never clean and tend to give a range of side products depending on the conditions [10]. The synthesis of the monoanion **4** only requires the addition of two electrons, together with the loss of three carbonyl units and the addition of a proton. We have observed that in this case, the reducing agent **1** is used up only if a 1:4 ratio of samarium to rhenium is present in the starting mixture. We therefore propose a mechanism (Scheme 2) in which the $Re(CO)_5^-$, **3**, formed initially is not stable for extended periods in toluene at temperatures above 60°C. Hence, when it is formed it oligomerizes with the $Re_2(CO)_{10}$ in solution, losing CO to give **2** which is stable to further reduction. By carrying out the reaction at lower temperatures and crystallizing the reaction mixture quickly the intermediate species, **3**, may be trapped before it reacts further. The forma-



Scheme 2.

tion of **4** then results by protonation of **2** by adventitious water. Attempts to prepare **4** deliberately by addition of water to samples of **2** were complicated by the hydrolysis of the $[Sm(Tp^{Me,Me})_2]$ cation.

Thus, the formation of **2** is a direct result of the rate at which the samarium(II) reagent is able to transfer electrons to the rhenium starting material. Owing to the extreme insolubility of the $[Sm(Tp^{Me,Me})_2]$ starting material in common solvents [20,21], the rate of electron transfer may be assumed to be quite slow, giving time for carbonyl elimination to occur. In this respect the reaction is similar to that observed previously for $Co_2(CO)_9$ which yields $Co_4(CO)_{12}$ in addition to the salt $[Sm(Tp^{Me,Me})_2]Co(CO)_4$ [22].

In conclusion, the results presented here suggest that samarium(II) reagents may provide a subtle alternative to other more powerful reducing agents such as sodium or sodium benzophenone ketyl for the preparation of higher clusters.

3. Experimental

All preparations and manipulations were carried out using standard Schlenk line and dry-box techniques in an atmosphere of dinitrogen [23]. Oxygen-free nitrogen was purified by passage over columns containing 3 Å molecular sieves and MnO [24]. Toluene was pre-dried over sodium wire and distilled under nitrogen over sodium before use. $[Sm(Tp^{Me,Me})_2]$ was prepared from sodium hydro-tris-(3,5-dimethyl)pyrazolylborate [25] and samarium diiodide [26].

Infrared spectra were recorded as KBr pellets on a Nicolet 205 FTIR spectrometer. ^1H- and ^{13}C-NMR spectra in solution were recorded on Bruker AM300 and Varian VXR-400 spectrometers at 300, and 400 and 100.6 MHz, respectively. Spectra were calibrated using residual proton (^1H) and solvent resonances (^{13}C), respectively, and are reported relative to tetramethylsilane. Elemental analyses were determined by Mr Alan Stones of UCL Analytical Services.

3.1. *Preparation of of* $[Sm(Tp^{Me,Me})_2]_2[Re_4(CO)_{17}]$, **2**

To a purple slurry of $(Tp^{Me,Me})_2Sm$ (250 mg, 0.33 mmol) in toluene was added a colourless solution of $Re_2(CO)_{10}$ (109 mg, 0.17 mmol) in toluene. The mixture was warmed to 80°C and stirred for 5 h during which time the solid dissolved and the solution turned orange. After cooling to room temperature, the solution was filtered and the volume of solvent reduced to 15 cm^3. Cooling to -20°C gave pink needles. Yield: 44 mg (19%). Elemental analysis: Calc. for $C_{77}H_{88}B_4N_{24}O_{17}$-$Re_4Sm_2$: C 34.12, H 3.27, N 12.40; Found: C 34.24, H 3.29, N 12.30. IR ν_{BH} 2559; ν_{CO} 2083, 2006, 1964, 1914, 1905, 1881. ^1H-NMR (C_6D_6, 298 K) 4.93 (s, 4-CH); 2.13 (s, 5-Me); -2.63 (s, 3-Me).

3.2. *Preparation of of* $[Sm(Tp^{Me,Me})_2][Re(CO)_5]$, **3**

To a purple slurry of $(Tp^{Me,Me})_2Sm$ (194 mg, 0.26 mmol) in toluene was added a colourless solution of $Re_2(CO)_{10}$ (109 mg, 0.13 mmol) in toluene. The mixture was warmed to 60°C and stirred for 4 h during which time the solid dissolved and the solution turned yellow. After cooling to room temperature, the solution was filtered and the volume of solvent reduced to 5 cm^3. Cooling to -20°C gave yellow microcrystals. Yield: 75 mg (27 %). Elemental analysis: Calc. for $C_{35}H_{44}B_2N_{12}O_5ReSm$: C 39.25, H 4.14, N 15.69; Found: C 38.97, H 4.29, N 15.79. IR ν_{BH} 2555; ν_{CO} 1912, 1868. ^1H-NMR (C_6D_6, 298 K) 4.96 (s, 4-CH); 2.20 (s, 5-Me); -2.55 (s, 3-Me).

3.3. *X-ray diffraction study of* **4**

3.3.1. *Crystal data for* **4**

$C_{47}H_{45}B_2N_{12}O_{17}Re_4Sm$, yellow crystal of dimensions $0.24 \times 0.20 \times 0.04$ mm, $M = 1966.72$, triclinic space group $P\bar{1}$, $a = 10.4574(7)$ Å, $b = 11.4168(8)$ Å, $c = 26.1519(19)$ Å, $\alpha = 88.088(2)°$, $\beta = 78.298(2)°$, $\gamma = 78.804(2)°$, $U = 2999.1(4)$ Å^3, $Z = 2$, $F(000) = 1838$, $D_c = 2.178$ g cm^{-1}, μ(Mo–K$_\alpha$) 9.081 mm^{-1}, $2\theta_{max} = 50.00°°$, $T = 160$ K. 18 308 reflections (10 312 unique with $R_{int} = 0.0418$) were collected on a Bruker AXS SMART CCD area detector diffractometer with narrow frames (0.3° in ω) and three-dimensional profile fitting using graphite monochromated radiation Mo–K$_\alpha$ ($\lambda = 0.71073$ Å). Data were corrected semi-empirically for absorption based on symmetry equivalent and repeated reflections. Cell parameters were refined by locally written software from the observed ω angles of 14 076 reflections in the range $1.82 \leq \theta \leq 28.36°$ with $I > 10\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values. All non-H atoms were refined anisotropically, H atoms were constrained. Final $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1118$ {where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ and $P = (F_o^2 + 2F_c^2)/3$} for 763 refined parameters, conventional $R = 0.0453$ [for F values of 7686 data with $F^2 > 4\sigma(F^2)$]. The largest features in the final difference synthesis were within ± 2.65 eÅ^{-3}, close to the metal atoms. The following programs were used: Bruker AXS SHELXTL [27] for structure solution and refinement and molecular graphics, Bruker AXS SMART (control), and SAINT (integration) and local programs [28].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 118784. Copies of this information may be obtained free of charge from The

Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH, New York, 1990.
[2] C.-M.T. Hayward, J.R. Shapley, Inorg. Chem. 21 (1982) 3816.
[3] C.-M. Hayward, J.R. Shapley, Organometallics 7 (1988) 448.
[4] T.J. Healy, S.R. Wilson, J.R. Shapley, Inorg. Chem. 6 (1987) 2618.
[5] S.-Y. Liu, G.H. Maunder, A. Sella, M. Stephenson, D.A. Tocher, Inorg. Chem. 35 (1996) 76.
[6] A.C. Hillier, Ph.D. Thesis, University of London, 1998.
[7] J.M. Boncella, R.A. Andersen, Inorg. Chem. 23 (1984) 432.
[8] J.C. Hileman, D.K. Huggins, H.D. Kaesz, Inorg. Chem. 1 (1962).
[9] A.C. Hillier, S.Y. Liu, A. Sella, M.R.J. Elsegood, Angew. Chem. Int. Edn. Engl., accepted for publication (1999).
[10] N.M. Boag, H.D. Kaesz, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon, Oxford, 1982, pp. 161–242.
[11] F.W.B. Einstein, V.J. Johnston, R.K. Pomeroy, Organometallics 9 (1990) 2754.
[12] V.G. Albano, G. Ciani, M. Freni, P. Romiti, J. Organomet. Chem. 96 (1975) 259.
[13] L.F. Dahl, E. Ishishi, R.E. Rundle, J. Chem. Phys. 26 (1957) 1750.
[14] M.R. Churchill, R. Bau, Inorg. Chem. 7 (1968) 2606.
[15] T.J. Henly, Coord. Chem. Rev. 93 (1989) 269.
[16] J. O'Connor, Chapter 9, in: E. Abel, F. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 6, Pergamon, Oxford, 1995.
[17] F.W.B. Einstein, V.J. Johnston, A.K. Ma, R.K. Pomeroy, Organometallics 9 (1990) 52.
[18] G. Ciani, G. D'Alfonso, M. Freni, P. Romiti, J. Organomet. Chem. 170 (1979) C15.
[19] G. Ciani, V.G. Albano, A. Immirzi, J. Organomet. Chem. 121 (1976) 237–248.
[20] J. Takats, X.W. Zhang, V.W. Day, T.A. Eberspacher, Organometallics 12 (1993) 4286.
[21] G.H. Maunder, A. Sella, D.A. Tocher, J. Chem. Soc. Chem. Commun. (1994) 885.
[22] A.C. Hillier, S.-Y. Liu, A. Sella, O. Zekria, M.R.J. Elsegood, J. Organomet. Chem. 528 (1997) 209.
[23] S. McNally, N.J. Coope, in: A.L. Wayda, M.Y. Darensbourg (Eds.), Experimental Organometallic Chemistry : A Practicum in Synthesis and Characterization, vol. 357, American Chemical Society, 1987, pp. 6–22.
[24] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, Wiley, New York, 1986.
[25] S. Trofimenko, J. Amer. Chem. Soc. 89 (1967) 6288.
[26] G. Maunder, A. Sella, J. Takats, X. Zhang, unpublished results.
[27] G.M. Sheldrick, SHELXTL User Manual, Version 5, Bruker AXS Inc, Madison, WI, 1994.
[28] SMART and SAINT Software for CCD Diffractometers, Bruker AXS Inc., Madison, WI, 1994.