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Electron Distribution in the Two-Electron Reduced Isopolytungstate $[W_{10}O_{32}]^{6-}$

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Reduced polyoxometalates form an important class of polynuclear mixed-valence compounds.[1−3] They are commonly called "blues", or "heteropoly blues" in the case of heteropolyoxometalates, due to their intense blue color generated by the intervalence electron transfer. Oxidized precursor polyoxometalates can often accept not only one but several "excess" electrons. As a rule, polyoxoanions (POA) conserve their structures under reduction. In the chemistry of mixed-valence clusters, the distribution pattern of the excess electrons in binuclear clusters can be referred to as localized or delocalized.[4] However, the high nuclearity and the high symmetry of POA sometimes result in electron delocalization over a part of the metal−oxygen framework. The electron distribution of excess electrons in POA has a number of important chemical and physical consequences.[5−12] It is an essential factor determining possible protonation sites in the POA structure whereas the modifications of the protonation state can be used to tune the redox potentials. Besides, delocalization, not antiferromagnetic exchange, is responsible for stabilization of a spin-singlet state in two-electron reduced POA.[13−15]

The recent NMR studies by Duncan and Hill revealed an asymmetric excess electron distribution in the two-electron reduced unprotonated isopolytungstate $[W_{10}O_{32}]^{6-}$.[8] The decatungstate POA is made of two compact W_5O_{14} moieties linked by four corner-sharing oxygen atoms (Figure 1). Each W_5O_{14} fragment consists of five edge-sharing tungsten−oxygen octahedra. Therefore, the total symmetry of the POA is D_{4h}. Eight equatorial and two terminal sites can be distinguished for the tungsten atoms. The equatorial sites and the terminal sites form each a set of equivalent sites. The experimental results indicate that the two excess electrons in the two-electron reduced isopolytungstate are mainly distributed between the eight equatorial sites. Since only two lines are observed in ^{183}W NMR spectra, i.e., one for the equatorial sites and one for the terminal ones, a quasi-homogeneous two-electron distribution over the equatorial sites can be suggested. This suggestion seems quite surprising as the electronic repulsion favors a charge distribution in which the electrons are located at the more distant terminal tungsten sites. Apparently, the gain in the energy due to the electron delocalization between equatorial sites exceeds the loss associated the electronic repulsion. A simple model is proposed here which permits analysis of the origin of bielectronic distributions in the doubly reduced decapolytungstate.

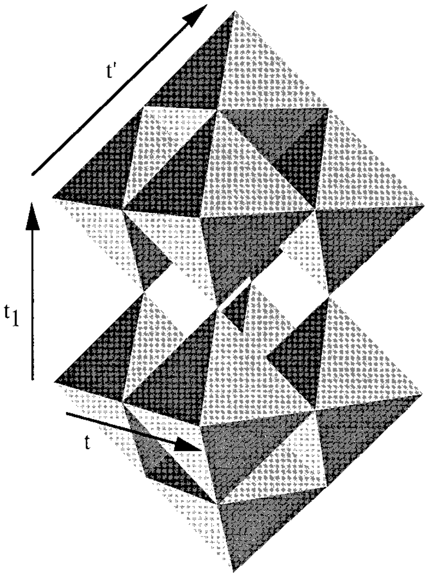

Figure 1. Polyhedral model of $[W_{10}O_{32}]$. The arrows show possible types of electron transfer with corresponding parameters.

We suppose that at the *i*th tungsten site the excess electron can occupy a localized electronic state ϕ_i which has mainly d character but is delocalized toward oxygen ligands. Our approach is based on the model Hamiltonian originally introduced in solid-state physics and called the Hubbard Hamiltonian.[16] Three basic interactions are included in this Hamiltonian: (i) the resonance interaction between the localized electronic states (the Hückel integral) which is responsible for electron transfer and is usually taken into account only for nearest neighbors; (ii) the Coulomb repulsion between electrons localized at different sites; (iii) the energy cost associated with two spin-paired excess electrons which occupy the same localized orbital (the Hubbard *U* parameter). We recently used a similar approach to explain the origin of the magnetic properties of the Keggin-type heteropoly blues with a paramagnetic heteroatom.[14]

Two electron-transfer parameters describe the interactions between the edge-sharing octahedra. One of them (t) connects four equatorial sites of each W_5O_{14} unit, another (t') gives the interaction between a terminal site and the nearest equatorial

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metal atoms. The Hückel integrals between the corner-sharing octahedra are much smaller, and we will retain only the coupling (t_1) between the two W_5O_{14} fragments.

We also approximate the intercenter Coulomb repulsion between the electrons at *i*th and *j*th centers by the simplest form $V(R_{ij}) = ke^2/R_{ij}$, where R_{ij} is the distance between two metal sites and k is the effective screening coefficient. If we consider the $W_{10}O_{32}$ structure as consisting of ideal octahedra with all W−O−W angles equal to 90 or 180°, all R_{ij} could be expressed through the average tungsten−oxygen distance $a = 1.95$ Å.[17]

The electronic configuration of tungsten atoms in the oxidized decatungstate $[W_{10}O_{32}]^{4-}$ is d^0, so the doubly reduced POA can be treated as a two-electron system. Only spin-singlet and -triplet electronic states are possible. The double exchange interaction[18] which is due to the electron delocalization between paramagnetic metal cores does not appear in POA. As polyoxometalates reduced by an even number of electrons are generally diamagnetic, we only consider spin-singlet electronic states. The orbital parts of the singlet wave functions for radical (the two electrons being localized at different sites) and ionic (the two electrons being localized at a single site) states, ϕ_{ij}^{S} and ϕ_{ii}^{S} respectively, are symmetric against electron permutation and can be written as

$$\phi_{ij}^{S} = \frac{1}{\sqrt{2}}(\phi_i(1)\phi_j(2) + \phi_i(2)\phi_j(1)) \tag{1}$$

$$\phi_{ii}^{S} = \phi_i(1)\phi_i(2)$$

Taking into account the decatungstate structure 45 radical states and 10 ionic states can be formed. The matrix of our model Hamiltonian can be built in the basis of these 55 functions according to the following simple rules:

$$\langle \phi_{ii}\, H_{\mathrm{m}}\, \phi_{ii}\rangle = U$$

$$\langle \phi_{ij}\, H_{\mathrm{m}}\, \phi_{kl}\rangle = t_{ik}\delta_{jl} + t_{jl}\delta_{ik} + t_{il}\delta_{jk} + t_{jk}\delta_{il}\ (i \neq j,\, k \neq 1) \tag{2}$$

$$\langle \phi_{ij}\, H_{\mathrm{m}}\, \phi_{kk}\rangle = \sqrt{2}t_{ij}(\delta_{ik} + \delta_{jk})$$

The formulas for matrix elements (2) are only valid if the orbitals ϕ_{i} are orthogonal. Diagonalization of the Hamiltonian matrix gives the energies and eigenfunctions of our bielectron system in the space of five free parameters: t, t', t_1, U, k. The charge distribution between the 10 tungsten sites can be determined from the ground-state wave function which takes the form

$$\Phi_0 = \sum_{i,j} c_{ij}^{0}\, \phi_{ij} \tag{3}$$

However, the number of free parameters in our theory can be reduced. The intracenter electronic repulsion parameter U was estimated earlier from the intervalence band of the tetranuclear tungsten clusters in which metal atoms are also placed in an octahedral oxygen environment.[19] We use in all calculations the estimated value $U = 7000$ cm^{-1}.[19] The relationship between the one-electron transfer parameters t and t' has been estimated from a simple Hückel-type calculation. We performed calculations on the $W_5O_{18}^{7-}$ cluster, where the W_5O_{14} fragment is completed by four bridging oxygen atoms and the total charge corresponds to valence state $4W^{VI}+1W^{V}$. The Cartesian frame has been chosen with the z axis perpendicular to the equatorial plane. The excess electron occupies the HOMO which involves d_{xz} and d_{yz} orbitals of the equatorial tungsten atoms and the d_{xy} orbital of the terminal metal atom. The functions centered at the equatorial atoms contribute with the same weight, while the contribution of the terminal tungsten atom is less important. The same system can be modeled within our phenomenological approach by a five-center square-pyramidal cluster with one excess electron. Two parameters for electron transfer, t and t' are taken into account in the model cluster (see Figure 1). If we set $|t/t'| \approx 2.3$ we get the same weight ratio of the terminal and four base centers in the ground-state wave function as the one found from the Hückel calculation for the d functions of corresponding tungsten atoms. Under this requirement we varied t and t_1 in the range 4000−6000 cm^{-1}. Earlier estimations[19] of the electron-transfer parameters between tungsten−oxygen octahedra with shared corner (analogous to our t_1) gave the value 8000 cm^{-1}. However, in our case the conditions for orbital overlap are less favorable and lead to a reduced value of t_1. The electronic repulsion at shortest metal−metal distance $\sqrt{2}a$ was varied in the range 2000−4000 cm^{-1}, as in any case it must be much smaller than the one-center repulsion U.

The electronic Hamiltonian was diagonalized for different values of parameters and the composition of the ground state wave function was analyzed. It was found that for any combination of parameters the bielectronic ground state has a negligibly small probability density at the terminal sites. It means that almost all electronic density of the excess electrons is distributed between equatorial sites. Although all eight equatorial sites are equally populated, the total asymmetry of electronic distribution in the doubly reduced decatungstate is much higher than that of the singly reduced system. The weight of different types of the bielectronic wave functions of different types can be estimated by adding up the squares of the corresponding coefficients in the ground-state wave functions. We analyzed the weight of the bielectronic valence configurations in the ground state and found that the total contribution of the configurations describing two electrons at different equatorial planes varies between 0.60 and 0.65. This value is not very sensitive to the interplane electron-transfer t_1. We conclude that the delocalized electronic distribution is due not to strong electronic interaction through quasilinear oxygen bridges between equatorial layers (as was proposed for the isostructural polyoxomolybdate cluster[12]) but to the correlated delocalization of two electrons within two equatorial planes.

Similar electronic effects are probably responsible for the nonequivalence of metal sites in the two-electron reduced Wells−Dawson heteropoly tungstate a-$[P_2W_{18}O_{62}]^{8-}$.[20] The electronic density of two excess electrons is homogeneously distributed within two “delocalization belts”. Evidently, electron distribution patterns are also strongly determined by vibronic interaction.[21,22] The participation of vibrations can transform

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an electron pair into bipolaron.[23] As it was recently shown, the intramolecular electron delocalization can also modify the kinetics of redox processes by reducing the reorganization energy.[24] These effects will be addressed in future publications.

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