

Condensation of all-*cis*-tetraphenylcyclotetrasiloxanetetraol in ammonia: new method for preparation of ladder-like polyphenylsilsesquioxanes

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1. Experimental

1.1. General Considerations

Solvents were purified according to described procedures.¹ Toluene was distilled from calcium hydride under argon. Sodium hydroxide, pyridine, chlorotrimethylsilane, HCl were purchased from Aldrich. All-*cis*-tetraphenylcyclotetrasiloxanol was obtained by our published method.²

NMR spectra were recorded on a Bruker Avance™ 600 spectrometer (Germany) operating at 600.22 and 119.26 MHz for ¹H and ²⁹Si, respectively. The chemical shifts for ¹H were indirectly referenced to TMS *via* the solvent signals. The chemical shifts for ²⁹Si were measured with TMS as an external standard.

IR spectra were obtained using a Bruker Tensor 37 FT-IR spectrometer (Germany). The samples were prepared by pressing KBr pellets.

The X-ray powder diffraction pattern of polymer **4** was obtained using a Bruker D8 Advance Vario diffractometer equipped with LynxEye 1D detector and Ge(111) monochromator utilizing CuK α radiation in transmission mode. The specimen was placed between Kapton films under argon and evacuated to prevent hydration. The pattern was indexed using SVD-Index algorithm as implemented in Bruker TOPAS 5.0 software.

Thermogravimetric investigations were performed using a Derivatograph-C instrument (MOM, Hungary) under air or argon at heating rate 10 K min⁻¹.

Reduced viscosity of the dilute solution of polymer **4** in toluene was measured using an Ubbelohde suspended level capillary viscosimeter in the concentration range of 0.25–1 dl g⁻¹ at 25±0.05° C.

GPC analysis was performed using a Shimadzu chromatograph with refractometer RID-20A detector, PSS SDV 100 000Å analytical column (300 x 8 mm) and THF as eluent.

1.2. Synthesis

1.2.1. Hydrolytic condensation of all-*cis*-tetraphenylcyclotetrasiloxanol in liquid ammonia.

all-*cis*-1,3,5,7-Tetraphenyl-1,3,5,7-tetrahydroxycyclotetrasiloxane **1** (1.0 g, 1.9 mmol) was loaded into an autoclave equipped with a magnetic stirrer, then the autoclave was filled with NH₃ under chill-down using an IN-FLOW mass flow meter (Bronkhorst, Netherlands). The reaction mixture was heated at 100°C for 4 h and then decompressed. The condensation product **2** was obtained as a white powder. Yield 0.961 g (96%).

1.2.2. OH groups capping reaction in condensate polymer **2**

A solution of polymer **2** (0.961 g, 1.8 mmol) in THF (15 ml) was added to a solution of trimethylchlorosilane (1.56 g, 14.4 mmol) and pyridine (1.14 g, 14.4 mmol) in THF (15 ml). The reaction mixture was stirred at room temperature for 24 h, then filtered through silica gel to remove precipitated material. The solvent was evaporated *in vacuo* (10 mmHg, 40 °C, then 1 mmHg, 100 °C, 6 h). The capped product **3** was obtained as white film-forming polymer. Yield 0.711 g (74%). ¹H NMR (600 MHz, CDCl₃) δ: -0.76–0.32 (br. s), 6.21–7.80 (br. s).

²⁹Si NMR (150 MHz, CDCl₃) δ: -80 – -75 (PhSiO₃), 10.6 (Me₃SiO).

IR (KBr, ν/cm⁻¹): 3094–3008, 1595, 1430, 1101–997, 842, 725, 692, 477–407.

1.2.3. Preparation of polymer **4**

A solution of blocked polymer **3** (1.2 g) in THF–ethanol (C = 1%) was fractionated at room temperature to give high molecular weight polymer **4**. Yield 0.9 g (75%).

¹H NMR (600 MHz, CDCl₃) δ: -0.78–0.19 (br. s), 6.04–7.79 (br. s).

²⁹Si NMR (150 MHz, CDCl₃) δ: -80 – -75, 10.5.

IR (KBr, ν/cm⁻¹): 3074–2851, 1748, 1596, 1463, 1432, 1379, 1134, 1042, 732, 697, 506.

2. NMR, IR spectra

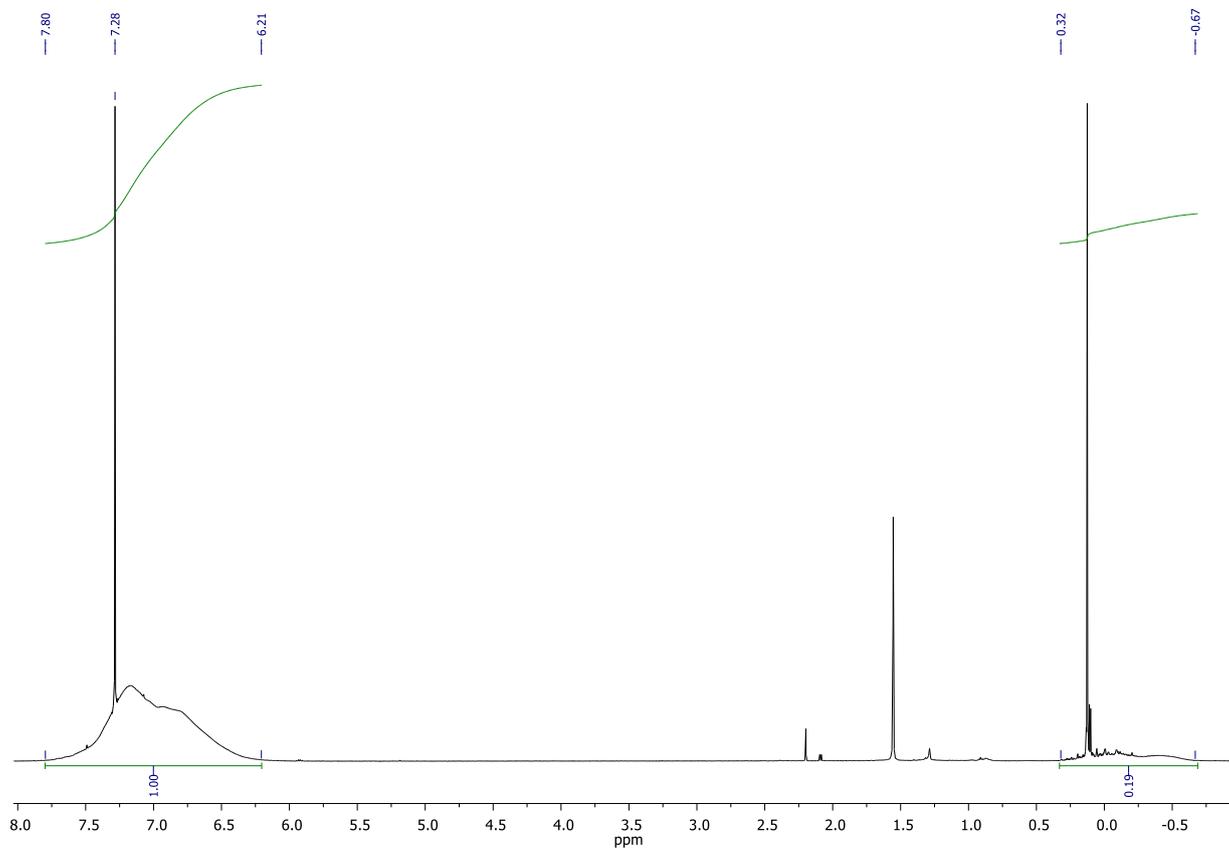


Figure S1 ^1H NMR (600 MHz, CDCl_3) of polymer **2**.

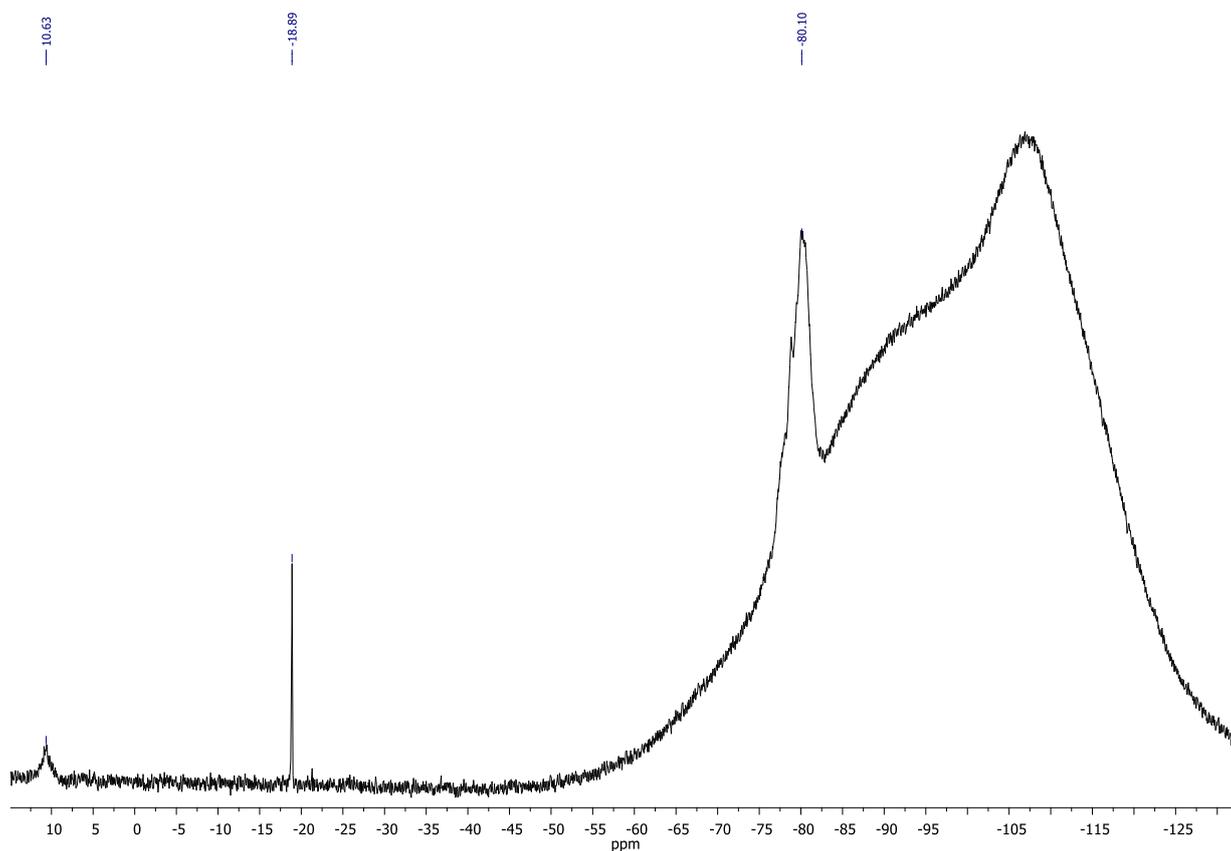


Figure S2 ^{29}Si NMR (119 MHz, CDCl_3) of polymer **2**.

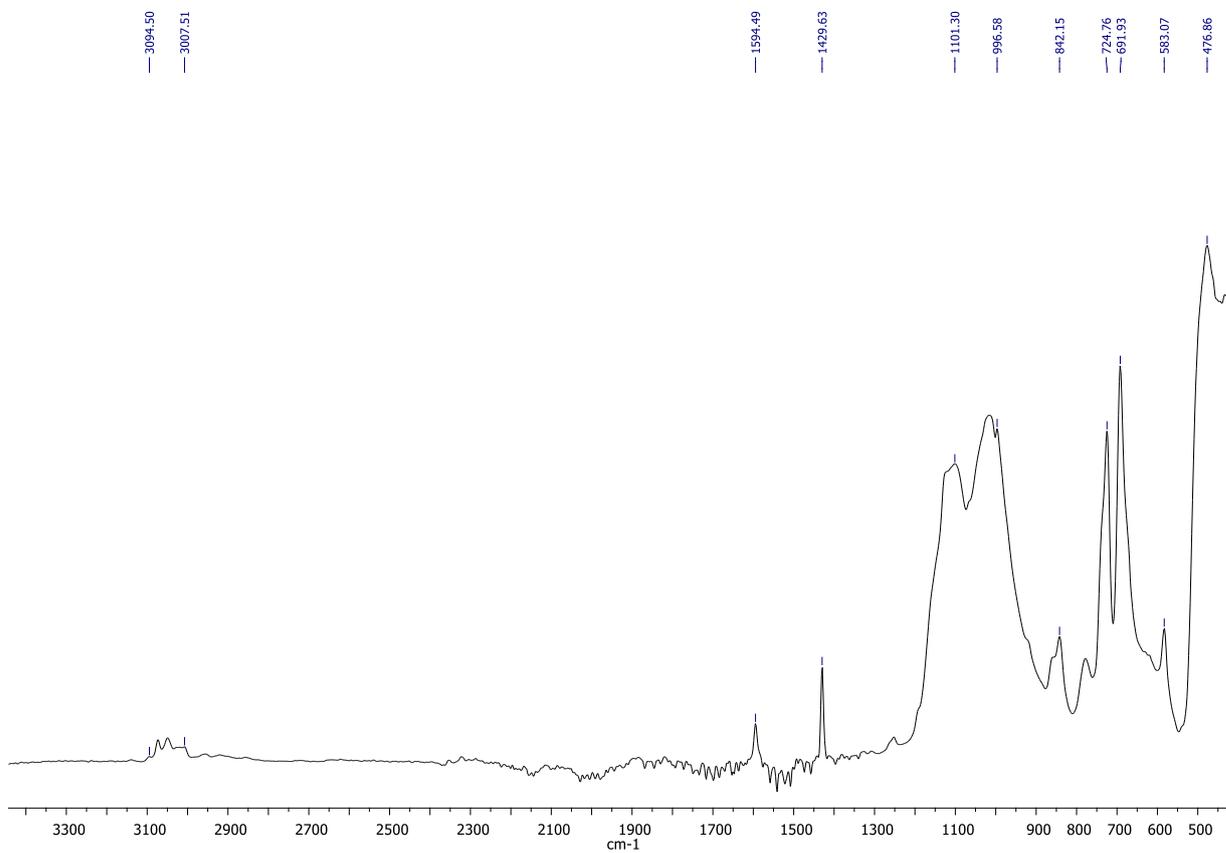


Figure S3 IR spectrum of polymer **2**.

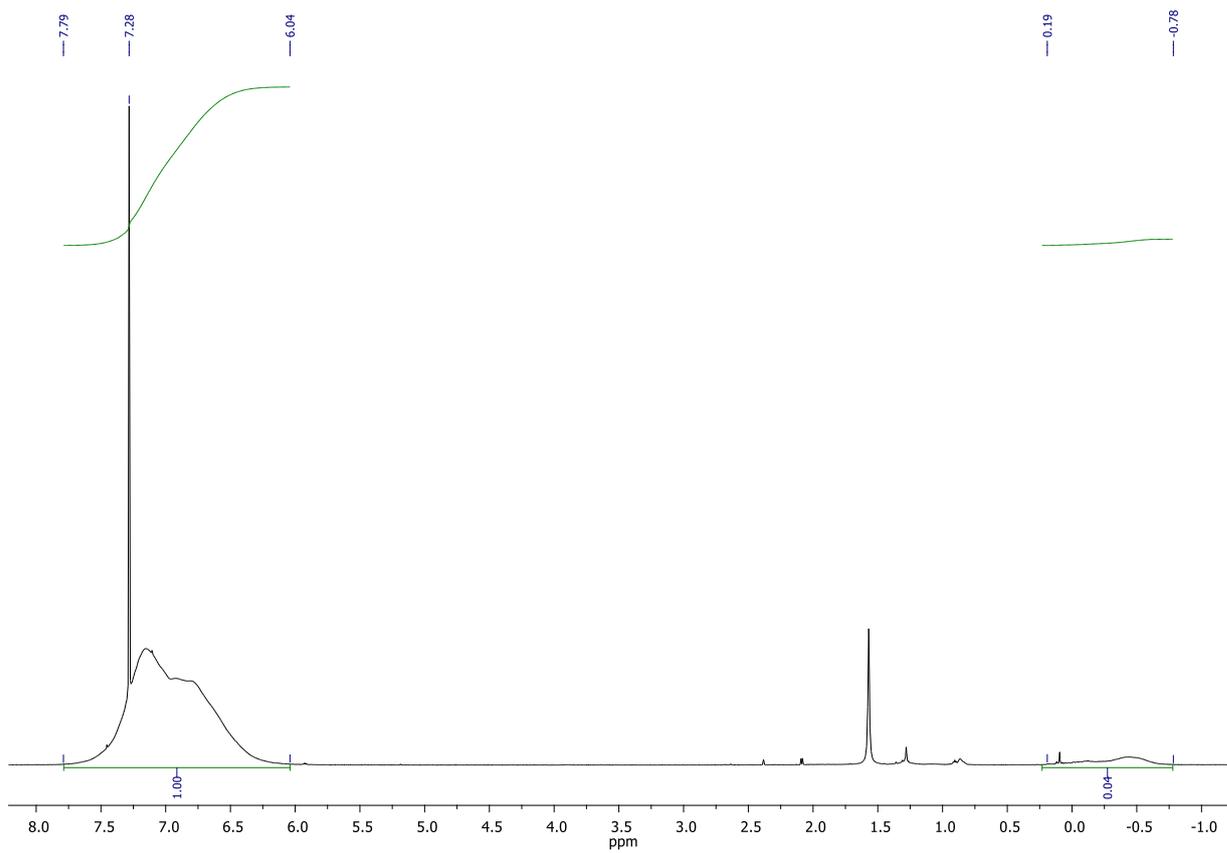


Figure S4 ^1H NMR (600 MHz, CDCl_3) of polymer **4**.

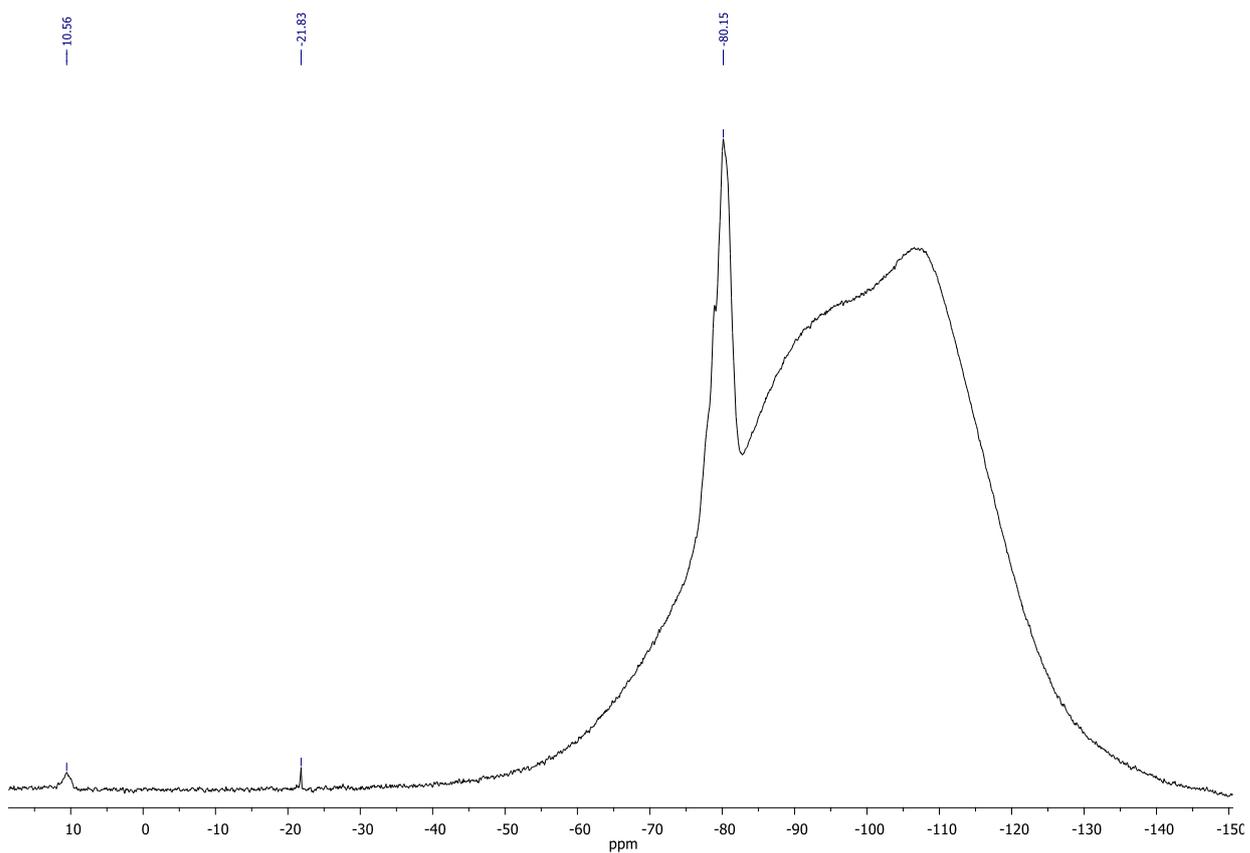


Figure S5 ^{29}Si NMR (119 MHz, CDCl_3) of polymer **4**. The weak signal at -22 ppm corresponds to silicone vacuum grease.

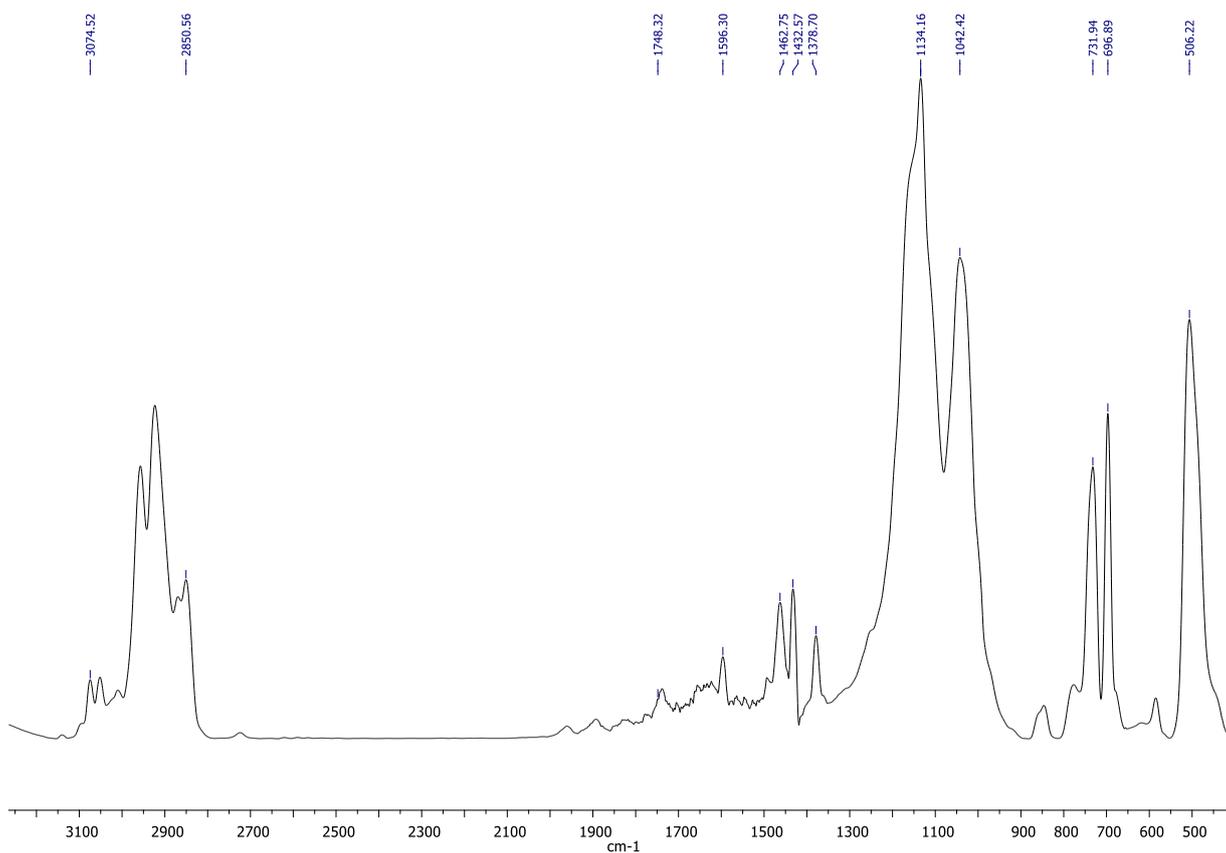


Figure S6 IR spectrum of polymer **4**.

3. References

- 1 A. J. Gordon, R. A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, Wiley, New York, 1973.
- 2 O. I. Shchegolikhina, Yu. A. Pozdnyakova, Yu. A. Molodtsova, S. D. Korkin, S. S. Bukalov, L. A. Leites, K. A. Lyssenko, A. S. Peregudov, N. Auner and D. E. Katsoulis, *Inorg. Chem.*, 2002, **41**, 6892.