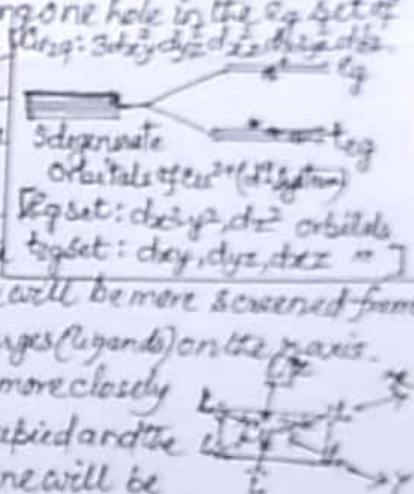


Jahn-Teller Effect:

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In 1937, Jahn & Teller put forward a remarkable theorem to explain why some octahedral complexes undergo distortion and have distorted octahedral geometry. It states that "any nonlinear molecular system/complex in a degenerate electronic state will be unstable and will undergo some kind of distortion which will lower its symmetry and split the degenerate state resulting more stable molecule/complex". The distortion in geometry of non-linear system due to Jahn-Teller effect is called Jahn-Teller distortion.

To illustrate this theorem, suppose Cu^{2+} ion finds itself in the center of an octahedron of ligands. This ion may be thought of as possessing one hole in the e_g set of d-orbitals and the electronic state of the ion is hence a degenerate, E_g state. According to Jahn-Teller theorem, the octahedron cannot remain perfect at equilibrium but must become distorted in some way. The reason for this is that, of the two e_g orbitals, it is the $d_{x^2-y^2}$ orbital which is doubly occupied while the d_{z^2} orbital is only singly occupied. This must mean that the four negative charges or negative ends of dipoles in the xy plane will be more screened from the electrostatic attraction of the Cu^{2+} ion than will the two charges (ligands) on the z-axis. Naturally, the latter two ligands will be drawn in some what more closely than the other four. Conversely, if the d_{z^2} orbital is doubly occupied and the $d_{x^2-y^2}$ orbital only singly occupied, the four ligands in the xy plane will be drawn more closely to the Cu^{2+} than will the other two on z-axis. It is also possible that the unpaired electron could be in an orbital which is some linear combination of $d_{x^2-y^2}$ & d_{z^2} , in which case the resulting distortion would be some related combination of the simple ones considered above. On above discussions, some important facts relating to operation of the Jahn-Teller effect given as:



1. The theorem only predicts that for degenerate states a distortion must occur. It does not give any indication of the geometrical nature of the distortion, and extent of distortion.
2. In order to make a prediction of the nature and magnitude of the distortion, detailed calculation must be made of the energy of the entire complex as a function of all possible types and degrees of distortion. The configuration having the lowest energy may then be predicted to be the equilibrium one. However, the calculations are extremely laborious.
3. It may be noted that there is one general restriction on the nature of distortion: if the undistorted configuration has a center of symmetry, so also must the distorted equilibrium configuration.

Distortions shown by octahedral complexes of d^n system ($n=0$ to 10):

- Octahedral complexes of d^n system are grouped as follows w.r.t. nature of distortion:
- *1. Octahedral complexes having d^0 ($t_{2g}^0 e_g^0$), d^3 ($t_{2g}^3 e_g^0$), d^5 high spin ($t_{2g}^3 e_g^2$), d^8 low spin ($t_{2g}^6 e_g^2$), d^8 high spin ($t_{2g}^5 e_g^3$), d^{10} ($t_{2g}^6 e_g^4$) confs do not show any distortion due to either vacant/empty or symmetrically filled orbitals. In such cases, Jahn-Teller effect not observed i.e. complexes have regular geometry. e.g., $[TiX_6]^{3-}$, $[CrOX_6]^{3-}$, $[FeX_6]^{3-}$, $[NiX_6]^{4+}$, $[ZnX_6]^{2+}$ etc.
 - *2. Octahedral complexes having d^2 ($t_{2g}^2 e_g^0$), d^4 low spin ($t_{2g}^4 e_g^0$), d^5 low spin ($t_{2g}^5 e_g^0$), d^6 high spin ($t_{2g}^4 e_g^2$), d^7 high spin ($t_{2g}^5 e_g^2$) configurations show slight distortion. Here t_{2g} set of orbitals is asymmetrically filled ($t_{2g}^4, t_{2g}^5, t_{2g}^6$) and e_g set of orbitals is symmetrically filled.

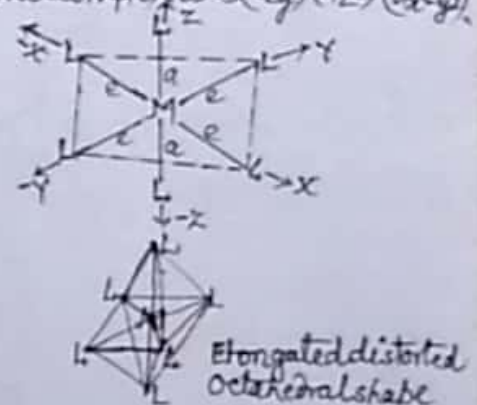
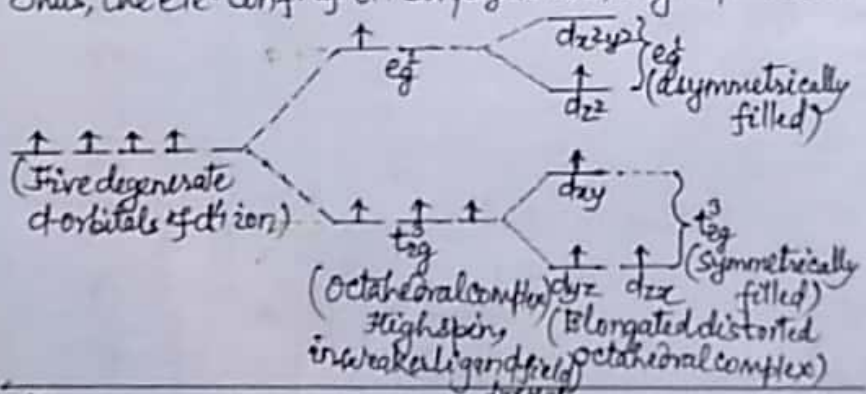
ally-filled. Small distortion is because of the fact that since the lobes of the three asymmetrically filled orbitals of t_{2g} set don't lie directly in the path of the ligands, the electron present in t_{2g} set of orbitals cause small distortion in octahedral complexes. e.g. $[CoF_6]^{3-}$

*3. Octahedral Complexes having $d^1(t_{2g}^1 e_g^0)$, d^4 high spin ($t_{2g}^3 e_g^1$), d^7 low spin ($t_{2g}^6 e_g^1$), d^8 low spin ($t_{2g}^6 e_g^2$), $d^9(t_{2g}^6 e_g^3)$ configurations show strong/large distortions (compressed or elongated).

In this case, Jahn-Teller effect studied distortion in geometry as follow:

(i) d^1 system: e.g. $[Ti(H_2O)_6]^{3+}$ or Ti^{3+} is a d^1 system. In the ground state, d^1 configuration is represented as $t_{2g}^1 e_g^0$. t_{2g} electron may be present in d_{xy} and xz/d_{yz} orbital. When t_{2g} electron is present in d_{xy} orbital, Ti^{3+} ion or $[Ti(H_2O)_6]^{3+}$ ion undergo strong distortion and assumes compressed distorted octahedral geometry. On the other hand, if t_{2g} electron present in d_{xz} or d_{yz} orbital, $[Ti(H_2O)_6]^{3+}$ undergoes strong distortion and assumes elongated distorted octahedral geometry.

(ii) d^4 system (High spin complexes): $[MnF_6]^{3-}$ or Mn^{2+} & $[Cr(H_2O)_6]^{3+}$ or Cr^{2+} are d^4 systems. Since the configuration of these ions in weak ligand field/high spin, $t_{2g}^3 e_g^1$ has symmetrically filled e_g set. These complex ions show strong distortion in octahedral geometry/shape. One electron present in e_g set may be present either in d_{z^2} or $d_{x^2-y^2}$ orbital. If an electron in $d_{x^2-y^2}$, it is repelled by four ligands lying on $+x, -x, +y$ & $-y$ axes. On the other hand, if an electron present in d_{z^2} orbital, it is repelled by two ligands lying on $+z$ & $-z$ axes. Thus, the energy of $d_{x^2-y^2}$ orbital increases relative to d_{z^2} orbital. This leaves $d_{x^2-y^2}$ orbital empty. Thus, the ele. conf. of d^4 ion/system in high spin octahedral complexes is $(t_{2g})^3 (d_{z^2})^1 (d_{x^2-y^2})^0$.



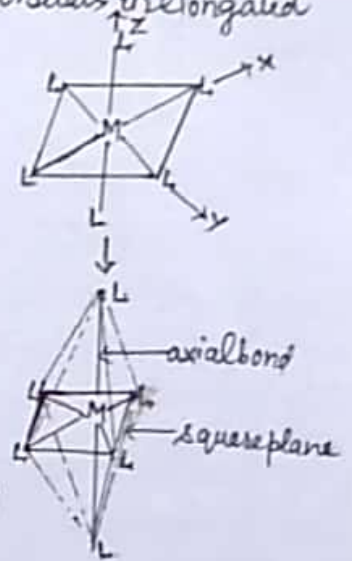
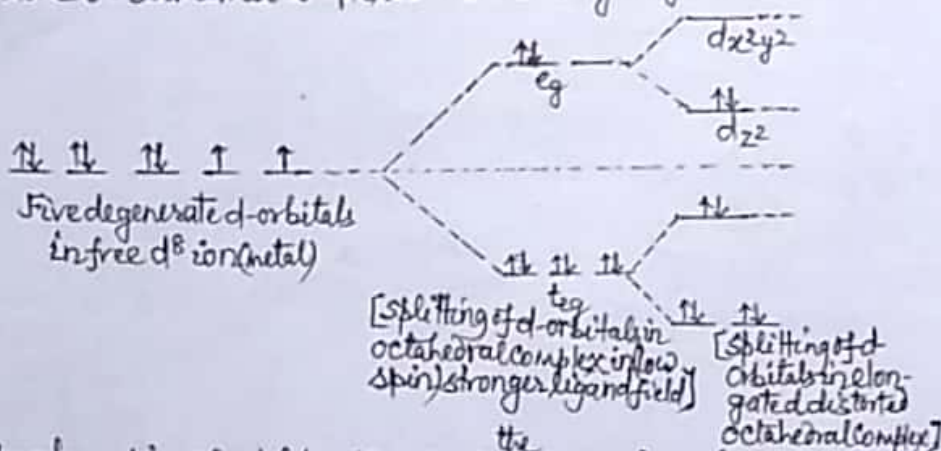
The repulsion between the electron in d_{z^2} orbital and two ligands (axial) results in the elongation of two axial or trans ligands (i.e. $+z$ & $-z$ axes). Thus, two trans M-L bonds are long and four M-L bonds in xy square plane are short resulting elongated distorted octahedral geometry/shape.

(iii) d^7 system (low spin complexes): $[CoF_6]^{3-}$ or Co^{2+} is a d^7 system (low spin, i.e. strong ligand field). The electronic conf. of d^7 ion/system in low spin octahedral complex is $t_{2g}^6 e_g^1$. This configuration has symmetrically filled t_{2g} orbitals and asymmetrically filled e_g orbitals. e_g^1 electron is present in d_{z^2} & $d_{x^2-y^2}$ orbital is vacant, i.e. $(d_{z^2})^1 (d_{x^2-y^2})^0$. Due to presence of asymmetrically filled e_g orbitals in $t_{2g}^6 e_g^1$ or $t_{2g}^6 (d_{z^2})^1 (d_{x^2-y^2})^0$ conf; low spin octahedral complex of d^7 ion undergo large distortion.

(iv) d^8 system (low spin complexes): $[M(diam)_2]^{2+}$ or M^{2+} (where $M = Ni, Pd, Pt$) are d^8 system (in low spin, i.e. strong ligand field). The electronic conf. of d^8 system in low spin state is $t_{2g}^6 e_g^2$ or $t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^1$. In this configuration, t_{2g} orbitals are symmetrically filled.

(3)

e_g orbitals are asymmetrically filled, since both the e_g electrons are present in d_{z^2} orbital. Hence, the complexes having d^8 ion in low spin state show large distortion giving elongated distorted octahedral geometry/shape. The splitting of t_{2g} & e_g orbitals in elongated distorted octahedral complexes shown in figure given below:



The elongation of axial bond lengths in the complex is so larger that the complex assumes square planar geometry.

(d^9 system): $[Cu(H_2O)_6]^{2+}$ or Cu^{2+} is d^9 system. The electronic configuration of d^9 system ion is $t_{2g}^6 e_g^3$. In this configuration, t_{2g} orbitals are symmetrically filled while e_g orbitals are asymmetrically filled. Due to presence of asymmetrically filled e_g orbitals, the complex ions undergo large distortion, either elongated or compressed distorted octahedral geometry. If $t_{2g}^6 e_g^3$ configuration is $t_{2g}^6 (d_{z^2})^2 (d_{x^2-y^2})^1$, octahedral complexes assume elongated distorted octahedral geometry. On the other hand, if $t_{2g}^6 e_g^3$ conf. is $t_{2g}^6 (d_{z^2})^1 (d_{x^2-y^2})^2$, the octahedral complexes assume compressed distorted octahedral geometry, since axial M-L bonds shorten and planar (equatorial) M-L bonds larger.

The effect of the asymmetric arrangement of 1 or 3 electrons in e_g orbitals on the octahedral geometry of the complex ions is called Jahn-Teller effect.

⇒ Interpretation of Electronic spectra on the basis of Jahn-Teller effect:

Jahn-Teller effect successfully explain the bands observed in electronic absorption spectra of a number of octahedral complexes having asymmetric ele. conf. (e.g. d^1, d^9 system).

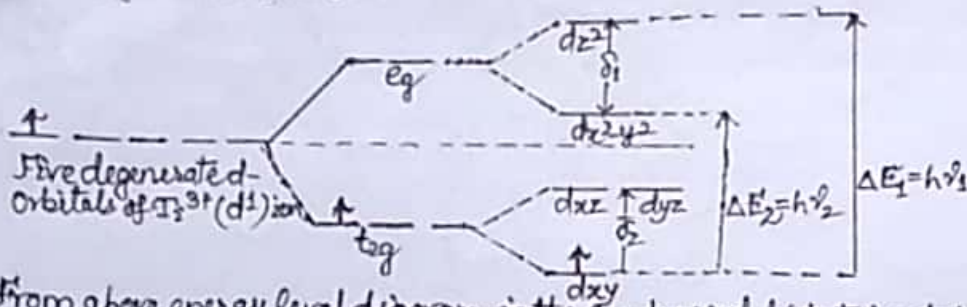
1. Electronic spectrum of $[Ti(H_2O)_6]^{3+}$: The absorption spectrum of $[Ti(H_2O)_6]^{3+}$ ion has two bands, which overlap to give a composite unsymmetrical absorption band, and peak is not symmetrical. This can be explained by Jahn-Teller effect as follows:

$[Ti(H_2O)_6]^{3+}$ ion has Ti^{3+} ion, which ground state electronic configuration is $3d^1$ or $t_{2g}^1 e_g^0$. t_{2g}^1 electron may be present in d_{xy} or d_{yz}/d_{zx} orbitals.

Case-I If t_{2g}^1 electron present in d_{xy} orbital; it would screen the nucleus of Ti^{3+} ion more effectively in xy plane than yz or xz plane. This reduces the attraction between Ti^{3+} ion and negative end of dipole of H_2O (ligand) in xy plane, which produces elongation of $Ti^{3+}-OH_2$ bonds in xy plane, and shorter in z-axis. Since ligand (H_2O) along z-axis come closer to Ti^{3+} and along x & y axes move away from Ti^{3+} , the repulsion between d-electron of Ti^{3+} ion and negative end of dipole of H_2O (ligand) would become less in xy plane in comparison to that of xz or yz plane. As a result, energy of d_{xy} orbital decrease and energies of d_{yz}, d_{zx}

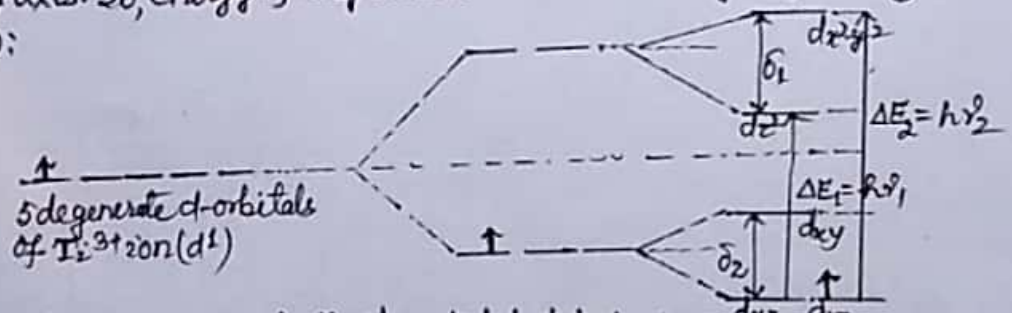
(4)

increase as shown below:



From above energy level diagram, in the compressed distorted octahedral geometry of $[Ti(H_2O)_6]^{3+}$ ion, the ground state of $Ti^{3+}(d^1)$ ion is d_{xy} and the excited states are dx^2y^2 & dz^2 , of which dx^2y^2 has lower energy. The two bands observed in the spectrum of $[Ti(H_2O)_6]^{3+}$ ion are due to (a) transition of one electron from d_{xy} orbital to dx^2y^2 orbital (i.e. $d_{xy}^1 \rightarrow dx^2y^2$) and (b) transition of one electron from d_{xy} orbital to dz^2 orbital (i.e. $d_{xy}^1 \rightarrow dz^2$ transition). Now, since the energy difference (δ_2) between d_{xy} & (dxz, dyz) pair very small, the above two transitions (a, b) are generally written as $t_{2g} \rightarrow dx^2y^2$ & $t_{2g} \rightarrow dz^2$ respectively. Again, since the energy gap (ΔE_1) is not very different from ΔE_2 , the two transitions are close in energy, and hence the frequencies (ν_1 & ν_2) of the two bands are close to each other, overlap to give a composite absorption band in the spectrum of $[Ti(H_2O)_6]^{3+}$ ion.

Case-II If t_{2g} electron present in dyz or dxz orbital, it would screen the Ti^{3+} nucleus more effectively in xz or yz plane than xy plane. This decreases the attraction between +ve nuclear charge on Ti^{3+} ion and the negative end of H_2O dipole along z -direction and increase along x & y axes. As a result, $Ti^{3+}OH_2$ bonds get elongated along z -axis. Since the ligands along z -axis move away from Ti^{3+} and those along x & y axes come closer to Ti^{3+} , repulsion between d -electron of Ti^{3+} & negative end of H_2O dipole become less in z -axis and more in x & y axes. So, energy of d_{xy} orbital increases & energies of dxz & dyz decrease, as shown below:



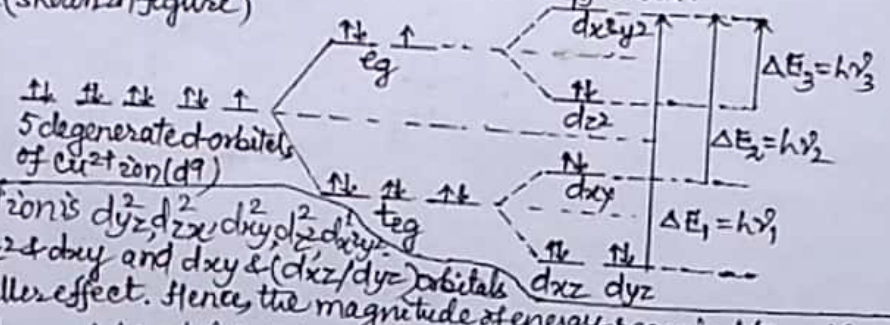
From above energy level diagram, in the elongated distorted octahedral geometry of $[Ti(H_2O)_6]^{3+}$ ion, the ground state of $Ti^{3+}(d^1)$ ion is (dxz, dyz) and excited states are dx^2y^2 & dz^2 , of which dz^2 has lower energy. The two bands observed in the spectrum of $[Ti(H_2O)_6]^{3+}$ ion are due to (a) transition of one electron from (dxz/dyz) or t_{2g} to dz^2 orbital (i.e. $(dxz/dyz)^1 \rightarrow dz^2$ transition) (b) transition of one electron from (dxz/dyz) or t_{2g} to dx^2y^2 (i.e. $(dxz/dyz)^1 \rightarrow dx^2y^2$ transition). Now, since the energy difference (δ_2) between (dxz, dyz) orbital pair & d_{xy} is very small, the above two transitions (a, b) are generally written as $t_{2g} \rightarrow dz^2$ & $t_{2g} \rightarrow dx^2y^2$ respectively. Since the energy gap (ΔE_1) is not very different from ΔE_2 , the two transitions are close in energy and hence the frequencies (ν_1 & ν_2) of two bands are close to each other, overlap to give a composite absorption band in the spectrum of $[Ti(H_2O)_6]^{3+}$ ion.

It is evident from above discussion that the complex ions show an asymmetric absorption band whatever be the electronic arrangement/distortion (elongated or compressed)

2. Interpretation of electronic spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion has elongated distorted octahedral geometry, in which axial $\text{Cu}^{2+}-\text{OH}_2$ bonds are longer than equatorial (i.e. equatorial) $\text{Cu}^{2+}-\text{OH}_2$ bonds. The absorption spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ has three bands. These bands are closer frequencies (ν_1, ν_2 & ν_3) which overlap to give a composite, unsymmetrical absorption band. This can be explained by Jahn-Teller effect as follows:

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion has Cu^{2+} (d^9 system) whose ground state electronic configuration is $t_{2g}^6 e_g^3$. The distribution of three electrons in e_g orbitals may be $d_{z^2}^2 d_{x^2-y^2}^1$ or $d_{z^2}^1 d_{x^2-y^2}^2$. Thus, electronic conf. of Cu^{2+} ion can be written as $t_{2g}^6 (d_{z^2})^2 (d_{x^2-y^2})^1$ or $t_{2g}^6 (d_{z^2})^1 (d_{x^2-y^2})^2$. Now, since the complex ion has elongated distorted octahedral geometry, $t_{2g}^6 (d_{z^2})^2 (d_{x^2-y^2})^1$ conf. is more stable than $t_{2g}^6 (d_{z^2})^1 (d_{x^2-y^2})^2$ conf. In this case, the relative order of the energies of different orbitals obtained by the splitting of t_{2g} & e_g orbitals of Cu^{2+} ion is as follows:
 $d_{yz} = d_{zx} < d_{xy} < d_{z^2} < d_{x^2-y^2}$ (shown in figure)



Hence, the electronic conf of Cu^{2+} ion is $d_{yz}^2, d_{zx}^2, d_{xy}^2, d_{z^2}^1, d_{x^2-y^2}^1$. The difference in energy of d_{z^2} & d_{xy} and d_{xy} & (d_{xz}/d_{yz}) orbitals is very small due to Jahn-Teller effect. Hence, the magnitude of energy required to excite an electron from d_{yz} (or d_{xz}), d_{xy} and d_{z^2} orbitals to partially filled $d_{x^2-y^2}$ orbital is nearly the same. The three bands, in the spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ are due to following electronic transitions: (a) transition of an electron from d_{yz}/d_{xz} orbital to $d_{x^2-y^2}$ orbital by absorbing energy ΔE_1 (or $h\nu_1$), i.e., $d_{xz} \rightarrow d_{x^2-y^2}$ transition.

(b) transition of an electron from d_{xy} orbital to $d_{x^2-y^2}$ orbital by absorbing energy ΔE_2 (or $h\nu_2$) i.e., $d_{xy} \rightarrow d_{x^2-y^2}$ transition.

(c) transition of an electron from d_{z^2} orbital to $d_{x^2-y^2}$ orbital by absorbing energy ΔE_3 (or $h\nu_3$) i.e., $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. All the transitions (a, b, c) have been shown in above figure.

If Jahn-Teller effect is not present in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion, the spectrum must have a single symmetrical band due to $t_{2g}^6 e_g^3 \rightarrow t_{2g}^5 e_g^4$ transition. Above discussion, also pointed out that the peak is not symmetrical in the spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ irrespective of an asymmetric absorption by the elongated distorted octahedral complex, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.