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Solid-state Nuclear Magnetic Resonance Studies on the Co-ordination Geometry of Boron in Polyoxotungstates

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The co-ordination geometry of boron in derivatives of a polyoxotungstate with the Keggin structure, $K_5[BW_{12}O_{40}]\cdot 11H_2O$, has been studied by solid-state magic-angle-spinning NMR spectroscopy (in tandem with Fourier-transform infrared spectroscopy) which is shown to be a sensitive tool for probing the immediate environment of ^{11}B in polyoxotungstates, yielding new information on the local symmetry.

Polyoxotungstates with the Keggin structure (Fig. 1) have attracted considerable attention due to their potential applications in catalysis, medicine and other areas.[2,3] This class of compounds includes the parent Keggin anions, $[XW_{12}O_{40}]^{n-}$ (X = P, As, B, Si, Ge or other metals), their lacunar derivatives, $[XW_{11}O_{39}]^{(n+4)-}$, and metal complexes of the latter, $[XW_{11}O_{39}M^{m+}(H_2O)]^{(n+4-m)-}$.[1]

Solid-state NMR has not been previously used to study the status of boron of polyoxometalates. Because the technique probes local, rather than long-range, order it does not suffer from the drawbacks inherent in other structural methods. Boron-11 is a quadrupolar nucleus with spin $I = \frac{3}{2}$. The quadrupolar interaction is a tensor interaction which may be defined by two parameters, $eq(=V_{zz})$ and $\eta[=(V_{xx}\text{-}V_{yy})/V_{zz}]$, where V_{xx}, V_{yy}, V_{zz} are the principal elements of a tensor describing the electric field gradient (e.f.g.). For a polycrystalline sample magic-angle spinning (MAS) yields an NMR spectrum which is a powder pattern with a characteristic shape determined by the quadrupole coupling constant $C_Q = eQV_{zz}/h$ and by η.[4] Hence, the spectrum provides valuable information on the local symmetry around the ^{11}B nucleus. Here we report ^{11}B solid-state MAS NMR studies of α-$K_5[BW_{12}O_{40}]\cdot 11H_2O$, lacunar $K_9[BW_{11}O_{39}]\cdot 11H_2O$ and $K_6[BW_{11}O_{39}Co(H_2O)]\cdot 15H_2O$.* The NMR results are complemented by Fourier-transform infrared (FTIR) data.

A selected region of the FTIR spectra of α-$K_5[BW_{12}O_{40}]\cdot 11H_2O$, lacunar $K_9[BW_{11}O_{39}]\cdot 11H_2O$ and $K_6[BW_{11}O_{39}Co(H_2O)]\cdot 15H_2O$ is shown in Fig. 2. In spectrum (*a*) the bands in the range 816–960 cm^{-1} are assigned to W–O$_b$–W (916 cm^{-1}), W–O$_c$–W (816 cm^{-1}), W–O$_d$ (960 cm^{-1}) and B–O (910 cm^{-1}) vibrations.[5] When a tungsten atom is removed from $[BW_{12}O_{40}]^{5-}$ (forming $[BW_{11}O_{39}]^{9-}$) the two broad peaks centred at about 816 and 910 cm^{-1} split into several lines. The peak at *ca.* 960 cm^{-1} remains unchanged. This suggests that the highly symmetric Keggin unit has been distorted.[9] In particular, the local symmetry around the boron atom has probably been lowered. Insertion of Co^{III} is likely to restore partially the symmetry of the Keggin unit and consequently the splitting of the bands is not observed for $K_6[BW_{11}O_{39}Co(H_2O)]\cdot 15H_2O$. Close inspection of Fig. 2(*a*) and (*c*) reveals that, although similar, the spectra are not identical. This might indicate that the local boron symmetry has not been fully recovered.

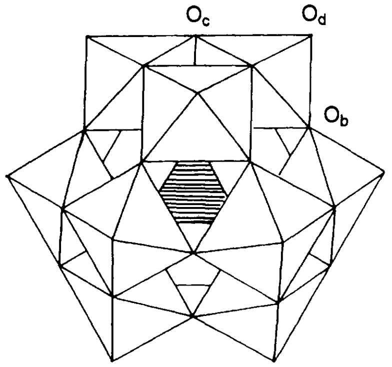

Fig. 1 Structure of α-$[XW_{12}O_{40}]^{n-}$, the most common isomer of the parent Keggin anion, which has been confirmed by a large number of techniques[1] and assumed for a variety of derivatives. The central atom, X, is tetrahedrally co-ordinated to oxygen and is surrounded by 12 WO_6 distorted octahedra in a T_d symmetry

Central-transition ($m = +\frac{1}{2} \longleftrightarrow m = -\frac{1}{2}$) ^{11}B MAS NMR spectra of the three polyoxometalates are shown in Fig. 3. The spectrum of α-$K_5[BW_{12}O_{40}]\cdot 11H_2O$ displays a rather sharp and symmetric resonance with a full-width-at-half-maximum (Δ) of 15 Hz, centred at δ −7.4. This implies a highly symmetric e.f.g. around ^{11}B due to the four oxygens to which boron is tetrahedrally co-ordinated. The spectrum of lacunar $K_9[BW_{11}O_{39}]\cdot 11H_2O$ displays a broad and characteristic second-order quadrupolar powder pattern[4] which has been simulated (Fig. 4) to yield the isotropic chemical shift δ_{iso} (−6.8), C_Q (0.74 MHz) and η (0.16). This clearly shows that boron is in a relatively distorted environment. It has been previously suggested that the lacunar Keggin unit contains trigonal rather than tetrahedral boron (ref. 3, p. 79); however, C_Q values for BO_3 units in borates and boron oxides are in the range 2.5–2.75 MHz (η = 0–0.2),[10] much larger than the value measured in this work. In addition, the δ_{iso} found is characteristic of BO_4 units.[10] Therefore, lacunar $K_9[BW_{11}O_{39}]\cdot 11H_2O$ contains boron in a distorted tetrahedral environment. Although FTIR suggests that the local symmetry of boron changes when the lacunar polyoxometalate forms, NMR alone

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* α-$K_5[BW_{12}O_{40}]\cdot 11H_2O$ and $K_9[BW_{11}O_{39}]\cdot 11H_2O$ were prepared by published methods.[5,6] $K_6[BW_{11}O_{39}Co(H_2O)]\cdot 15H_2O$ was prepared by the reaction of $K_9[BW_{11}O_{39}]\cdot 11H_2O$ with $CoSO_4\cdot 7H_2O$ followed by oxidation of the isolated Co^{II} complex with $K_2S_2O_8$, as described by Weakley and co-workers[7,8] for similar compounds. The purity of the prepared compounds was checked by X-ray powder diffraction.

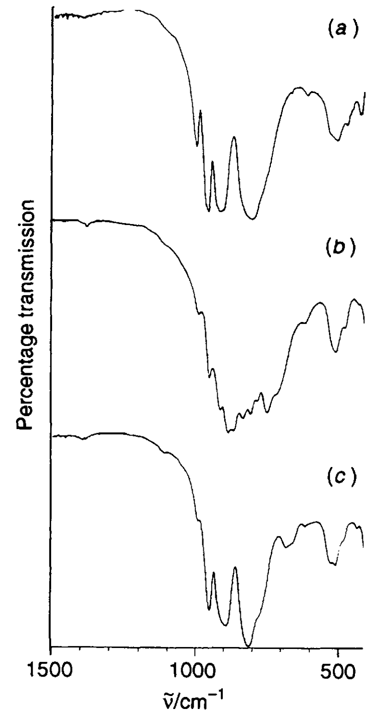

Fig. 2 Selected region of the FTIR spectra (Mattson Polaris, KBr wafer technique): (*a*) α-$K_5[BW_{12}O_{40}]\cdot 11H_2O$, (*b*) $K_9[BW_{11}O_{39}]\cdot 11H_2O$ and (*c*) $K_6[BW_{11}O_{39}Co(H_2O)]\cdot 15H_2O$

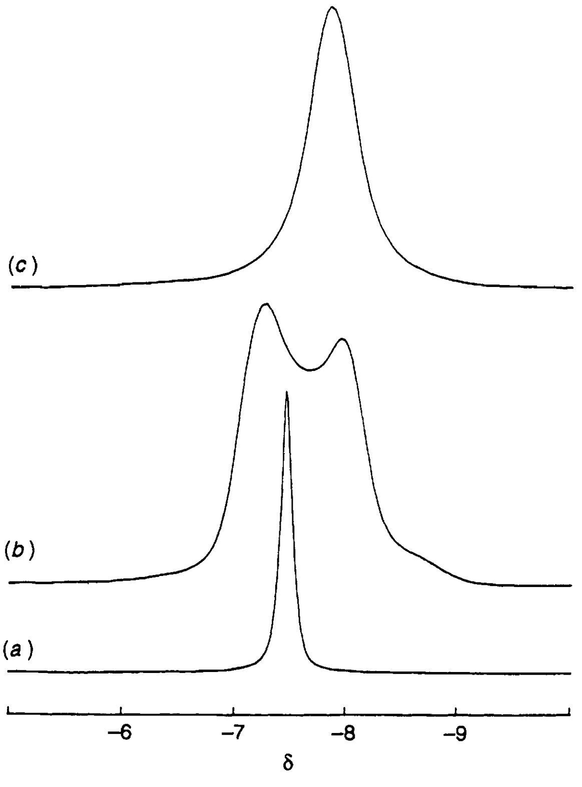

Fig. 3 Central-transition ^{11}B MAS NMR spectra recorded at 128.34 MHz (9.4 T) on a Bruker MSL-400 spectrometer with very short, 0.6 μs (< 15°),[4] radiofrequency pulses and 2 s recycle delays. Rotors were spun in air at 15 kHz. The chemical shifts are relative to external $Na_2B_4O_7\cdot 10H_2O$. (*a*) α-$K_5[BW_{12}O_{40}]\cdot 11H_2O$, (*b*) $K_9[BW_{11}O_{39}]\cdot 11H_2O$ and (*c*) $K_6[BW_{11}O_{39}Co(H_2O)]\cdot 15H_2O$

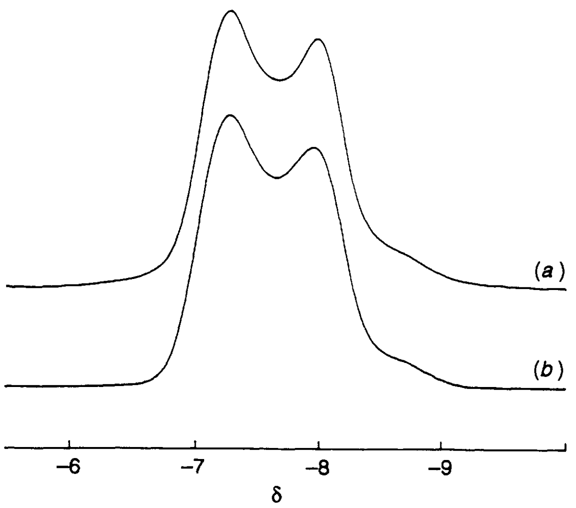

Fig. 4 Experimental (*a*) and simulated (*b*) (C_Q = 0.74 MHz, η = 0.16, $\delta_{iso} = -6.8$) central-transition ^{11}B MAS NMR spectra of $K_9[BW_{11}O_{39}]\cdot 11H_2O$

clearly shows that the co-ordination geometry remains tetrahedral. The spectrum of $K_6[BW_{11}O_{39}Co(H_2O)]\cdot 15H_2O$ displays a peak at δ −7.9 which does not exhibit a second-order pattern. Despite this, the width Δ of the line is 65 Hz, over four times that observed for α-$K_5[BW_{12}O_{40}]\cdot 11H_2O$. This indicates that the local boron symmetry has not been fully restored. Assuming that the residual linewidth is solely due to second-order quadrupole effects (with no consideration of dipolar interaction with ^{59}Co) simulations allow C_Q to be estimated at about 0.3 MHz and δ_{iso} at δ −7.6.

In conclusion, solid-state NMR has been shown to be a sensitive technique to probe the immediate environment of ^{11}B in polyoxotungstates yielding important information on the local symmetry, which is not forthcoming from other techniques.

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References

1 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983.
2 M. T. Pope and A. Mueller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
3 W. P. Griffith, *Trans. Met. Chem.*, 1991, **16**, 548; Y. Ono, in *Perspectives in Catalysis*, eds. J. M. Thomas and K. I. Zamaraev, Blackwell, Oxford, 1992, p. 431.
4 G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, Wiley, New York, 1987.
5 C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207.
6 P. Souchay, *Ann. Chim.*, 1949, **20**, 96.
7 T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2935.
8 C. M. Tourné, G. F. Tourné, S. A. Malik and T. J. R. Weakley, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3875.
9 C. Rocchiccioli-Deltcheff and R. Thouvenot, *J. Chem. Res.* (*S*), 1977, 46.
10 K. F. M. G. J. Scholle and W. S. Veeman, *Zeolites*, 1985, **5**, 118.

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