Kinetic study for the interaction of Nd(III) with creatine in different organic solvents using 4*f*-4*f* transition spectra as a probe

N. Mohondas Singh*, Ramananda Singh Naorem, H. Lalthlamuanpuii, Lalhmingmawia and Dhritiman Borgohain

Department of Chemistry, School of Physical Sciences, Mizoram University, Aizawl-796 004, Mizoram, India

*E-mail: nmdas08@rediffmail.com

The 4*f*-4*f* spectra involving the interaction between Nd(III) with creatine in the presence and absence of Zn(II) is discussed using four solvents such as methanol, dioxane, acetonitrile, DMF. The energy of interaction parameters namely, Slater-Condon (F^K) factor, Lande spin-orbit coupling constant (ξ_{4f}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and percent covalency (δ), have been evaluated for the interaction between Nd(III) and creatine. The variation in these parameters revealed the formation of bond between Nd(III)-creatine. The oscillatory strength, as well as Judd-Ofelt parameters, is also evaluated for the complexation. It was found that the reaction followed the first-order kinetics, and the rate of reaction for the complexation was found to be 0.03574×10^{-6} mol L^{-1} s^{-1}.

Keywords: 4*f*-4*f* Spectra, Nd(III), creatine, organic solvents, Judd-Ofelt parameters.

Introduction

Creatine is an important substance which is usually found in muscle cells of our body. Creatine in our body is mainly from amino acids such as glycine and arginine[1]. It keeps our body healthy and helps in improving athletic performance[2]. Supplementation of creatine increases phosphocreatine stores which is a form of energy store inside the cells. Consequently, high energy molecules are produced known as ATP. ATP gives energy to the body, especially during exercise[3]. It also plays an essential role in gaining muscles in many ways viz. boosted workload, improve cell signalling, raised anabolic hormones, increased cell hydration, reduced protein breakdown etc.[4–9] Moreover, creatine keeps the brain healthy by increasing the phosphocreatine stores, and it protects the brain from neurological disease[10,11]. On the other hand, lanthanide ions are also well known as it has many applications such as luminescence, biosensors, bioimaging, etc.[12–15] The electronic signals due to 4*f* electron transition lie in the accessible region and make the electrochemical study very simple. These transitions are very sensitive toward the minor change of their coordination environment. Hence, the coordination chemistry of lanthanides can be understood using their absorption spectroscopy. Moreover, the formation of inner and outer-sphere complexes can be understood using intra 4*f*-4*f* transitions[16].

In this paper, 4*f*-4*f* spectral analysis involving praseodymium/neodymium interaction with creatine is discussed using different solvents. Spectral analysis of 4*f*-4*f* transition have been employed, evaluating the oscillator strength and Judd-Ofelt electronic dipole intensity parameters, T_λ (λ = 2, 4, 6) for the complexation of Pr(III)/Nd(III) with creatine in presence and absence of Zn(II) were evaluated. It is believed that the study will have some significance in biological applications.

Experimental

The chemicals used for the experiment are $NdCl_3 \cdot H_2O$ and creatine from Alfa Aesar, $ZnCl_2$, DMF, methanol, acetonitrile, dioxane from Himedia. In the preparation steps, 0.01 *M* solutions of Nd(III), creatine and Zn(II) were prepared using different solvents such as DMF, methanol, acetonitrile, dioxane. For studying the absorption spectra of Nd(III) and Nd(III):creatine in four solvents, the Nd(III):ligand molar ratio is fixed at 1:1. Nd(III):creatine:Zn(II) ratio was kept 1:1:1 in all solvents for the multimetal interaction. Thermo Scientific Evolution 220 UV-Visible spectrophotometer was used for recording the absorption spectra. All the measurements were done at room temperature.

Methods:

The information on covalency can be earned from the nephelauxetic ratio value. Again the nephelauxetic ratio can be determined from calculating the values of Racah parameter and Slater-Condon parameters.

$$\beta = \frac{F_k^C}{F_k^f} \; or \; \frac{E_C^k}{E_f^k} \tag{1}$$

F_k stands for the Slater-Condon parameter for the free ions (*f*) and the complex (*C*). The other parameters such as bonding parameter and the percent covalency can be measured as:

$$b^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2} \tag{2}$$

$$\delta\% = \left[\frac{1-\beta}{\beta}\right] \times 100 \tag{3}$$

E_{so} from the electronic transition in the 4*f*-4*f* energy interaction mostly arises from the magnetic interactions. The following expression can give a better idea about the spin-orbit interaction[17].

$$E_{so} = A_{so}\xi_{4f} \tag{4}$$

In the above equation, A_{so} stands for the angular spin-orbit interaction and ξ_{4f}, also known as Lande's parameter, indicates the radial integral. The energy of the *j*-th level as follow[18]:

$$E_j(F_k, \xi_{4f}) = E_{0j}(F_k^0, \xi_{4f}^0) +$$

$$\Sigma_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta\xi_{4f} \tag{5}$$

where E_{0j} indicates the zero-order energy. F_k and ξ_{4f} can be expressed as follows:

$$F_k = F_k^0 + \Delta F_k \; and \; \xi_{4f} = \xi_{4f} + \Delta\xi_{4f} \tag{6}$$

The difference in the energy between the zero-order value and the observed value is expressed as:

$$\Delta E_j = \Sigma_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta\xi_{4f} \tag{7}$$

ΔF_k and $\Delta\xi_{4f}$ be evaluated from the above equation by solving it with least square method[18]. Putting their value in eq. (6), the values of ΔF_2, ΔF_4, ΔF_6 and $\Delta\xi_{4f}$ can be evaluated.

The intensities of the bands can be calculated from the theoretical treatments given by Judd and Ofelt. They assumed the transitions to be electrically dipolar. The oscillator strength of the induced dipole in the $\psi J \rightarrow \psi'J'$ the transition can be expressed as[19]

$$P = \sum_{\lambda=2,4,6} T_\lambda^- \langle f^n \Psi J \rightarrow |U^\lambda||f^n \Psi'J'\rangle^2 \tag{8}$$

where $U^{(\lambda)}$ indicates, the λth ranked matrix element. T_2, T_4, and T_6 are the radial parts of the wave function $4f^N$, near the wave function $4f^{N-1} 5d$. The probability of radiant energy P is related to the measured absorption intensity.

$$P_{obs} = 4.6 \times 10^{-9} \times \xi_{max} \times \Delta_{1/2}^- \tag{9}$$

where ξ represents molar absorptivity and $\Delta_{1/2}^-$ is half band width. From the values of the above equation, one can find the values of the factors T_2, T_4, and T_6 as follows:

$$\frac{P_{obs}}{\nu} = [(U^2)]^2 T_2 + [(U^4)]^2 T_4 + [(U^6)]^2 T_6 \tag{10}$$

The following equation depicts the formation of the complex through the Arrhenius equation. To find the rate, one can plot ln *k* vs 1/*T*.

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \tag{11}$$

where *A* is the pre-exponential frequency factor, and the calculation of E_a can be done as follows:

$$E_a = Slope \times 2.303 \times R \tag{12}$$

Results and discussion

Because of the transitions between the levels of f^N configuration, lanthanides exhibit sharp peaks. Even in minor changes in coordination, some of the 4*f*-4*f* transitions show good sensitivity[20]. These types of transitions are known to be hypersensitive transitions. Neodymium shows five highly intense peaks due to five different transitions. Those are $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$ respectively[21,22]. Absorption spectra of Nd(III); Nd(III): creatine; Nd(III):creatine:Zn(II) in different solvents is shown in Fig. 1, which shows the increase in the intensity of the peak with the addition of the ligand in all the four different solvents. Among which, the highest intensity is shown in DMF. This intensity is a sign of complexation of the ligand with
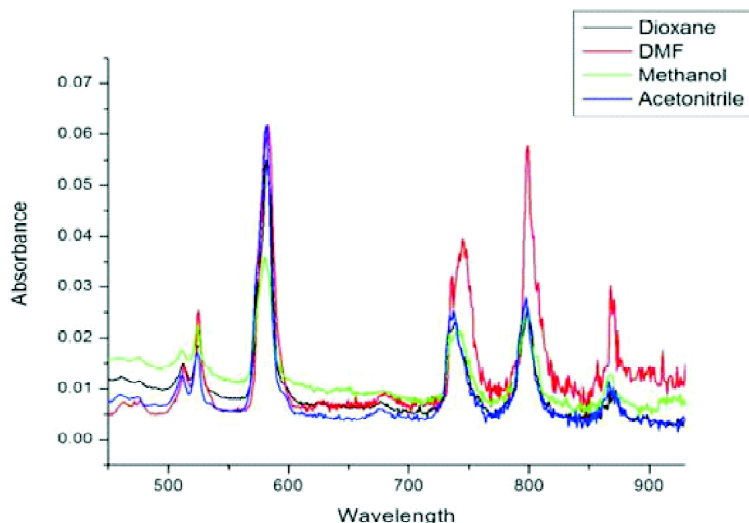
Fig. 1. Comparative absorption spectra for Nd(III):creatine in four different solvents at 303.45 K.

Table 1. Calculated values of energy interaction spin-orbit interaction, ξ_{4f} (cm^{-1}), Slater-Condon, F_k (cm^{-1}), bonding ($b^{1/2}$), nephelauxetic ratio (β), and covalency (δ) parameters of Nd(III):creatine and Zn(II) in DMF

DMF	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
NdS2	325.474	49.02113	5.354628	990.8769	1.049609	0.689344	4.726411
NdS2L	325.7995	49.17434	5.349684	984.4384	1.04658	0.690442	4.450718
NdSZn	326.0121	49.16195	5.344974	982.0272	1.045163	0.690955	4.32111

Table 2. Experimental data for the observed and calculated values for oscillatory strength and Judd-Ofelt parameters Nd(III), Nd(III):ligand, Nd(III):ligand:Zn(II) in DMF

DMF	P_{obs1}	P_{cal1}	P_{obs2}	P_{cal2}	P_{obs3}	P_{cal3}	P_{obs4}	P_{cal4}	P_{obs5}	P_{cal5}	T_2	T_4	T_6
Nd	1.388519	0.878928	4.359641	6.651925	2.690017	0.322385	2.197775	2.49979	0.80137	0.657356	2.16	1.6	3.63
NdL	1.560871	0.689958	4.857483	7.410522	2.981624	0.302848	2.086145	2.485018	0.595196	0.468422	2	1.51	4.15
NdLZn	1.817385	0.932438	4.6153	6.638889	2.682108	0.298155	1.637973	2.269068	0.913503	0.648861	2.69	0.69	4.6

lanthanide in the DMF environment. The absorption intensities of Nd(III):creatine:Zn(II) in DMF in a different interval of time were measured at 303.45 K.

Further, more intense peaks are observed in the presence of Zn(II) ion. Table 1 explains the calculated values of energy interaction spin-orbit interaction, ξ_{4f} (cm^{-1}), Slater-Condon, F_k (cm^{-1}), bonding ($b^{1/2}$) nephelauxetic ratio (β), and covalency (δ) parameters of Nd(III):creatine and Zn(II) in DMF. The nephelauxetic effect plays a vital role here to show the nature of the metal-ligand bond. The table clearly shows that the values were more than 1, which showed the formation of ionic bond[23–25].

Table 3 shows calculated values of energy interaction

spin-orbit relation, ξ_{4f} (cm^{-1}), Slater-Condon, F_k (cm^{-1}), bonding ($b^{1/2}$), nephelauxetic ratio (β), and covalency (δ) parameters of Nd(III):creatine and Zn(II) in DMF by differing the reaction time intervals. Table 4 shows both observed and calculated oscillatory strength as well as Judd-Ofelt parameter (T) for Nd(III):creatine:Zn(II) in DMF. The tables' analysis revealed an increase in both the parameters mentioned above when Zn(II) is added. The observation is similar to the addition of the ligand too. The magnitude of Judd-Ofelt parameters increases as ligand and Zn(II) are added and results in Nd(III) enhancement-ligand interaction in the solution. The T_λ values alter considerably. Here, T_4 in this study is not considered due to its negative values. Both parameters show an excellent relation concerning the instantaneous change

Table 3. Calculated values of energy interaction spin-orbit relation, ξ_{4f} (cm^{-1}), Slater-Condon, F_k (cm^{-1}), bonding ($b^{1/2}$), nephelauxetic ratio (β), and covalency (δ) parameters of Nd(III):creatine and Zn(II) in DMF at different time intervals 303.45 K

Time (h)	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
1	327.2668	48.62106	5.2889	971.4249	1.036297	0.694155	3.502553
2	327.6823	48.6745	5.284301	966.1523	1.033629	0.695115	3.253509
3	327.6691	48.61631	5.295455	969.287	1.035514	0.694437	3.429637
4	327.8295	48.5213	5.283422	967.5546	1.033928	0.695008	3.281489
5	327.2205	48.63401	5.292663	972.2452	1.036892	0.693941	3.5579
6	327.2709	48.60344	5.287372	971.429	1.036192	0.694193	3.492793
7	327.3898	48.55569	5.27563	969.2196	1.034492	0.694805	3.334173
8	327.7091	48.65075	5.288359	967.0955	1.034213	0.694905	3.30815
9	327.7904	48.62354	5.273733	964.2798	1.032136	0.695652	3.113574
10	327.5699	48.797	5.282945	964.5732	1.033074	0.695315	3.201482
11	326.2673	48.32141	5.511596	1024.177	1.071068	0.681517	6.635269
12	328.0398	48.75694	5.283601	961.5032	1.031501	0.69588	3.053868
13	327.9138	48.55884	5.260125	962.0288	1.030298	0.696313	2.940662
14	327.659	48.69364	5.292473	967.4578	1.034666	0.694742	3.35049

Table 4. The experimental values of the oscillatory strength (observed and calculated) and Judd-Ofelt intensity parameter (T) for Nd(III): creatine:Zn(II) in DMF for different times(upto 14 h) at 303.45 K

Time	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$				
(h)	P_{obs1}	P_{cal1}	P_{obs2}	P_{cal2}	P_{obs3}	P_{cal3}	P_{obs4}	P_{cal4}	P_{obs5}	P_{cal5}	T_2	T_4	T_6
1	0.319476	0.167533	4.396733	2.559206	1.916883	1.429036	0.948057	0.758455	0.128327	0.111502	2.49	−1.02	3.05
2	0.396856	0.208103	4.556609	2.654726	1.956158	1.49547	1.516075	1.213755	0.136113	0.118294	2.5	−0.37	3.2
3	0.465172	0.243931	4.616062	2.689779	2.037146	1.519038	1.531251	1.224036	0.159423	0.138602	2.68	−0.08	3.28
4	0.489271	0.256241	4.735174	2.756587	2.06372	1.537801	1.573762	1.258884	0.241643	0.209927	2.74	0.01	3.33
5	1.066696	0.558021	4.785816	2.784436	2.071089	1.544763	1.607198	1.284762	0.279862	0.243127	2.77	0.03	3.36
6	1.210316	0.633915	4.813384	2.804037	2.08187	1.551264	1.61043	1.289358	0.297256	0.258426	2.82	0.05	3.38
7	1.264965	0.662475	4.898814	2.85449	2.086626	1.556435	1.62046	1.29642	0.302711	0.263359	2.83	0.06	3.46
8	1.278907	0.67062	4.908846	2.858765	2.118328	1.579489	1.648662	1.318929	0.316629	0.27568	2.84	0.32	3.46
9	1.321027	0.691822	4.961791	2.890243	2.154063	1.606156	1.681015	1.343837	0.317556	0.275281	2.86	0.49	3.67
10	1.325302	0.694154	5.02408	2.925974	2.225568	1.660095	1.703013	1.362496	0.321773	0.27955	3.03	0.52	3.69
11	1.474187	0.077208	5.050336	2.940255	2.265561	1.678878	1.726598	1.381227	0.341966	0.297298	3.11	0.87	3.78
12	1.643693	0.861887	5.132429	2.986201	2.355336	1.689497	1.787309	1.430098	0.353439	0.307057	3.13	0.89	3.83
13	1.805494	0.94561	5.170026	3.009214	2.367732	1.757175	2.429394	1.941961	0.356514	0.319458	3.3	0.96	3.93
14	2.071641	1.085022	5.508174	3.208676	2.516443	1.899255	2.811559	2.24756	0.494226	0.429349	3.55	1.58	4.26

in the compound's coordination and the other symmetry characteristics of the formed complex. In this experiment, the T_6 values are low and significantly show the formation of outer-sphere complex[26].

The kinetic study is performed by observing the changes in the intensity of 4f-4f spectra with time (Fig. 2). The experimental values of oscillator strength and the Judd-Ofelt intensity parameters involving the complexation of Nd(III):creatine and Zn(II) in DMF were calculated for different reaction time.

The increase in absorption spectra was observed with increased time (shown in Fig. 2). Table 4 indicates that T_2, T_4 and T_6 parameters show a positive increase in the transitions' oscillator strengths. The addition of Zn(II) to Nd(III):creatine leads to intense changes in the oscillator strengths and deviates in T_λ parameters.

At the first stage, the reaction seems to be very slow, which is shown by the marginal change in oscillator strength and supported by the increase in T_2, T_6, T_2 and T_6 param-
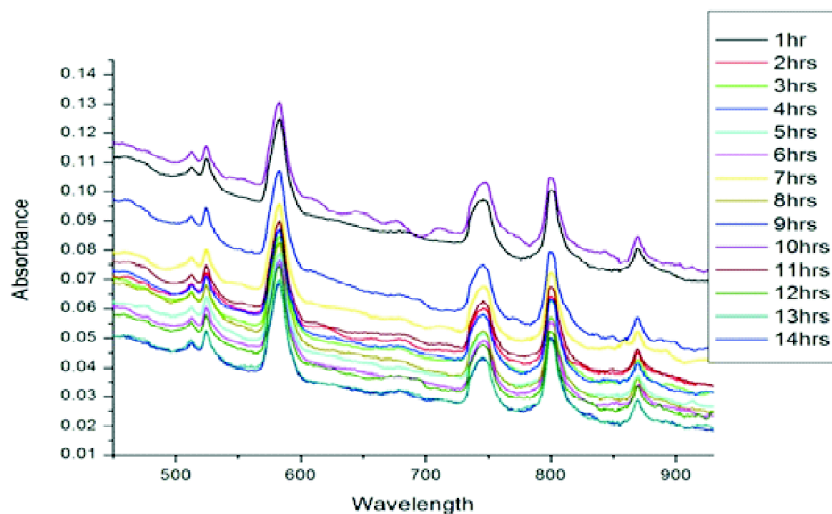
Fig. 2. Absorption spectra of Nd(III):creatine:Zn(II) in DMF at different times (upto 14 h) at 303.45 K.
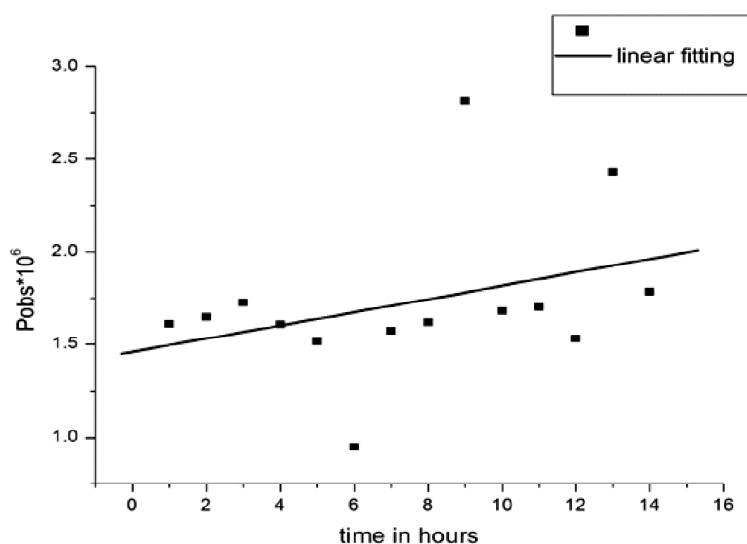

Fig. 3. Plot of P_{obs} and time (h) for the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd(III):creatine:Zn(II) in DMF.

eters are familiar with their responsive nature even when the coordination environment changes a bit[27–29]. Therefore, mere variation in these two parameters can be credited to even a minimal difference in Nd(III)'s coordination atmosphere. The reaction rate was calculated by plotting a graph of P (observed) vs time and taking its slope, as shown in Fig. 3. The slope's value was calculated, which gives the required rate and found as 0.03574×10^{-6} mol L^{-1} s^{-1}.

Conclusions

Nd(III) interaction with creatine was discussed using their 4f-4f transition spectra in four different solvents such as acetonitrile, dioxane, DMF, and methanol. Out of the four solvents, DMF was found to promote 4f-4f electric dipole intensity more than the other three solvents. Further, the complexation is stimulated by the presence of Zn(II) showing the heterobimetallic complexation of Nd(III):creatine:Zn(II) is more stable comparing the binary mixture of Nd(III) and creatine. Formation of an ionic bond between Nd(III) and creatine was confirmed from the observed energy interaction and intensity parameter. Judd-Ofelt parameter study showed the forma-

tion of outer-sphere complex. The rate of complexation was also calculated and found to be 0.03574 mol L^{-1} $s^{-1}\times10^{-6}$ at 303.45 K.

Acknowledgements

References

1. R. Cooper, F. Naclerio, J. Allgrove and A. Jimenez, *J. Int. Soc. Sports Nutr.,* 2012, **9**, 33; https://doi.org/10.1186/1550-2783-9-33.

2. J. Volek, N. Duncan, S. Mazzetti, R. S. Staron, M. Putukian, A. L. Gómez, D. R. Pearson, W. J. Fink and W. J. Kraemeret, *Med. Sci. Sports Exerc.,* 1999, **31(8)**, 1147.

3. A. M. Persky and G. A. Brazeau, *Pharmacol. Rev.,* 2001, **53(2)**, 161.

4. M. D. Becque, J. D. Lochmann and D. R. Melrose, *Med. Sci. Sports Exerc.,* 2000, **32(3)**, 654.

5. B. Dangott, E. Schultz and P. E. Mozdziak, *Int. J. Sports Med.,* 2000, **21(1)**, 13.

6. L. Deldicque, M. Louis, D. Theisen, H. Nielens, M. Dehoux, J. P. Thissen, M. J. Rennie and M. Francaux, *Med. Sci. Sports Exerc.,* 2005, **37(5)**, 731.

7. D. Häussinger, W. Gerok, E. Roth and F. Lang, *Lancet,* 1993, **22:341(8856)**, 1330.

8. G. Parise, S. Mihic, D. MacLennan, K. E. Yarasheski and M. A. Tarnopolsky, *J. Appl. Physiol.,* 2001, **91(3)**, 1041.

9. A. Saremi, R**.** Gharakhanloo, S. Sharghi, M. R. Gharaati, B. Larijani and K. Omidfar, *Mol. Cell Endocrinol.,* 2010, **12**, 317(1-2), 25. doi: 10.1016/j.mce.2009.12.019

10. C. Rae, A. L. Digney, S. R. McEwan and T. C. Bates, *Proc. Bio. Sci.,* 2003, **22**, 270(1529), 2147.

11. P. Dechent, P. J. Pouwels, B. Wilken, F. Hanefeld and J. Frahm, *Am. J. Physiol.,* 1999, **277(3)**, 698.

12. N. P. Singh, N. R. Singh, N. R. Singh and N. M. Singh, *Indian J. Phys.,* 2018, **92**, 1461.

13. S. V. Eliseeva and J. C. G. Bünzli, *Chem. Soc. Rev.,* 2010, **39(1)**, 189.

14. E. J. Werner, A. Datta, C. J. Jocher and K. N. Raymond, *Angew. Chem. Int. Ed.,* 2008, **47(45)**, 8568.

15. P. Hermann, J. Kotek, V. Kubíèek and I. Lukes, *Dalton Trans.,* 2008, **23**, 3027.

16. M. Woods, D. E. Woessner and A. D. Sherry, *Chem. Soc. Rev.,* 2006, **35(6)**, 500.

17. S. N. Misra and O. Sommerer, *Appl. Spectrosc. Rev.,* 1991, **26(3)**, 151.

18. N. Yaiphaba, T. D. Singh, M. I. Devi and N. R. Singh, *Asian J. Chem.,* 2008, **20(2)**, 901.

19. E. Y. Wong, *J. Chem. Phys.,* 1963, **38(4)**, 976.

20. G. S. Ofelt, *J. Chem. Phys.,* 1962, **37**, 511.

21. C. Sumitra, T. D. Singh, M. I. Devi and N. R. Singh, *Spectrochim. Acta, Part A,* 2007, **66**, 1333.

22. D. M. Gruen and C. W. DeKock, *J. Chem. Phys.,* 1966, **45(2)**, 455.

23. B. R. Judd, *Phys. Rev.,* 1962, **127(3)**, 750.

24. R. D. Peacock, *J. Chem. Soc.,* 1971, **2028**, 2031.

25. C. K. Jørgensen and B. R. Judd, *Mol. Phys.,* 1964, **8(3)**, 281.

26. H. D. Devi, Ch. Sumitra, T. D. Singh, N. Yaiphaba, N. M. Singh and N. R. Singh, *Int. J. Spectrosc.,* 2009, 1. https://doi.org/10.1155/2009/784305.

27. B. Huidrom and N. R. Singh, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.,* 2014, **118**, 367.

28. T. D. Singh, N. M. Singh, N. Yaiphaba, H. D. Devi, C. Shumitra, T. Kriyananda, M. I. Devi, N. R. Singh, *Chem. Environ. Res.,* 2003, **12(3&4)**, 295.

29. R. S. Naorem, N. P. Singh and N. M. Singh, *Chem. Afr.,* 2020, **3(1)**, 171. https://doi.org/10.1007/s42250-019-00111-9.