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John-Teller Distortion in Octahedral hexaaquacopper (II) Transition for S=1/2, d9 Metal Complex

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تشويه John–Teller في انتقال هيكساكواكوبر ثماني السطوح (II) لـ$S = 1/2$ ، d^9 المركبات معدني

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ABSTRACT

Jahn–Teller effect (JTE) describe how specific electrons distributions induce geometric deformation in molecules or ions. The distortion of Jahn–Teller (JT) takes place because of the uneven occupation of orbitals with the identical energies is disapproving. To prevent such inappropriate electronic arrangements, molecules distort (lose regularity), causing these orbitals to become non-degenerate. This distortion is most frequently seen in octahedral compounds, at which two axial bonds could be squeezed (compressed) or extend (elongated), leading to bond lengths that the different from equator bonds. The degeneracy of electronic states really isn't accurately measured, but it would be measured precisely by the disparity in a concentration of electron among metal and the ligands upon on axil direction. The density functional theory has been used to calculate bond length in both cases $Z - in\ and\ Z - out$ geometry for $[Cu[OH]6]^{2+}$, $Spin(S) = 1/2,\ d^9$ octahedral metal-complexes, the majority ordinary mechanism of distortion is elongation (z-out). In perfectly octahedral complexes deformation, the e_g orbitals energy is changed more than the t_{2g} orbitals energy, causing elongation z-out distortion. The d-levels energy would be splitting in a ligand field throughout transition metal centers can frequently result in degenerate electron configurations that are subject to Jahn–Teller effects. In six-coordinate complexes of d^9copper II ions. It is also significant in fewer regular oxidation levels of other transition ions with that $d - electrons$ count.

Key words: Jahn–Teller effect(JTE), compression, elongation and distortion

الخلاصة

تشويه جان تيلر يوضح كيف تؤدي توزيعات الإلكترون المحددة إلى حدوث تشوه هندسي في الجزيئات أو الأيونات .يحدث تشويه جان تيلر بسبب الأشغال غير المتكافئ للمدارات ذات الطاقات نفسها وهو أمر مرفوض. لمنع مثل هذه الترتيبات الألكترونية غير المناسبة، تتشوه الجزيئات (تفقد الأنتظام) ، مما يتسبب في أن تصبح هذه المدارات غير منحلة . يظهر هذا التشوه بشكل متكرر في مركبات ثماني السطوح ، حيث يمكن تقليص (ضغط) أو تمديد (استطالة) رابطين محوريين ، مما يؤدي إلى أطوال روابط تختلف عن الروابط الأستوائية. لا يتم قياس انحلال الحالات الألكترونية بدقة ، ولكن سيتم قياسه بدقة من خلال التباين في تركيز الألكترون بين المعدن والليكاندات باتجاه محوري. تم استخدام نظرية الكثافة الدالية لحساب طول الرابطة في كلتا حالتي الهندسة Z–in و Z–out لـ $[Cu[OH]6]^{2+}$ ،, S = 1/2 ، d9 مركبات معدنية ثماني السطوح ،ا لية التشوه الأكثر شيوعًا هي الاستطالة (Z–out)، في تشوه المركبات ثمانية السطوح المثالية، تتغير طاقة المدارات e_g على سبيل المثال أكثر من طاقة المدارات t_{2g} ، مما يؤدي إلى استطالة تشوه (Z–out) . يمكن أن تنقسم طاقة المستويات d في مجال الليكاند عبر المراكز المعدنية الأنتقالية بشكل متكرر إلى توزيعات إلكترونية منحلة تخضع لتأثيرات جان تيلر. في مركبات ذات ستة إحداثيات من أيونات النحاس II d^9 . كما أنه مهم أيضًا في عدد أقل من مستويات الأكسدة المنتظمة لأيونات الانتقال الأخرى مع عدد الإلكترونات d .

الكلمات المفتاحية:: تأثير جان تيلر ، الضغط ، الأستطالة والتشويه

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INTRODUCTION

The effect Jahn-Teller (JTE) is really a geometric deformation of non- chemical molecule systems and ions that reduces their regularity and energy, they have been tied to specific electron arrangements. This influence is based on the JTE testified on $[Cu[OH]6]^{2+}$, $Spin(S) = 1/2$, d^9 .Transition metal complexes to octahedral regularity, and clarifies that why does JTE come from an unpaired electron in the $dz^2$of a d^9metal compound. The deformation of Jahn-Teller occurs when there is a compression $(z - in)$ and elongation $(z - out)$. In terms of its electronic state, Hermann Jahn and Edward Teller proposed an idea in 1937 stating that "degeneracy & stabilization" are unlikely to occur concurrently unless the molecule would be linear." This tends to cause a break in degeneracy, which regulates the molecule as well as, as a result, reduces its symmetry [1]. An electronically degenerate state is one in which an electron has access to more than one degenerate orbital. The two possible degenerate states for S = 1/2, d^9 $[t2g6\ eg3]$ octahedral transition metal complexes are shown in Figure.1. The electronic distortion will induce energy levels to split and also a change in geometric distortion. This distortion of Jahn-Teller is often seen in octahedral (Oh) structures with elongation $(z - out)$, which is a complex with 2 longer axial bonds and 4 lesser equatorial bonds, which would be the opposite of $[z - in]$ octahedral systems. The d-electron stabilization energy could be used to objectively understand octahedral Jahn-Teller elongated structures. If a metal with two ligands on the z-coordinate has a far greater electron density accumulation than metal with 4 ligands on the $xy - coordinate$, i.e.

$$D(e^-)[K - L]xy - Plane < D(e^-)[K - L]z - axis \tag{1}$$

$D(e^-)$: $density\ of\ electron$, k: $metal\ ion$. The metal will be more electrostatically repelled by the two ligands on the $Z - axis$ in contrast to the other four ligands in the $x - y\ plane$. Bond elongation along $z - axis$ is caused by electrostatic repulsion through the $[z - out]$ situation. As a result, the energy of those $d - orbitals$, namely orbitals d_{z^2} , d_{xy}, and d_{yz}, is decreased by a factor of z. As the bonds all along $z - Axis$ lengthen, orbitals d_{z^2} , d_{xy}, and d_{yz}form, which indicated in figure.2 b [2].

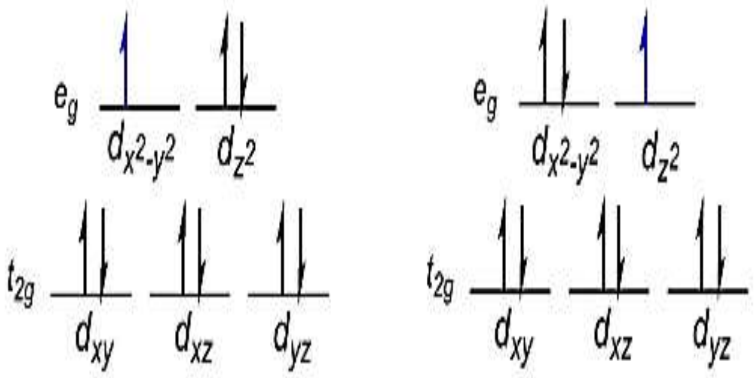

Figure.1: Energy level diagrams e_2 and t_{2g}, illustrating the two degenerate states discovered for $S = 1/2, d^9$

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The z-out situation is more noticeable when degeneracy takes place at the e_g level, as in d^9 transition metals [3]. In contrast to the $z-axis$, the equatorial plane has a higher fraction of electron density (large numbers) among the ligands metal.

$$D(e^-)[K-L]z-axis < D(e^-)[K-L]xy-Plane \tag{2}$$

Rather than, it causes bond elongation through the $X,Y-Axis$, while Compression deformation occurs whenever bonds are squeezed along the z-axis. in order to have a better knowledge of the impact of higher electron density among particular ligands and metal. A density functional theory -based computational experiment for the same compound ion-containing metal (Cu) with electron filling d^9 and $S = 1/2$, hexaaquacopper (2+) complex ion, $[Cu[OH]6]^{2+}$is defined here. The outcome indicates why an unpaired electron in the same d_{z^2} of a $spin(S) = 1/2, d^9$ transition metal compound displays z-in rather than a loaded electron pair in $d_{x^2-y^2}$.

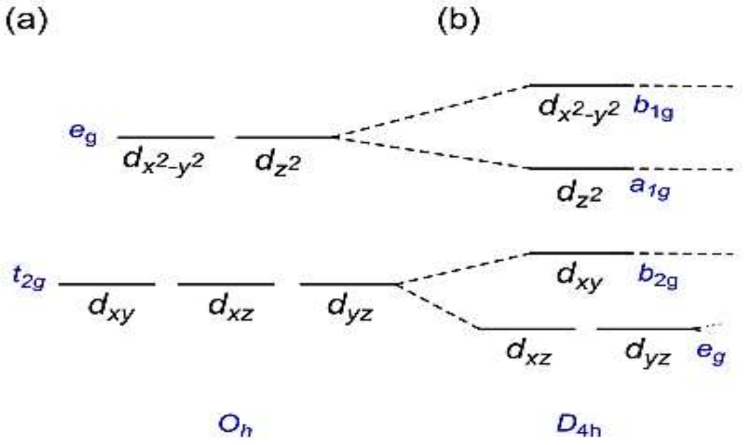

Figure 2: (a) A ordinary environment of e_g and t_{2g} levels. (b) Splitting of both the degenerate $e_g$and t_{2g} occurs to reduce energy in order to achieve stabilization energy.

In addition, the distortion of Jahn-Teller is generally reported in transition metal compounds. The phenomenon is so much more popular in bivalent copper hexacoordinated complexes. The distortion is typically caused by the elongation of metal-ligand bonds along the z-axis, but it can also be caused by the shortening of the same bonds. In general, symmetry results in stability; however, the Jahn-Teller distortion is an exception to this rule. Thus, it is necessary to discuss the driving force behind this behavior. Where the electron density associated with the degenerate set orbitals is much more concentrated, the magnitude of the Jahn-Teller effect is greater. Therefore, the effect of Jahn-Teller is crucial in evaluating the structure of metal complexes. The case study of d^9complexes explicates the entire energetics of the Jahn-Teller [4]. By reducing the symmetry of the molecule, the degeneracy of orbitals could be expelled. It could be accomplished either through elongating or shortening bonds through z-axial $[Z-out\ or\ Z-in]$. The energies value of d-orbitals with z factors d_{z^2} $, d_{xy}, and\ d_{yz}$ be reduced in the presence of Z-out deformation, as illustrated in figure 3. That's the most popular distortion and can be seen in the majority of instances, particularly whenever the degeneracy happens at the e_g $and\ t_{2g}$ levels [5].

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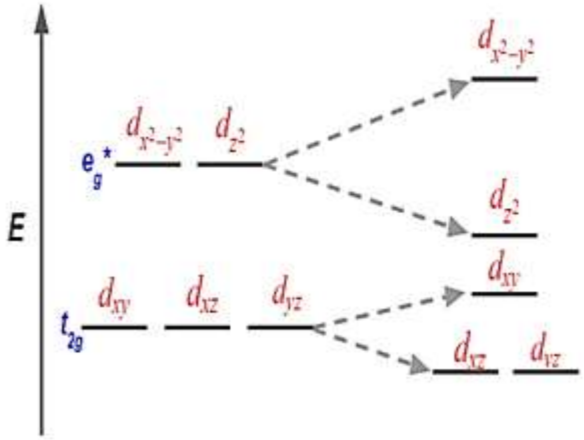

Figure.3: d-orbitals undergo an Elongation Distortion

As for the Z-in situation, the strength of orbitals with the z factor increases in this position because their bonds near the z-axis are shortened. Throughout the case of octahedral configuration, this sort of distortion is noted, in addition, the z-out distortion will not erase the degeneracy since there are always two degenerate orbitals existing for the electron to fill after distortion that is d_{xz} and d_{yz} , which is expression in the figure 4. Furthermore, keep in mind that the Jahn-Teller theorem doesn't quite anticipate the size of the distortion.

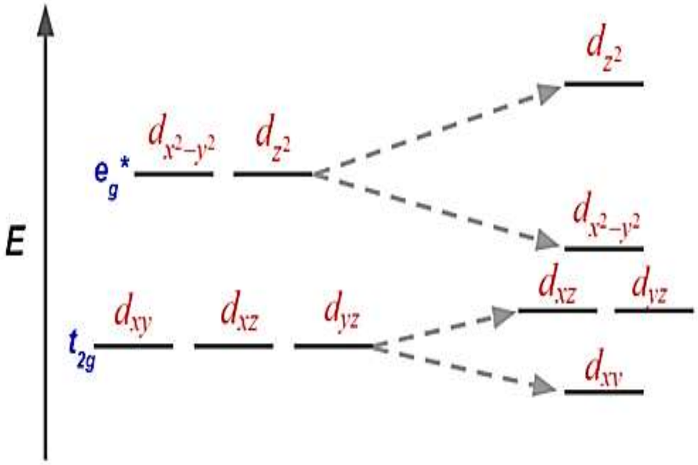

Figure.4: d-orbitals undergo a compression Distortion

Materials and Methods

- **Computational Method**

The $spin\ (S) = 1/2, d9$ hexaaquacopper (2+) compound ions, $[Cu[OH]6]^{2+}$, were the focus of this study. To optimize the structures, the density functional theory [DFT] technique, density Functional program [ADF2016] was used. The triple polarized operations, as well as the iB3LYP functional were used [6, 7]. In the data input that lacked symmetry converged to close $D2h$ symmetry for $[Cu[OH]6]^{2+}$through using elongated and compression shapes such as starting geometry, the compression and elongated optimized geometries have been achieved. The existence of minima was verified via analyses of frequency. The improved Geometric parameters stay available in the Supplementary information. Using Bader's QTAIM, these octahedral restrained models, as well as the confined symmetry compression of $S = 1/2, d^9$ $[Cu[OH]6]^{2+}$were exposed to QTAIM computation, as executed in [ADF2016] at the matching theoretical level, and it was also performed using DFT with B3LYP functional in 2018 [8-10]. The same quantifiable picture acquired here for the B3LYP functional is predicted with another function computation. Similarly, this same doublet of the hexaaquacopper (2+) compound ion, $[Cu[OH]6]^{2+}$, configured to the electronic states $d_{xy}^2\ d_{xz}^2 d_{yz}^2 d_{z^2}^2\ d_{x^2-y^2}^1$ and $d_{xy}^2\ d_{xz}^2 d_{yz}^2\ d_{x^2-y^2}^2 d_{z^2}^1$, for an z-in and z-out geometry [11].

Table.1: DFT comparison energies (eV) and average metal-O ionic bonds size (Å) were computed for complexes described exclusively utilizing the range of experimentally measured bond dimensions values from X-ray data, [12,13].

Complex	$d-electrons$	occupation	$K-L$ $[z-axis]$ $(ave) in A^o$	$K-L$ $[xy-plane]$ $(ave) in A^o$	$functional$ (DFT)
$[Cu[OH]6]^{2+}$	d^9	$d_{xy}^2\ d_{xz}^2 d_{yz}^2 d_{z^2}^2\ d_{x^2-y^2}^1$ $d_{xy}^2\ d_{xz}^2 d_{yz}^2\ d_{x^2-y^2}^2 d_{z^2}^1$	2.289 1.980	2.024 2.169	$[z-out\ elongation]$ $[z-in\ compression]$

Results and Discussion

As it is usual for Cu II compounds with six coordinates, the d9 $[Cu[OH]6]^{2+}$structure only has a single spin state [$S = ½$]. For and S = 1/2, d9 $[Cu[OH]6]^{2+}$clusters, it is possible to achieve two different electronic states with comparable stabilized energies. One demonstrates Z-out distortion, while the other demonstrates Z-in distortion. Table 1 also contains DFT computed copper-bond distances for $[Cu[OH]6]^{2+}$ molecular structures. Likewise, 2 different optimized configurations for the $S = 1/2, d^9$ hexaaquacopper (2+) complex ion, $[Cu[OH]6]^{2+}$have been gained. Throughout all configurations, a couple of the copper bond sizes estimated by DFT are either taller or shorter (roughly 0.27) or smaller (approximately 0.19) compared to the four other copper bonds. This seems to be indicative of the presence of both Z-out and Z-in in the two different optimization structures of Cu (Table 1). The copper-bond lengths determined by DFT in both stretching and compression Jahn-Teller deformed structures were within the range of practically measured bond-sizes, which are $(0.24\ and\ -0.16)$ respectively see [14]. The $[Cu[OH]6]^{2+}$read between lines d-based border molecular energy levels. The relevant orbitals, including the compression and elongation geometries, gave the following perspectives:

i- The crystal field splitting energy level diagram into a normal octahedral environment Oh levels $e_g\ and\ t_{2g}$. Figure 5 depicts the splitting energy level along with degeneracy of eg energy levels, as well as the splitting of the t2g level, under $D4h$ symmetry for $S = 1/2, d^9$ $[t2g6\ eg3]$ transition metal compound. The divisions of energy levels aren't drawn to scale.

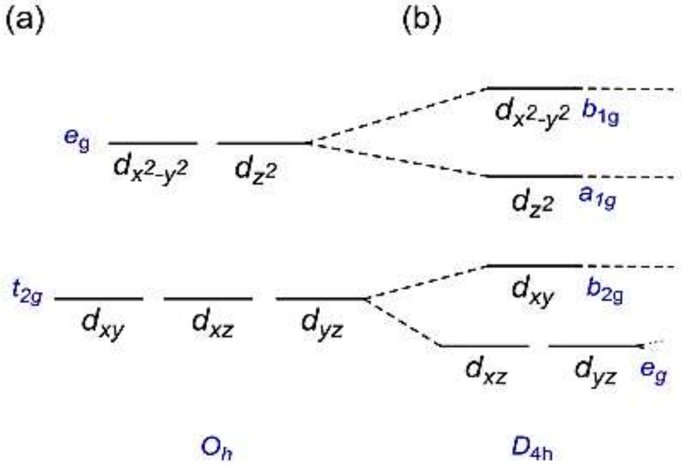

Figure.5: (a) a normal octahedral level $e_g\ and\ t_{2g}$. (b)Splitting takes place, for both of them eg levels and t2g level to lower energy. [13]

ii- In contrast, for the $S = 1/2, d^9$ $[Cu[OH]6]^{2+}$ complex, a greater density of electron (z-out) could well take place on the z-axis among two ligands and metal d_{z^2} with occupied by two electron , but also between the metal and the four ligands in on plane-xy [$d_{x^2-y^2}$ with filled by one electron], guessing $z - out$ alteration for $S = 1/2, d^9$ $[Cu[OH]6]^{2+}$, illustrates in Figure.6(b, c)In the presence of Z-in alteration even within d9 complex, the d-level filled with lower electron density through $Z - axial$ because of this circumstances this condition valid $(Z - in)$ [14].

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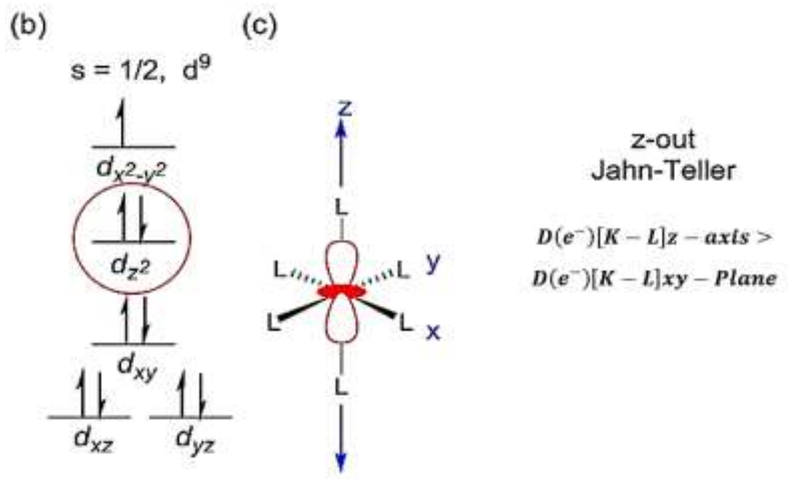

Figure.6: (b) $S=\frac{1}{2}, d^9$ with copper ion (2+). (c) z- out (elongation) exist caused by the higher density of electron

iii. In the $d_{x^2-y^2}$orbital for all unpaired electron of $S=\frac{1}{2}, d^9$ octahedral transition metal substance, such as Cu II, displays elongation demonstrates in Figures 6(b,c). $Z-in$ will appear instead if the unpaired electron would be in the d_z^2 orbital of a $S=\frac{1}{2}, d^9$ metal transition substance, as can be seen in Figures 7 (e, f). The same result illustrates that the $Z-in$ appears due to a lower electron density. [15]

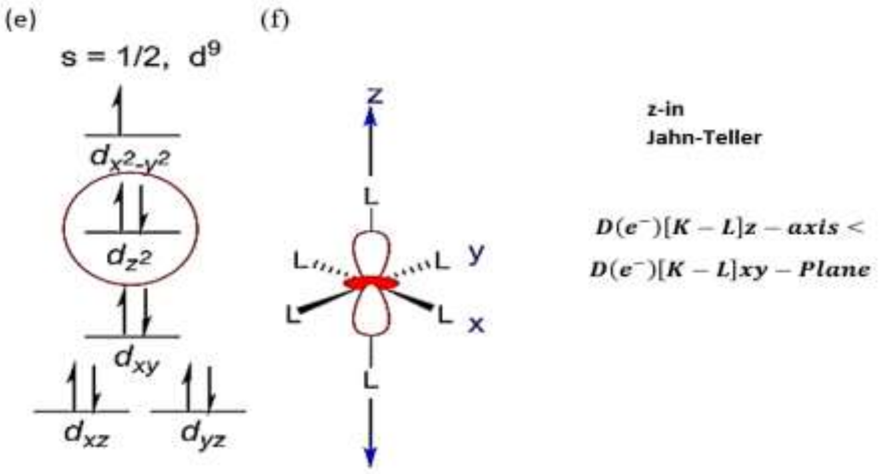

Figure.7: (e) S = ½, d9 metal transition compound. (f) Z-in (compression) exist caused by the higher density of electron

Figures 7(e,f) In light of this, the greater density of electron (large concentration) is realized among the four ligands and metal on $plane-xy$ of $[Cu[OH]6]^{2+}$, that has also degenerate orbital energies. The distortion happens inside the electron density in the plane of x-y, causing their degenerate levels of energy to divide, reducing the regularity and even its overall energy so, Z-in is achieved .

$$D(e^-)[copper(cu)-L]z-axis < D(e^-)[copper(cu)-L]xy-Plane \quad (3)$$

Figure 6(b,c) As a result of the higher density(greater concentration), Copper Cu has bigger electrostatic repulsion with the 2 ligands on the z-axis than with the other 4 ligands on the $xy - plane$, resulting in $Z - out$ of the bonds within z-axis . QTAIM analysis on octahedral restrained models was done, to obtain computational support for this investigation of the found distortion of Jahn-Teller, as described via electrostatics owing to variations in density of electron, QTAIM's results are comparable to ours [15,16].

$$D(e^{-})[copper(cu) - L]z - axis > D(e^{-})[copper(cu) - L]xy - Plane \quad (4)$$

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Conclusion

the distortion of Jahn-Teller, which would be geometric shapes influence on a chemical compound caused by the energy decreasing of significantly degenerate electronic state, which is caused by an imbalance in electron concentration (before distortion) among both the two ligands and the metal on the z-axis instead of the shape of the highest occupied orbital, as already generally believed. And the density of electrons among the 4 ligands and metal the in $xy - plane$, if the concentration of electrons is larger along the z-axis, the resulting disparity in electron density would result in z-out distortion. If the electron density along the z-axis is smaller, the disparity would instead cause Z-in distortion. Since $d_{x^2-y^2}$ consists of an electron pair in comparison, octahedral metal-complexes with a d_{z^2} that included an unpaired electron also display z-in distortion. In comparison to other studies, we achieve the same result and characterization.

Conflict of interests.

There are non-conflicts of interest.

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