

covalent character of the bond concerned. In the electronic spectrum of the complex (d) also, three bands are observed in the region 7000 cm^{-1} (ν_1), 18600 cm^{-1} (ν_2) and 21000 cm^{-1} (ν_3) attributed to the assignments ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$; ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively showing octahedral symmetry. The ligand field parameters $10 Dq$ and B have been calculated with the help of the expressions available in literature⁴.

On examination of the ir spectra of the ligands and their corresponding complexes with cobalt(II) it has been found that most of the frequencies are perturbed on complexation. The lowering of the frequencies in the order of 50 cm^{-1} for $>C=O$ and $20\text{--}25\text{ cm}^{-1}$ for $-N=N-$ respectively during chelation indicates that these two groups are participating in the reaction. The antisymmetric carbonyl stretch of the $-COOH$ at 1680 cm^{-1} is replaced by a very strong band at 1580 cm^{-1} in the complex (d). This is due to the antisymmetric stretch of the coordinated carboxylate ion. The coordination through oxygen atom of carboxyl group is further supported by the disappearance of $-OH$ deformation vibrations^{5,6}. Several new bands at $480\text{--}510\text{ cm}^{-1}$ and $450\text{--}475\text{ cm}^{-1}$ are due to ν_{Co-N} and ν_{Co-O} respectively.

References

1. L. KNORR, *Ann.*, 1891, 279, 237.
2. H. S. VERMA and R. C. SAXENA, *Z. Naturforsch.*, 1978, 33b, 1001.
3. R. G. CAVELIS, E. D. DAY, W. BYERS and P. M. WATKINS, *Inorg. Chem.*, 1972, 11, 1759.
4. W. J. EBBECK, F. HOLMES and A. E. UNDERHILL, *J. Chem. Soc.*, 1967, 757.
5. C. A. MCAULIFFE and W. D. PERRY, *J. Chem. Soc.*, 1969, 634.
6. G. G. BARRALLOUGH, R. L. MARTIN and I. M. STENWART, *Aust. J. Chem.*, 1969, 22, 891.

Spectral, Magnetic and Thermal Studies of Some Transition Metal Ions with N-m-Tolyl-p-Methoxy Benzohydroxamic Acid (TMBHA)

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NUMBER of hydroxamic acids have been found in microorganism products¹ of pharmacological and analytical^{2,3} interest. Complex formation studies of hydroxamic acids with several metal ions in solution have been undertaken by various workers⁴⁻⁸. However, not much attention has been paid to the structural studies of solid complexes of hydroxamic acid with transition metal ions. In most of the cases the studies are restricted to colour, solubility and elemental analysis of solid complex formed. In very few cases spectral and magnetic studies have been undertaken for their characterisation⁹⁻¹¹. Recently N-m-tolyl-p-methoxy benzohydroxamic acid (TMBHA) has been used in this laboratory^{4,6}

as an analytical reagent. In the present report we describe the chelating ability and tentative geometry of the N-m-tolyl-p-methoxy benzohydroxamic acid with some transition metal ions on the basis of elemental, conductance, thermal analysis, magnetic and spectral (electronic, ir, esr) data.

Experimental

Materials and methods: All chemicals were of AnalaR or chemically pure grade. The ligand N-m-tolyl-p-methoxy benzohydroxamic acid was prepared by known method^{4,12}.

Preparation of metal chelates: Metal salts of Fe(II), Fe(III) were taken as ferrous ammonium sulphate and ferric nitrate respectively, while the metal salts of Co(II), Ni(II) and Cu(II) were used in the form their acetates. Solutions of metal salts were prepared in distilled water and the ligand solution in ethyl alcohol.

Alcoholic solution of ligand and aqueous solution of metal salt were mixed in 2 : 1 (L : M) ratio for Fe(II), Co(II), Ni(II) and Cu(II) chelates and 3 : 1 (L : M) in case of Fe(III) chelate and digested on boiling water bath for about 15 min. The separated complexes were filtered and washed several times with hot water and finally with aqueous ethanol (1 : 1) and dried in desiccator over calcium chloride. The purity of the metal chelates was tested by thin layer chromatography.

Physical measurements: Electronic spectra of the ligand and the complexes were recorded on Beckman DU2 spectrophotometer in methanol (250-1000 nm). A Carl Zeiss USU-2p spectrophotometer was used for measurement of reflectance spectra (400-1000 nm). IR spectra (nujol mull) were recorded on Specord IR-75 at CIC, Nagpur. Magnetic measurements of all the complexes were made at room temperature and Co(II), Ni(II) and Cu(II) complexes were studied down to liquid nitrogen temperature with Gouy balance at Bhabha Atomic Research Centre, Bombay. Diamagnetic constants were calculated by the method given in literature¹³. The esr spectra of the Cu(II) chelates was obtained from the L. I. T., Bombay. Conductance measurements were made using a Toshniwal Conductivity Meter at $25 \pm 0.1^\circ$ with conventional closed type cell. Elemental analysis were performed at the Central Drug Research Institute, Lucknow. TG and dta studies were performed as described earlier¹⁴.

Results and Discussion

Analytical results and some physical properties of the complexes are shown in Table I. All the complexes are stable in air and Fe(II), Fe(III) and Cu(II) complexes are soluble in common organic solvents. Complexes of Co(II) and Ni(II) are slightly soluble in chloroform, acetone, DMF and ethanol but soluble in methanol, benzene, nitrobenzene. Molar conductance values in nitrobenzene,

NOTES

TABLE 1—ANALYTICAL DATA, COLOUR, MOLAR CONDUCTANCE IN NITROBENZENE AND μ_{eff} AT ROOM TEMPERATURE

Chelate	M% Found (Reqd.)	O% Found (Reqd.)	H% Found (Reqd.)	N% Found (Reqd.)	Colour	M*	μ_{eff} B.M. at room temperature
Fe(II)(TMBHA) $_2$.2H $_2$ O	9.35 (9.24)	59.95 (59.60)	5.16 (5.29)	4.60 (4.63)	Red	13.5	4.95
Fe(III)(TMBHA) $_2$.3H $_2$ O	6.40 (6.36)	60.70 (61.51)	5.40 (5.36)	4.90 (4.78)	Red	11.2	5.95
Co(TMBHA) $_2$.2H $_2$ O	9.82 (9.70)	60.00 (59.31)	5.20 (5.27)	4.70 (4.61)	Pink	10.5	5.02
Ni(TMBHA).2H $_2$ O	9.65 (9.67)	59.80 (59.33)	5.30 (5.27)	4.65 (4.61)	Light green	3.20	3.07
Cu(II)(TMBHA).2H $_2$ O	10.20 (10.39)	58.60 (58.86)	5.30 (5.23)	4.60 (4.57)	Light green	5.35	1.92

* Molar conductance M ($\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) in $1 \times 10^{-3} M$ solution of nitrobenzene at 25°.

TABLE 2—SPECTRAL DATA OF THE METAL CHELATES IN VISIBLE REGION WITH SOME OF THEIR ASSIGNMENTS

Chelate	Reflectance spectra λ kK	Absorption spectra λ kK	Assignments	Crystal field parameters ($\text{cm}^{-1} \times 10^{-3}$)*
Fe(II)-TMBHA	10.52 17.85 22.72	20.83	${}^6T_{2g}(D) \rightarrow {}^6E_g$ Charge transfer	$Dq = 1.052$ $B = 0.582$ $\beta = 0.568$ (B for free ion = 1024 cm^{-1})
Fe(III)-TMBHA	12.20 14.28 20.00 23.80	20.40	${}^6A_{1g} \rightarrow {}^4T_{1g}$ ${}^6A_{1g} \rightarrow {}^4T_{2g}$ ${}^6A_{1g} \rightarrow {}^4E_g$	
Co(II)-TMBHA	10.63 18.51 21.73	10.41 18.86	${}^4T_{1g}(F) \rightarrow {}^4T_{2g} \nu_1$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g} \nu_2$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) \nu_3$	$Dq = 1.19$ $B = 0.0825$ ν_3 (calculated) = 22.54 kK $\beta = 0.7366$
Ni(II)-TMBHA	14.28 23.25	14.28 25.64	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Calculated $\nu_1 = 8.54 \text{ kK}$ $B = 0.953$ $\beta = 0.882$ $B^0 = 11.75\%$
Cu(II)-TMBHA	11.76 15.38 22.22 24.39	15.38 17.85	${}^2B_{1g} \rightarrow {}^2A_{1g}$ Charge transfer	

* Reference No. 39.

viz., $3\text{--}14 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ indicate non-electrolytical nature of the complexes.

IR spectra: As is anticipated, a band around 3100 cm^{-1} , assigned to the hydrogen bonded OH stretching¹⁶⁻²⁸ for the ligand (TMBHA), disappears in the spectra of all metal complexes. The band due to C=O stretching vibration ($=1625 \text{ cm}^{-1}$) in the free ligand is displaced towards lower frequency in the metal complexes to more or less the same extent. The C–N stretching frequency¹⁰ (near 1400 cm^{-1}) in the free ligand is found to be displaced to higher frequency on complexation. Such lowering of C=O frequencies and increase of C–N frequencies indicate that coordination of hydroxamic acid occurs through oxygen of carbonyl group. The band due to N–O stretching vibration (940 cm^{-1}) in free ligand gets shifted to higher frequency side on complexation. Metal-oxygen stretching vibration ($510\text{--}530 \text{ cm}^{-1}$) and observation of lattice water ($3200\text{--}3550 \text{ cm}^{-1}$) are arrived on the literature data^{11,20,22}.

Magnetic and electronic spectral studies: A magnetic moment value (4.95 B. M.) for Fe(II) complex indicates octahedral spin-free geometry²³. A broad band around $17\text{--}22 \text{ kK}$ (reflectance spectrum) and an intense band near 20 kK (absorption spectrum) could be assigned for charge transfer spectra, while the band near 10.52 kK may be assigned ${}^6T_{2g} \rightarrow {}^6E_g$. Magnetic study, spectral study and crystal field parameters favour octahedral geometry for Fe(II)-TMBHA complex²⁴.

Fe(III)-TMBHA shows a magnetic moment value 5.95 B. M. This indicates its spin free state^{25,26}. The various bands observed in electronic spectra are incorporated in Table 2. Magnetic and spectral studies suggest octahedral geometry for Fe(III)-TMBHA complex²⁶.

The magnetic moment of Co(II) complex is 5.02 B.M. The susceptibility follows the Curie-Weiss law with moderate θ values of 10°K (Table 3) and suggests octahedral geometry²⁷. Spectral assignments and crystal field parameters for Co(II)-TMBHA complex are shown in Table 2. A broad

band near 10 kK and a strong band around 18 kK indicate the merging of ν_a transition with ν_g and shoulder near 21 kK (observed in reflectance spectra) suggests octahedral geometry to Co(II) complex. The observed energy value of ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition is found to be lower than the theoretical value calculated by the relationship $\nu_a = \nu_1 + 10 Dq$. This suggests the lower symmetry i.e. distorted octahedral geometry for Co(II)-TMBHA complex²⁸.

TABLE 3—MAGNETIC DATA

Co(TMBHA)₂·2H₂O

Temperature °K	Diamagnetic correction : -92.79×10^{-6} erg G ⁻² mole ⁻¹	$\chi_{Co} \times 10^6$ (erg G ⁻² mole ⁻¹)	$\chi_{Co} \times 10^{-3}$ (G ² mole erg ⁻¹)	μ_{eff} (B.M.)
294.5		10,682	0.9361	5.02
250.0		12,552	0.7966	5.01
198.2		15,556	0.6428	5.01
145.5		20,992	0.4763	4.95
120.0		25,505	0.3920	4.95
102.5		29,542	0.3385	4.91

Ni(TMBHA)₂·2H₂O

Temperature °K	Diamagnetic correction : -92.79×10^{-6} erg G ⁻² mole ⁻¹	$\chi_{Ni} \times 10^6$ (erg G ⁻² mole ⁻¹)	$\chi_{Ni} \times 10^{-3}$ (G ² mole erg ⁻¹)	μ_{eff} (B.M.)
294.5		3,996	2.502	3.07
273.0		4,177	2.394	3.02
240.5		4,760	2.100	3.02
200.5		5,880	1.700	3.06
152.0		7,246	1.380	2.97
110.0		10,1178	0.982	2.98

Cu(TMBHA)₂·2H₂O

Temperature °K	Diamagnetic correction : -92.79×10^{-6} erg G ⁻² mole ⁻¹	$\chi_{Cu} \times 10^6$ (erg G ⁻² mole ⁻¹)	$\chi_{Cu} \times 10^{-3}$ (G ² mole erg ⁻¹)	μ_{eff} (B.M.)
294.5		15,690	6.373	1.92
273.0		16,773	5.961	1.91
250.5		18,039	5.543	1.90
210.5		21,462	4.659	1.90
152.5		29,552	3.383	1.89
120.0		37,381	2.675	1.89
104.5		41,936	2.384	1.87

Magnetic susceptibility studies of Ni(II)-TMBHA complex (Table 3) suggest its magnetically normal behaviour with a small θ value of $+10^\circ K$. Electronic spectra (Table 2) consists of a broad band in the region 15 kK-17 kK which may be assigned to ${}^8A_{2g} \rightarrow {}^8T_{1g}$ while strong shoulder near 25.64 kK can be assigned to ${}^8A_{2g} \rightarrow {}^8T_{1g}$ (P) transition. Calculated values of crystal field parameter, magnetic and spectral studies suggest octahedral geometry for Ni(II)-TMBHA complex²⁸.

Magnetic moment values of Cu(II)-TMBHA complex (Table 3), obey the Curie-Weiss law with $\theta = 9^\circ K$ and indicates neither inter nor intramolecular Cu-Cu interaction²⁹. Distorted octahedral geometry is suggested due to the appearance of two bands in the region 11 kK-16 kK in electronic spectral studies (Table 2). The band near 24 kK with high intensity is assigned to charge transfer. The g values of Cu(II)-TMBHA chelate ($g_{\parallel} = 2.253$, $g_{\perp} = 2.040$, $|g| = 2.111$) indicate a tetragonal or distorted octahedral symmetry³⁰⁻³³.

Thermal analysis: Thermal analysis studies indicates that there is a dehydration around $60-140^\circ$, $70-150^\circ$, $100-180^\circ$, $100-170^\circ$ and $50-165^\circ$ respectively in Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of TMBHA. According to Nikolev *et al*³⁴ water eliminated below 150° can be considered as the crystal water and water eliminated above 150° as coordinated water to the metal ion. Metal oxide formation is observed around $400-560^\circ$. Endothermic dta peaks around $140-180^\circ$ indicate dehydration of the complexes. Exothermic broad dta peaks are observed in the temperature range of $400-550^\circ$ as seen in other cases³⁵⁻³⁷. Above observations may be interpreted in terms of dissociation of the complex (endothermic peak) followed by an exothermic oxidation-reduction reaction as observed by Chang *et al*³⁸.

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References

1. S. MIZUKAMI and K. NAGATA, *Coord. Chem. Rev.*, 1968, **3**, 267.
2. Y. K. AGRAWAL, *Analyst*, 1972, **97**, 578.
3. V. K. GUPTA and S. G. TANDON, *J. Indian Chem. Soc.*, 1971, **48**, 753.
4. S. B. GHOLSE and R. B. KHARAT, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1681.
5. S. P. BAG and A. K. CHAKRABARTI, *J. Indian Chem. Soc.*, 1975, **52**, 492.
6. S. B. GHOLSE and R. B. KHARAT, *J. Indian Chem. Soc.*, 1975, **55**, 492.
7. N. N. GHOSH and D. K. SARKAR, *J. Indian Chem. Soc.*, 1975, **52**, 195.
8. A. K. MAJUMDAR and G. DAS, *Anal. Chem. Acta*, 1966, **36**, 454.
9. B. C. BHATTACHARYA, S. K. BHOWAL and G. BASAK, *Indian J. Chem.*, 1976, **14A**, 354.
10. B. CHATTERJEE, *J. Indian Chem. Soc.*, 1973, **50**, 758.
11. N. N. GHOSH and S. K. MUKHOPADYAY, *J. Indian Chem. Soc.*, 1973, **50**, 553.
12. Y. K. AGRAWAL and S. G. TANDON, *J. Chem. and Engg. Data*, 1973, **16**, 371.
13. B. N. FIGGIS and D. J. MARTIN, *Inorg. Chem.*, 1966, **5**, 100.
14. N. S. BHAVE and R. B. KHARAT, *J. Inorg. Nuclear Chem.*, (In press).
15. G. J. SUTTON, *Aust. J. Chem.*, 1959, **12**, 122.
16. D. R. AGRAWAL and S. G. TANDON, *J. Indian Chem. Soc.*, 1971, **48**, 571.
17. D. HADAZI and PREVORSER, *Spectrochimica Acta*, 1957, **10**, 38.
18. J. P. SHUKLA, Y. K. AGRAWAL and K. P. KUCHYA, *J. Indian Chem. Soc.*, 1974, **51**, 437.
19. S. P. BAG and S. LAHIRI, *J. Indian Chem. Soc.*, 1975, **52**, 36.
20. A. E. MARTEL, "Coordination Chemistry", Von Nostrand Reinhold Co., New York, 1971, vol 1, p. 258.
21. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, 1970.
22. K. NAKAMOTO and S. J. MCGARTHY, "Spectroscopy and Structure of Metal Chelate Compounds", John Wiley & Sons, London, 1968, p. 286.
23. B. N. FIGGIS and J. LEWIS, *Prog. Inorg. Chem.*, 1964, **6**, 37.
24. S. P. GHOSH and L. K. MISHRA, *Inorganic Chimica Acta*, 1973, **7**, 545.
25. N. N. GHOSH and G. SIDDHANTA, *J. Indian Chem. Soc.*, 1969, **46**, 488.

26. P. SINGH, V. SINGH, B. P. SINGH, G. P. POKHARYAL and R. P. MAHESH, *J. Indian Chem. Soc.*, 1976, **53**, 355.
27. S. S. SANDHU and G. K. SANDHU, *Indian J. Chem.*, 1974, **12**, 830.
28. A. B. P. LEVER, *J. Chem. Soc., A*, 1967, 2041.
29. M. R. KIDD and W. H. WATSON, *Inorg. Chem.*, 1969, **8**, 1886.
30. S. FUJIWARA, S. KATSUMATA and T. SEKI, *J. Phys. Chem.*, 1967, **71**, 155.
31. D. E. O'REILLY, *J. Chem. Phys.*, 1959, **29**, 1188.
32. F. M. ROBERTS and W. S. KOSHI, *J. Amer. Chem. Soc.*, 1960, **82**, 3006.
33. R. H. SANDS, *Phys. Rev.*, 1955, **99**, 1222.
34. A. V. NIKOLAEV, V. A. LAGVIENKO and L. I. MYACHINA, "Thermal Analysis", Academic Press, New York, 1969, vol 2, p. 779.
35. Y. K. AGRAWAL and T. P. SHARMA, *J. Indian Chem. Soc.*, 1977, **54**, 771.
36. C. G. SCENEY, J. O. HILL and R. J. MAGEE, *Thermochimica Acta*, 1975, **11**, 301.
37. C. G. SCENEY, J. F. SMITH, J. O. HILL and R. J. MAGEE, *J. Thermal Anal.*, 1976, **9**, 415.
38. F. C. CHANG and W. W. WENDLANDT, *Thermochimica Acta*, 1973, **7**, 103.
39. K. C. PATEL and D. E. GOLDBERG, *J. Inorg. Nuclear Chem.*, 1972, **34**, 637.

Rare Earth Complexes with N, O-Donor Ligands—Part II. Complexes of Gd(III), Tb(III), Dy(III) and Ho(III) with 2-(2'-Hydroxyphenyl)benzimidazole

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IN a previous communication¹, we described the 8-coordinated complexes of the type $[M(\text{HO-PhBzH})_2(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}]$ where HO-PhBzH stands for the title ligand and M is Y(III), La(III), Ce(III), Pr(III), Nd(III) or Sm(III). We report here similar complexes with Gd(III), Tb(III), Dy(III) and Ho(III).

The nitrates of these middle rare earth elements (procured as hydrated crystals from Indian Rare Earths Ltd., Kerala, in 99.9-99.99% purity), when interacted with HO-PhBzH in 1 : 2 molar proportions in refluxing ethyl acetate, yield pale yellow 8-coordinate complexes of the type $[M(\text{HO-PhBzH})_2(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}]$ in solid state. The 1 : 1 electrolyte nature of the complexes is supported by their molar conductance values** lying in the range 117-128 ohm⁻¹ cm² in DMF. The water of crystallisation is lost by heating upto 120° and no further loss is recorded upto 180°.

The room-temperature magnetic moment values are in good agreement with the values calculated on the formula², $\mu_{\text{eff}} = g[J(J+1)]^{\frac{1}{2}}$ and confirm the terpositive state of the metals in these complexes.

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** All physical measurements were made as described in Ref. 1.

Infrared spectra : The existence of both coordinated (C_{2v}) and uncoordinated (D_{3h}) nitrate groups are inferred from the ir spectra of the complexes.

Of the six fundamentals expected³ for a coordinated nitrate, five are exhibited by Gd-, Tb- and Ho-complexes, whereas four by the Dy-complex. The $\nu_4(\text{B}_1)$ mode appears as a triplet (1470, 1462, 1455 cm⁻¹) in each complex and $\nu_1(\text{A}_1)$ appears as a doublet (Gd, Tb : 1300, 1288 cm⁻¹) or a singlet (Dy : 1295 ; Ho : 1298 cm⁻¹). The $\nu_2(\text{A}_1)$ mode which appears at 1022 cm⁻¹ in Gd-, Tb- and Ho-complexes is obscured in the Dy-complex. The weak bands at 800 cm⁻¹ and 700 cm⁻¹ (Gd, Tb : 700 ; Dy : 695 ; Ho : 698 cm⁻¹) are assigned to the $\nu_5(\text{B}_2)$ and $\nu_6(\text{B}_1)$ modes respectively. On arguments mentioned earlier¹, we treat the coordinated nitrate ions as bidentate groups in these complexes also, supported by the magnitude⁴ of $\nu_4 - \nu_1$ (~170 cm⁻¹).

The presence of uncoordinated nitrate⁵ is substantiated by appearance of shoulders at 1350 cm⁻¹ ascribed to $\nu_3(\text{E}')$ mode and at 850 cm⁻¹ ascribed to $\nu_3(\text{A}'')$ mode uniformly in each complex.

The assignment of bands for $\nu_{(\text{OH})}$ and $\nu_{(\text{NH})}$ have been discussed in detail in our previous paper¹. In accordance with that, the strong broad band at 3200 cm⁻¹ is assigned to $\nu_{(\text{OH})}$ and a shoulder at 3060-3050 cm⁻¹ to $\nu_{(\text{NH})}$ in each complex. The $\delta_{(\text{HOH})}$ is exhibited¹ at 1642 cm⁻¹ as a weak band on account of water of crystallisation of the complexes. Extra bands in the 3μ region at 3525 cm⁻¹ in the Tb- and Ho-complexes indicate the presence of non-hydrogen bonded OH groups also.

Electronic spectra : The spectra of Tb(III)-, Dy(III)- and Ho(III)-complexes have been recorded in DMF and assignment of bands made with reference to the levels of the metal ions in LaCl₃-host.

As the first excited level (⁶P) of Gd(III) lies 32000 cm⁻¹ above the ground term (⁸S_{7/2}), all bands of the metal ion are expected to be in the ultraviolet region. Because of intense ligand bands appearing in this region, the spectrum of Gd(III)-complex could not be studied.

The bands due to transitions, ${}^7F_6 \rightarrow {}^7F_3$ (4.34 kK) and ${}^7F_6 \rightarrow {}^7F_2$ (4.95, 5.06 kK) of Tb(III) in the given complex show little red-shifts from the LaCl₃-host reference⁶. However, the ${}^7F_6 \rightarrow {}^7F_1$ (5.19, 5.37 kK), ${}^7F_6 \rightarrow {}^7F_0$ (5.52 kK) and ${}^7F_6 \rightarrow {}^5D_3$ (25.64 kK) bands suffer 2-4% red-shifts with reference to the same.

The two hypersensitive bands due to ${}^6H_{15/2} \rightarrow {}^6H_{9/2}$ and ${}^6H_{15/2} \rightarrow {}^6F_{11/2}$ transitions of Dy(III) appear to have mixed up at 7.72 kK in the given complex. Similarly, ${}^6H_{15/2} \rightarrow {}^6H_{7/2}$ and ${}^6H_{15/2} \rightarrow {}^6F_{9/2}$ give rise to a single band at 5.03 kK. The transitions from ${}^6H_{15/2}$ to other levels, ${}^6H_{5/2}$ (10.20 kK), ${}^6F_{7/2}$ (11.00 kK), ${}^6F_{5/2}$ (12.35 kK) and ${}^6F_{3/2}$ (13.16 kK) also appear almost at the same positions as they do in LaCl₃-host⁶.