DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 17, No. 5, 1973
Printed in Republic of Korea

Note

케긴형 헤테로다중 블루들의 전자 구조. 분자궤도론적 연구

蘇 玄 秀
서강대학교 이공대학 화학과

(1972. 12. 26 접수)

Electonic Structure of Keggin-Type Heteropoly Blues. A Molecular Orbital Approach

Hyunsoo So
Department of Chemistry, Sogang University, Seoul, Korea

(Received Dec. 26, 1972)

Heteropoly blues with the Keggin structure[1] have been the subjects of two recent papers by Pope, *et al.*[2,3] They studied the formation and properties of some blues by polarographic and potentiometric methods and measured their electron spin resonance and electronic spectra. So a considerable amount of experimental data is available; however, many of these data are yet to be interpreted.

One of the basic questions is whether the extra electron (or electrons) is delocalized over the whole anion or localized on a single metal ion. Pope *et al.* prefer the latter model to the former. But their observation that two-electron blues show no esr absorptions is much easier to interpret in terms of the former model.[3] Can the electronic spectra be interpreted also in terms of the delocalized molecular orbitals? With this question in mind, we have derived simple molecular orbitals for Keggin-structure heteropoly blues and obtained their energies as functions of Coulomb and resonance integrals.

Let us consider a 12-tungstate anion. This anion belonging to the point group *Td* consists of 12 WO_6 groups, the approximate symmetry of which is C_{4v} (See *Fig.* 1). In order to derive molecular orbitals, we use the five *d* orbitals on each metal and mix them with appropriate *d* orbitals on all other centers and with appropriate oxygen orbitals. Then it is noticed that a *d* orbital can mix only with its own type, if d_{xz} and d_{yz} orbitals are considered to be of the same type. Thus there are four subsystems of molecular orbitals based on different types of the *d* orbital. In each subsystem the molecular

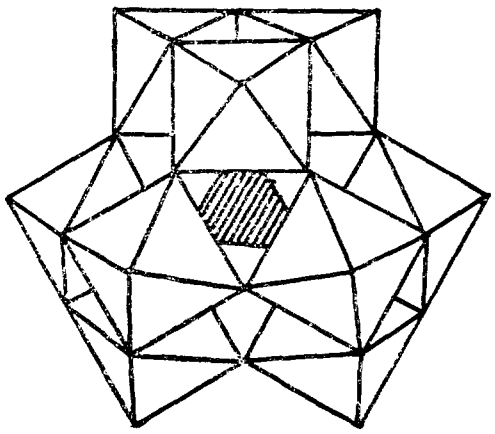


Fig. 1. Polyhedral model of the Keggin-structure anion

orbital ordering is determined by metal-metal and metal-ligand interactions. Of course, a molecular orbital of a certain subsystem can mix with molecular orbitals of the same symmetry of other systems. But the structure of the anion makes this mixing zero or negligibly small.

Since we are not prepared to evaluate the exact magnitudes of all interactions, we assume that the metal-ligand interactions lift the d manifolds bodily upward without splitting them. The manifold ordering is the same as the d orbital ordering in a WO_6 moiety. Here the terminal oxygen is of oxo type and the local symmetry is close to C_{4v}. If the W=O bond is taken as the z axis and the x and y axes are chosen to coincide roughly with the planar W—O bonds, the d orbital ordering is quite certainly $d_{xy}<d_{xz}\simeq d_{yz}<d_{x^2-y^2}<d_{z^2}$. For a typical oxotungsten compound such as $WOCl_5^{2-}$, the $d_{xz}d_{yz}$ and $d_{x^2-y^2}$orbitals are 14 and 25 kK above the d_{xy} orbital, respectively. Each manifold is then split by the metal-metal interactions.

In the case of the d_{z^2} and $d_{x^2-y^2}$ orbitals, there are no direct metal-metal overlaps and thus no appreciable splittings. Within the $d_{xz}d_{yz}$ and d_{xy} sets, the metal-metal interactions split the energy levels in the manner shown in *Fig* 2. In order to obtain the energy levels, we have first derived symmetry orbitals by the standard group theoretical procedure, and then solved the secular determinants neglecting all overlap integrals. Listed in *Table* 1 are the energies thus obtained in terms of Coulomb intergrals α and α', and resonance integrals β, β', γ and γ'. These expressions determine the molecular orbital ordering in each subsystem unequivocally, but not the ordering of the orbitals in different subsystems.

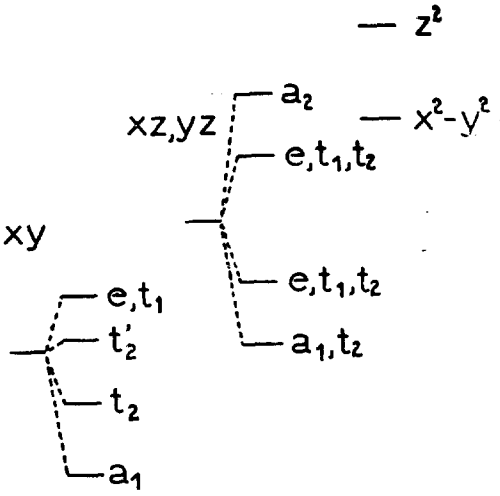


Fig. 2. Schematic energy level diagram

Table 1. Energies of molecular orbitals

Set	Symmetry	Energy
d_{xy}	a_1	$\alpha+2(\beta+\beta')$
	t_2	$\alpha+\frac{1}{2}(\beta+\beta')-\frac{1}{2}\sqrt{9\beta^2+9\beta'^2-14\beta\beta'}$
	t_2	$\alpha+\frac{1}{2}(\beta+\beta')+\frac{1}{2}\sqrt{9\beta^2+9\beta'^2-14\beta\beta'}$
	e, t_1	$\alpha-\beta-\beta'$
$d_{xz}d_{yz}$	a_1, t_2	$\alpha'+\gamma+\gamma'$
	e, t_1, t_2	$\alpha'-\sqrt{\gamma^2+\gamma'^2-\gamma\gamma'}$
	e, t_1, t_2	$\alpha'+\sqrt{\gamma^2+\gamma'^2-\gamma\gamma'}$
	a_2, t_1	$\alpha'-\gamma-\gamma'$

* α and α' represent the energies of the d_{xy} and d_{xz} (or d_{yz}) orbitals in a WO_6 moiety, respectively. Each tungsten atom has two different kinds of neighboring tungsten atoms. The two different resonance integrals between the neighboring d_{xy} orbitals are represented by β and β', and similar intergrals between the neighboring d_{xz} (or d_{yz}) orbitals by γ and γ'.

In order to interpret the optical spectra of one- and two-electron blues, we have to identify the lowest energy molecular orbital. Now if we choose the a_1 orbital of the d_{xy} set as the ground state orbital, the transitions to the t_2 orbitals are allowed and others are forbidden in the same subsystem. The orthogonality of the d orbitals in different subsystems forbids transitions between subsystems.

The characteristic optical spectra of some 12-tungstates show two or three bands between 8 and 21 kK.[3] The two low energy bands common to all species can be assigned to the two allowed transitions. The highest energy band, usually the weakest of the three, is observed as a maximum for the phosphate or silicate, and as a shoulder for the ferrate, but it is completely missing for the cobaltate and metatungstate. This is then probably the forbidden trasition to the e or t_1 orbitals, partially allowed by distortion of the anion. In an acid medium where the spectra of the phosphate and silicate were recorded, protonation may cause the anion deviate slightly from the Td symmetry. But appearance of a shoulder for the ferrate cannot be attributed to this mechanism, for the spectrum was measured in a buffer of pH 6.6. At the present moment we cannot offer any explanation for the high energy band of the ferrate.

So the d_{xy} subsystem gives a reasonable account for the two or three band spectra, if the highest energy band is taken as a forbidden transition. But it is not possible to reproduce exactly the three transition energies by choosing any two values for β and β'. The best fitting based on $\beta=\beta'=-3.33$ kK predicts transitions at 6.7, 13.3, and 20.0 kK, while experimental values for $PW_{12}O_{40}^{3-}$ are 8.0, 13.3, and 20.5 kK. But the discrepancy may be removed by introducing other parameters such as overlap integrals, which have been neglected for the derivation of the energies in the table.

The structure of the anion shows that the metal-metal interactions in the $d_{xz}d_{yz}$ set is considerably larger than those in the d_{xy} set. Still the $a_1(d_{xz}d_{yz})$ orbital is not probably as low as the $a_1(d_{xy})$ orbital, for α' is greater than α by approximately 14 kK. (See above.) Anyhow, if we choose the $a_1(d_{xz}d_{yz})$ orbital or the degenerate t_2 orbitals as the lowest, a qualitative interpretation of the two or three band spectra is equally possible. However, a quantitative fitting is much worse than the above: the best fitting based on $\gamma=\gamma'=-4.43$ kK gives 4.4, 13.3, and 17.7 kK for $PW_{12}O_{40}^{3-}$. So the assignment to the transitions in the d_{xy} set is more satisfactory.

The same method can be used to interpret the optical spectra of the 12-molybdosilicates. Two isomers are known for this species and two different spectra were reported for the two-electron blues: one maximum at 12.8 kK for the α-form and two maxima at 9.5 and 14.7 kK for the β-form.[6] It is possible that another low energy transition for the α form occurs outisde the energy range measured (9-25 kK). A careful study of the electronic structures of the two blues may reveal the structural difference between them.

The four-electron blue of the β form has an additional peak at 12 kK, while the band at 9.5 kK is now diminished to a shoulder.[6] The assignment of the new peak depends upon the ordering of the $t_2(d_{xy})$ and $a_1, t_2(d_{xz}d_{yz})$ orbitals. If the former is lower, the new transition must be $t_2 \rightarrow t_1, e$ in the d_{xy} set; $t_2 \rightarrow t_2'$ should occur at a much lower energy. And the band corresponding to $a_1 \rightarrow t_2$ should broaden for two of the upper levels are already occupied by electrons. If the latter is lower, the new band must be one of the allowed transitions in the $d_{xz}d_{yz}$ set. However, in this case the transition

$a_1(d_{xy})\rightarrow t_2(d_{xy})$ should not be affected. Thus the former assignment is more reasonable.

References

1. J. F. Keggin, *Proc. Roy. Soc.* (London), **A144**, 75 (1934).
2. M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).
3. G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970).
4. E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).
5. H. So and M. T. Pope, *J. Chem. Phys.*, **55**, 2786 (1971).
6. P. Souchay, "Ions Minéraux Condensés," p. 330, Masson ET Cie, Paris, France, 1969.