

Characterization and bio-chemical synthesis of Gd³⁺ rare metal Complex with benzoxazole derivative

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Abstract: The grouping of some rare metal ions with an significant 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide (BSPA) ligand to form coordination compounds is an important area of present research. Less explored biologically important 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide ligand is allowed to react with solution of some rare metal perchlorates and attempt has been made to synthesize solid 2-(1,3-benzoxazole -2-yl-sulfanyl)-N-phenyl acetamide complexes. These 2-(1,3-benzoxazole-2-yl-sulfanyl)-N-phenyl acetamide complex are subjected to U.V Visible Spectroscopy, IR Spectroscopy, TGA Analysis, elemental analysis of these complex has been evaluated by standard methods and attempts have been made to correlate structural characteristics with properties of these 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide complex.

Keywords: Spectroscopic analysis, characterization, 2-(1,3-Benzoxazole-2-yl-sulfanyl)-N-phenyl acetamide(BSPA) complex.

1. INTRODUCTION

The rare–earth metals are by definition, the group IIIb elements Sc, Y, La and the 14 lanthanides Ce–Lu. [1,2,3]

2. EXPERIMENTAL

A definite volume of 70% acid was diluted with water to obtain 0.2M perchloric acid solution in 500 ml flask. The exact strength was determined by pH metric titration against 0.2M NaOH solution (standardized with 0.2N oxalic acid previously prepared). 75 ml 0.2M perchloric acid was taken and excess solid metal carbonate was added. The solution was stirred for 30 minutes and filtered (this way 0.133 M lanthanide was obtained).

The formation of complexes was carried out by mixing 75 ml 0.133 M metal perchlorate solution and 50ml 0.2 M BSPA ligand in DMSO solution. The mole ratio of ligand and metal was (1:1). The reaction mixture was refluxed for 2.5 to 3.0 hours at 95 °C temperature. After 3 hours the reaction mixture was cooled. There was no immediate precipitation. The pH of the above solution was then raised up to 6.5 using 0.1M sodium hydroxide solution which resulted in the precipitation of the semi solid sticky material. Then, this sticky product was dissolved in methanol to remove stickiness. This mixture with methanol was slightly heated for total dissolution and after that cooled. Then after around 30 ml of cold water was added for precipitation of the complex in non sticky form. The complex thus obtained was washed well with double distilled water to remove unreacted metal perchlorate and ligand. All the complexes were dried in oven at 40°C to 50°C.

Table 1: Rare metal of the complexes

Sr. No.	Ligand	Brief name
1	Ligand BSPA	BSPA
2	Gd(III)-BSPA	Gd-BSPA

2.1 Analyses and Physical Measurements:-

M.P. and TLC were taken with usual apparatus[solvent system for TLC 70% toluene + 30% methanol]. TLC indicated single spot confirming complex formation. Elemental analyses were performed with a Vario-MICRO CUBE C, H, N, S analyzer. The metal content was determined by titration with a solution of standardized disodium salt of EDTA [4]. Magnetic susceptibilities were measured by the Gouy's method [5], at room temperature using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as calibrant. The IR spectra were recorded on a BRUKER ALPHA FT-IR 400 – 4000 cm^{-1} spectrophotometer. The UV – visible spectra were measured on a UV-1800 Shimadzu (Double beam) spectrophotometer. Thermal measurements were performed using a METTLER TOLEDO STAR[®] system TGA/DSC1(1150 $^{\circ}$ C) thermal analyzer. The mass spectra analyses were performed with a model QDA of Waters and Alliance 2690 analyzer.

Table 2: Physical characterization of BSPA ligand with Gd³⁺ Complexes

Sr. No.	Compound Name	M.P (°C)	Rf value	Molar Cond. mho cm^{-1}	Mole. weight gm mol^{-1}	Uv – vis spectral λ_{max} (nm)	Color	Magn. Sus. (BM)	Elemental Analysis											
									% C		% H		% N		% S		% Cl		% M	
									Cal.	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	Fou.
1	BSPA Ligand	127	0.72	0.43	284.33	349.5, 286.5, 279, 255.5, 240.5, 226.5, 208.5	Creamy White	----	63.01	63.30	4.09	4.22	9.94	9.85	29.79	11.25	---	---	---	---
2	Gd-BSPA	179	0.67	0.248	1308.74	341, 286.5, 279.5, 252.5, 235.5, 220	light yellow	7.87	61.30	41.26	4.08	3.07	9.61	6.41	28.10	7.33	8.13	---	10.36	12.01

BSPA = 2-(1,3-Benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide, Mole.=molecular, Mag.Sus.=Magnetic susceptibility,

Cal. = calculated, Fou. = Found,

Cond. = conductance,

%M carried out by EDTA method,

*Solvent system for TLC = 70% toluene + 30% methanol

The physical data of the complex and ligand are presented in the table no.2. The Gd(III) complex was colored while BSPA is colorless. The melting point of ligand is different than the complex. The TLC of solid was carried out using silica gel as the stationary phase and toluene : methanol (7:3) as the mobile phase. The Rf value of complex are different than ligand. Together, all these provide confirm formation of single complex in each case. The molar conductance of complex confirms that are quite low and these complex are nonionic.

2.2 Infrared Spectra study:-

IR bands corresponding to BSPA and its complexes are shown in table no.3. The IR spectra of ligand and metal complexes were recorded in the 4000-400 cm^{-1} range using KBr pellet. IR spectral[6,7] analysis confirms the presence of characteristic groups in the compound. In the ligand bands at~3344 and 3333 cm^{-1} is assigned to the $\nu(\text{N-H})$ stretching of the amine group. The sharp band at 1598 cm^{-1} can be attributed to the $\nu(\text{C=N})$ stretching mode in the ligand. This band shifted in the complexes. This indicates participation in coordinate bond. The band at 1675 cm^{-1} of the ligand is due to the C=O stretching. In the Gd-BSPA, it is shifted to 15-40 cm^{-1} either at lower energy or at higher energy indicating the coordination by the carbonyl-oxygen atom. [6,7]

Further conclusive evidence of this ligand with metal ion was shown by the appearance of weak low frequencies new bands at 650-750 cm^{-1} and 450-510 cm^{-1} . These were assigned to the metal[8,9] nitrogen (M-N) and metal oxygen (M-O) vibration respectively, and were observed in the spectra of the metal complexes and not in the spectra of the ligand. Thus, this is the confirmation that the N and O atoms participated in the coordination[8,9].

Table 3: IR spectra of BSPA ligand with Gd³⁺ complex

Compound	v[Ar(C-H)] stre.	v(C=N) stre.	v(C=O) stre.	v(N-H) stre.	v(M-N) stre.	v(M-O) stre.	v(M-Cl) stre.	v(C-O-C) stre.	v(C-S) stre.	ClO ₄ vibrations	Scissoring and other bending Vibrations
BSPA ligand	2912 2978	1440 1454	1598 1675	3529 3671	-----	-----	-----	1236 1251	757 781 807 858	-----	1454- CH ₂ Scissoring 1369- wagging and twisting
Gd-BSPA	2979	1441 1454 1473	1509 1528 1599 1636	3475 3550	653 665 678 690 702	453 464 479 499	510 596 624	1236 1251	757 781 807 858	(s) 1111 (b)624 (b)653	1454- CH ₂ Scissoring 1370- wagging and twisting

(1) *Metal –Sulphur stretching (below 300 cm⁻¹) could not be measured by the instrument (2) All figures are in cm⁻¹

2.3 Electronic Spectra and Magnetic Studies:-

The Gd-BSPA are analyzed for UV- Visible spectra and magnetic moments. These f- block metals have a usual characteristic of absence of d-d transition because no space for excited electron is present in the d orbital which is completely filled in these ions. The results indicate paramagnetic nature of the complexes along with metal to ligand charge transfer band.[10,11]

The room temperature magnetic moment of the solid Gd-BSPA was found to be 7.87 BM. This indicates seven unpaired electrons per Gd (III) ion in tricapped distorted trigonal prism [12] environment.

The group with longest wavelengths lies to near 3100 Å. The ground state of Gd³⁺ is ⁸S_{7/2}, the only known level of any of the triply ionized rare earth ions which has primarily S character (where thus L= 0, with angular momentum entirely due to the spin) which in first approximation does not interact with the electric crystal field. The 8S level is, therefore, single, or at least [13,14] appears to be so unless very high resolution is employed, in which case a structure of the order of 0.1 cm⁻¹ is revealed. [13,14] There are nominal S levels for the other rare earth ions, but their eigenvectors always have so much mixture with L ≠ 0 that they are split quite appreciably in a crystal field.[13,14]

Table 4: Literature information: Electronic structure and Magnetic properties

Ion/ Configuration	Colour of common salts	Ground State term	Excited state levels of hypersensitive transitions	Usual Magnetic moment values (B.M)	Number of unpaired electrons	Total orbital angular momentum
Gd ^{III} /f ⁷	colorless	⁸ S _{7/2}	none	7.94	7	0

Reference: - [15,16]

Table 5: Electronic spectra of Gd³⁺ complex

Complexes	cm ⁻¹	Assignment
Gd-BSPA	29325.5 34904 35778.1 39603.9 42462.8	⁸ S _{7/2} → ⁶ I _{7/2} (D ₁) ⁸ S _{7/2} → ⁶ D _{9/2} (K ₅) ⁸ S _{7/2} → ⁶ D _{5/2} (O ₃)

2.4 Thermal analysis:-

Thermal analysis of metal complexes is carried out by thermo gravimetric analyzer. The heating was carried out until there was [17.18] no further loss in weight (up to ~ 1000 °C). Change in weight was recorded with time. A regular temperature change makes possible to plot a graph of weight as a function of temperature. Thermo grams were analyzed by increasing the temperature at a uniform rate of 10 °C minute^{-1} . The temperature range wise % weight loss data of metal complexes are shown in table.6 [17.18]

Loss in weight of the sample between room temperature and approximately, upto 150 °C – correspond to water of crystallization. Loss in weight of the sample between approximately 150 °C to 250 °C correspond to loss in weight due to water of coordination. After approximately 800 °C, almost constant weight is observed. [17.18 This is due to oxide of corresponding metal hence from this constant weight, percentage of metal can be obtained.

Table 6: TGA data of Complexes of BSPA

Compound	RT-150 °C			150 °C - 250 °C		
	% Loss	Loss of weight(gm) for 1 mole complex	Corresponding water molecules	% Loss	Loss of weight(gm) for 1 mole complex	Corresponding water molecules
BSPA ligand	0.15	0.42	0	1.50	4.28	0
Gd-BSPA	0.13	0.73	0	1.21	6.55	0

RT = Room temperature

Table 7: Complexes and Coordination numbers

Complexes	Coordination number of metal in the probable structures	Usual coordination number * of metal ion
Gd-BSPA	8	7, 8

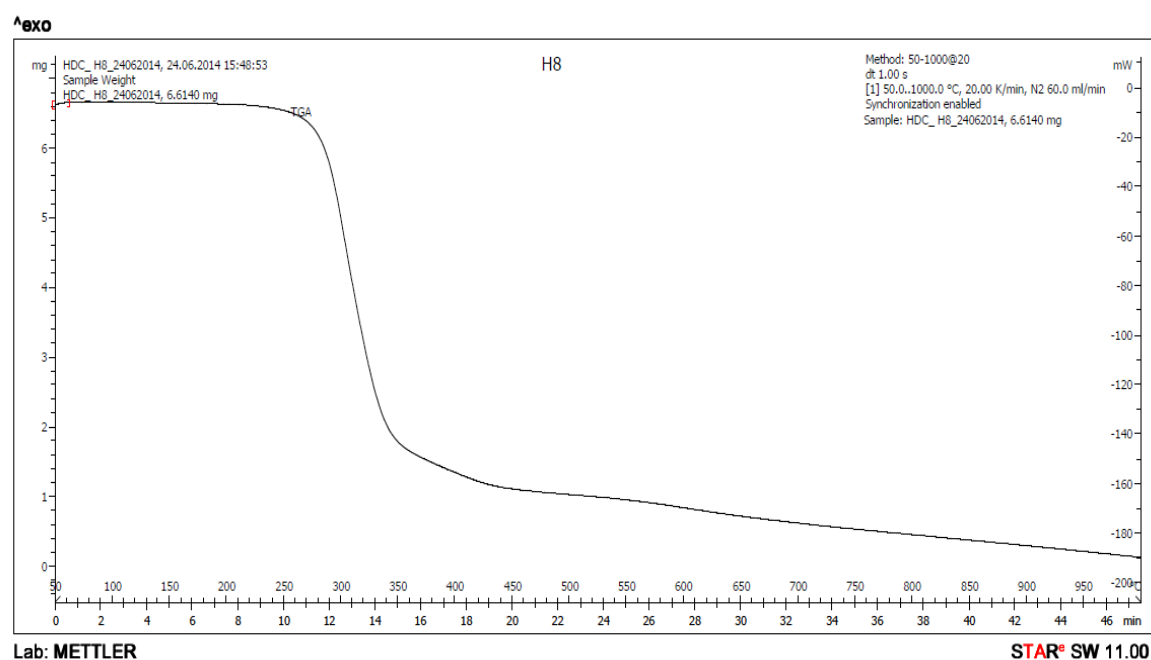


Figure 1: TGA spectrum of BSPA Ligand

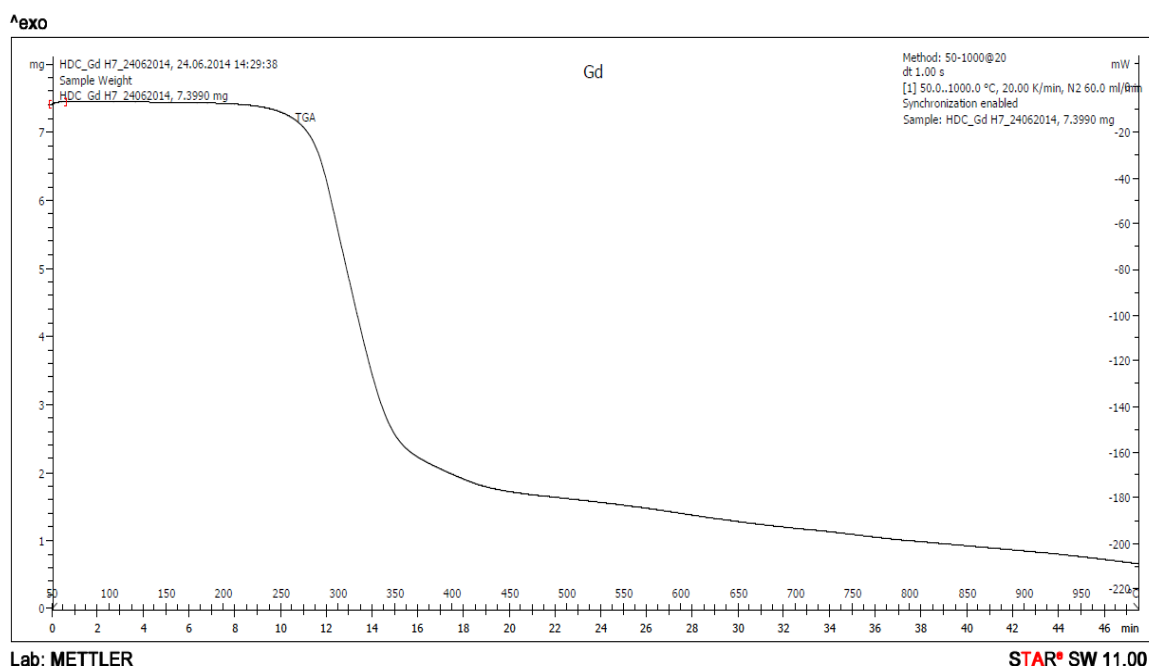


Figure 2: TGA spectrum of Gd-BSPA

It has been observed that Gd-BSPA does not show any loss in weight in the range 150°C - 250°C . there are no water molecules that coordinate with gadolinium ion in the Gd-BSPA complex. It has been also observed that Gd-BSPA lose weight corresponding to no water molecules up to 150°C hence, no water molecules are there for water of crystallization.

The reported values for Gd-BSPA are based upon the results of complexes without water of crystallization. When thermal analysis was carried out, the sample, because of its hygroscopic nature, absorbed water molecules from air and all the corresponding results were uniformly lower than anticipated. Therefore, the results have been expressed for the complex on dried basis. This hygroscopic complex was dried at 50°C for 90 minutes in oven to remove absorbed water.

2.5 Mass spectroscopy

The most common use of mass spectrometry by the organic chemist is for the accurate determination of molecular weight and from that molecular formula so is the case for the inorganic chemist. A second important use is to provide information about the structure of compounds by an examination of the fragmentation pattern and also from the relative intensities of M+1, M+2, M+4 peaks.[19,20] The individual information and interpretation of mass spectra is shown below.

Gd-BSPA

Probable peak – 441 amu (Metal + Ligand) (weak)

Base peak (B. P.) - 211.2 amu (ES+), 166.0 amu (ES-), 297 amu and 497.7 amu (ES-)

(B. P. +1) is 16 % of B.P. therefore 15 carbon atoms present in fragment corresponding to base peak

Peak, peak +2, peak + 4 (ratio 3:3:1) in certain fragments therefore 3 chlorine atoms may be present in the fragment and hence in the molecule.

Ligand (-) Ph- NH₂ + 1 (ES+) peak = 192.1 amu

Ligand (-) Ph-NH-CO peak = 164.1 amu (ES+)

Ligand (-) 1,3-benzoxazole (118) peak = 166.0 amu

Metal + Ligand - 1,3-benzoxazole (118) peak = 323.0 amu

Metal + Ligand - 1,3-benzoxazole (118) – CH₂ peak = 307.1 amu

Metal + Ligand – Ph – (ES-) peak = 362.5 amu

Molecular weight of all complexes are higher than 1000 amu, the mass spectra are taken upto 600 amu only. The fragments present in the spectra largely confirm the probable structures proposed.

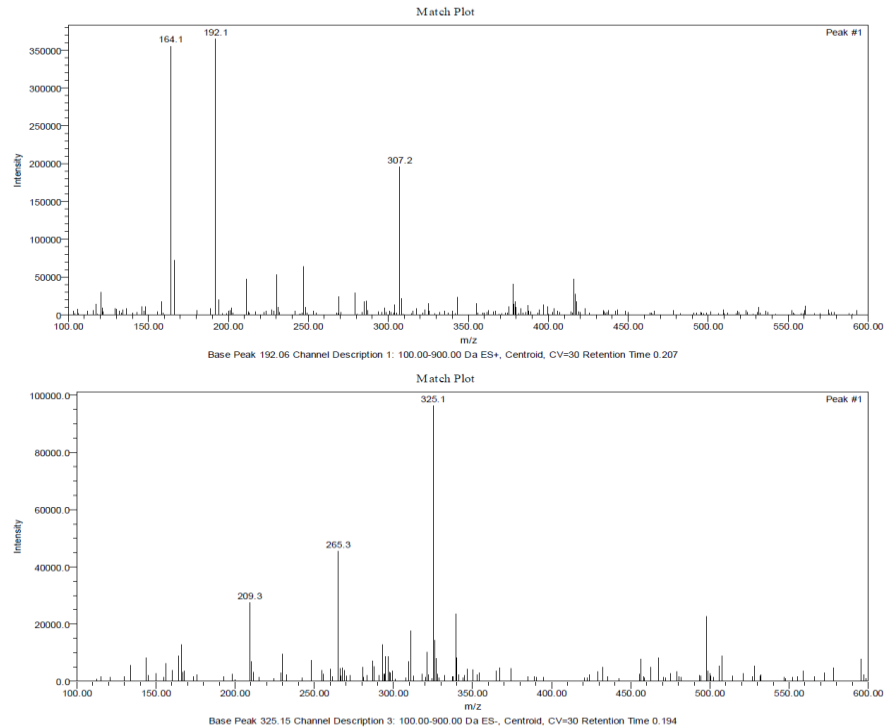


Figure 3: Mass Spectra Ligand BSPA

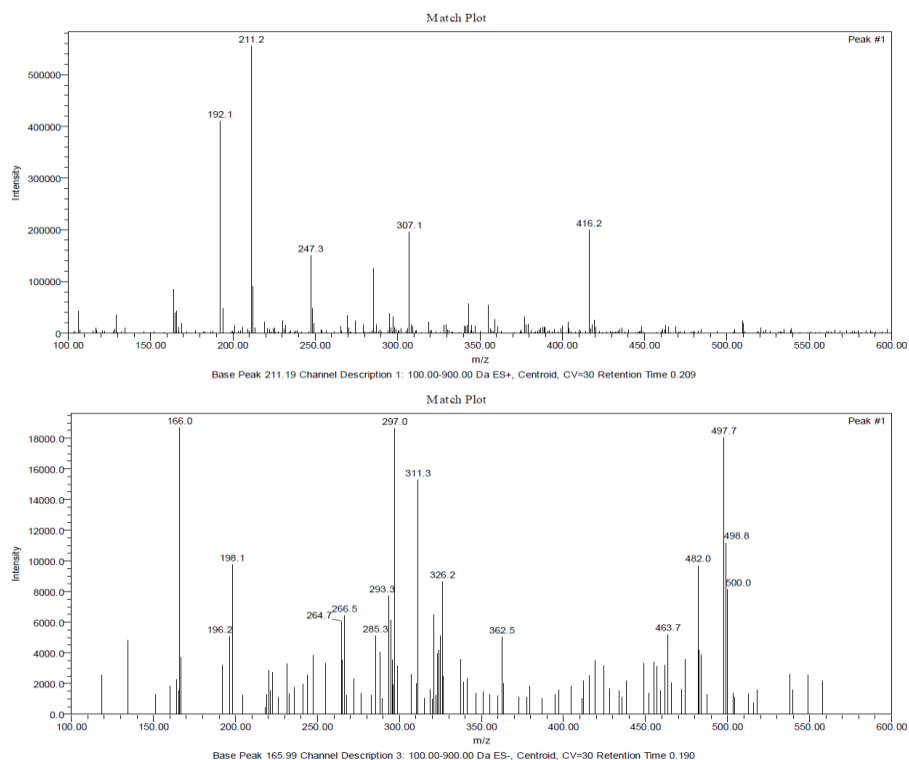


Figure 4: Mass Spectrum of Gd-BSPA

Based upon all the experimental data of physico chemical analyses, the structures of the Gd^{3+} metal complex can be shown as below.

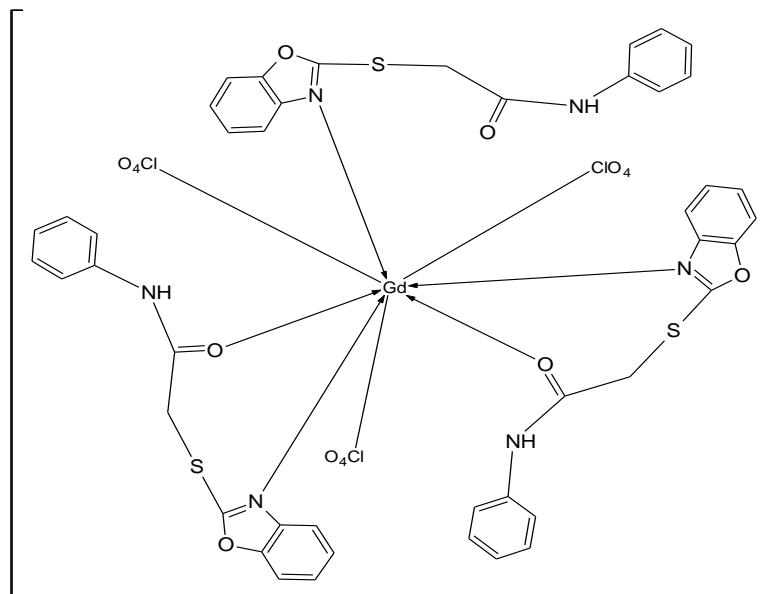


Figure 5: Gd-BSPA probable structure

3. CONCLUSION

This portion describes preparation of the ligand BSPA and its complexes with three lanthanide ions. Usual laboratory tests (M.P., U.V-visible spectra, TLC, colour etc.) confirmed formation [21,22,23] of coordination compounds which were finally characterized by (IR, Mass, TGA etc.). Electronic spectra and magnetic moment values gave information regarding number of unpaired electrons, spin-orbit coupling [21,22,23], charge transfer bands, probable geometry etc. Combining all these information, the tentative structures were assigned to the new complex. [21,22,23]

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