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Preliminary communication

STRUCTURE OF $H_3Os_3(CO)_9CCH_3$ BY NEMATIC-PHASE PMR AND X-RAY POWDER PHOTOGRAPHY

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Summary

The structure of $H_3Os_3(CO)_9CCH_3$ has been determined by a combination of nematic-phase PMR and X-ray powder photography; the compound is isostructural with the analogous $H_3Ru_3(CO)_9CCH_3$, with an osmium to (bridging) hydride proton distance of 1.82 Å and an Os—H—Os angle of 103°.

The positions of hydride protons in transition-metal compounds, particularly those of the second and third rows, are difficult to establish accurately. Nuclear magnetic resonance studies of these hydrides dissolved in a nematic liquid crystal can yield information about the positions of the spin-½ nuclei. In practice, however, there are severely limiting criteria for molecules suitable for study in this way: they should possess reasonably high symmetry, fewer than ten spins, a sufficient number of independent dipolar interactions, and at least one known distance with which to calibrate the dipolar couplings. One such study [1] has been reported for the compound $H_3Ru_3(CO)_9CCH_3$ (I), which has also been studied by single-crystal X-ray diffraction [2]. We wish to report an investigation of the structure of $H_3Os_3(CO)_9CCH_3$ (II) using the complementary methods of nematic-phase proton magnetic resonance and X-ray powder photography.

The isotropic proton NMR of (II) consists of two singlets at τ 5.55 and 28.58 [3], corresponding to the methyl and hydride protons respectively. A saturated solution of (II) in the Vari-Light liquid crystal VL-3268-N (less than 10 mg of solute in the 0.5 ml of solvent) in a 5 mm NMR tube was held in a concentric 12 mm tube containing D_2O as a heteronuclear lock. Several spectra were obtained (non-spinning) on a Varian XL-100-15 spectrometer working in Fourier-transform mode at a probe temperature of 37°C. Line widths at half-height of 15 Hz were obtained using a spectral width of 5000 Hz.

X-ray powder photographs of (I) and (II) taken with a Guinier focusing camera, using Cu-K_α radiation and a silicon calibrant (α = 5.4306 Å) revealed that the compounds were isostructural (viz. space group *Pnma*). Iterative refinement of the line positions resulted in a unit cell of a = 17.55(3), b = 14.57(2), c = 6.76(1) Å, which is identical, within experimental error, to that found for (I) [2].

Assuming (II) has C_{3v} symmetry like (I), only one orientation parameter S_{zz} is required to characterise the orientation of (II) in the nematic solvent. The spectra were nearly first order and displayed two triplets of quartets. The dipolar couplings T_{ij}, defined by

$$T_{ij} = -\frac{\hbar\gamma_i\gamma_j}{2\pi r_{ij}{}^3}(3\cos^2\beta_{ij} - 1)S_{zz} \qquad (1)$$

where r_{ij} is the distance between nuclei i and j, γ_i is the gyromagnetic ratio of the ith nucleus and β_{ij} is the angle between the internuclear vector and the z axis (the symmetry axis in this case), were obtained from the spectra using a modified [4] version of the LAOCOON2 program. This program fits the experimental spectrum by adjusting the values of T_{ij} and chemical shifts until the r.m.s. error between computed and experimental spectra is minimised. The best-fit dipolar couplings and their uncertainties (computed from approximate errors in experimental frequency measurements of 5 Hz) are shown in Table 1.

TABLE 1

NMR PARAMETERS FOR (II) DISSOLVED IN VL-3268-N at 37°

Parameter	Spectrum 1	Spectrum 2
$\lvert T(\text{intra-Me})\rvert$	781.6 ± 3.3 Hz	873.2 ± 1.7 Hz
$\lvert T(\text{intra-hydride})\rvert$	286.4 ± 1.6 Hz	317.8 ± 3.3 Hz
$\lvert T(\text{inter})\rvert$	80.4 ± 3.1 Hz	88.1 ± 3.0 Hz
r.m.s. error in line fitting	1.7 Hz	1.0 Hz
$\lvert S_{zz}\rvert$	0.0367 ± 0.0002 Hz	0.0410 ± 0.0001 Hz

Indirect couplings between methyl and hydride protons were taken as zero [3] and the indirect couplings between magnetically equivalent nuclei do not affect the spectrum.

Because of the nearly identical unit cells of (I) and (II) (see above), the geometry of the non-proton part of the molecule was assumed identical to the geometry of (II) (Table 2), as found in the single crystal X-ray diffraction study

TABLE 2

ASSUMED AND CALCULATED GEOMETRICAL PARAMETERS FOR (II)

Parameter	
r(intra-Me) [a]	1.780 Å
r(C—C) [b]	1.52 Å
r(C—Os) [b]	2.08 Å
r(Os—Os) [b]	2.84 Å
r(Os—H) [c]	1.82 Å
Angle Os—H—Os [c]	103°

[a] Assumed value from reference 1. [b] See text. [c] Calculated. See ref. 2 for a discussion of likely errors.

of this molecule [2]. S_{zz} was computed from eqn. 1 using r(intra-Me) and the observed T(intra-Me). A numerical integration program which evaluated T(inter) (the methyl-hydride proton dipolar coupling) from equation 1 for a rapidly rotating methyl group was used to obtain r(AD) (Fig. 1). In order to obtain a reasonable geometry it was necessary to take T(inter) to have the opposite sign to the other two couplings (owing to the nearly first-order nature of the spectrum, these signs are not determined unambiguously). Values of r(AD) and r(intra-hydride) were then used to calculate an osmium—(bridging) hydride proton distance of 1.82 Å (average) and an Os—H—Os angle of 103°. These values are identical within experimental error to those found for (I), which suggests that the coordination about each osmium atom is approximately octahedral [2].

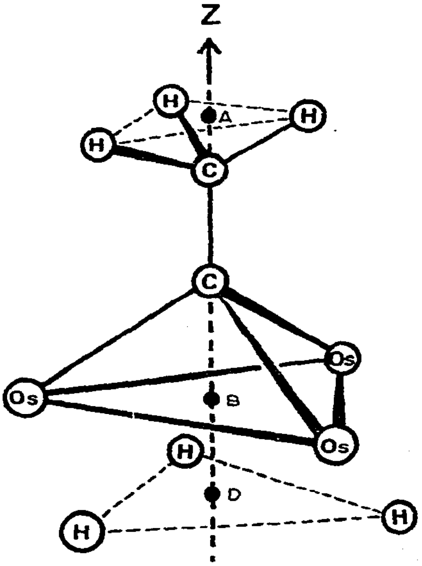

Fig. 1. Schematic diagram of $H_3Os_3(CO)_9CCH_3$ (II), not showing carbonyl groups.

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