

Optical Absorption, Kinetics and Thermodynamic Studies of Pr(III) and Nd(III) Ions with N-Acetyl L-Cysteine in Presence of Ca(II) ions

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Interaction of N-acetyl-L-cysteine (NAC) with Pr³⁺ (Pr(NO₃)₃·6H₂O) and Nd³⁺ (Nd(NO₃)₃·6H₂O) ions are studied in presence of Ca²⁺ (Ca(NO₃)₂·4H₂O) ion in an aqueous and organic solvent by applying the spectroscopic technique for quantitative probe of 4f-4f transition. The complexation was determined by the variation in the intensities of 4f-4f absorption spectral bands and by applying the change of symmetric properties of electronic-dipole known as Judd-Ofelt parameters T_λ (λ = 2,4,6). On the addition of Ca²⁺ ion in the binary complexation of praseodymium and neodymium with N-acetyl-L-cysteine (NAC) there is an intensification of bands which shows the effect of Ca²⁺ toward the heterobimetallic complex formation. Other parameters like Slater-Condon (F_k), bonding (b^{1/2}), the Nephelauxetic ratio (β), percentage covalency (δ) are also used to correlate the complexation of metals with N-acetyl-L-cysteine (NAC). With the minor change in coordination around Pr³⁺ and Nd³⁺ ions, the sensitivity of 4f-4f bands is detected and further used to explain the coordination of N-acetyl-L-cysteine (NAC) with Pr³⁺ and Nd³⁺ in presence of Ca²⁺. The variation in oscillator strength (P_{obs}), energy (E_{obs}) and dipole intensity parameter help in supporting the heterobimetallic complexation of N-acetyl-L-cysteine. In kinetics investigation, the rate of the complexation of both hypersensitive and pseudo-hypersensitive transition is evaluated at various temperature in DMF solvent. The value of the thermodynamic parameters such as ΔH°, ΔS° and ΔG° and activation energy (E_a) also evaluated.

Keywords: N-Acetyl-L-cysteine, Nephelauxetic effect, Judd-Ofelt, Hypersensitive, Pseudo hypersensitive, Oscillator strength.

INTRODUCTION

The biological peculiar similarity among the paramagnetic lanthanides Ln³⁺ and Ca²⁺ in the binding pattern, coordination character, rate of exchange of water and coordination number which is used as absorption probes [1-3] in explaining the reaction mechanism and function including the interchange of isomorphous Ca²⁺ by Ln³⁺ [4-6]. Based on the multiple photon excitation and time-resolved detection lanthanide are mainly use in biosensing and imaging [7-10]. Nowadays chemist gives more importance to the intensity variation of hypersensitive and pseudo hypersensitive transitions to explain detail structure of Ln³⁺ complex using absorption 4f-4f transition. The induce electric dipole transition is the main reason for an optical transition of Ln³⁺. They do not depend on the environment and dipole strength. But some are found sensitive to the environment and known as hypersensitive transition. As electric quadrupole transitions, hypersensitive transitions also follow the selection rule [11].

Henrie & Choppin *et al.* [12] explained the foremost the coordination of Nd³⁺ and bovine serum albumin (BSA) by using the change in the intensity of pseudo hypersensitive and hypersensitive transitions. The studies of Ln³⁺ and amino acid containing sulphur interaction are less thus it will be valuable to explore the complexation of Nd³⁺ and Pr³⁺ with N-acetyl-L-cysteine (NAC) in the sight of Ca²⁺. The present work mainly deals with the study of spectral energy interaction parameters and the change in pseudo hypersensitive and hypersensitive transitions of Nd³⁺ and Pr³⁺ with slight coordination changes to determine the rate of complexation. The kinetics of two different metal ions Nd³⁺ and Ca²⁺ with NAC forming heterobimetallic complexation are reporting at different temperature using DMF solvent, to explain the feasibility of the complexation of the activation energy (E_a) and thermodynamic parameters such as ΔH°, ΔS° and ΔG° evaluated.

EXPERIMENTAL

N-Acetyl-L-cysteine (NAC) was purchased from Sigma-Aldrich and used without any further purification. Neodymium

(Nd(NO₃)₃·6H₂O) and praseodymium (Pr(NO₃)₃·6H₂O) of 99.0% purity from Central Drug House (P) Ltd., India. The solvents were acetonitrile, methanol, dimethyl formamide and dioxane of A.R. grade from E. Merck. The different solutions of praseodymium and neodymium, ligand NAC (N-acetyl-L-cysteine) and calcium salt Ca(NO₃)₂·4H₂O were prepared at the concentration of 10⁻² mol L⁻¹. The Pr³⁺ and Nd³⁺ with N-acetyl-L-cysteine (NAC) were kept at 1:1 ratio and Pr³⁺ and Nd³⁺ a binary complex of NAC on addition of Ca²⁺ ions at 1:1:1 ratio. The absorption spectral data are recorded using Perkin-Elmer Lambda-35 UV-Vis Spectrometer in the range 350-920 nm for Nd³⁺ and 410-650 nm for Pr³⁺. At various temperatures *i.e.* 298 K (25 °C), 303 K (30 °C), 308 K (35 °C), 313 K (40 °C), 318 K (45 °C), the electronic spectra of Nd³⁺: NAC:Ca²⁺ in DMF medium was used for kinetics and thermodynamic studies. Perkin Peltier Temperature Controller was used to maintain all the temperature. Perkin-Elmer FTIR spectrophotometer spectrum two was used for the measurement of infrared spectra.

Detection method: When a covalent bond is formed between the 4*f*-orbitals and ligand then metal wave function can be determined [12] by using eqn. 1:

$$\phi 4f = (1-b)^{1/2} < 4f | -b^{1/2} < \phi \text{ ligand} | \quad (1)$$

where $b^{1/2}$ is used to measure the mixing of 4*f*-orbital known as covalency and δ scale is used to express covalency [13]. Both $b^{1/2}$ and δ are correlated with the nephelauxetic effect. The Nephelauxetic ratios are expressed regarding Racah and Slater-Condon parameters employing the ratio of the complex concerning to free ions [14,15].

$$\beta = \frac{F_K^C}{F_K^f} \text{ or } \frac{E_C^K}{E_K^f} \quad (2)$$

$$\beta = \left(\frac{\beta_1 + \beta_2}{2} \right) \quad (3)$$

where, F_K^C and F_K^f is the Slater-Condon parameters for the complex and metal free ions and electrostatic repulsion E_C^K and E_K^f is the Racah parameter for complex and metal free ions. Nephelauxetic effect and per cent covalency are co-related to the bonding parameter ($b^{1/2}$) as:

$$b^{1/2} = \left(\frac{1-\beta}{2} \right)^{1/2} \quad (4)$$

$$\delta (\%) = \left(\frac{1-\beta}{\beta} \right) \times 100 \quad (5)$$

The two main components of the 4*f*-4*f* transitions are the energy (E_{obs}) that appears within the magnetic interaction and the spin-orbital interaction can be written as:

The electronic transition of 4*f*-4*f* contains two main components, the energy of spin-orbital (E_{obs}) arises from the

$$E_{\text{obs}} = f^A F_K + A_{\text{so}} \xi_{4f} \quad (6)$$

here, the Slater-Condon parameter is F_K , ξ_{4f} is the Lande's radial integral parameter and A_{so} is the spin orbital angular part [16,17].

The energy E_j of the j^{th} level of first-order approximation is given by Wong [18], as:

$$E_j(F_K^0, \xi_{4f}^0) = E_{\text{oj}}(F_K^0, \xi_{4f}^0) + \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_K} \Delta F_K + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (7)$$

where zero-order energy of the j^{th} level is E_j and the values of F_K , ξ_{4f} are calculated as:

$$F_K = F_K^0 + \Delta F_K \quad (8)$$

and

$$\xi_{4f} = \xi_{4f}^0 + \Delta \xi_{4f} \quad (9)$$

From Richman & Wong [19], the energy of zero-order and the value, partial derivatives equation (8 and 9) can be explained by using the least square's technique and ΔF_K and $\Delta \xi_{4f}$ can also be evaluated. The variation among the E_j and the zero-order ΔE_j is determined by using the following equation as:

$$\Delta E_j = \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_K} \Delta F_K + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (10)$$

The band intensities are calculated on a theoretical basis explained by Judd and Ofelt [20,21]. The key electric dipole and oscillator strength are characterized by $\Psi_J \rightarrow \Psi'_J$ induced electric dipole transition which can be calculated by:

$$P_{\text{cal}} = \sum_{\lambda=2,4,6} T_\lambda \bar{v} \left\langle f^n \Psi_J \left\| U^\lambda \right\| f^n \Psi'_J \right\rangle^2 \quad (11)$$

$$\frac{P_{\text{cal}}}{v} = \left[(U^2) \right]^2 T_2 + \left[(U^4) \right]^2 T_4 + \left[(U^6) \right]^2 T_6 \quad (12)$$

Here T_2 , T_4 , T_6 are the three-variable of radial parts correlated with the wave function $4f^N$, the nearest perturbing wave function configuration is $4f^{N-1}5d$ and the matrix element of λ is U^λ . The absorption band intensity is calculated from the observed oscillatory strength and fits directly to the absorption curve using Gaussian analysis [22] as

$$P = 4.6 \times 10^{-9} \times \epsilon_{\text{max}} \times \Delta v_{1/2} \quad (13)$$

where the molar absorptivity is ϵ_{max} and half bandwidth is $\Delta v_{1/2}$.

RESULTS AND DISCUSSION

Sharp absorption spectra of lanthanides are developed from transitions among the level of f^N electronic configuration. Crystal field-effect employs the configuration of (2J+1) fold degeneracy. Within 4*f*-4*f* transitions of lanthanides absorption spectra, few of them exhibited high sensitivity after the small coordination variation throughout lanthanide these can be explained by the value of U^2 matrix elements and provide significant variation of T_2 parameter in explaining the symmetry of the complex. In contrast, to spin-orbital interaction, the crystal field gives more detail information about the transition elements. Due to the polarisation of $5s^2$ and $5p^6$ close shells, there is more or less shielded from the influence of lattice in 4*f*-electrons of lanthanides. Normally, lanthanides ions have a small crystal field splitting effect in the range of 200-300 cm⁻¹.

On the spectral analysis of lanthanides in a different solution, the correlation between the change in the value of nephelauxetic

xetic and symmetry of complex is of great delight in the investigation. The variation of the nephelauxetic effect in complexation and with the decrease in the coordination number and reduction of bond length in the metal-ligand follows [23]. The decrease in value of free ions of F_k and ξ_{sf} parameters (Tables 1 and 2) exhibit the change of different energy interaction parameter like nephelauxetic ratio, Slater-Condon, percentage covalency, Lande's spin orbital angular factor for Pr^{3+} and Nd^{3+} with ligand NAC in presence of Ca^{2+} in a different solvent. The decrease and variation in the value of binary complex and hetero-bimetallic complex from the free metal ions used to explain the complexation. The central metal ions orbital on complexation are found to be expand the main reason is the increase of percentage covalency value and the nephelauxetic effect comparing with the comparable metal free ion parameters. The covalent types of bond are formed between the metal-ligand bond is explained by the value of the nephelauxetic ratio which is below unity and the positive value of bonding parameter (Figs. 1 and 2).

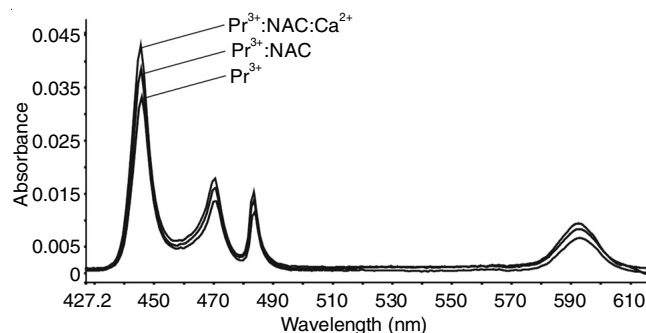


Fig. 1. Comparative absorption spectra of Pr^{3+} , $\text{Pr}^{3+}:\text{NAC}$, $\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$ in DMF

In Tables 3 and 4, Judd [24] unraveled the hypersensitive and pseudo-hypersensitive transition of the lanthanide ions with the variation in the symmetry and hypersensitive transitions are observed at lanthanides possessing Dihedral (D_{nh}) symmetry [25]. The phenomenon of hypersensitive and pseudo-hypersensitive transition is derived that follow transition rules

TABLE-1
CALCULATED VALUES OF ENERGY INTERACTION SLATER CONDON (F_k), SPIN ORBITAL INTERACTION (ξ_{sf}), THE NEPHELAUXETIC RATIO (β), BONDING PARAMETER ($b^{1/2}$) AND COVALENCY (δ) OF Pr^{3+} , $\text{Pr}^{3+}:\text{NAC}$ AND $\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$ SYSTEM AT AQUEOUS AND ORGANIC SOLVENT

System	Parameters	F_2	F_4	F_6	ξ_{sf}	β	$b^{1/2}$	δ
Solvent-Water	Pr^{3+}	309.34	42.70	4.67	722.26	0.9472	0.1624	5.57
	$\text{Pr}^{3+}:\text{NAC}$	309.32	42.70	4.67	722.28	0.9472	0.1624	5.57
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	309.30	42.70	4.67	721.93	0.9470	0.1629	5.60
Solvent-Methanol	Pr^{3+}	308.13	42.54	4.65	721.23	0.9448	0.1662	5.85
	$\text{Pr}^{3+}:\text{NAC}$	308.17	42.54	4.65	721.21	0.9448	0.1661	5.84
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	308.16	42.54	4.65	720.88	0.9446	0.1665	5.87
Solvent-DMF	Pr^{3+}	307.96	42.51	4.65	720.06	0.9437	0.1678	5.96
	$\text{Pr}^{3+}:\text{NAC}$	307.94	42.51	4.65	720.22	0.9438	0.1677	5.96
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	307.91	42.51	4.65	720.21	0.9437	0.1677	5.96
Solvent-Dioxane	Pr^{3+}	307.83	42.50	4.65	720.95	0.9441	0.1671	5.92
	$\text{Pr}^{3+}:\text{NAC}$	307.81	42.49	4.65	720.50	0.9438	0.1676	5.96
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	307.93	42.51	4.65	722.19	0.9451	0.1657	5.81
Solvent- CH_3CN	Pr^{3+}	308.42	42.58	4.66	725.06	0.9478	0.1615	5.51
	$\text{Pr}^{3+}:\text{NAC}$	308.34	42.57	4.66	724.73	0.9475	0.1621	5.55
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	308.01	42.52	4.65	723.66	0.9462	0.1639	5.68

TABLE-2
CALCULATED VALUES OF ENERGY INTERACTION SLATER CONDON (F_k), SPIN ORBITAL INTERACTION (ξ_{sf}), NEPHELAUXETIC RATIO (β), BONDING PARAMETER ($b^{1/2}$) AND COVALENCY (δ) OF $\text{Nd}^{3+}:\text{NAC}$ AND $\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$ SYSTEM AT AQUEOUS AND ORGANIC SOLVENT

Solvent	Parameters	F_2	F_4	F_6	ξ_{sf}	β	$b^{1/2}$	δ
Solvent-Water	Nd^{3+}	332.195	48.639	5.099	895.91	0.0669	0.9910	0.90402
	$\text{Nd}^{3+}:\text{NAC}$	332.135	48.614	5.097	896.51	0.0664	0.9912	0.88881
	$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	332.119	48.614	5.097	896.70	0.0660	0.9913	0.87811
Solvent-Methanol	Nd^{3+}	329.987	48.545	5.200	934.12	0.0835	1.0140	1.37558
	$\text{Nd}^{3+}:\text{NAC}$	329.950	48.575	5.201	934.14	0.0839	1.0141	1.38965
	$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	330.766	47.991	5.172	932.90	0.0738	1.0109	1.07768
Solvent-DMF	Nd^{3+}	329.187	48.872	5.284	949.75	0.1140	1.0260	2.53242
	$\text{Nd}^{3+}:\text{NAC}$	329.181	48.858	5.284	950.14	0.1144	1.0262	2.54914
	$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	329.116	48.813	5.288	952.28	0.1168	1.0273	2.65714
Solvent-Dioxane	Nd^{3+}	330.669	47.602	5.192	944.34	0.0907	1.0165	1.61994
	$\text{Nd}^{3+}:\text{NAC}$	330.533	47.577	5.196	946.67	0.0941	1.0177	1.7415
	$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	330.580	47.648	5.188	943.63	0.0896	1.0161	1.58126
Solvent- CH_3CN	Nd^{3+}	330.983	47.803	5.210	941.23	0.0899	1.0162	1.59098
	$\text{Nd}^{3+}:\text{NAC}$	330.648	47.718	5.210	945.70	0.0954	1.0182	1.78709
	$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	330.414	47.543	5.220	952.61	0.1039	1.0216	2.11442

TABLE-3
OBSERVED AND CALCULATED VALUE OF OSCILLATOR STRENGTHS ($P \times 10^6$) AND JUDD-OFELT ($T\lambda \times 10^{10}$)
PARAMETER Pr^{3+} , $\text{Pr}^{3+}:\text{NAC}$ AND $\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$ IN AQUEOUS AND DIFFERENT ORGANIC SOLVENT

Solvent	Parameters	${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$	${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$	${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$	T_2	T_4	T_6	RMS
Solvent-Water	Pr^{3+}	1.6978 (1.6978)	0.619 (0.619)	0.2466 (0.242)	0.514 (0.5138)	-30.724	1.193	5.245	102.04
	$\text{Pr}^{3+}:\text{NAC}$	3.2938 (3.2938)	1.182 (1.182)	0.458 (0.45)	0.784 (0.7844)	-40.825	2.261	10.189	101.37
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	3.5772 (3.5772)	1.344 (1.344)	0.4635 (0.456)	0.804 (0.8043)	-55.077	2.492	11.057	105.66
Solvent-Methanol	Pr^{3+}	2.7728 (2.7728)	1.046 (1.046)	0.324 (0.32)	0.646 (0.6461)	-37.327	1.894	8.610	127.37
	$\text{Pr}^{3+}:\text{NAC}$	3.8218 (3.8218)	1.305 (1.305)	0.4626 (0.457)	0.829 (0.8291)	-65.249	2.443	11.910	126.66
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	3.7751 (3.7751)	1.347 (1.347)	0.4316 (0.426)	0.849 (0.8491)	-57.433	2.458	11.749	133.21
Solvent-DMF	Pr^{3+}	4.952 (4.952)	1.722 (1.722)	0.6835 (0.675)	1.187 (1.1875)	-59.083	3.330	15.406	125.51
	$\text{Pr}^{3+}:\text{NAC}$	5.5968 (5.5968)	3.25 (3.25)	0.7316 (0.722)	1.246 (1.2457)	-90.917	5.506	16.947	122.68
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	5.5766 (5.5766)	1.889 (1.889)	0.7064 (0.698)	1.321 (1.3207)	-70.126	3.593	17.392	124.48
Solvent-Dioxane	Pr^{3+}	3.5002 (3.5002)	1.178 (1.178)	0.3649 (0.361)	0.683 (0.6826)	-75.667	2.132	10.907	179.20
	$\text{Pr}^{3+}:\text{NAC}$	3.6707 (3.6707)	1.282 (1.282)	0.3309 (0.327)	0.816 (0.8161)	-56.443	2.228	11.446	179.30
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	3.7598 (3.7598)	1.368 (1.368)	0.4059 (0.401)	0.755 (0.7548)	-77.058	2.451	11.677	157.97
Solvent- CH_3CN	Pr^{3+}	2.9329 (2.9329)	1.116 (1.116)	0.3384 (0.334)	0.723 (0.7227)	-29.721	2.008	9.055	139.49
	$\text{Pr}^{3+}:\text{NAC}$	4.0642 (4.0642)	1.262 (1.262)	0.432 (0.426)	0.888 (0.888)	-66.627	2.340	12.676	139.02
	$\text{Pr}^{3+}:\text{NAC}:\text{Ca}^{2+}$	4.3618 (4.3618)	1.255 (1.255)	0.4305 (0.425)	0.869 (0.8686)	-90.058	2.329	13.661	160.12

TABLE-4
OBSERVED AND CALCULATED VALUE OF OSCILLATOR STRENGTHS ($P \times 10^6$) AND JUDD-OFELT ($T\lambda \times 10^{10}$)
PARAMETER Nd^{3+} , $\text{Nd}^{3+}:\text{NAC}$ AND $\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$ IN AQUEOUS AND DIFFERENT ORGANIC SOLVENT

Parameters	${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$	${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{5/2}$	${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{7/2}$	${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$	${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{7/2}$	T_2	T_4	T_6	RMS
Solvent- Water									
Nd^{3+}	0.8823 (0.5601)	2.4736 (2.4877)	3.0647 (3.0020)	2.5755 (2.6533)	0.3791 (0.3694)	1.32	0.15	5.21	118.29
$\text{Nd}^{3+}:\text{NAC}$	0.9235 (0.4981)	3.1427 (3.1642)	3.5872 (3.3276)	2.5020 (2.8007)	0.4275 (0.2625)	1.98	-0.40	5.83	120.25
$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	0.9085 (0.4226)	2.7685 (2.7769)	3.6854 (3.3870)	2.4665 (2.8130)	0.4179 (0.2275)	1.80	-0.56	5.95	127.08
Solvent-Methanol									
Nd^{3+}	0.5203 (0.4341)	2.6485 (2.6467)	1.3138 (1.3186)	1.2088 (1.2048)	0.1822 (0.2022)	1.52	0.22	2.28	149.36
$\text{Nd}^{3+}:\text{NAC}$	0.3307 (0.5460)	4.0963 (4.0777)	1.9176 (1.9216)	1.6730 (1.6617)	0.2756 (0.1962)	2.53	-0.06	3.36	150.33
$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	0.6547 (0.5621)	3.4882 (3.4820)	1.4213 (1.4378)	1.3513 (1.3364)	0.2132 (0.2508)	1.99	0.36	2.46	153.65
Solvent-DMF									
Nd^{3+}	0.9831 (0.7854)	6.1518 (6.1688)	2.7863 (2.6277)	2.0676 (2.2551)	0.3524 (0.2506)	3.89	-0.15	4.61	161.78
$\text{Nd}^{3+}:\text{NAC}$	1.3618 (1.0154)	7.8629 (7.8720)	3.4041 (3.1920)	2.5109 (2.7618)	0.4326 (0.3283)	4.93	-0.09	5.59	163.75
$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	1.5216 (1.0594)	7.9970 (8.0176)	3.4410 (3.2152)	2.5262 (2.8061)	0.4374 (0.3565)	4.98	0.01	5.62	169.95
Solvent-DXN									
Nd^{3+}	1.0522 (0.5031)	2.7113 (5.8504)	0.7328 (0.6789)	0.6637 (0.7475)	0.1099 (0.2423)	1.44	0.65	1.11	152.4
$\text{Nd}^{3+}:\text{NAC}$	2.1077 (1.0091)	5.7875 (5.8504)	1.7154 (1.5727)	1.4248 (1.6359)	0.2333 (0.4612)	3.18	1.12	2.61	161.03
$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	1.7885 (0.9451)	5.7739 (5.8220)	1.5644 (1.4586)	1.3363 (1.4925)	0.2181 (0.4027)	3.25	0.94	2.43	173.83
Solvent- CH_3CN									
Nd^{3+}	1.9715 (0.9258)	5.5806 (5.6377)	1.5273 (1.3904)	1.2375 (1.4357)	0.1783 (0.3971)	3.13	0.95	2.31	143.32
$\text{Nd}^{3+}:\text{NAC}$	2.4863 (1.2283)	8.0053 (8.0748)	2.1870 (1.9842)	1.6797 (1.9654)	0.2512 (0.4799)	4.64	1.02	3.33	142.51
$\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$	2.5115 (1.4328)	8.2661 (8.3409)	1.6645 (1.4771)	1.4674 (1.7268)	0.4159 (0.6336)	4.49	1.83	2.37	144.28

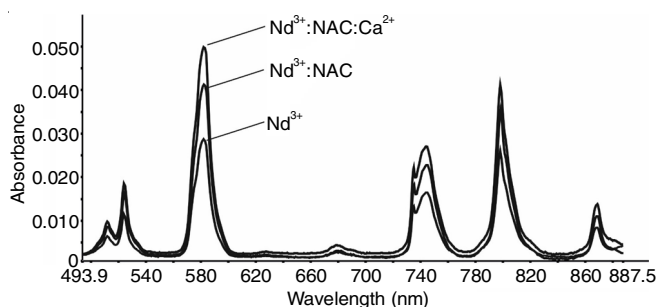


Fig. 2. Comparative absorption spectra of Nd^{3+} , $\text{Nd}^{3+}:\text{NAC}$, $\text{Nd}^{3+}:\text{NAC}:\text{Ca}^{2+}$ in DMF

[26]. The four transitions ${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$, ${}^3\text{P}_0$, ${}^3\text{P}_1$ and ${}^3\text{P}_2$, of Pr^{3+} ion do not follow the selection rule but they are notice to be sensitive toward the change environment on complexation. So, they term as a pseudo hypersensitive transition. The five transitions ${}^4\text{I}_{9/2}$

$\rightarrow {}^4\text{G}_{7/2}$, ${}^4\text{G}_{5/2}$, ${}^4\text{F}_{7/2}$, ${}^4\text{F}_{5/2}$ and ${}^4\text{F}_{3/2}$ of Nd^{3+} ion is observed in the spectra of Nd^{3+} complex in different organic solvent shows a characteristic transition, among five transitions only two ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{7/2}$ and ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$ show stronger intensity $4f-4f$ absorption transition and sensitive on the change of chemical environment, which lead to known as hypersensitive [27]. The higher oscillator strength and absorption intensity of ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$ and ${}^4\text{G}_{7/2}$ transition are mainly due to the polarizability of the solvent [28]. The other pseudo hypersensitive transition ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{7/2}$, ${}^4\text{F}_{5/2}$ and ${}^4\text{F}_{3/2}$ don't follow the selection or transition rules [23], whereas these five-transition exhibit sensitivity in the complex formation [29] or with the variation of the coordination environment, they are known as pseudo or non-hypersensitive transition. The correlation between the hypersensitive transitions and the coordination between ligand and the lanthanide ions are explain by few researchers [30,31].

In Pr^{3+} complex, Judd-Ofelt electron transition theory is not applicably comparing to those of other lanthanides due to difficulties in filling both ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$, ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition. Among the absorption intensities of Nd^{3+} transitions ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$, ${}^4\text{G}_{7/2}$ exhibit significant sensitivity to the different solvent environment. This transition arises around about 580 nm and possesses a wide range of U^λ matrix elements [32]. The polarizability of the solvent is the main reason for the excessive value and enhance oscillator strength [33].

Similarly, with the addition of NAC and Ca^{2+} ion respectively to Pr^{3+} and Nd^{3+} ions complex in aqueous and different organic solvent, we can monitor an increase in electric-dipole oscillator strength of calculated and observed values. The Judd-Ofelt parameter (T_λ , $\lambda = 2, 4, 6$) which are present in Tables 3 and 4, respectively. The increasing interaction of $4f$ -orbital is expressed by the intensification of the bands. DMF solvent have doner site nitrogen which can engage in the complexation, oscillator strength and intensification are maximum and the accuracy of various energy parameters is shown by the RMS value. The root mean square deviation (RMS) is the weighted difference between the square of observed and calculated values of energies denoted:

$$\text{R.M.S.} = \left(\frac{\sum (E_{\text{cal}} - E_{\text{obs}})^2}{4} \right)^{1/2} \text{ for } \text{Pr}^{3+}$$

$$\text{R.M.S.} = \left(\frac{\sum (E_{\text{cal}} - E_{\text{obs}})^2}{5} \right)^{1/2} \text{ for } \text{Nd}^{3+}$$

The values of T_2 parameters are negative gives no meaning or information but T_6 and T_4 are used significantly. Both the parameters T_4 and T_6 are used to explain the change in symmetry properties of the complex. The $4d$ and $4f$ -orbital mixing also explain by the T_6 parameter. Due to the involvement of ligands in the inner sphere coordination.

Absorption spectra of binary complex Pr^{3+} : NAC in different solvent shows DMF (Fig. 3) induce a strong influence on complexation and minimum in case of CH_3OH (methanol) due to oxygen show stronger binding capacity and lower in nitrogen hence it follows the order of $\text{DMF} > \text{CH}_3\text{CN} > \text{dioxane} > \text{CH}_3\text{OH}$. Solvent DMF prefers to bind with oxygen when its coordinates with hard acid-like lanthanide ions (Ln^{3+}) whereas CH_3CN prefer to bind through nitrogen.

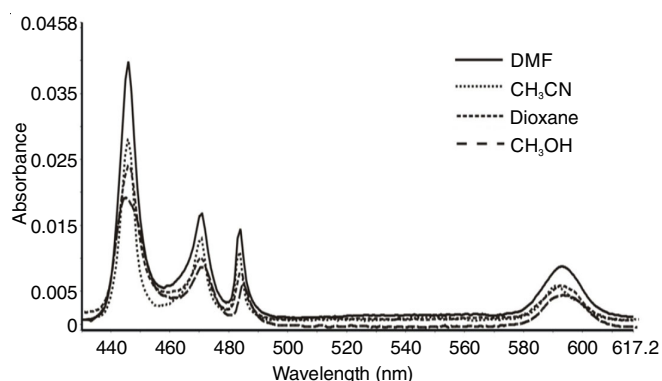


Fig. 3. Absorption spectra of Pr^{3+} :NAC in different solvents- DMF, CH_3CN , dioxane, CH_3OH

FTIR spectral studies: The $\nu(\text{N-H})$, $\nu(\text{S-H})$, $\nu(\text{COO}^-)$ (amide), $\nu(\text{C-N})$ stretching frequency of NAC is observed at 3573 cm^{-1} , 2552 cm^{-1} , 1635 cm^{-1} and 1356 cm^{-1} upon complexation (Pr^{3+} :NAC) stretching frequency shift at 3562 cm^{-1} , 2574 cm^{-1} , 1642 cm^{-1} and 1380 cm^{-1} , respectively indicates the coordination with the metal ion (Fig. 4). But the $\nu(\text{COO}^-)$ stretching frequency of both NAC and the complex found to be unchanged. The broad absorption band in the $3100\text{-}1800 \text{ cm}^{-1}$ range belong to $\nu(\text{OH})$ stretching frequency of intermolecular interaction OH- a group of COOH [34,35].

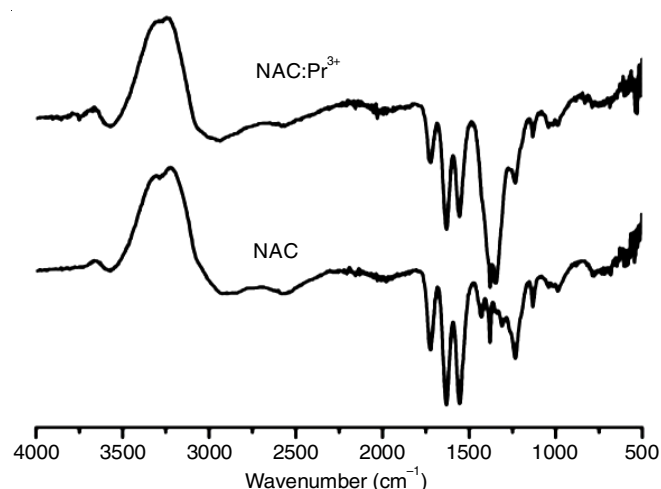


Fig. 4. FTIR spectra of NAC, Pr^{3+} :NAC in the range $4000\text{-}500 \text{ cm}^{-1}$ in a water medium

The thermodynamic parameters and activation energy depend on temperature are further analyzed in the characterization of heterobimetallic complex NAC with Nd^{3+} and Ca^{2+} ions. The activation energy for the complexation in DMF solvent medium is evaluated by applying Arrhenius linear equation.

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad (14)$$

Having rate constant $\ln k$ and the pre-exponential or frequency factor 'A' and temperature in kelvin. At 298 K, 303, 308, 313 and 318 K the value of rate constant is shown in Table-5. The activation energy (E_a) is derived from the slope as:

$$E_a = -\text{Slope} \times R \quad (15)$$

From Table-6 with the increase in temperature rate constant k also increases from this we can calculate the thermodynamic parameters and the coordination of the complexes. The thermodynamic parameters change in enthalpy (ΔH°) and change in entropy (ΔS°) for the complexation of Nd^{3+} :NAC: Ca^{2+} ion is experimentally calculate using van't Hoff plot ($\ln k$ against $1/T$) [36,37]:

$$\ln k = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} = -\frac{\Delta G^\circ}{RT} \quad (16)$$

or

$$\ln k = -\frac{\Delta G^\circ}{RT} \quad (17)$$

By using hypersensitive transition absorption spectra ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$ of Nd^{3+} ion, on the steady rise of time the absorption

TABLE-5
OBSERVED VALUE OF ABSORBANCE OF
(HYPERSENSITIVE TRANSITION ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ OF Nd^{3+})
OF $Nd^{3+}:NAC:Ca^{2+}$ AT 303, 308, 313 AND 318 K

Time (h)	Absorbance (${}^4I_{9/2} \rightarrow {}^4G_{5/2}$)				
	298 K	303 K	308 K	313 K	318 K
0	7.219	7.219	7.219	7.219	7.219
2	7.242	7.264	7.276	7.280	7.294
4	7.286	7.319	7.340	7.354	7.371
6	7.329	7.369	7.399	7.422	7.448
8	7.367	7.418	7.456	7.488	7.525
10	7.417	7.469	7.518	7.556	7.602
12	7.458	7.521	7.571	7.625	7.679
14	7.502	7.572	7.638	7.696	7.756
16	7.545	7.624	7.699	7.765	7.844
18	7.593	7.675	7.759	7.834	7.921
20	7.623	7.728	7.820	7.904	7.999
22	7.670	7.777	7.881	7.972	8.076
24	7.710	7.829	7.942	8.040	8.153
26	7.761	7.881	8.002	8.109	8.241
28	7.814	7.933	8.061	8.181	8.307

band transitions also increase and can be used as a probe of the kinetics of the complex formation at the different temperature 303, 308, 313 and 318 K. The value of rate (K) calculated from the absorbance of ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd^{3+} ion complex formation *versus* time (h). The activation energy (E_a) of the complex $Nd^{3+}:NAC:Ca^{2+}$ calculated from the slope of the plot of $\ln K$ against $1/T$ (Fig. 5) using the Arrhenius rate equation.

Table-7 summarizes the value of ΔH° , ΔS° , ΔG° . Positive values of ΔH° and ΔS° designated that complexation of Nd^{3+} :

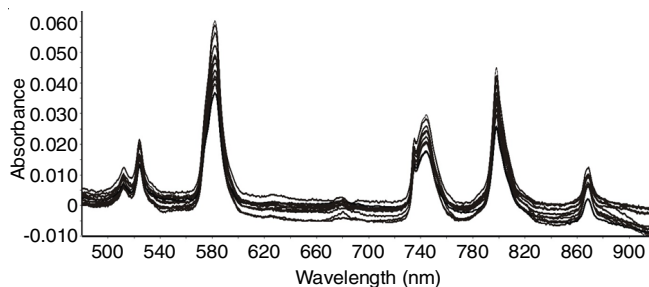


Fig. 5. Absorbance spectra of $Nd^{3+}:NAC:Ca^{2+}$ at 313 K at DMF medium

$NAC:Ca^{2+}$ is an endothermic and entropy (ΔS°) increasing random operation due to $T\Delta S^\circ > \Delta H^\circ$. The negative value of ΔG° specified that the complexation reaction is the spontaneous process as well as found to be favourable in studies of complexation. It is observed that the value of ΔG° is negative to predict the complex formation is favourable and spontaneous. The rate of reaction has been found to increase with temperature and from which the activation energy has been determining.

Conclusion

From the above study, it can be affirmed that the variation of energy exchange and intensity parameters, the binary complexation of $Nd^{3+}/Pr^{3+}:NAC$ is weaker than the heterobimetallic complexation of N-acetyl-L-cysteine (NAC) showing that the accelerated effect of Ca^{2+} ion against the complexation of Nd^{3+}/Pr^{3+} ions with NAC. This study mainly focussed on the flexibility of comparative adsorption spectral studies to explain the coordination and binding nature of complexation, by know-

TABLE-6
OSCILLATOR STRENGTH (P_{obs}) AND JUDD-OFELT INTENSITY PARAMETER T_i
FOR THE COMPLEXATION $Nd^{3+}:NAC:Ca^{2+}$ 313 K IN DMF MEDIUM

Time (h)	${}^4I_{9/2} \rightarrow {}^4G_{7/2}$	${}^4I_{9/2} \rightarrow {}^4G_{5/2}$	${}^4I_{9/2} \rightarrow {}^4F_{7/2}$	${}^4I_{9/2} \rightarrow {}^4F_{9/2}$	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$	T_2	T_4	T_6
0	1.2719	7.219	2.8485	2.2581	0.2839	4.460	0.050	2.700
2	1.3845	7.280	3.1135	2.4254	0.2844	4.500	0.063	4.910
4	1.4311	7.354	3.1216	2.4362	0.2899	4.540	0.071	5.200
6	1.4463	7.422	3.1583	2.4463	0.2923	4.550	0.090	5.250
8	1.4465	7.488	3.2278	2.4558	0.3193	4.560	0.150	5.210
10	1.4583	7.556	3.2717	2.4825	0.4151	4.590	0.150	5.340
12	1.4639	7.625	3.2809	2.5016	0.4542	4.650	0.160	5.350
14	1.5075	7.696	3.3068	2.5088	0.4579	4.680	0.170	5.430
16	1.5118	7.765	3.3104	2.5287	0.468	4.700	0.330	5.420
18	1.5236	7.834	3.3113	2.565	0.4735	4.840	0.360	5.480
20	1.5693	7.904	3.3225	2.5803	0.4749	4.890	0.510	5.481
22	1.5796	7.972	3.4209	2.5961	0.4792	4.900	0.513	5.583
24	1.7204	8.040	3.4344	2.6077	0.4862	4.910	0.590	5.585
26	1.8898	8.109	3.4547	2.6083	0.49	5.060	0.710	5.592
28	1.8955	8.181	3.4604	2.6473	0.636	5.110	0.990	5.597

TABLE-7
RATE CONSTANT AND THERMODYNAMIC PARAMETER FOR THE
COMPLEXATION OF $Nd^{3+}:NAC:Ca^{2+}$ AT 298, 303, 308, 313 AND 318 K

Temp. (K)	$1/T \times 10^3$	Rate constant ($Mol L^{-1} S^{-1}$)	$\ln K$	E_a ($KJ mol^{-1}$)	ΔH° ($KJ mol^{-1}$)	ΔS° ($J K^{-1} mol^{-1}$)	ΔG° ($J K^{-1} mol^{-1}$)
298	3.356	5.833	1.763	0.2437	0.2437	0.1472	-43.628
303	3.300	7.083	1.957			0.1625	-49.244
308	3.247	8.378	2.125			0.1764	-54.348
313	3.195	9.556	2.257			0.1873	-58.648
318	3.145	10.886	2.387			0.1981	-63.026

ing the complexation reaction between the heterobimetallic complex of NAC with Nd³⁺/Pr³⁺ and Ca²⁺ ions. These studies indicate the change of electric-dipole oscillator strengths of 4*f*-4*f* transition concerning with time and the temperature explain the kinetics nature of heterobimetallic complexation of NAC with Nd³⁺/Pr³⁺ and Ca²⁺ ion in DMF solution medium. With the steady rise in temperature the rate of the complexation reaction also elevated and activation energy (E_a) is reported as 0.2437 KJ mol⁻¹. The thermodynamic parameters were also calculated, the positive value of change in enthalpy (ΔH°) and entropy (ΔS°) can use in explaining the endothermic and entropy increasing process (spontaneous) in heterobimetallic complexation reaction. The negative value of ΔG° also indicates the reaction is favoured.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- N. De Vries and S. De Flora, *J. Cell. Biochem.*, **53**(S17F), 270 (1993); <https://doi.org/10.1002/jcb.240531040>
- J.A. Cotruvo Jr, *ACS Cent. Sci.*, **5**, 1496 (2019); <https://doi.org/10.1021/acscentsci.9b00642>
- A. Kothari and S.N. Misra, *Can. J. Chem.*, **61**, 1778 (1983); <https://doi.org/10.1139/v83-304>
- S.N. Misra and K. John, *J. Appl. Spectrosc. Rev.*, **28**, 285 (1993); <https://doi.org/10.1080/05704929308018115>
- N. Bendangsenla, T. Moaienla, Th. David Singh, Ch. Sumitra, N. Rajmuhon Singh and M. Indira Devi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **103**, 160 (2013); <https://doi.org/10.1016/j.saa.2012.11.011>
- J. Legendziewicz, H. Kozlowski, B. Jezowska-Trzebiatowska and E. Huskowska, *Inorg. Nucl. Chem. Lett.*, **15**, 349 (1979); [https://doi.org/10.1016/0020-1650\(79\)80109-9](https://doi.org/10.1016/0020-1650(79)80109-9)
- K. Bukietynska and A. Mondry, *Inorg. Chim. Acta*, **130**, 145 (1987); [https://doi.org/10.1016/S0020-1693\(00\)85944-7](https://doi.org/10.1016/S0020-1693(00)85944-7)
- B. Huidrom, N. Ranjana Devi, Th. Devid Singh and N. Rajmuhon Singh, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **85**, 127 (2012); <https://doi.org/10.1016/j.saa.2011.09.045>
- R.C. Holz and L.C. Thompson, *Inorg. Chem.*, **27**, 4640 (1988); <https://doi.org/10.1021/ic00298a027>
- M.T. Devlin, E.M. Stephens and F.S. Richardson, *Inorg. Chem.*, **27**, 1517 (1988); <https://doi.org/10.1021/ic00282a003>
- G.H. Brittain, F.S. Richardson and R.B. Martin, *J. Am. Chem. Soc.*, **98**, 8255 (1976); <https://doi.org/10.1021/ja00441a060>
- D.E. Henrie and G.R. Choppin, *J. Chem. Phys.*, **49**, 477 (1968); <https://doi.org/10.1063/1.1670099>
- S.P. Sinha, *Spectrochim. Acta A*, **22**, 57 (1966); [https://doi.org/10.1016/0371-1951\(66\)80008-5](https://doi.org/10.1016/0371-1951(66)80008-5)
- W.T. Carnall, R.P. Fields and B.G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965); <https://doi.org/10.1063/1.1695840>
- T.D. Singh, C. Sumitra, N. Yaiphaba, H.D. Devi, M.I. Devi and N.R. Singh, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **61**, 1219 (2005); <https://doi.org/10.1016/j.saa.2004.06.044>
- L. Di Sipio, E. Tondell, G. De Michelis and L. Oleari, *Inorg. Chem.*, **9**, 927 (1970); <https://doi.org/10.1021/ic50086a047>
- S.P. Tandon and P.C. Mehta, *J. Chem. Phys.*, **52**, 5417 (1970); <https://doi.org/10.1063/1.1672792>
- E.Y. Wong, *J. Chem. Phys.*, **38**, 976 (1963); <https://doi.org/10.1063/1.1733794>
- I. Richman and E.Y. Wong, *J. Chem. Phys.*, **37**, 2270 (1962); <https://doi.org/10.1063/1.1732998>
- W.D. Horrocks Jr and D.R. Sudnick, *Acc. Chem. Res.*, **14**, 384 (1981); <https://doi.org/10.1021/ar00072a004>
- G.S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962); <https://doi.org/10.1063/1.1701366>
- S.F. Mason, R.D. Peacock and B. Stewart, *Mol. Phys.*, **30**, 1829 (1975); <https://doi.org/10.1080/00268977500103321>
- S.N. Misra, G. Ramchandriah, M.A. Gagnani, R.M. Shukla and M. Indira Devi, *Appl. Spectrosc. Rev.*, **38**, 433 (2003); <https://doi.org/10.1081/ASR-120026330>
- G. Lakshminarayana, H. Yang and J. Qiu, *J. Alloys Compd.*, **475**, 569 (2009); <https://doi.org/10.1016/j.jallcom.2008.07.083>
- A.D. Shery and E. Pascual, *J. Am. Chem. Soc.*, **99**, 5871 (1977); <https://doi.org/10.1021/ja00460a004>
- T. Moaienla, T.D. Singh, N.R. Singh and M.I. Devi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **74**, 434 (2009); <https://doi.org/10.1016/j.saa.2009.06.039>
- T. Moaienla, N. Bendangsenla, Th. David Singh, Ch. Sumitra, N. Rajmuhon Singh and M. Indira Devi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **87**, 142 (2012); <https://doi.org/10.1016/j.saa.2011.11.028>
- S.N. Misra and M.I. Devi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **53**, 1941 (1997); [https://doi.org/10.1016/S1386-1425\(97\)00064-4](https://doi.org/10.1016/S1386-1425(97)00064-4)
- C.K. Jorgensen and B.R. Judd, *Mol. Phys.*, **8**, 281 (1964); <https://doi.org/10.1080/00268976400100321>
- D.G. Karraker, *Inorg. Chem.*, **6**, 1863 (1967); <https://doi.org/10.1021/ic50056a022>
- S.N. Misra and S.O. Sommerer, *Appl. Spectrosc. Rev.*, **26**, 151 (1991); <https://doi.org/10.1080/05704929108050880>
- C.V. Devi and N.R. Singh, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **78**, 1180 (2011); <https://doi.org/10.1016/j.saa.2010.12.078>
- W.T. Carnall, P.R. Fields and K. Rajnak, *J. Chem. Phys.*, **49**, 4412 (1968); <https://doi.org/10.1063/1.1669892>
- P.P. Corbi, F. Cagnin and A.C. Massabni, *J. Coord. Chem.*, **61**, 3666 (2008); <https://doi.org/10.1080/00958970802108809>
- B.B. Ivanova, V.D. Simeonov, M.G. Arnaudov and D.L. Tsalev, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **67**, 66 (2007); <https://doi.org/10.1016/j.saa.2006.06.025>
- P. Carette and A. Hocquet, *J. Mol. Spectrosc.*, **131**, 301 (1988); [https://doi.org/10.1016/0022-2852\(88\)90241-X](https://doi.org/10.1016/0022-2852(88)90241-X)
- L.W. Zhang, K. Wang and X.X. Zhang, *Anal. Chim. Acta*, **603**, 101 (2007); <https://doi.org/10.1016/j.aca.2007.09.021>