

The demetalation step is itself rather slow and is not detected by cyclic voltammetry, even at scan rates as low as 20 mV/s. Also, the demetalation of PbPc is clearly induced by reduction of the ligand. This is at variance with mechanisms for demetalations of silver and thallium porphyrins, where the central cation is reduced and then expelled owing to the large increase of its size that the ligand cannot accommodate.²⁶ It is in agreement, however, with a similar mechanism that we

have observed for reduced HgTPP in bonding solvents such as pyridine.²⁷

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Registry No. PbPc, 15187-16-3; Pc³⁻, 90741-23-4; Au, 7440-57-5; Pt, 7440-06-4; Hg, 7439-97-6; Pb, 7439-92-1.

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Electrochemical and Photochemical Reduction of Decatungstate: A Reinvestigation

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The electrochemical study of the potassium, tetrabutylammonium and tributylammonium salts of Wy strongly suggests that they contain the $(W_{10}O_{32})^{4-}$ anion, the structure of which has been described by Fuchs. The observed differences in electrochemical behavior are assigned to medium effects (i.e., solvent, acidity, counterions). The complete optical spectrum of the 1e-reduced species has been obtained for the first time. It exhibits a new band around 6500 cm^{-1} , which seems characteristic of the presence of quasi-linear W-O-W bridges, as already observed in 2/18 structures. The low-temperature ESR spectrum has been recorded for the first time, and the orthorhombic spectrum is consistent with a localization in equatorial sites. The photochemical reduction gives the same reduced species as the electrochemical reduction.

Introduction

During the course of a study on the electrochromic properties of tungstic acid gels,² we found that colloidal solutions obtained through acidification of a tungstate solution contained appreciable amounts of decatungstate $(W_{10}O_{32})^{4-}$. This polyanion exhibits a marked photochromism in the presence of an organic reducing agent. It was thus interesting to correlate its photochemical and electrochemical behaviors.

The first electrochemical study was performed by Boyer.³ At this time, the polyanion called "Wy" was formulated as a dodecatungstate $(HW_{12}O_{39})^{5-}$. Later on, Termes and Pope⁴ gave some evidence for the identification of Wy with the tributylammonium decatungstate, described by Fuchs and having the structure⁵ depicted in Figure 1. However, some doubts remained since it was observed, in our laboratory, that the reversible reduction of the Wy polyanion in protic medium (pH 2.5) required $1/12$ faraday/mol of tungsten. Furthermore, despite of their precautions, Termes and Pope's experiments were not carried out in a strictly aprotic medium, owing to the use of $HNBu_3^+$ as counterion. Finally, it appeared that the published electronic spectra of the reduced species were not complete and that no ESR spectra were reported. This led us to reinvestigate the properties of the reduced decatungstate ions. Very recently, a similar study was reported

by Yamase,⁶ but still without any detailed analysis of the electronic and ESR spectra.

In the present study, we used three different salts: (i) the $HNBu_3^+$ salt, since it was used in the crystal structure determination by Fuchs et al.;⁵ (ii) the NBu_4^+ salt, since it contains a proton-free counterion; (iii) the K^+ salt, since it was the first characterized compound and allows an easy electrochemical reduction in water.

Experimental Section

(i) Sample Characterizations. Thermogravimetric analysis (TG) coupled with careful spectroscopic measurements throughout the sample preparation and purification allowed us to define unambiguously the compounds. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as KBr pellets; TG curves were carried out in air on a Cahn RG electrobalance.

(ii) Studied Samples. $K_4(W_{10}O_{32}) \cdot 4H_2O$ (I). The potassium salt was prepared according to a procedure previously described.⁷ Anal. Calcd for $K_4W_{10}O_{32} \cdot 4H_2O$: WO_3 , 89.9; K_2O , 7.3; H_2O , 2.79. Found: WO_3 , 89.9; K_2O , 7.6; H_2O , 2.8. Calcd for $HW_{12}O_{39}K_4 \cdot 4H_2O$: WO_3 , 89.78; K_2O , 7.6; H_2O , 2.3. IR (cm^{-1}): 1005 (w), 985 (m), 970 (s), 960 (s), 944 (s), 910 (m), 895 (m), 805 (vs), 595 (w), 438 (m), 405 (m), 350 (w), 337 (w), 325 (w).

$((C_4H_9)_4N)W_{10}O_{32}$ (II). The tetrabutylammonium salt was prepared by mixing boiling solutions of 16 g of $Na_2WO_4 \cdot 2H_2O$ in 100 mL of water and 33.5 mL of 3 M HCl. After boiling for a few minutes, the clear yellow solution was precipitated by addition of an aqueous solution of tetrabutylammonium bromide (6.4 g/10 mL). The white precipitate was filtered, washed with boiling water and ethanol, dried with diethyl oxide, and then recrystallized in hot dimethylformamide to give yellowish prismatic crystals: yield 10 g;

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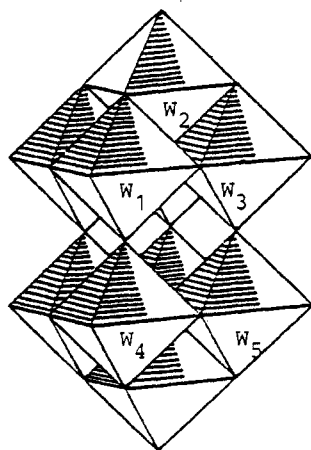


Figure 1. Structure of $(W_{10}O_{32})^{4-}$ according to ref 5.

TG for $((C_4H_9)_4N)_4W_{10}O_{32}$ (cation content) 29.2 (calcd), 29.2 (found). IR (cm^{-1}): 991 (vw), 958 (vs), 942 (s), 890 (s), 802 (vs), 582 (vw), 434 (m), 425 (sh), 405 (s), 345 (w), 331 (m).

$((C_4H_9)_3NH)_4W_{10}O_{32}$ (III). The tributylammonium salt was prepared following a slightly modified Fuchs procedure:⁵ to a solution of 35 g of $NaWO_4 \cdot 2H_2O$ in 200 mL of water was added 200 mL of 1 M HCl while boiling. The mixture was then quickly cooled down to 0 °C (1 min) and precipitated by addition of a solution of 2 M tributylammonium chloride (30 mL). The precipitate was filtered, washed with ethanol and ether, and then recrystallized in refluxing acetonitrile: yield 20 g of colorless crystals; TG for $((C_4H_9)_3NH)_4W_{10}O_{32}$ (cation content) 24.04 (calcd), 24.11 found. IR (cm^{-1}): 998 (w), 962 (s), 951 (s), 891 (s), 792 (vs), 745 (sh), 580 (w), 431 (m), 421 (sh), 394 (s), 341 (w), 329 (m).

(iii) **Electrochemical Studies.** These were performed as previously described.⁸ Amperometric titration (I/Q plot) permits accurate coulometric determination by the extrapolation of the curve. The zero-current point gives the exact quantity of electricity needed for stoichiometric reduction. The solvents used were either water containing a buffer and 0.25 M Na_2SO_4 or dimethylformamide (for UV and IR spectrography) containing 0.1 M tetrabutylammonium tetrafluoroborate. A saturated calomel electrode (SCE) with a double junction was used as reference electrode. The reduced solutions were transferred into spectrophotometer cells or ESR tubes by using an argon-inflated glovebag. Electronic and ESR spectra were recorded as already described.⁸

Results and Discussion

Identity of the Anions of the Three Salts. Electronic spectra of the three salts, dissolved in suitable solvents, exhibited the absorption band around 325 nm that seems characteristic of the $(W_{10}O_{32})^{4-}$ structure. A better identification can however be obtained by polarography, and consequently the three salts were studied by this method. The tetrabutylammonium salt, dissolved in DMF, exhibits two mono-electronic waves at -1.02 and -1.6 V on a dropping-mercury electrode. These waves are found to be reversible by cyclic voltammetry. The tributylammonium salt in the same medium gives a different polarogram with a bi-electronic wave at -0.82 V (reversible) and a higher one at -1.66 V (irreversible). Finally, the potassium salt can only be dissolved in water. Under such conditions it gives a third type of polarogram where the two waves are more positive and less spaced than for the other salts (-0.12 and -0.37 V at pH 2.5 in the presence of 0.25 M Na_2SO_4).

Thus, at first sight, the identity of the three salts was not obvious. The situation was clarified by additional experiments. Thus, addition of $HNEt_3^+Cl^-$ to a solution of the NBu_4^+ salt makes its polarogram identical with the one of the $HNBu_3^+$

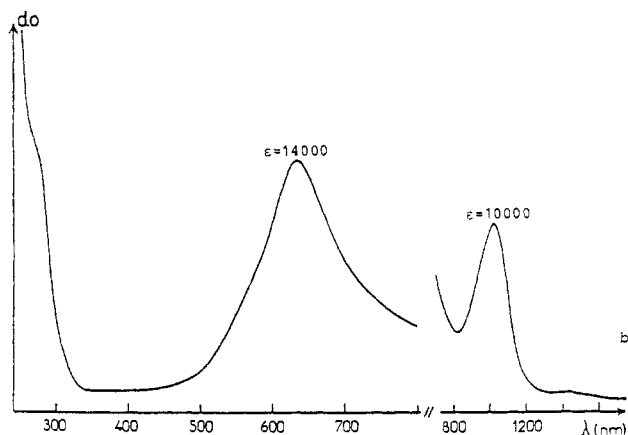
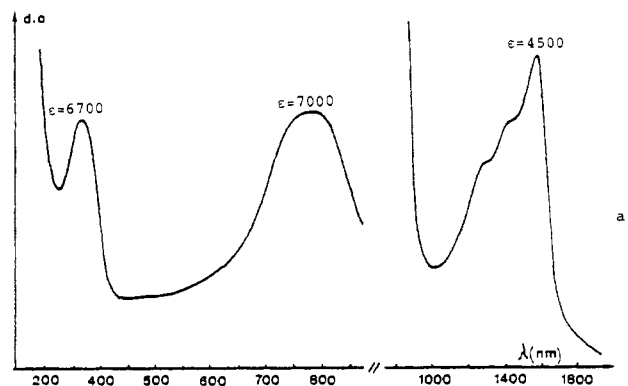


Figure 2. Electronic spectra of electrochemically reduced decatungstate: (a) 1e-reduced $(W_{10}O_{32})^{5-}$; (b) 2e-reduced $(H_xW_{10}O_{32})^{(6-x)-}$.

salt. This shows that the polarogram of the $HNBu_3^+$ salt has been perturbed by the H^+ ions brought by the $HNBu_3^+$ cations. The reversible wave at -0.82 V corresponds to the direct 2e reduction in a protic medium, while the irreversible wave at -1.66 V is ascribed to a proton reduction, since it can be suppressed by addition of $NBu_4^+OH^-$.

The potassium salt, which is normally insoluble in organic solvents, can be dissolved in DMF by adding a crown ether (18-crown-6) that can complex the K^+ ion. Then, the same polarogram as for the NBu_4^+ salt is observed, providing strong support for the identity of the anions of both salts. The difference between the polarograms in water and in DMF is ascribed to solvent and counterion effects. This last one is suggested by the drastic influence of Na^+ ions on the polarogram in DMF. The addition of $NaBPh_4$ causes a marked shift of the waves toward positive values, the effect being greater on the second wave.

Electrochemical Reduction. Controlled-potential reduction at -1.3 V of the NBu_4^+ salt in DMF yields the 1e-reduced from $(W_{10}O_{32})^{5-}$. Coulometry indicates 1 e/10 W atoms, thus confirming that the polyanion is decacondensed. The same experiment carried out in water at 0 °C with the K^+ salt (pH 2.5; -0.25 V imposed) needed 1 e/12 W atoms, in agreement with Boyer's results³ and later observations in our laboratory. However, the spectrum of the reduced species, which is very characteristic (see below), was identical with the one obtained in DMF. We believe that the coulometry in water is in error by default, owing to the presence of small amounts of pseudo-metatungstate, which is not reducible at the potential at which the electrolysis³ is performed. This pseudo-metatungstate can either be formed during the electrolysis by spontaneous evolution of decatungstate⁹ or be already present in the K^+ salt. The last hypothesis appears likely since a

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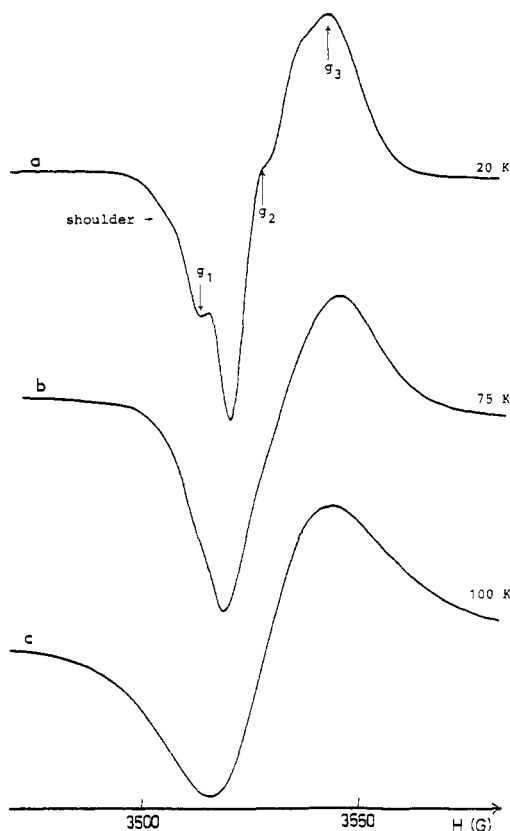


Figure 3. ESR spectra of 1e-reduced decatungstate ($\text{W}_{10}\text{O}_{32}$) $^{5-}$. Recording temperature: (a) 20 K; (b) 75 K; (c) 100 K.

careful observation of the Raman spectrum revealed extra bands belonging to a polyanion different from ($\text{W}_{10}\text{O}_{32}$) $^{4-}$.

The electronic spectrum of ($\text{W}_{10}\text{O}_{32}$) $^{5-}$ is shown in Figure 2a. Two new features that have never been reported before can be pointed out. First, the band around 325 nm, corresponding to the parent oxidized form has completely disappeared. The polyanion being extremely oxidizable, the appearance of this band in the spectrum of ref 4 could be ascribed to a partial reoxidation of the solution. ($\text{W}_{10}\text{O}_{32}$) $^{5-}$ exhibits a band at a longer wavelength (370 nm). Second, a very characteristic band with some fine structure is observed in the near-infrared range, around 1500 nm (see Figure 2a).

The ESR spectrum, recorded at 30 K on a frozen solution of ($\text{W}_{10}\text{O}_{32}$) $^{5-}$ in DMF, is shown in Figure 3a. It is typical of a W(V) ion in an orthorhombic ligand field. The g values are $g_1 = 1.848$, $g_2 = 1.842$, and $g_3 = 1.830$. A shoulder can be seen on the low-field side of the spectrum. It could correspond to an hyperfine line arising from the 14.8% abundant ^{183}W ($I = 1/2$).

A broadening of the ESR signal occurs above 50 K. g_1 and g_2 components collapse first, giving rise to an axial spectrum around 75 K (Figure 3b). A Lorentzian isotropic signal centered around $g = 1.84$ and about 27 G wide is observed at 100 K (Figure 3c). The line then broadens continuously, and the signal is not visible anymore above room temperature.

The 2e-reduced species could be easily prepared only in aqueous media and is thus formulated ($\text{H}_x\text{W}_{10}\text{O}_{32}$) $^{(6-x)-}$, with x most likely 2. It has been obtained either from the potassium salt electrolyzed at -0.4 V or from the tributylammonium salt electrolyzed in DMF at -1.0 V. In this last case, an excess of HNET_3^+ , acting as a proton donor, was found to be necessary. The electronic spectrum is given in Figure 2b; only the visible part was reported in previous works.^{3,4} We see that,

in addition to the intense 630-nm band responsible for the strong photochromic effect ($\epsilon = 14\,000\text{ M}^{-1}\text{ cm}^{-1}$), a sharp band is observed at 970 nm in DMF or 1024 nm in water. During the electrolysis process leading from the 1e to the 2e stage, the intensity of the ESR spectrum decreases steadily without change of the g value, suggesting that the 2e form is diamagnetic.

Photochemical Reduction. It has been known for some time that decatungstate solutions or salts turn blue when exposed to daylight in the presence of traces of organic solvents or impurities. If the solid compounds are pure and free from crystallization solvent molecules, no photochromic effect is observed. We studied this effect by irradiating solutions of the NBU_4^+ salt in DMF with a mercury-vapor lamp. The photochemical reduction required the addition of either ethanol or poly(vinyl alcohol). According to UV-visible spectroscopy, irradiation then leads to the same species as obtained by electrochemistry, i.e. ($\text{W}_{10}\text{O}_{32}$) $^{5-}$ and ($\text{H}_x\text{W}_{10}\text{O}_{32}$) $^{(6-x)-}$. Generally, a mixture of both forms is produced. However, the ratio of 2e species increases with the irradiation time, and it can even be obtained alone when the irradiation time is long enough (>1 h). A direct reduction to the 2e form occurs when the medium contains a large amount of ethanol (50–50 by volume). This can be related with the well-known tendency of polyanions to give bielectronic waves in protic media. The ESR spectrum of the photochemically reduced solutions shows the presence of ($\text{W}_{10}\text{O}_{32}$) $^{5-}$. However the low-temperature spectrum is slightly different from the one obtained by electrochemistry ($g_3 = 1.837$ instead of 1.830). This could be due to some slight modification of the local symmetry around W(V) arising from a change in the solvation or protonation state.

Electronic Structure of ($\text{W}_{10}\text{O}_{32}$) $^{5-}$. Several features in the electronic spectrum of ($\text{W}_{10}\text{O}_{32}$) $^{5-}$ suggest a unique electronic structure with extensive ground-state delocalization. The characteristic 325-nm charge-transfer band of the fully oxidized form has completely disappeared, showing that the overall electronic structure of the polyanion has been altered. By contrast, in heteropolyanions possessing the Keggin structure ($\text{XW}_{12}\text{O}_{40}$) $^{n-}$, the charge-transfer band does not disappear upon reduction but is only reduced in intensity.¹⁰ We should notice however that the 370-nm band of ($\text{W}_{10}\text{O}_{32}$) $^{5-}$ cannot, in principle, be assigned to such a transition since a blue shift for the oxygen to tungsten charge-transfer band would be anticipated upon reduction. The two bands at 370 and 780 nm are tentatively assigned to the d-d transitions ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ of W^{V} in C_{4v} symmetry. There is in particular a striking analogy with the spectrum of (WOCl_5) $^{2-}$.¹¹ However, the intensities are much stronger in ($\text{W}_{10}\text{O}_{32}$) $^{5-}$, which would imply a large amount of ground-state delocalization. For the 780-nm band, an intervalence nature could be also considered.

The 1500-nm band is more safely assigned to an intervalence transition, owing to (i) its position outside the usual range for d-d transitions, (ii) its asymmetrical shape with a fine structure, as predicted by the vibronic coupling (PKS) model,¹² and (iii) its solvent dependence (it shifts from 6470 cm^{-1} in DMF up to 6660 cm^{-1} in H_2O). The unusual position of this band, at a particularly low energy, seems intimately related to the presence of nearly linear W–O–W bridges, linking both halves of the polyanion. Similar low-energy intervalence transitions were observed¹³ in ($\text{As}_2\text{W}_{18}\text{O}_{62}$) $^{7-}$ and

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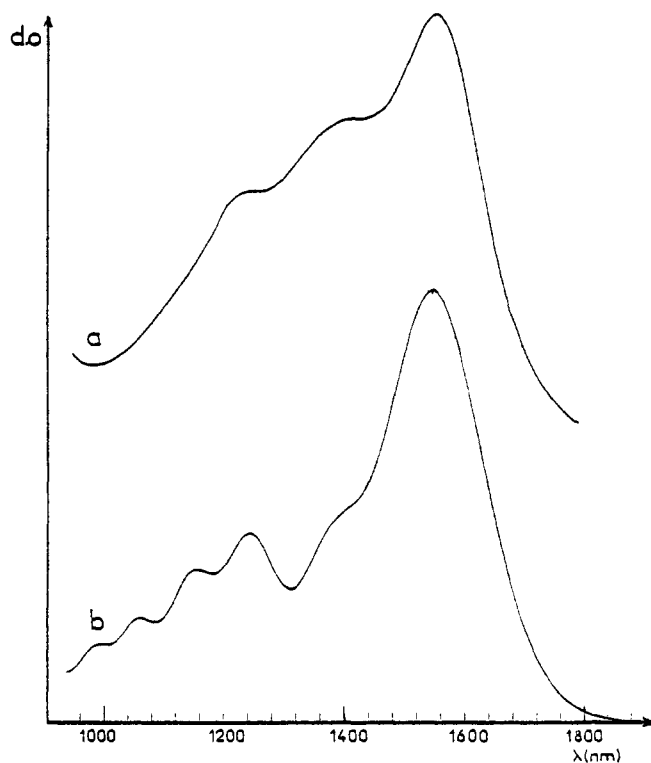


Figure 4. Intervalence-transfer absorption band for $(W_{10}O_{32})^{5-}$: (a) experimental; (b) simulated following PKS model.¹²

$(AsH_2W_{18}O_{60})^{8-}$. These polyanions also have dimeric structures with linear W–O–W bridges. We have argued elsewhere¹³ that a complete delocalization across this bridge could account for the low energy of these bands. In this hypothesis the intervalence band would correspond to an electron transfer between two pairs of WO_6 octahedra linked by the nearly linear bridges, i.e. between a pair such as W_1 --- W_4 (see Figure 1) and a pair such as W_3 --- W_5 .

A simulation of the intervalence band profile has been performed in the frame of the PKS model. This allows an experimental determination of the two basic parameters describing the mixed-valence system: ϵ , the electronic coupling parameter, and λ , the electron phonon coupling constant.¹² The vibrational quantum ($h\nu$) was taken as 500 cm^{-1} . The best results (see Figure 4) were obtained when $\epsilon h\nu = 3000\text{ cm}^{-1}$ and $\lambda^2 h\nu = 5000\text{ cm}^{-1}$. These values of the parameters correspond to a class II system, since $\epsilon < \lambda^2$, but nevertheless are very near to the class III edge.¹⁴

More information on the electronic structure can be obtained from ESR. The orthorhombic nature of the spectrum clearly shows that the reduction bears on the "equatorial" tungsten sites (W_1 for instance; Figure 1), instead of the outer most sites (W_2 for instance), which would give an axial spectrum.¹³ The hyperfine structure could give information on the amount of ground-state delocalization. In the case of $(W_6O_{19})^{3-}$, the unpaired electron is trapped on a single tungsten. The hyperfine structure is then clearly resolved with $A_{\perp} = 74\text{ G}$ and $A_{\parallel} = 158\text{ G}$.¹³ Unfortunately the resolution is not so good in $(W_{10}O_{32})^{5-}$, but if the shoulder on the low-field side of the spectrum is actually due to a hyperfine coupling, we could notice that no other hyperfine feature can be seen on the high-field side. This would mean that the hyperfine coupling parameter A is smaller than the spectrum width, i.e. 60 G . This would suggest a complete delocalization of the

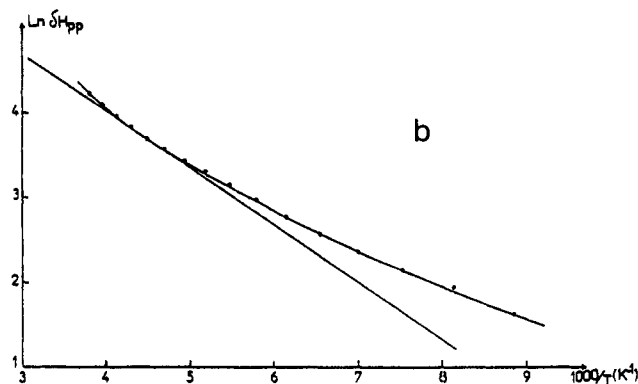
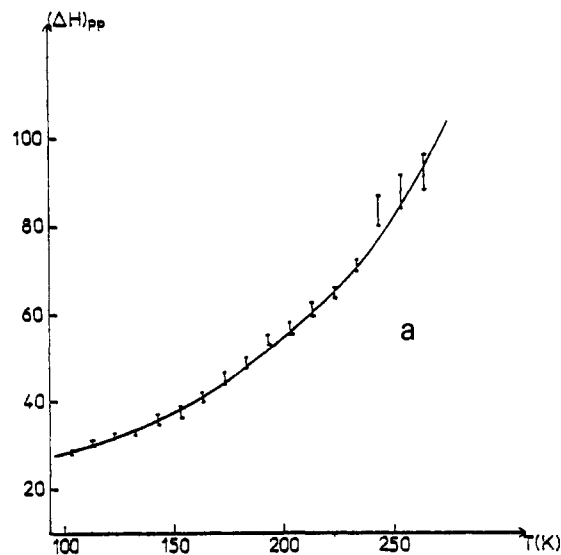


Figure 5. (a) Temperature dependence of the ESR line width ΔH_{pp} . (b) Plot of $\ln \delta H_{pp} = f(T^{-1})$ where δH_{pp} corresponds to the temperature-dependent part of the ESR line width.

unpaired electron over two tungsten atoms since, according to isotopic abundances, one should find 24% of W_2 pairs containing one ^{183}W ($I = 1/2$) and one other isotope ($I = 0$). Thus, the unpaired electron would interact half of the time with ^{183}W , giving a hyperfine parameter roughly half the value for a localized electron.

Finally, the broadening of the ESR signal with temperature can be used to determine the activation energy for thermal electron transfer. In the high-temperature range, where a single isotropic Lorentzian signal is observed, the ESR line width can be directly measured on the spectrum. Following an analysis previously described,⁸ the peak to peak line width $\Delta H_{pp(T)}$ can be expressed as

$$\Delta H_{pp(T)} = \Delta H_{pp(0)} + \delta H_{pp(T)}$$

The temperature-independent line width $\Delta H_{pp(0)}$ is obtained by extrapolation at low temperature of the $\Delta H_{pp(T)} = f(T)$ plot (Figure 5). This gives $\delta H_{pp(T)}$, which is assumed to be proportional to the hopping frequency $\nu = \nu_0 \exp(-E/kT)$. Thus, a plot of $\ln \delta H_{pp}$ vs. $1/T$ (Figure 5) gives the activation energy, which is found to be 0.06 eV . This low value is consistent with a weakly localized system and would correspond to an electron transfer between different pairs of WO_6 octahedra, according to the hypothesis above. The electron transfer inside a pair

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such as W_1 --- W_4 would not require any thermal activation energy.

Conclusion

Decatungstate appears to be a promising candidate for photochromic applications due to the high values of the extinction coefficients. Moreover, the simultaneous uptake of

two electrons in certain media should be useful for photocatalytic applications (water splitting for instance).

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Dynamic Intersystem Crossing in Solid Bis(phenanthroline)bis(cyanotrihydroborato)iron(II)¹

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Variable-temperature Mössbauer, magnetic susceptibility, and infrared studies of $Fe(phen)_2(NCBH_3)_2$ reveal the occurrence of a reversible, gradual singlet/quintet intersystem crossing above room temperature. Mössbauer spectra of the complex in the transition region are interpreted as showing the occurrence of a novel (for Fe(II)), fast singlet/quintet interconversion.

Introduction

The solid complexes $Fe(phen)_2X_2$ constitute a class of compounds in which the *cis*- $Fe(phen)_2X_2$ structure provides the opportunity, through the choice of X^- , for selection of the electronic ground-state configuration of Fe(II). With $X = Cl^-$, Br^- , and I^- the ground state is a quintet state,³ while for $X = CN^-$, $CNBH_3^-$, and $CNBPh_3^-$ the ground state is a singlet to temperatures well above ambient.⁴ With $X^- = NCS^-$ and $NCSe^-$ the ground electronic state changes, rather sharply, from singlet to quintet at temperatures of 174 and 232 K, respectively.⁵ For these last two complexes there is believed to be considerable cooperativity in the transitions,⁶ due to the importance of intermolecular interactions in the solid state. Emphasizing in another way the importance to intersystem crossing of intermolecular interactions in solution and solids is the fact that the complex with $X^- = NCBPh_3^-$ remains low spin to 400 K as a solid but exhibits rapid intersystem crossing at 273 K in CH_2Cl_2 solution.⁷

The phenomenon referred to here as "intersystem crossing" has been referred to in the literature as "spin crossover" and "spin equilibrium". Since the molecular event in question is clearly that of change in the spin multiplicity of the molecular wave function and since such a change is widely designated by experimentalists and theorists in all areas of science as intersystem crossing, we prefer the generally accepted semantics, particularly since this removes an unnecessary element of mystique from the phenomenon.

The purpose of this paper is to report our studies on certain variable-temperature properties of the compound $Fe(phen)_2(NCBH_3)_2$. Our earlier studies of this compound at room

temperature led to the conclusion that this compound exists as a spin triplet at room temperature.⁸ New experimentation on this compound at temperatures other than ambient shows that $Fe(phen)_2(NCBH_3)_2$ does not have a spin triplet ground state but that it exhibits a singlet/quintet intersystem crossing equilibrium that becomes pronounced only above room temperature. Variable-temperature Mössbauer studies of ⁵⁷Fe-enriched samples of $Fe(phen)_2(NCBH_3)_2$ further reveal new effects at the molecular level that are not found in the intersystem crossing of other Fe(II) intersystem-crossing compounds.

Experimental Section

Preparation of $KNCBH_3$. The compound was prepared according to a previously developed synthesis.⁹

Preparation of $Fe(phen)_2Br_2$. The compound was synthesized by a new method introduced by J. P. Zapata, which may also be used in making the Cl^- and NCS^- complexes.⁴ $Fe(phen)_3Br_2$ (6 mmol), prepared by literature methods,¹⁰ was refluxed (438 K) in 150 mL of dry dimethylacetamide (DMA). The color of the solution changed from red ($Fe(phen)_3Br_2$) to dark blue ($Fe(phen)_2Br_2$) (dark blue for Cl^- and purple for NCS^-). After removal of the heating mantle, 100 mL of benzene was added quickly to the refluxing solution through the reflux condenser. (*Caution:* large amounts of boiling benzene are produced.) The solid was filtered, washed with diethyl ether, and dried in vacuo over P_2O_5 at 373 K. Occasionally, unreacted $Fe(phen)_3Br_2$ would appear in the product; in such cases, the process was simply repeated with the crude product as the starting material.

- (1) Presented at the 185th National Meeting of American Chemical Society, Seattle, WA, 1983, Abstract INOR 259.
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- (8) Purcell, K. F.; Yeh, S. M.; Eck, J. *Inorg. Chem.* **1977**, *16*, 1708. König has cast an element of doubt on all claims of triplet ground state $Fe(phen)_2X_2$ complexes with his findings that certain of his complexes, previously interpreted as possessing triplet ground states, are actually composed of $Fe(phen)_3^{2+}$ cations and $Fe(dianion)_3^{3-}$ anions in which the cation has a singlet electronic state and the anion exhibits a sextet state. His syntheses are performed in water, where air oxidation may occur. Rigorous exclusion of air leads to, for example, $Fe(phen)_2(ox)\cdot 5H_2O$, which exhibits intersystem crossing. $Fe(phen)_2(NCBH_3)_2$ is not a $Fe(phen)_3^{2+}$ salt; the cause of our earlier assignment of a spin triplet stems from the unusual effects reported here and their failure to appear in the IR and Mössbauer spectra at room temperature. See: König, E.; Ritter, G.; Goodwin, H. A. *Inorg. Chem.* **1981**, *20*, 3677; König, E.; et al. *Inorg. Chim. Acta* **1979**, *35*, 239.
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