Theoret. chim. Acta (Berl.) 28, 193—199 (1973)

The Electronic Structure of the Oxygen Double-Bridged $\mu\mu'$-Dioxo-bis (Oxodichloroaquo) Dimolybdate (V)-Ion by SCCC MO Method

Leszek Natkaniec, Mikołaj F. Rudolf, and Bogusława Jeżowska-Trzebiatowska
Institute of Chemistry, University of Wrocław, Wrocław, Poland

Received May 31, 1972

Results of SCCC MO calculations for the dimeric oxygen double-bridged $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ ion are reported. On the basis of these results the previously reported spectra and magnetic properties may be explained. The strong direct molybdenum – molybdenum interaction in the $Mo_2O_4^{2+}$ core was proved to exist.

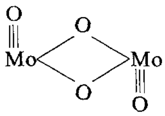
Die Ergebnisse von SCCC MO-Rechnungen für das zweikernige Ion $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ mit zweifacher Sauerstoffbrücke werden mitgeteilt. Danach können die früher angeführten magnetischen und spektralen Eigenschaften dieses Ions verstanden werden. Die Existenz starker unmittelbarer Molybdän-Molybdän Wechselwirkungen innerhalb des $Mo_2O_4^{2+}$ Kerns wird nachgewiesen.

Résultats de calculs SCCCMO pour l'ion dimère $Mo_2O_4Cl_4(H_2O)_2^{2-}$. Sur la base de ces résultats les propriétés spectrales et magnétiques précédemment obtenues peuvent être expliquées. L'existence d'une forte interaction directe molybdène-molybdène dans le coeur $Mo_2O_4^{2+}$ est clairement démontrée.

Introduction

Theoretical and experimental investigations of both-monomeric and polymeric oxocomplexes of *d*-electronic elements are since many years the subjects to intensive studies. The problem of binuclear systems with single oxygen bridges, such as $Cr-O-Cr$, $Fe-O-Fe$, $Re-O-Re$, $Ru-O-Ru$ and $Mo-O-Mo$, have been considered and led to the elaboration of the theory of linear oxygen bridge-bonding [1–4]. Theoretical calculations performed with regard to all interatomic interactions for the $Re_2OCl_{10}^{4-}$ ion indicated the specific features of electronic structure of two paramagnetic ions bonded by an anion, and showed also the influence of ligands coordinated on such a nuclei.

Studies on the chemistry of quinquevalent molybdenum proved, that in the $MoOCl_5^{2-}$ and $MoOBr_5^{2-}$ ions hydrolysis reactions, the bi- and tetranuclear oxomolybdates (V) are formed, in which the molybdenum atoms are bonded by double oxygen bridges [5]. The results of studies on spectral (UV, IR) and magnetic properties of synthetized polymeric oxomolybdates (V) not only confirmed the existence of the dimeric cores of the



type in those complexes, but indicated also their specific electronic structure. The interatomic interactions within such cores were recognized (magnetic moment reduction to 0.3–0.5 BM) [6, 7].

In spite of attempts to theoretical interpretation of the electronic structure of copper (II) acetate dihydrate, made with simplified methods, the satisfactory and reliable interpretation was reported by Bersuker [8] who considered in the SCCC MO approximation the complete atomic arrangement, the ligand – ligand and metal – metal interactions.

In the present work the results of the electronic structure calculations of the $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ ion, carried out by the SCCC MO method [9], are reported.

The Calculation and Results

Since the X-Ray structure of the $\mu\mu'$-dioxo-bis (oxodichloroaquo) dimolybdate (V) ion has not been determined yet, its geometrical configuration and bond lengths were determined indirectly, using the known X-Ray data for mono- and binuclear oxomolybdates (V) [10–15]. The structure of the complex is shown on Fig. 1. The symmetry of the complex ion was assumed to be C_{2h} and all the angles in the bridge core were assumed to be equal to 90°. For the diatomic overlap integrals calculations, the Mo–O_t, Mo–O_b, Mo–Cl and Mo–H_2O bond lengths were assumed to be equal to: 1.67, 1.90, 2.63 and 2.27 Å respectively. On Fig. 2 the coordinate system of the $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ ion is presented. At the calculations the 4*d*, 5*s* and 5*p* molybdenum valence orbitals, *ns* and *np* valence orbitals of oxygen and chlorine atoms and one σ-orbital (sp^3 hybrid) for each water molecule were taken into account in the function basis. Therefore the complete function basis contained 52 orbitals from all the atoms in the molecule.

The analytical expressions of orbitals were taken for Mo^{1+} as reported by Basch [16], for Cl^0 as reported by Freeman [17] and for O^0 as reported by Ballhausen [18]. The diagonal matrix elements for molybdenum were approxi-

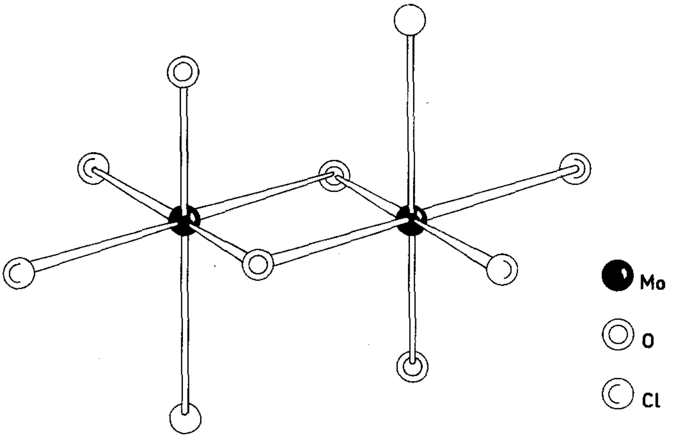


Fig. 1

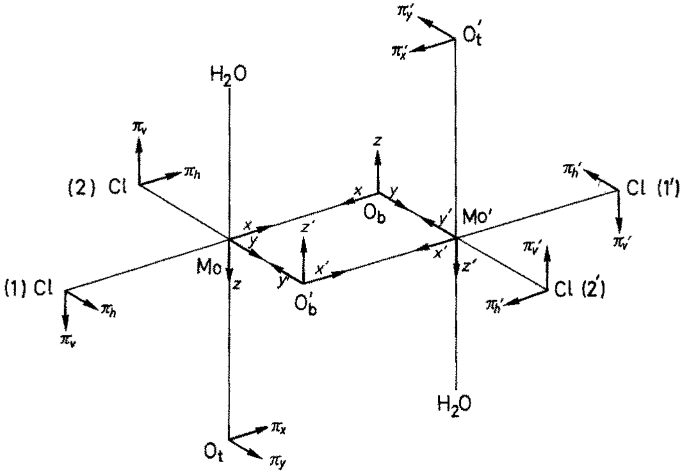


Fig. 2

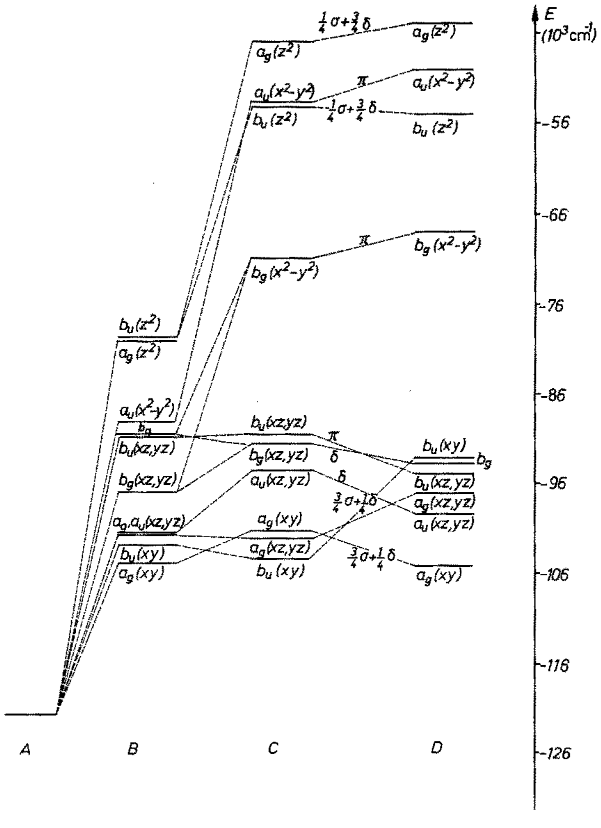


Fig. 3. *A* Molybdenum *d*-Valence orbitals; *B* *A* + MO–O_t, Cl, H_2O interaction; *C* *B* + MO–O_b interaction; *D* *C* + MO–MO interaction

Table 1. Energies and symmetries of molecular orbitals of the $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ ion

Energy	Symmetry	Contribution of molybdenum and ligands orbitals			
$[10^3 \cdot cm^{-1}]$					
−276.1	$1a_g$	s_{O_b} (0.487)	s_{O_t} (0.448)		
−264.3	$1b_u$	s_{O_t} (0.968)			
−262.8	$1a_u$	s_{O_b} (0.958)			
−259.1	$2a_g$	s_{O_t} (0.480)	s_{O_b} (0.432)		
−208.5	$3a_g$	s_{Cl} (0.914)			
−207.1	$2b_u$	s_{Cl} (0.976)			
−205.2	$2a_u$	s_{Cl} (0.943)			
−204.2	$1b_g$	s_{Cl} (0.963)			
−160.6	$3b_u$	σ_{H_2O} (0.488)	d_{xz} (0.145)	$p_{z_{O_b}}$ (0.122)	
−158.7	$4a_g$	σ_{H_2O} (0.583)			
−151.0	$5a_g$	$p_{x_{O_b}}$ (0.410)	d_{xy} (0.343)		
−150.8	$4b_u$	d_{xz} (0.229)	$p_{\sigma_{O_t}}$ (0.220)	σ_{H_2O} (0.192)	π_x (0.132)
−150.7	$2b_g$	d_{xz} (0.348)	π_x (0.290)	$p_{z_{O_b}}$ (0.286)	
−143.8	$5b_u$	$p_{x_{O_b}}$ (0.423)	$p_{\sigma_{Cl}}$ (0.139)	d_{xy} (0.119)	
−141.4	$6a_g$	$p_{\sigma_{O_t}}$ (0.705)			
−139.6	$3a_u$	π_x (0.505)	d_{xz} (0.309)		
−139.3	$6b_u$	$p_{\sigma_{O_t}}$ (0.584)			
−136.4	$3b_g$	$p_{x_{O_b}}$ (0.661)	$d_{x^2-y^2}$ (0.252)		
−136.1	$4a_u$	$p_{x_{O_b}}$ (0.415)	$d_{x^2-y^2}$ (0.228)	$p_{\sigma_{Cl}}$ (0.202)	
−135.4	$7a_g$	$p_{\sigma_{Cl}}$ (0.360)	π_x (0.286)		
−127.4	$4b_g$	$p_{\sigma_{Cl}}$ (0.543)	$d_{x^2-y^2}$ (0.148)		
−127.0	$7b_u$	$p_{\sigma_{Cl}}$ (0.539)	π_h (0.135)		
−125.8	$8a_g$	$p_{\sigma_{Cl}}$ (0.384)	π_x (0.229)	d_{xz} (0.191)	
−119.8	$5a_u$	$p_{\sigma_{Cl}}$ (0.428)	$p_{x_{O_b}}$ (0.396)		
−118.3	$5b_g$	π_x (0.286)	$p_{z_{O_b}}$ (0.250)	$p_{\sigma_{Cl}}$ (0.177)	π_v (0.149)
−117.0	$8b_u$	$p_{z_{O_b}}$ (0.485)	π_x (0.178)		
−116.9	$9a_g$	π_h (0.473)	$p_{x_{O_b}}$ (0.261)	d_{xy} (0.207)	
−110.4	$9b_u$	π_h (0.473)	π_v (0.324)		
−109.7	$10a_g$	π_v (0.862)			
−108.2	$10b_u$	π_v (0.466)	π_h (0.200)		
−108.2	$6a_u$	π_v (0.849)			
−106.2	$7a_u$	π_h (0.982)			
−105.5	$6b_g$	π_h (0.952)			
−105.2	$11a_g$	π_h (0.471)	d_{xy} (0.367)	$p_{x_{O_b}}$ (0.138)	
−102.2	$7b_g$	π_v (0.620)	d_{xz} (0.150)	π_x (0.137)	
− 99.3	$8a_u$	d_{xz} (0.532)	π_x (0.319)		
− 97.1	$12a_g$	d_{xz} (0.684)	π_x (0.225)		
− 94.8	$11b_u$	d_{xz} (0.490)	π_x (0.269)	$p_{z_{O_b}}$ (0.144)	
− 93.7	$8b_g$	d_{xz} (0.430)	$p_{z_{O_b}}$ (0.269)	π_x (0.148)	π_v (0.133)
− 93.1	$12b_u$	d_{xy} (0.701)	$p_{x_{O_b}}$ (0.203)		
− 68.0	$9b_g$	$d_{x^2-y^2}$ (0.551)	$p_{\sigma_{Cl}}$ (0.217)	$p_{x_{O_b}}$ (0.193)	
− 54.9	$13b_u$	d_{z^2} (0.521)	$p_{z_{Mo}}$ (0.124)	σ_{H_2O} (0.123)	
− 50.1	$9a_u$	$d_{x^2-y^2}$ (0.541)	$p_{\sigma_{Cl}}$ (0.196)	$p_{x_{O_b}}$ (0.118)	
− 44.8	$13a_g$	d_{z^2} (0.475)	$p_{z_{Mo}}$ (0.190)		
12.8	$14b_u$	s_{Mo} (0.501)	$p_{z_{Mo}}$ (0.250)	$p_{x_{Mo}}$ (0.196)	
18.2	$10b_g$	$p_{x_{Mo}}$ (0.953)			
30.5	$14a_g$	$p_{z_{Mo}}$ (0.354)	$p_{x_{O_b}}$ (0.305)		
67.0	$10a_u$	$p_{x_{Mo}}$ (0.892)			
74.7	$15b_u$	$p_{x_{Mo}}$ (0.833)	s_{Mo} (0.120)		
79.8	$15a_g$	$p_{x_{Mo}}$ (0.757)			
134.8	$16b_u$	$p_{z_{Mo}}$ (0.575)	s_{Mo} (0.326)		
168.2	$16a_g$	s_{Mo} (0.488)	$p_{z_{Mo}}$ (0.382)		

mated with negative values of VOIP similarly as reported by Gołębiewski [19]. For ligands it was assumed, that the H_{ii}'s are independent on charge and are equal to the negative values of VOIP for the neutral ligands. The non-diagonal matrix elements were approximated as given by Cusachs [20]. The calculations were carried out employing the Mulliken population analysis [21] until the charge and configuration selfconsistence were obtained [22]. The results of these calculations are presented in Table 1 and shown on Fig. 3.

Discussion

To examine the influence of different types of interactions on the MO ordering, the calculations of the electronic structure of the $\mu\mu'$–dioxo–bis (oxodichloroaquo) dimolybdate (V) ion were carried out stepwise starting with the model of simple molybdenum-non-bridging ligand interactions (Fig. 3 B). If one considers this type of interactions only, the molybdenum d-orbitals are splitted into two groups: the first one being strongly antibonding with respect to the molybdenum-ligand σ-interaction, originating from octahedral e_g orbitals and the second group of orbitals originating from octahedral t_{2g} orbitals. For this approximation the following energetic ordering of orbitals was obtained (Fig. 3 B)

$$a_g, b_u(d_{z^2}) \gg a_u, b_g(d_{x^2-y^2}) > a_g, a_u, b_g, b_u(d_{xz}, d_{yz}) > a_g, b_u(d_{xy}) .$$

That the both nuclei are bonded by the bridging oxygen atoms results in the energy increase of antibonding orbitals $a_g, b_u(d_{z^2})$ and $a_u, b_g(d_{x^2-y^2})$ (Fig. 3 C). The changes in energy of π-orbitals are small and their direction can not be explicitly justified.

The metal-metal interaction has the peculiar character (Fig. 3 D). In the group of σ-MO's it has mainly the character of π–π or δ–δ interactions and is not the cause of essential changes in energy. In the group of π–MO's essential changes in the energetic ordering of MO's due to the metal-metal interaction are observed. Under the influence of that interaction, first of all of the σ-type, the $a_g(d_{xy})$ and $b_u(d_{xy})$ orbitals became the bonding and antibonding ones, respectively. Since the $a_g(d_{xy})$ orbital is occupied by two electrons, the metal-metal interaction through d_{xy} orbitals is in that case the factor leading to an additional stabilization of the complex and deciding on the molybdenum-molybdenum bond order. Taking the foregoing analysis into account it should be stated, that the ligands have the strongest influence on energetic splitting of d-orbitals of molybdenum. The metal-metal interaction is less important, except of the σ-type interaction.

To analyze the character of particular bonds in the examined compound the bond orders, overlap populations and gross atomic populations were calculated. The bond order definition and population analysis, both given by Mulliken were applied [21]. In Table 2 some of the obtained results are presented. The electron overlap populations are calculated per one ligand atom. Hence they comprise the total electron density in the overlap area between one ligand and two molybdenum atoms. For nonbridging ligands they are practically reduced to the overlap populations between one ligand and one molybdenum atom.

Table 2. Overlap populations for individual bonds in the $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ ion

Bond symmetry	Mo–Mo[a]	Mo–Mo[b]	Mo–O_b	Mo–O_t	Mo–Cl	Mo–O_{H_2O}
A_g	0.0373	0.0464	0.0182	0.1049	0.0616	0.0774
B_u	0.0047	−0.0184	0.0576	0.0863	0.0135	0.0712
A_u	0.0078	0.0055	0.0187	0.0617	0.0504	
B_g	−0.0090	−0.0077	0.0577	0.0324	0.0265	
Total O. P.	0.0408	0.0258	0.1522	0.2853	0.1520	0.1486

[a] Only *d*-orbitals considered.

[b] All *s*, *p* and *d*-valence orbitals of molybdenum are considered.

Metal-Metal Bond. The largest contribution have the a_g orbitals (Table 2), and first of all the $a_g(d_{xy})$ orbital. It is the result of the large value of the overlap integral between d_{xy} orbitals, corresponding mainly to the σ-type interaction and of the presence of two electrons on the $a_g(d_{xy})$ molybdenum orbital.

Molybdenum-Oxygen (Terminal) Bond. The subtotal overlap populations decrease in the ordering:

$$a_g > b_u > a_u > b_g .$$

It is clear because in the representations a_g and b_u there appear the d_{z^2} and p_z molybdenum orbitals which cause the strong bonding with the O_t atoms. The d_{xz}, d_{yz} orbitals of b_g and b_u symmetries and p_z molybdenum orbitals of b_u symmetry are very much involved in the π-bonding with the bridge-oxygen atoms. Therefore their contributions in the Mo–O_t π-bonding are smaller if compared with orbitals a_g and a_u. The more it is clear if one compare the contributions of a_g and b_u orbitals in the total overlap populations for Mo–O_t and Mo–H_2O bonds. In the later case these contributions are comparable, because the water molecule is only a σ-bonding ligand.

Molybdenum-Oxygen (Bridge) Bonds. The b_u and b_g orbitals have the largest contribution, while the a_g and a_u orbitals exhibit a remarkably lower bonding effect. It is caused by the contribution in molecular orbitals b_u and b_g of $p_{z_{O_b}}$ orbitals which forms with the d_{xz}, d_{yz} orbitals of molybdenum (for symmetry b_u also with p_z molybdenum orbitals) the strongly bonding π-MO's in the plane perpendicular to the bridge ring. Moreover, the interaction of p-orbitals of molybdenum and of the bridge-oxygen atoms is much stronger for the b_g symmetry than for the a_u one (overlap integral values amounts 0.430 and 0.084 respectively). On the other hand the $d_\pi - p_\pi$ interaction in the bridge plane gives the stronger bonding effect for b_u symmetry than for the a_g one, because two electrons are located on the $a_g(d_{xy})$ orbital, which is antibonding with respect of that interaction.

Molybdenum-Chlorine Bonds. The strongest bonding effects give the a_g and a_u orbitals. Also in that case it is due to the stronger π-interaction between d_{xz} orbitals of molybdenum and π_v orbitals of chlorine. The p_x and p_y orbitals of molybdenum of a_u symmetry could combine with σ- and π_h orbitals of chlorine rather than $b_g(p_x, p_y)$ orbitals because the latter ones are already very much involved in the bonding with bridge oxygen atoms.

Results of theoretical calculations are in agreement with experimental data previously obtained by us [5–7]. Complexes of the $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ type exhibit only a small, practically temperature independent paramagnetism of the magnitude of $300 \cdot 10^{-6}$ cm^3/mole. On the highest occupied energy level $a_g(d_{xy})$ two paired electrons are located. The energy distance between this orbital and the next one of higher energy amounts 6000 cm^{-1}. Therefore any contribution of excited triplet states e.g. $a_g(d_{xy})^1\ a_u(d_{xz})^1\ {}^3A_u$ leading to a temperature dependent paramagnetism must be neglected.

Acknowledgements. This research was supported by a grant from the Polish Academy of Sciences.

References

1. Dunitz, I. D., Orgel, L. E.: J. chem. Soc. **1953**, 2594.
2. Jeżowska-Trzebiatowska, B., Kozłowski, H., Natkaniec, L.: Bull. Acad. polon. Sci., Sér. Sci. chim. **19**, 115 (1971).
3. Jeżowska-Trzebiatowska, B.: Pure Appl. Chem. **27**, 89 (1971).
4. Schmidtke, H. H.: Theor. chim. Acta (Berl.) **20**, 92 (1971).
5. Jeżowska-Trzebiatowska, B., Rudolf, M. F.: Roczniki Chem. **41**, 453 (1967; **42**, 1221 (1968).
6. Jeżowska-Trzebiatowska, B., Rudolf, M. F.: Bull. Acad. polon. Sci., Sér. Sci. chim. **17**, 419 (1969).
7. Jeżowska-Trzebiatowska, B., Rudolf, M. F.: Roczniki Chem. **44**, 745, 1031 (1970).
8. Bersuker, I. B., Titova, Yu. G.: Theoret. Exper. Chim. **6**, 469 (1970).
9. Ballhausen, C. J., Gray, H. B.: Molecular orbital theory. New York: Benjamin 1964.
10. Głowiak, T.: Dissertation, Wrocław 1967.
11. Atovmian, L., Dyachenko, O. A., Lobkovskii, E. B.: private information.
12. Scane, I. G.: Acta crystallogr. **23**, 85 (1967).
13. Cotton, F. A., Morehouse, S. M.: Inorg. Chemistry **4**, 1377 (1966).
14. Knox, J. R., Prout, C. K.: Acta Crystallogr. B **25**, 1857 (1969).
15. Delbaere, L. T. J., Prout, C. K.: Chem. Comm. **1971**, 162.
16. Basch, H., Gray, H. B.: Theoret. chim. Acta (Berl.) **4**, 367 (1966).
17. Freeman, A. J., Watson, R. E.: Physics Rev. **123**, 521 (1961).
18. Ballhausen, C. J., Gray, H. B.: Inorg. Chemistry **1**, 111 (1962).
19. Gołębiewski, A., Kowalski, H.: Theoret. chim. Acta (Berl.) **12**, 293 (1968).
20. Cusachs, L. C.: J. chem. Physics **43**, 157 (1965).
21. Mulliken, R. S.: J. chem. Physics **23**, 1833, 1844 (1955).
22. Basch, H., Viste, A., Gray, H. B.: J. chem. Physics **44**, 10 (1966).

Prof. Dr. B. Jeżowska-Trzebiatowska
Institute of Chemistry
University of Wrocław
Wrocław, Poland