

ferences in bond lengths between the *saldpt* complexes and our *saldien* complex are small at best. Sterically, the *saldpt* and *saldien* appear to be very similar with bond angles close to 90° and 180° as expected. Consequently, the difference in the chemical behavior of *saldpt* vs. *saldien* complexes is difficult to explain. One explanation may involve the tenacity of the sixth ligand in the *saldien* complexes compared to those of *saldpt*. The more rigid nature of *saldien* may provide a barrier to easy substitution of the sixth group, which would have a pronounced effect on the chemistry of *saldien* complexes. We are currently reexamining the chemistry of *saldien* complexes, particularly the cobalt case, with this concept in mind.

**Acknowledgment.** We thank the NSF Instrumentation Program for a grant for the purchase of the Nicolet diffractometer.

**Supplementary Material Available:** Tables of the final positional and thermal parameters, distances and angles, and hydrogen atom parameters (5 pages); a table of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

(15) Permanent address: Department of Crystallography, Institute of Chemistry, M. Curie-Skłodowska University, 20-031 Lublin, Poland.

Center for Molecular Structure  
Department of Chemistry  
University of Florida  
Gainesville, Florida 32611

A. E. Koziol<sup>15</sup>  
R. C. Palenik  
G. J. Palenik\*

Received July 22, 1986

## Articles

Contribution from Laboratoire de spectrochimie du solide and Laboratoire de chimie des polymères inorganiques, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

### ENDOR Study of a One-Electron 2:18 Reduced Fluoropolytungstate

D. Gourier,<sup>\*1a</sup> P. Doppelt,<sup>1b,c</sup> and C. Sanchez<sup>1a</sup>

Received November 18, 1985

One-electron electrochemical reduction of the  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{8-}$  polyanion led to a mixed-valence compound. Electron trapping has been studied by fluorine and proton ENDOR spectroscopy using  $\text{W}^{\text{V}}$  as a probe.  $^{19}\text{F}$  ENDOR has shown that the unpaired electron is trapped inside the equatorial rings of the 2:18 structure.  $^1\text{H}$  ENDOR has shown that the  $\text{WO}_5\text{F}$  polyhedron is not strongly solvated.

#### Introduction

Fluoropolytungstates have recently been reported.<sup>1-4</sup> One of them  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{8-2}$  belongs to the 2:18 series, the structure of which was described by Dawson.<sup>5</sup> This polyanion is composed of two  $\text{XW}_9\text{O}_{39}$  subunits that can be derived from the well-known Keggin structure<sup>6</sup> by removing one  $\text{WO}_6$  octahedron from three different edge sharing  $\text{W}_3\text{O}_{13}$  groups (Figure 1).

Two basic  $\text{WO}_6$  units can be distinguished in such polyanion, those belonging to  $\text{W}_3\text{O}_{13}$  caps and those belonging to equatorial belts.

$^1\text{H}$  and  $^{19}\text{F}$  NMR experiments performed<sup>2</sup> on  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{8-}$  have shown that the six fluorine atoms are distributed in two groups with three fluorine located at the corners of the two tetrahedral cavities surrounding the hydrogen atoms. Two sets of tungsten sites arise from such a structure, those  $\text{WO}_6$  situated at the caps of the polyanion and those  $\text{WO}_5\text{F}$  situated at the equatorial belts.

Like other polyanions, these fluoropolytungstates can be electrochemically reduced,<sup>8</sup> leading to a mixed valence compound. We recently used ESR and optical spectroscopy<sup>8</sup> to study the electron delocalization process in the one-electron-reduced  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{9-}$  compound.

The problem of electron trapping in the 2:18 structure is not yet clearly understood. Previous work<sup>9</sup> suggested that it should be trapped on one of the equatorial rings, i.e. on the  $\text{WO}_5\text{F}$  octahedron of the fluoropolytungstate unit  $((\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{8-})$ . However our ESR experiments<sup>8</sup> did not reveal any superhyperfine coupling with  $^{19}\text{F}$  nuclei even at very low temperature.

The aim of the present paper was to extend the characterization of the reduced polyanion  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{9-}$  by using ENDOR spectroscopy. This approach provides a much better resolution than is available with ESR.

#### Experimental Section

$(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{8-}$  fluoropolytungstate was prepared according to a procedure previously described.<sup>1</sup> The purity of this polyanion was determined by  $^{19}\text{F}$  NMR and chemical analysis.<sup>2</sup> Electrochemical reduction was performed under an argon atmosphere with a mercury cathode. The imposed potential (-150 mV vs. SCE) was given by a Tacussel PRT 500 LC. The reduction of the  $10^{-1}$  M solution ( $\text{HCl}$  0.1 M,  $\text{NaCl}$  1 M) was followed by coulometry using an IGSN integrator.

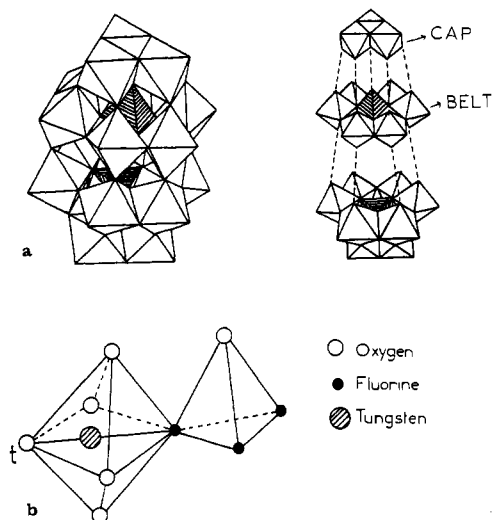
ESR and ENDOR spectra were recorded on a Bruker ER 220D ESR spectrometer equipped with the Aspect 2000 computer-monitored ENDOR unit. The maximum rf power in the ENDOR coil was 100 W. The modulation scheme employed was frequency modulation of the radiofrequency. All experiments were carried out at temperatures between 4 and 10 K produced by using a helium-flow cryostat ESR 9 from Oxford Instrument. The maximum ENDOR enhancement was obtained by using an hf power of 2 mW and the maximum rf power available. The  $10^{-1}$  M solution was merely frozen at these temperatures, without glass-forming additives.

#### Results and Discussion

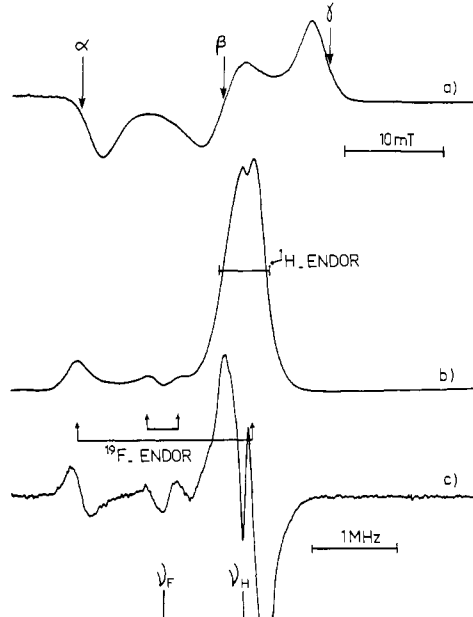
The ESR of a frozen solution at 4 K of the one-electron-reduced  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{9-}$  polyanion is shown in Figure 2a. This spectrum

- (1) (a) Laboratoire de spectrochimie du solide. (b) Laboratoire de chimie des polymères organiques. (c) Present address: Laboratoire de cristallographie et chimie, structurale, Institut Le Bel, Université L. Pasteur, 67070-Strasbourg Cedex, France.
- (2) Chauveau, F.; Doppelt, P.; Lefebvre, J. *Inorg. Chem.* **1980**, *19*, 2803. P. Doppelt, Thèse de Doctorat d'état, Université Pierre et Marie Curie, Paris 1981.
- (3) Chauveau, F.; Doppelt, P.; Lefebvre, J. *J. Chem. Res., Synop.* **1978**, 130; *J. Chem. Res., Miniprint* 1977; 1981 (*J. Chem. Res., Synop.* 155; *J. Chem. Res., Miniprint* 1937).
- (4) Doppelt, P.; Lefebvre, J. *Nouv. J. Chim.* **1981**, *5*, 463.
- (5) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 115.
- (6) Keggin, J. F. *Nature (London)* **1933**, *131*, 969.
- (7) Pope, M. T. *Heteropoly and Isopolyoxometallates*; Springer-Verlag: West Berlin, 1983; p 100.
- (8) Sanchez, C.; Livage, J.; Doppelt, P.; Chauveau, F.; Lefebvre, J. *J. Chem. Soc., Dalton Trans.* **1982**, 2439.
- (9) Prados, R. A.; Pope, M. P. *Inorg. Chem.* **1976**, *15*, 2547.

\* To whom correspondence should be addressed.



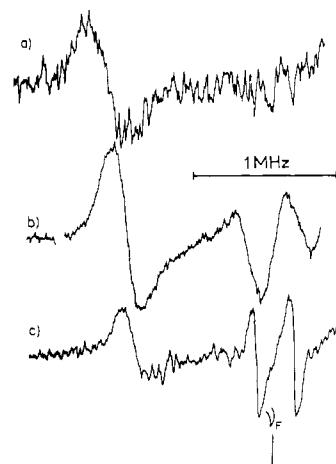
**Figure 1.** (a) Structure of  $[\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56}]^{8-}$  polyanion. (b) Partial view of the polyanion showing the central cavity and a belt site.



**Figure 2.** (a) ESR spectrum at 5 K of the one-electron-reduced  $[\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56}]^{8-}$  polyanion. The arrows indicate the magnetic fields corresponding to the ENDOR spectra of figures 2-4. (b) Spectrum obtained with integration of spectrum c. (c) ENDOR spectrum obtained with magnetic field setting  $\beta$ .  $\nu_F$  and  $\nu_H$  indicate the RMN frequencies of  $^{19}\text{F}$  and  $^1\text{H}$  nuclei.

is typical of a W<sup>V</sup> ion in a rhombic ligand field. No hyperfine coupling with the 14% abundant  $^{183}\text{W}$  nucleus ( $I = 1/2$ ) is observed. This is a general feature of the tungsten polyanions, due to the large ESR line width.<sup>8-10</sup> For the same reason, superhyperfine (shf) interactions with  $^{19}\text{F}$  and  $^1\text{H}$  nuclei are not resolved.

The ESR spectrum can be only described by the three magnetic parameters  $g_x = 1.811$ ,  $g_y = 1.852$ , and  $g_z = 1.917$ . These values were obtained by computer simulation of the ESR spectrum by using a Gaussian line shape ( $\Delta B = 3$  mT) and are in good agreement with those previously reported.<sup>8,9</sup> The ENDOR spectrum shown in Figure 2c was obtained by partially saturating the ESR spectrum at the magnetic field  $B_0$  labeled  $\beta$  while sweeping the rf field. With this field setting the ENDOR spectra clearly exhibit two different sets of components. The strongest one is an intense pair of closely spaced and broad lines centered



**Figure 3.**  $^{19}\text{F}$  ENDOR spectra. Spectra a-c correspond to magnetic field settings  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively (see Figure 2a).

at the proton frequency  $\nu_H$ . This response results from purely dipolar coupling of the unpaired electron spin with surrounding protons. In addition we observed other ENDOR components centered at the nuclear frequency  $\nu_F$  of the  $^{19}\text{F}$  nucleus. The  $^{19}\text{F}$  ENDOR line at high frequency is hidden by the proton ENDOR components. However the presence of the  $^{19}\text{F}$  ENDOR line is deduced from the distortion it produces on the high-frequency part of the proton ENDOR signal, as shown on the integrated spectrum in Figure 2b.

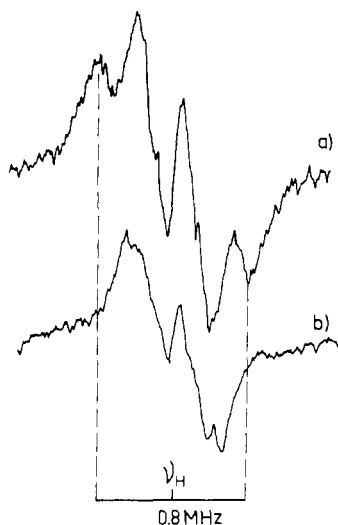
**$^{19}\text{F}$  ENDOR.** For the interpretation of the fluorine ENDOR spectra, we have to determine if the two pairs of lines belong to one or two different nuclei. This is possible by saturating the low- and high-field sides of the ESR spectrum (position  $\alpha$  and  $\gamma$  in Figure 2a). With the magnetic field set at position  $\alpha$ , we saturate only those molecules which have their  $g_z$  tensor axis parallel to  $B_0$ .<sup>11</sup> Since both  $\text{WO}_6$  and  $\text{WO}_5\text{F}$  polyhedra of the polyanion structure have a short  $\text{WO}_t$  bond (about 1.7 Å,  $\text{O}_t$  being the terminal oxygen), the  $z$  axis of the  $g$  tensor is almost collinear to this bond. The corresponding ENDOR spectrum is shown in Figure 3a. With this field setting the spectrum is very simple and consists of a single and nearly symmetrical ENDOR line corresponding to a W-F hyperfine (hf) coupling of 2.3 MHz. In contrast the ENDOR spectrum shown in Figure 3c, obtained with field setting  $\gamma$ , corresponds to molecules which have their  $g_x$  tensor axis parallel to  $B_0$ . In this case three ENDOR lines are resolved, corresponding to two hf couplings of 0.27 and 1.94 MHz. Since the field setting  $\gamma$  selects molecules with a specific orientation, the observation of two different hf interactions indicates that we are dealing with two different kinds of fluorine nuclei. If only one fluorine is involved in the ENDOR spectrum, the two pairs of lines should collapse when  $B_0$  is shifted gradually from position  $\beta$  to  $\gamma$ .<sup>12</sup> Consequently two different W-F couplings can be distinguished: one almost purely isotropic with  $|A_{\text{max}}^{\text{F}}| = 2.3$  MHz and  $|A_{\text{min}}^{\text{F}}| = 1.94$  MHz corresponding to a near fluorine nucleus, and a smaller coupling of  $\sim 0.27$  MHz corresponding to distant fluorine nuclei.

The existence of two very different types of fluorine atoms can be explained only if the electron is trapped on one of the belt sites, as previously proposed.<sup>9</sup> In that case one fluorine is directly bonded to the tungsten ion ( $\text{W-F} = 2.3$  Å) while the two others are more distant. The fact that the two extrema of the hf coupling for the near fluorine are obtained when  $B_0$  is respectively parallel and perpendicular to the short  $\text{WO}_t$  bond confirms this interpretation. In contrast, if the electron is trapped in one of the cap sites, the three fluorines are distant and should give rise to small, and almost purely dipolar coupling. Furthermore, the W-F directions are not collinear to the short  $\text{WO}_t$  bond in that case, and consequently the hf coupling measured when  $B_0$  is set at position  $\alpha$  and  $\gamma$  should

(10) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M. *J. Am. Chem. Soc.* **1983**, *105*, 6817.

(11) Rist, G. H.; Hyde, J. S. *J. Chem. Phys.* **1970**, *52*, 4633.

(12) Hoffman, B. M.; Martinsen, J.; Venters, R. A. *J. Magn. Reson.* **1984**, *59*, 110.



**Figure 4.**  $^1\text{H}$  ENDOR spectra. Spectra a and b correspond to magnetic field settings  $\alpha$  and  $\gamma$ , respectively (see Figure 2a).

not correspond to the extrema, contrary to the experimental results.

Owing to the short W–F distance of 2.3 Å,<sup>5</sup> the hf coupling appears surprisingly small and isotropic. This implies that the anisotropic part of the W–F coupling is very small ( $|A^F_p| = 0.1$  (4) MHz) and that the hf interaction is dominated by a small isotropic coupling ( $|A^F_s| = 2.0$  (8) MHz). Such a small value for  $A^F_{\text{iso}}$  can be explained considering the electronic ground state. Because of the short  $\text{WO}_t$  bond, the unpaired electron lies in the nonbonding  $5d_{xy}$  orbital, which is perpendicular to the  $\text{O}_t\text{W–F}$  direction. Consequently a direct transfer of fluorine 2s spin density to this  $5d_{xy}$  orbital is forbidden by symmetry.<sup>13</sup> If this mechanism is allowed, it should give rise to a large and positive value for  $A^F_s$ . However a small and negative value for  $A^F_s$  may result from a polarized transfer of fluorine 2s spin density to the empty  $5d_{z^2}$  orbital.<sup>13</sup> Furthermore a small and positive value is also possible if there exists a small admixture of  $5d_{z^2}$  in the  $5d_{xy}$  ground state. This implies a symmetry  $C_2$  or  $C_3$  for the  $\text{WO}_5\text{F}$  polyhedron, consistently with the crystallographic data, which indicate a  $C_3$  symmetry in nonreduced Dawson polyanions.<sup>5</sup>

The anisotropic part of the hf coupling  $|A^F_p| \approx 0.14$  MHz is considerably smaller than the value  $A^F_d \approx +6$  MHz expected from a point ion dipole expression  $A^F_d = gg_N\beta\beta_N/r^3$  with  $r = 2.3$  Å. This implies that the positive value of  $A^F_d$  is compensated by an important negative contribution to the hf coupling.

**$^1\text{H}$  ENDOR.** The proton matrix ENDOR signal obtained by saturating the ESR spectrum at position  $\beta$  is shown in Figure 2c. Despite this field setting, which gave the best sensitivity, we were unable to detect local ENDOR transitions.

However this signal clearly exhibits a resolved structure when  $B_0$  is set at position  $\alpha$ , corresponding to the selection of molecules with their  $\text{O}_t\text{–W}^V\text{–F}$  axes nearly parallel to  $B_0$  (Figure 4a). A pair of lines separated by 0.76 MHz, which appears only with this field setting, is absent when  $B_0$  is perpendicular to the  $\text{O}_t\text{–W}^V\text{–F}$  axis (field setting  $\gamma$  and  $\beta$ ; Figures 4b and 2c). These features suggest that the unpaired electron spin interacts with one or several

protons oriented approximately along the  $\text{O}_t\text{–W}^V\text{–F}$  direction ( $A^H_{\parallel} = +0.76$  MHz). The other part of the ENDOR signal centered at  $\nu_H$  corresponds to interactions with more distant protons and also to the perpendicular part of the hf coupling with the near protons. It is tempting to attribute this proton to the hydrogen inside the tetrahedral cavity  $\text{OF}_3$ . However two arguments invalidate this hypothesis:

(i) Since the proton is located approximately along the  $g_z$  tensor axis and the unpaired electron spin is trapped in the nonbonding  $5d_{xy}$  orbital, the W–H interaction should be purely dipolar. The proton in the tetrahedral cavity is situated at about 3.5–4 Å from the  $\text{W}^V$  probe, which should give rise to a larger shf coupling ( $A^H_d \approx +1.5$  MHz) than those observed ( $A^H_d \approx +0.4$  MHz).

(ii) A similar  $^1\text{H}$  ENDOR signal was observed in photoreduced  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  polyanion<sup>16</sup> with Keggin structure<sup>6</sup> in which the tetrahedral cavity contains a phosphorus atom instead of a proton.

Thus the observed ENDOR signal corresponds to protons located outside the polyanion. A proton trapped at the terminal oxygen  $\text{O}_t$  gives rise to strong dipolar interaction<sup>14</sup> while protons located at bridging oxygen W–O–W would be characterized by strong isotropic and dipolar coupling values.<sup>14</sup> The small coupling value measured corresponds to a W–H distance of about 6 Å, which is too large to be consistent with a proton located on the  $\text{WO}_5\text{F}$  polyhedron. It is more likely that these protons belong to the first shell of solvent molecules. However the results clearly indicate that these molecules are not randomly distributed but that the nearest  $\text{H}_2\text{O}$  molecules are approximately oriented along the  $\text{O}_t\text{–W–F}$  direction.

One unanswered issue is the lack of an ENDOR signal corresponding to the proton of the  $\text{OF}_3$  tetrahedral cavity. In the nonreduced polyanion  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{8-}$  this proton was detected by NMR.<sup>2</sup> Recent ENDOR experiments performed on  $[\text{PVW}_{17}\text{O}_{62}]^{8-}$   $\alpha_1$  and  $\alpha_2$  isomers<sup>15</sup> have shown that  $^{31}\text{P}$  ( $I = 1/2$ ) nuclei located inside the tetrahedral cavity can be readily detected. In addition NMR studies<sup>3,4</sup> performed on Keggin fluoropolytungstates have shown that these central protons are located near the oxygen atom and rotate around the ternary axis of the tetrahedral cavity. These compounds also exhibit proton exchange properties.<sup>4</sup> The strong broadening of the  $^1\text{H}$  NMR transitions observed in the  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{9-}$  polyanion<sup>2</sup> is also consistent with such proton mobility. Let us now consider the ENDOR response of this proton. Since it is trapped on the oxygen atom of the central cavity  $\text{OF}_3$ , the shf coupling is most probably purely dipolar. The slow motion of this proton would partially average this dipolar interaction, which should produce an important broadening of the ENDOR transitions.

## Conclusion

The present work represents the first ENDOR measurements on polyanions. The enhanced resolution offered by this technique provides considerable insight concerning electron trapping in this material. Fluorine and proton ENDOR spectra were consistent with one electron trapped at one tungsten ion located inside the equatorial belts of  $(\text{H}_2\text{W}_{18}\text{F}_6\text{O}_{56})^{9-}$ . They also indicate that the polyanions are not strongly solvated; i.e., there is no proton trapped on the  $\text{WO}_5\text{F}$  polyhedra. Investigations of other tungsten and vanadium polyanions are currently under way.

**Acknowledgment.** The technical assistance of D. Simons is gratefully acknowledged.

(13) Owen, J.; Thornley, J. H. M. *Rep. Prog. Phys.* **1976**, *29*, 675.  
 (14) Atherton, N. M.; Shackleton, J. F. *Mol. Phys.* **1980**, *39*, 147.  
 (15) Gourier, D.; Sanchez, C.; Fournier, M., submitted for publication.

(16) Unpublished results.