Quantitative Study of Racah Parameter of Manganese Ions in Co-ordination Compounds

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Abstract: *The origin of the spectrochemical series and the different dependence of crystal-field splitting (10Dq) and Racah parameters on the metal-ligand distanceis explored through rigorous calculations on Manganese Complexes.For this purpose, both periodic and cluster calculations have been performed.*

Background*: The importance of the transition metal complexes formed has significance in all areas of science due to its particular properties. The transition metal complexes are widely involved in active centers of proteins, catalysts, molecular electronics, electroluminescent devices, solid-state lasers, gemstones, high-pressure manometers.The spectrochemical series discuss many parameters very clearly. Such as it shows that monoatomic ionic ligands usually cause a poor perturbation in respect to polyatomic molecules or ions. The other series of ligands is 'Nephelauxetic series' which expresses the covalent tendency of ligands with respect to bond formation with the central metal ion. The magnitude of Nephelauxetic effect is expressed as the nephelauxetic ratio, ($\beta = B'/B$, which is given by the ratio of a given inter electronic repulsion parameter, i.e., Racah parameter value for metal ion in the complex (B') to its value in the gaseous ion (B).*

The current study gives a nice overview of the Racah parameters of An octahedral $MX6q-$ complex involves a central cation, M, and halide ligands, X (X = Cl, 2,4,5-trimethoxybenzaldehyde-S-benzyl dithiocarbazone (BBTC), NO3, CH3COO-) by exploring the metal-ligand distance through rigorous calculations on Manganese Complexes.

Materials and Methods*: An octahedral $MX6q-$ complex involves a central cation, M, and halide ligands, X (X = Cl, 2,4,5-trimethoxybenzaldehyde-S-benzyl dithiocarbazone (BBTC), NO3, CH3COO-).For this purpose, both periodic and cluster calculations have been performed.*

Results*: The current study gives a nice overview of the Racah parameters of An octahedral $MX6q-$ complex involves a central cation, M, and halide ligands, X (X = Cl, 2,4,5-trimethoxybenzaldehyde-S-benzyl dithiocarbazone (BBTC), NO_3, CH_3COO-) by exploring the metal-ligand distance through rigorous calculations on Manganese Complexes. The study shows that the Nephalauxetic effect (β) has been explored it is found that the manganese complexes $[Mn(BBTC)_2Cl_2]$, $[Mn(BBTC)_2(NO_3)_2]$, and $[Mn(BBTC)_2(CH3COO)_2]$ have Nephalauxetic effect of 6.66354, 4.5579, 7.06699. The calculation also shows that Racah parameters are 3.45413, 3.2802, 3.4273, respectively for all discussed complexes.*

Conclusion:*The study shows that the Nephalauxetic effect (β) has been explored it is found that the manganese complexes $[Mn(BBTC)_2Cl_2]$, $[Mn(BBTC)_2(NO_3)_2]$, and $[Mn(BBTC)_2(CH3COO)_2]$ have Nephalauxetic effect of 6.66354, 4.5579, 7.06699. The calculation also shows that Racah parameters are 3.45413, 3.2802, 3.4273, respectively for all discussed complexes.*

Key Word*: Racah Parameter; Manganese Ions; Co-ordination Compounds.*

I. Introduction

The importance of the transition metalcomplexes formed in all areas of science such as physics, chemistry, and biology due to its particular properties. The transition metal complexes are widely involved in active centers of proteins, catalysts, molecular electronics, molecular magnets, pigments,electroluminescent devices,solid-state lasers, gemstones,high-pressure manometers, and systems with ferroelectric distortions as well as giant magnetic anisotropy.

The spectrochemical series discuss many parameters very clearly. Such as it shows that monoatomic ionic ligands usually cause a poor perturbation in respect to polyatomic molecules or ions. Secondly, the polarizability of ligand is also an important factor in creation of a weak or a strong field. Thirdly, the ability of the ligand toparticipate in "-bonding with certain metal ion seems to enhance its perturbing power.Although these reasons are very important, but it is, however true that 10Dq is a complex quantity having contribution from at least four sources purely electronic perturbationeffect of π-lone pairs belonging to the ligandseffect of metal-ligand dπ-dπ bonding andeffect of ligand-metal pπ-dπ bonding.

The other series of ligands is 'Nephelauxetic series' which expresses the covalent tendency of ligands with respect to bond formation with the central metal ion. During the course of their study of the energy level diagram for transition metals ion of d^n configuration, Jorgensen and Schaterobserved that the separation between the various Russell-Saunders states is not exactly the same in the complex ion asin the free gaseous ion. The separation between different R-S states takes place due the repulsion between the d-electrons. Obviously, the decrease in the separation energy between d-electrons suggest that d-electron cloud have been expanded in the complex by ligands causing an increase in the mean distance between d-electron and thus decreasing the inter electronic repulsion. The different ligands are certainly differently effective in expanding the d-electronscloud. This effect of ligands in expanding the d-electron clouds is termed as 'Nephelauxetic effect'.

The magnitude of Nephelauxetic effect is ex- pressed as the nephelauxetic ratio, (which is given by the ratio of a given inter electronic repulsion parameter, i.e., Racah parameter value for metal ion in the complex (B') to its value in the gaseous ion (B). Thus β = B'/B.

Jorgensen and Schafter calculated the nephelauxetic effect and arranged ligand in the series as F– < H2O < urea < NH3 < oxalate ~ en < NCS– < Cl– ~ CN– ~ SCN– < Br– < I–. Since expansion of d-electrons cloud is correct with the extent to which covalent bond formation occurs, the nephelauxetic effect may be used as an index of such covalent complexing power. A perusal of the series obviously reveals that it follows the order of decreasing electronegativity of the atoms, e.g.: F> O > N > Cl > Br > I.

II. Material And Methods

An octahedral MX6q- complex involves a central cation, M, and halide ligands, X (X =Cl,2,4,5-trimethoxybenzaldehyde-S-benzyldithiocarbazone(BBTC), NO_3, CH_3COO-).The precursor, 2,4,5-trimethoxybenzaldehydewas procured from Lupin and S-benzyldithiocarbazatehas been purchased from Merck. The ligand wasprepared by the method reported by Islamet al. 0.01 mole (1.96 gram) of 2,4,5-trimethoxybenzaldehyde was dissolved in 25 mililitreof ethanol and 0.01 mole (1.98 gram) of S-benzyldithiocarbazate was also dissolved in 25mililitre of ethanol. The two solutions were mixedtogether and a little (about 2 mililitre) of concH_2SO_4 was added to it. The resulting solution wasrefluxed on water bath using air condenser forabout four hours. The yellow turbidity appearedwhich got solidified after leaving overnight. It wasfiltered by suction. The solid was recrystallized inethanol-acetone mixture. Its melting point was determined to be 184°C.The yield was 79%.

Dichloride-bis(2,4,5-trimethoxy   benzaldehyde-S-benzyldithiocarbazone)manganese(II)[Mn(BBTC)$_2$Cl$_2$] was prepared by following procedure. 0.1 mole (2.34 gm) of MnCl2.6H2O was dissolved in 20 mililitre of ethanol and 0.2 mole (6.56gm) of the ligand 2,4,5-trimethoxybenzaldehyde-Sbenzyl dithiocarbazone was dissolved separately in20 mililitre of ethanol. The two solutions weremixed together and the resulting solution was refluxed for 2 hours, using Leibig condenser on water bath. This solution was left overnight, whenmagneta coloured solid appeared which was filteredon suction and washed with ethanol and then bydistilled water. The solid was recrystallized in ethanol and it was dried in desiccator on dry anhydrous$CaCl_2$. Its melting point was determined and C, H,S and N were determined microanalytically.

Dinitrato-bis(2,4,5-trimethoxybenzaldehyde-S-benzyldithiocarbazone)manganese(II)[Mn(BBTC)$_2$(NO$_3$)$_2$] was prepared by following procedure. 1 m mole (0.287 gram) of Mn(NO$_3$)$_2$6H$_2$O wasdissolved in 20 millilitre of ethanol and 2 milimole(0.656 gram) of ligand BBTC was also dissolved in20 mililitre of ethanol. The two solution weremixed and was refluxed on water bath, usingLeibig condenser for two and half hours. This solution was left to stand whereby a dull red ppt appeared after 3 hours. It was filtered and recrystallized as above. The compound was dried in airoven and its melting point was noted down. Itsmelting point was 271°C.

Diacetato-bis(2,4,5-trimethoxybenzaldehyde-S-benzyldithiocarbazone)manganese(II)[Mn(BBTC)$_2$(CH$_3$COO)$_2$] was prepared by following procedure. 1 milimole (0.173 gram) of Mn(CH$_3$COO)$_2$was dissolved in 20 mililitre of ethanol and 2 milimole (0.656 gram) of ligand (BBTC was dissolvedin 20 mililitre ethanol seperately and the two solution were mixed. The resulting solution was refluxed on water bath using Leibig condenser forabout 3 hours. After cooling the solution red pptappeared which was filtered and recrystallised inalcohol. Its M.P. was measured and was found tobe 269°C, the yield was found nearly 71%.

III. Result

The molar conductivity of complexes has been determined on conductivity on conductivity meter (G. 857 Schott-Grate GmbH) in DMSO solution of 10^{-3}M concentration using Dip type cell having Pt- electrode. The value of molar conductivity of complexes have been given in table 01.

Table no 01: Molar conductivity of complexes

	Compounds		$\lambda m (Ohm^{-1} cm^2 mol^{-1})$
1.	$[Mn(BBTC)_2Cl_2]$	–	21
2.	$[Mn(BBTC)_2(NO_3)_2]$	–	23
3.	$[Mn(BBTC)_2(CH_3COO)_2]$	–	20
4.	$[Fe(BBTC)_2Cl_2]$	–	20
5.	$[Fe(BBTC)_2(NO_3)_2]$	–	18
6.	$[Fe(BBTC)_2(CH_3COO)_2]$	–	20
7.	$[Co(BBTC)_2Cl_2]$	–	21
8.	$[Co(BBTC)_2(NO_3)_2]$	–	23
9.	$[Co(BBTC)_2(CH_3COO)_2]$	–	23

The value of molar conductivity of complexes in Dimethyl sulfoxide (DMSO) Solution of concentration 10^{-3}M has been found in the range of18-23Ω^{-1} cm^2 mol^{-1}. The extremely low values of conductivity indicate the non-electrolytic nature of all the complexes.[1-7]
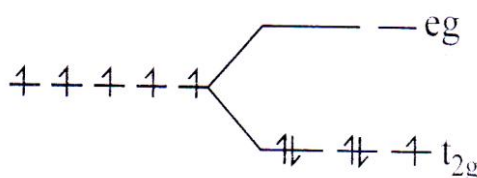
Magnetic moment of Mn(II) Complexes :

Magnetic moment of complexes has been determined on Gouy's Balance Method using $Hg[Co(CN)_4]$, [Mercuric tetra cyanide cobaltate (II)] as calibrant. The magnetic susceptibility value determined from this method were converted into magnetic moment using the expression $\mu = 2.828(\chi_{AT})^{1/2}$B.M.[8] The magnetic moment of Mn(II) complexes has been given in table 02.

Table no 02: Magnetic moment of Mn(II) complexes

Complexes		Magnetic Moment of Mn (II) Complexes $\mu = (B.M)$
1. $[Mn(BBTC)_2Cl_2]$	–	5.81
2. $[Mn(BBTC)_2(NO_3)_2]$	–	5.80
3. $[Mn(BBTC)_2(CH_3COO)_2]$	–	5.83

Mn (II) is a d^5-system which may from high spin complexes with weak ligand with S=5/2. But if the ligands are strong, Mn(II) may from low spin complexes with S=1/2. The spin only value of magnetic moment in spin free complexes of Mn(II) may be given as $\mu_s = \sqrt{4S(S+1)} = \sqrt{4 \times \frac{5}{2}\left(\frac{5}{2}+1\right)} = \sqrt{10\left(\frac{5+2}{2}\right)} = \sqrt{\frac{10 \times 7}{2}} = \sqrt{35} = 5.92 B.M$. Therefore; $\mu_s = \sqrt{35} = 5.92 B.M$

The value is independent of temperature irrespective of wheather the ligand arrangement around Mn(II) is tetrahedral, octahedral or low symmetry. The magnetic moment of a number of Mn(II) has been measured at room temperature and mostly has been found to be very close to 5.9 B.M.[9-10] In low spin octahedral complexes of Mn(II) there is only one unpaired electron and S=1/2. So, Magnetic moment may be given as $\mu_s = \sqrt{4S(S+1)} = \sqrt{4 \times \frac{1}{2}\left(\frac{1}{2}+1\right)} = \sqrt{2 \times \frac{3}{2}} = \sqrt{3} = 1.732 B.M$. Therefore; $\mu_s = \sqrt{3} = 1.732 B.M$

But such complexes exhibit magnetic moment nearly 2.5 B.M, which is temperature dependent.[11] The configuration in low spin octahedral complexes becomes $t_{2g}^5 eg^0$.

The t_{2g}^5 configuration produces $2T_{2g}$ ground term which should be under the influence of spin orbit coupling constant ($\lambda = 300 cm^{-1}$), the triply degenerate ground term $2T_{2g}$ makes an appreciable contribution to the magnetic moment of complexes and hence it becomes greater than spin only value i.e., 1.732 B.M.

Magnetically dilute$O_h$complexes of high spin Mn(II) have recorded magnetic moment 5.68-5.88 B.M.[12,13] In some cases of complexes of Mn(II) with Schiff base recorded magnetic moment 474-5.7 B.M at room temperature. The values are much below the spin only value. But no obvious explanation of these low values of magnetic moment of Mn(II) complexes could be advanced. A d^5-system has ^{6}S ground state term

which under octahedral symmetry gets transformed into $^6A_{1g}$. As it is orbitally singly degenerate, there is no orbital contribution to the magnetic moment of Mn(II) complexes. The slightly low value of magnetic moment may be due to spin orbit coupling which further restricts the spin as well as orbital motion of the electron to the little extent.

The magnetic moment of Mn(II) complexes in the present study are found 5.80-5.83 B.M. The value are very close to the magnetic moment corresponding to five unpaired electron. The values are indicative of the fact that Mn(II) complexes are high spin magnetically dilute octahedral complexes.
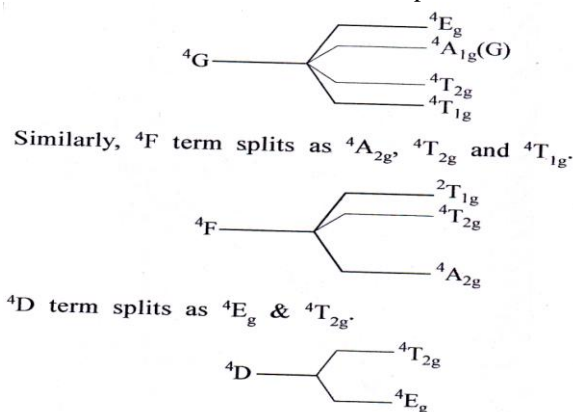
**Electronic Spectra of Mn(II) complexes :**

Mn, Z=25

Electronic configuration = $[Ar]3d^5 45^2$

$Mn^{2+} = [Ar]3d^5$

So, Mn^{2+} is a d5-system for which the ground state term is 6s and the next higher terms are ^4G, ^4F, ^4D, $4 \times {}^4P$, ^2H, $2 \times {}^2G$, $2 \times {}^2F$, $3 \times {}^2D$, ^2P, and ^2S. The total terms correspond to 252 micro states of d5-system.[14]

Similarly, ^4F term splits as $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$.

^4D term splits as ^4E_g & $^4T_{2g}$.

Out of these terms the Ground term ^1S is the non-degenerate term which doesn't further split by the perturbation of O_h crystal field or T^d or Sq. planner, C_{4V} or distorted octahedral (D_{4h}). However, under octahedral symmetry it is transfer into $^6A_{1g}$. The next higher term 4G undergoes splitting in octahedral crystal field into $^4T_{1g}$, $^4T_{2g}$, ^4E_g and $^4A_{1g}$.
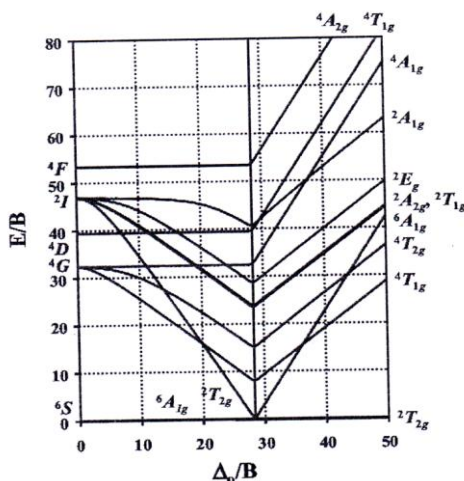
^4P term is triply degenerate but it doesn't split under octahedral symmetry. However, it gets also split into different crystal field term in various crystal field term in various crystal field perturbation. The energy level diagram at d5-system in an octahedral crystal field was given by Tanabe Sugano which shows the graph of variation of E/B and Dq/B Roughly it may be shown as below.[15]

Through the ground state crystal field term is 2A1g and the other higher terms are either quartet or doublet spin states. As three spin states are not similar, ther no spin allowed transition. However various spin forbidden transition are possible. In the present study Mn(II) complexes, four weak bands appeared in their electronic spectra which have been given in table 03.

Table no 03:

Complexes		Electronic Spectral Bands in cm^{-1}			
		v_1	v_2	v_3	v_4
(i)	$[Mn(BBTC)_2Cl_2]$	18,100	24,435	26,400	27,700
(ii)	$[Mn(BBTC)_2(NO_3)_2]$	18,050	24,190	26,300	27,600
(iii)	$[Mn(BBTC)_2(CH_3COO)_2]$	18,200	24,210	26,150	27,300

The assignment of these bands may be given as below.

$$v_1 \quad {}^6A_{1g} \quad \rightarrow \quad {}^4T_{1g}\,({}^4G)$$
$$v_2 \quad {}^6A_{1g} \quad \rightarrow \quad {}^4T_{2g}\text{ or }{}^4A_{1g}\text{ or }{}^4E_g\,({}^4G)$$
$$v_3 \quad {}^6A_{1g} \quad \rightarrow \quad {}^4E_g\,({}^4D)\text{ and}$$
$$v_4 \quad {}^6A_{1g} \quad \rightarrow \quad {}^4T_{1g}\,({}^4P)$$

IV. Discussion

Now, the electronic special data have been used to evaluate the different crystal field parameters, like Dq B (Racah Parameter). C (Again Racah Parameter, showing the difference of energy between terms of different spin multiplicity, Nephelauxetic effect (β) and C/B ratio using the Tanable Sugano diagram.

(i) **For Complex [Mn(BBTC)$_2$Cl$_2$] :**

$\frac{v_2}{v_1} = \frac{24,435}{1800} = 1.35$

In Tanabe Sugano diagram this ratio is obtained on E/B = 20.2 axis for Dq/B=1.4

So, $\quad \frac{v_1}{B} = 20.2$

or, $\quad B = \frac{18100}{20.2} 896.03 cm^{-1}$

Since $\quad$ Dq/B $\quad$ =1.4

or, $\quad$ Dq $\quad$ = B $\times$ 1.4

$\quad\quad\quad\quad\quad$ = 896.03 $\times$ 1.4

$\quad\quad\quad\quad\quad$ = 1,254.442 cm^{-1}

As we know, the B0 value for Mn (II) free ion is 960 cm^{-1}.

So, Nephelauxetic effect $(\beta) = \frac{B_0 - B}{B_0} \times 100$

$\quad\quad\quad\quad = \frac{960 - 896.03}{960} = \frac{6397}{960} = 6.66354\%$

Since $\quad\quad\quad\quad v_2 = 10B + 5C$

$\quad\quad\quad\quad$ 24,435 = 10 $\times$ 896 + 5C

$\quad\quad\quad\quad$ 5C = 24,435 - 8960

$\quad\quad\quad\quad$ 5C = 15,475

So, $\quad$ C $\quad = \frac{15475}{5} = 3095 cm^{-1}$

So, $\quad$ C/B $= \frac{3095}{896.03} = 3.45413$

The value of C/B for this Mn (II) complex is slightly less than the theoritical value of C/B = 3.8 for Mn2+.

(ii) **For Complex [Mn(BBTC)$_2$(NO3)$_2$] :**

$\quad\quad\quad$ E/B = 19.7 $\quad\quad\quad\quad \frac{Dq}{B} = 1.8$

$\quad\quad\quad \frac{v_2}{v_1} = \frac{24190}{18050} = 1.34017$

$\quad\quad\quad$ So, $\frac{v_1}{B} = 19.7$

$\quad\quad\quad B = \frac{18050}{19.7} = 916.24365$

$\quad\quad\quad$ Since,

$\quad\quad\quad$ Dq = 1.8 $\times$ B = 1.8 $\times$ 916.24365 = 1,649.23857

So, Nephalauxetic effect $(\beta) = \frac{B_0 - B}{B_0} \times 100$

$\quad\quad = \frac{960 - 916.24365}{960} \times 100$

$$= \frac{43.75635 \times 100}{960} = \frac{4375.635}{960} = 4.55795$$

Since $\nu_2 = 10B + 5C$

$$24190 = 10 \times 916.24365 + 5C$$
$$5C = 24190 - 9162.4365$$
$$C = \frac{15,027.5635}{5} = 3,005.5127$$

So, $C/B = \frac{3005.5127}{916.24365} = 3.28025$

(iii)   For Complex [Mn(BBTC)$_2$(CH$_3$COO)$_2$] :

$$\frac{\nu_2}{\nu_1} = \frac{24,210}{18,200} = 1.33022$$
$$E/B = 20.4 \qquad ,$$

So, $\frac{\nu_1}{B} = 20.4$

or, $B = \frac{18200}{20.4} = 892.1586$

Since,

$$Dq = B \times 1.6 = 892.15686 \times 1.6 = 1,427.45098$$

So, Nephalauxetic effect $(\beta) = \frac{B_0 - B}{B_0} \times 100$

$$= \frac{960 - 892.15686}{960} \times 100$$
$$= \frac{67.84314}{960} \times 100 = \frac{6784.314}{960} = 7.06699$$

Since, $\nu_2 = 10B + 5C$

$$24, 210 = 10 \times 892.15686 + 5C$$
$$5C = 24,210 - 8921-5686$$
$$C = \frac{15,288.4314}{5} = 3057.68628$$

So, $C/B = \frac{357.68628}{892.15686} = 3.4273$

On the basis of electronic spectral bands the various our crystal field parameter for all Mn(II) complexes have been calculated and the values are displayed in table 4.

Table no: 04

The values of crystal field parameters for Mn(II) Complexes.

	Complexes	ν_2/ν_1	Dq (Cm^{-1})	B (Cm^{-1})	C (Cm^{-1})	C/B	β
I	[Mn(BBTC)$_2$Cl$_2$]	1.35	1254.442	896.03	3095	3.45413	6.66354
II	[Mn(BBTC)$_2$(NO$_3$)$_2$]	1.34017	1649.238	916.243	3005.51	3.2802	4.55795
III	[Mn(BBTC)$_2$(CH$_3$COO)$_2$]	1.33022	1427.450	892.156	3057.68	3.4273	7.06699

The values of C/B derived here for Mn(II) complexes is closed to the theoretical value (3.5)[16]. The value of different crystal field parameter are in quite agreement with the values reported for O$_h$ complexes of Mn(II)[2,3,4,17-19]. On the basis of magnetic moment, molar conductivity, IR-spectra and electronic spectra. The tentative structure of Mn(II) complexes may be given as below.
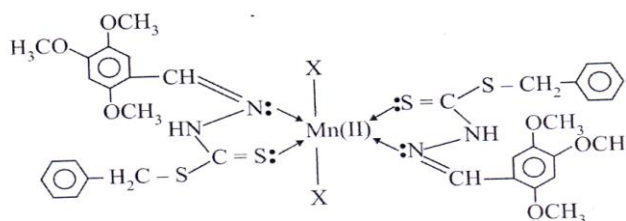
Where X = Cl$^-$, NO$_3^-$, CH$_3$COO$^-$

V. Conclusion

The current study gives a nice overview of the Racah parameters of An octahedral MX6q- complex involves a central cation, M, and halide ligands, X (X = Cl, 2,4,5-trimethoxybenzaldehyde-S-benzyl dithiocarbazone (BBTC), NO3, CH3COO-) by exploring the metal-ligand distance through rigorous calculations

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