EGE UNIVERSITY

INSTITUTE OF NATURAL AND APPLIED SCIENCES

(MSc THESIS)

SYNTHESES OF MULTINUCLEAR SCHIFF BASE COMPLEXES FORMED BY COPPER AND GADOLINIUM AND INVESTIGATION OF MAGNETIC PROPERTIES

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Code : 405.01.01

Presentation Date: 27.12.2006

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Bornova – IZMIR

Zeynep NAYMAN tarafindan yüksek lisans tezi olarak sunulan "Syntheses of multinuclear schiff base complexes formed by copper and gadolinium and investigation of magnetic properties" baslikli bu çalisma, E.Ü. Lisansüstü Egitim ve Ögretim Yönetmeligi ile E.Ü. Fen Bilimleri Enstitüsü Egitim ve Ögretim Yönergesi'nin ilgili hükümleri uyarinca tarafimizdan degerlendirilerek savunmaya deger bulunmus ve …… tarihinde yapilan tez savunma sinavinda aday oybirligi/oyçoklugu ile basarili bulunmustur.

Jüri Üyeleri: **Imza**

Jüri Baskani : ....

Raportör Üye: ....

Üye : ....

ÖZET

BAKIR ILE GADOLINYUMUN SCHIFF BAZLARI ILE OLUSTURDUGU ÇOK ÇEKIRDEKLI KOMPLEKSLERIN SENTEZLERI VE MAGNETIK ÖZELLIKLERININ INCELENMESI

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Aralik 2006, 81 sayfa

Ilk olarak, üç hafif lantanitin (Nd,Sm and Gd), N,N'-1,4-bütilenbis (salisilaldimin) kompleksleri hazirlanmistir.Söz konusu komplekslerin, $Ln(SbH_2)_2(NO_3)_3.nH_2O$ (Gd için n=0, Sm için n=2 ve Nd için n=3), formülleri ve yapilari element analizi, IR, TGA, DTA, XRD ve LC/MS ile belirlenmistir.Schiff bazi nötr halde olup, lantanit(III) iyonlarina oksijen atomlari araciligi ile iki disli olarak baglanmaktadir.Lantanit(III) iyonlari çevresindeki koordinasyon sayisi 10'dur.

Lantanit komplekslerinin, bakir (II) asetat monohidrat ile tepkimesi sonucunda olusan heteronüklüeer komplekslerin, $Ln(SbH_2)_2(NO_3)_3.nH_2O$ (Gd için n=4, Sm için n=2 ve Nd için n=3), formülleri ve yapilari element analizi, IR, TGA, DTA, XRD ve LC/MS ile aydinlatilmistir.Schiff bazi, bu komplekslerde, iki degerlikli anyon halinde olup lantanit (III) iyonuna iki disli, bakir (II) iyonlarina ise dört disli olarak baglanmaktadir.

Tüm komplekslerin manyetik momentleri ,oda sicakliginda yapilan manyetik alinganlik ölçümleri ile hesaplanmistir.

Anahtar Sözcükler: Lantanit, Schiff Bazi, Bakir, Manyetik Moment

ABSTRACT

SYNTHESES OF MULTINUCLEAR SCHIFF BASE COMPLEXES FORMED BY COPPER AND GADOLINIUM AND INVESTIGATION OF MAGNETIC PROPERTIES

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Master Thesis in Chemistry
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December 2006, 81 pages

Complexes of three lighter lanthanides (Nd,Sm and Gd) with N,N'-1,4- butylenebis (salicylaldimine) have been first prepared .The formulae and the structures of these complexes,$Ln(SbH_2)_2(NO_3)_3.nH_2O$ (n=0 for Gd, n=2 for Sm and n=3 for Nd),have been determined by means of elemental analyses, IR, TGA, DTA, XRD and LC/MS.Schiff base is in the neutral form and coordinated to lanthanide (III) ions in a bidentate fashion through oxygen atoms.The coordination number around lanthanide (III) ions is 10.

The formulae and the structures of heteronuclear complexes, $LnCu_2(Sb)_2(NO_3)_3.nH_2O$, (n=4 for Gd, n=2 for Sm and n=0 for Nd), which have been obtained as a result of reactions of previous lanthanide complexes with copper (II) acetate monohtdrate ,have been elucidated via elemental analyses, IR, TGA, DTA, XRD and LC/MS.Schiff base is dianionic in these complexes and coordinated to lanthanide (III) ion in bidentate fashion and to copper (II) ions in tetradentate mode.

The magnetic moments of all complexes have been calculated through magnetic susceptibility measurements carried out at room temperature.

Key words : Lanthanide, Schiff Base, Copper, Magnetic Moment

TESEKKÜR

Tez çalismamin basariya ulasmasinda büyük bir özveri ile bütün imkanlarini seferber eden, degerli bilgi ve tecrübeleriyle çalismalarima isik tutan, büyük destegini gördügüm danisman hocam Sayin Yrd. Doç. Dr. A. Sedat ÇELEBI' ye saygi ve sükranlarimi sunmayi bir borç bilirim.

Tez çalismalarimda yardimlarini esirgemeyen basta Yüksek Kimyager Gönül YAVUZ ve Ars.Gör.Mahmut ULUSOY olmak üzere degerli laboratuar arkadaslarima tesekkür ederim.

Tez çalismam için finansal destek saglayan E.Ü. Arastirma Fon Saymanligi' na (2004 FEN 060) tesekkür ederim.

Egitim hayatimda yoluma isik tutarak emek veren tüm ögretmenlerime, her konuda bana destek olan Sabriye Nermin ÇIÇEKÇIOGULLARI'na ve çalismalarim sirasindaki anlayisi için degerli esim Ilker ALSANCAK'a ve kizim Perim Su ALSANCAK'a tesekkürlerimi bir borç bilirim.

Hayatimin her asamasinda yanimda olan, maddi ve manevi desteklerini bir an olsun esirgemeyen, ömürlerini bana adayan aileme sükranlarimi sunmayi bir borç bilirim.

Zeynep NAYMAN

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ABBREVIATIONS

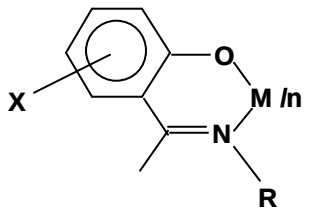
EtOH	Ethanol
HSAB	Hard-Soft Acid-Base Interactions
IR	Infrared Spectroscopy
SbH_2	N,N'-1,4-butylenebis(salicylaldimine)
Ln	Lanthanide
M	Metal
MS	Mass Spectrum
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
$?_{eff}$	Effective Magnetic Moment

1. INTRODUCTION

One of the oldest reactions in chemistry is the condensation of an amine with aldehyde, forming what is called a schiff base. Schiff base ligands coordinate to a metal through the amine nitrogen and another group, usually oxygen, situated on the original aldehyde. When diamino was first combined with 2 equiv. of salicylalhyde, the salen ligands came into being. The ligands feature two covalent and two coordinate covalent sites situated in a planar away. This makes the ligands ideal for the equatorial coordination of transition metals, leaving the two axial sites open for ancillary ligands. They are very much like porphyrins in this regard, but unlike porphyrins the salen ligands are easy to prepare and inexpensive. Evidence for the tremendous amount of transition-metal chemistry that has been conducted is demonstrated by the fact that the first reviews in this area were published in 1966. By incorporating additional group around the phenol portion of ligand, such as ^{t}Bu, the ligands can be made highly soluble in aryl and alkyl solvents. This form of the ligand, salen (^{t}Bu) has been used to great effect in Mn derivatives for olefin epoxylations. Incorporation of hydrophilic groups may also lead to ligands that are soluble in water and alcohols. The malleability inherent to salen ligands has led to their extensive use in transition-metal chemistry, particularly in modelling enzymes and in catalysis. More recent applications include use as metal containing liquid-crystalline polymers, as non radioactive models for T_c as anitviral agents and in asymmetric catalysis. However, only sporadic reports of main group salen complexes have appeared. (Atwood and Harvey, 2001)

1.1 Metal Complexes of Schiff-bases

Metal complexes derived from Schiff's bases have been known for over one hundred years. Preceding the work of S.M Jorgensen and Werner, Ettling in 1840 isolated a dark gren crystalline product from the reaction of cupric acetate, salicylaldehyde, and aqueous ammonia. This product was undoubtedly bis(salicylaldimino) Cu(II) (1,R=H). The corresponding R=phenyl and aryl derivatives were isolated in 1869 by Schiff who established the 1:2 metal ligand stochiometry. In this work Schiff discovered the exceedingly important synthetic techniqueue of preparing salicylaldimine complexes by reaction of the performed metal salicylaldehyde compound with primary amines. Subsequently Schiff prepared complexes obtained from the condensates of urea and salicylaldehyde. Delepine in 1899 prepared the complexes 1 with R=methyl and benzyl by reacting the metal acetate, salicylaldehyde, and primary amine in alcohol, and demonstrated the 2:1 stochiometry.



Scheme 1.1. Schiff's Baseses

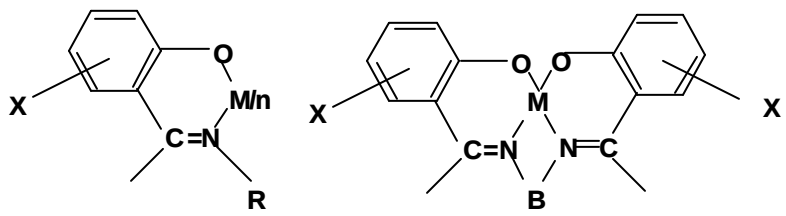
Metal complexes of Schiff-bases have occupied a central role in the development of coordination chemistry. This situation is manifested by the huge number of publications ranging from the purely synthetic to modern physicochemical to biochemically relevant studies of these

complexes. A tremendous variety of stable chemical species have been synthesized containing both transition and non transition metals and multifarious ligand system. Many of these complexes are of only incidental importance in modern coordination chemistry. However, a significant number of groups of complexes, defined by the basic structure of their ligand systems, have assumed significance in this field. (Holm and Everett, 1966)

1.2.Salicylaldimine Complexes

Of all Schiff-base complexes those derived from salicylaldimines have been by for the most thoroughly studied. Indeed, the particular advantage of the basic salicylaldimine ligand system has been the considerable flexibility of the synthetic procedure which has allowed the preparation of a wide variety of complexes with a given metal whose properties are often strongly dependent on the detailed ligand structure.

Currently, the most significant complexes of the salicylaldimines are of the structural types 1 and 2 in which R, X and B are generalized nitrogen, ring and bridging group substituents respectively. In practically all complexes of interest hydrogen is bound to azomethine carbon at position 7.



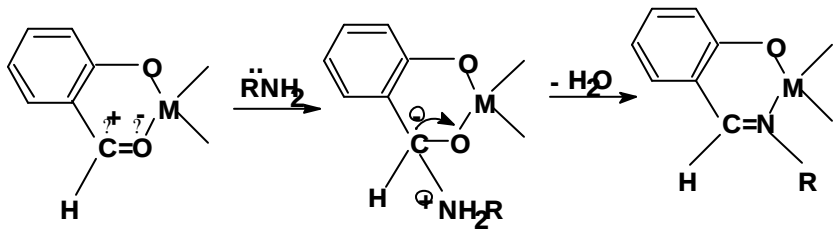
1 2

Scheme 1.2. Salicylaldimines Complexes

Salicylaldimine complexes are in general readily prepared and easily purified by recrystallization. The following three synthetic procedures have been employed.

? Reaction of metal ion and Schiff base in the presence of added base. These reactions are usually carried out homogeneously in alcohol or aquenous alcohol solution with a base such as acetate or hydroxide. This method useful for N-arylsalicylaldimines but occasionally fails for N-alkyl complexes due to hydrolysis of the Schiff base.

? Reaction of primary amino with bis-or tris (salicylaldehyde) metal complex. The preformed salicylaldehyde complex is refluxed with a slight mole excess of the amine in solvents such as ethonol, cholo roform or dicholormethane for a period of one hour or less, the crude product obtained by precipitation or volume reduction, and the purified. This method was first employed extensively by Pfeiffer and since then has come into general use.



? Template reactions. This method has thus for been applied to the synthesis of planar quadridentate complexes. (Holm and Everett, 1966)

1.3. d-f Complexes of Schiff Base Ligands

Studies of heteronuclear metal complexes started at the end of the 1960s due to an interest in the physicochemical properties arising from the presence of dissimilar metal ions in close proximity. The heteronuclear complexes first studied contained different d metal ions, and little attention was paid to d-f heteronuclear complexes until 1985 when Bencini reported unique magnetic properties for $Cu^{II}Gd^{III}$ complexes. In the first attempt to prepare discrete d-f complexes, Cu(salen) and analogus complexes of quadridentate Schiff bases wery extensively used as 'complex ligands' to provide di(μ-phenoxo) $Cu^{II}Ln^{III}$ complexes. (Bencini, 1985, 1986; Benelli, 1990) The synthetic strategy using appropriate d metal complexes as ligands proved to be of general use for d-f complexes of various bridging ligands, such as oxamide, oxamidate. The emergence of compartmental ligands with two dissimilar metal-binding sites, one being specific for the d metal ion and another for the f metal ion, has greatly contributed to developments in the solution chemistry of d-f complexes. Now non-compartmental ligands such as diaminoalcohols, diaminophenols, carboxylates, amino acidates, betaines and 2-pyridones are shown to afford discrete d-f complexes, and rare d-f cluster compounds have been synthesized. (Sakamoto et al., 1991; Ramade et al., 2002, Kahn et al., 2000, Vigato and Tamburini, 2004)

1.4. General Properties of Lanthanides

The term lanthanides strictly defined refers to the 14 elements following lanthanum in the periodic table, but as normally used also includes lanthanum itself. From lanthanum (Z = 57) to lutetium (Z = 71) we go from a $[Xe]4f^{o}$ to a $[Xe]4f^{14}$ configuration. Since the 4f electrons are relatively uninvolved in bonding, these highly electropositive

elements have as their prime oxidation number +3 and, overall, closely resemble one another chemically and physically. They generally occur together in nature.

The element promethium occurs in Nature only in trace of uranium ores, where it forms by spontaneous fission of ^{238}U.

The element yttrium, Y, (Z = 39) lies above La and has a similar +3 ion with a noble gas core, [Ar], has atomic and ionic radii close to those for terbium and dysprosium. It therefore resembles them closely in its chemistry and is generally found in Nature with the lanthanides. The lanthanides plus yttrium are commonly called the rare earths, although many of them are relatively abundant.

An important feature of the lanthanide elements is the occurrence of the lanthanide contraction, a steady decrease in atomic and ionic size with increasing atomic number.

A major cause of the lanthanide contraction is the electrostatic effect of increasing nuclear charge very imperfectly screened by the 4f electrons. In this sense it is comparable to the smaller contractions observed through each of the d – block transition series. Since the 4f electrons screen the outer electrons even more poorly than do the and electrons, and because there are 14 lanthanides, cumulative effect is greater. The chemistry of the Ln^{+3} ions (Ln being a generic symbol for these elements) thus changes gradually across the series in the ways that would be expected for increasing charge to radius ratio, but the trend is not completely smooth.

It has been concluded in recent years that the lanthanide contraction is also partly due to relativistic effects which influence the shielding characteristics of inner shell electrons.

The sum of the first three ionization enthalpies is comparatively low, so that the elements are highly electropositive. They readily form +3 ions in solids like oxides and in aqua ions, $[M(H_2O)_n]$, and complexes. However, Cerium can give Ce^{+4} and Sm, Eu, and Yb, the M^{+2} ions, in aqueous solutions and in solids.

Formerly the existence of +2 and +4 oxidation states was simply ascribed to the extra stability associated with the formation of stable empty $4f^0$ (Ce^{+4}), half – filled $4f^7$ (Eu^{+2}, Tb^{+4}), and filled $4f^{14}$ (Yb^{+2}) subshells. This argument is unconvincing when Sm and Tm give M^{+2} species having f^6 and f^{13} configurations but no M^+ ion, whereas Pr and Nd give M^{+4} ion, with configurations f^1 and f^2 but no penta – or hexavalent species.

The existence of the various oxidation states is best interpreted by consideration of the ionization enthalpies, enthalpies of sublimation of the metals, lattice energies, and so on, in Born – Haber cycles.

In their magnetic and spectroscopic properties the lanthanides show important differences from the d – block elements. This happens because the 4f electrons a pretty well (although not totally) shielded from external fields by the overlying $5s^2$ and $5p^6$ shells. The states arising from the various $4f^n$ configurations therefore tend to remain nearly invariant for a given ion.

The most common coordination numbers are 8 and 9. Many previously accepted examples of coordination number 6 are actually

invalid because coordinated solvent molecules are present and raise the true coordination number to 7, 8 or 9.

The differences between the properties of transition metal ions and lanthanide ions can be summarized as shown below(Karraker,1970).

Table 1.1. The differences between the properties of transition metal ions and lanthanide ions

	Lanthanide Ions	**First Series Transition Metal Ions**
Metal Orbitals	4f	3d
Ionic Radii	106-85 pm (1.06-0.85 ?A)	75-60 pm(0.75-0.6?A)
Common Coordination Numbers	6,7,8,9	4,6
Typical Coordination Polyhedra	Trigonal prism, Square antiprism Dodecahedron	Square planar, Tetrahedron Octahedron
Bonding	Little metal-ligand orbital interaction	Strong metal-ligand orbital interaction
Bond Direction	Little Preference in bond direction	Strong preference in bond direction
Bond Strengths	Ligands bond in order of electronegativity: F^-,OH^-, H_2O,NO_3^-,Cl^-	Bond strengths determined by orbital interaction normally in following order: CN^-, NH_3,H_2O,OH, F^-
Solution Complexes	Ionic,rapid ligand exchange	Often covalent;covalent complexes may exchange slowly

Table 1.2. Some of lanthanides properties

Lanthanides	Properties
Neodymium $_{60}Nd$: $[Xe]6s^2 4f^4$	The metal has a bright silvery metallic luster, Neodymium is one of the more reactive rare-earth metals and quickly tarnishes in air, forming an oxide that spalls off and exposes metal to oxidation. The metal, therefore, should be kept under light mineral oil or sealed in a plastic material. Neodymium exists in two allotropic forms, with a transformation from a double hexagonal to a body-centered cubic structure taking place at 863^oC.
Samarium $_{62}Sm$: $[Xe]6s^2 4f^6$	Samarium has a bright silver luster and is reasonably stable in air. Three crystal modifications of the metal exist, with transformations at 734 and 922^oC. The metal ignites in air at about 150^oC. The sulfide has excellent high-temperature stability and good thermoelectric efficiencies up to 1100^oC.
Gadolinium $_{64}Gd$: $[Xe]6s^2 4f^7 5d^1$	As with other related rare-earth metals, gadolinium is silvery white, has a metallic luster, and is malleable and ductile. At room temperature, gadolinium crystallizes in the hexagonal, close-packed alpha form. Upon heating to 1235^oC, alpha gadolinium transforms into the beta form, which has a body-centered cubic structure. The metal is relatively stable in dry air, but tarnishes in moist air and forms a loosely adhering oxide film which falls off and exposes more surface to oxidation. The metal reacts slowly with water and is soluble in dilute acid. Gadolinium has the highest thermal neutron capture cross-section of any known element (49,000 barns).

Aqua ions found in crystalline compounds are generally nine–coordinate with the tri–capped trigonal prism being the favored structure. The $[Ln(H_2O)_n]^{+3}$ ions in aqueous solution are either eight – or nine coordinate and this may vary with ionic strength.

Despite the general similarities to be expected from the electronic structures and sizes of the elements and their ions, there are, nevertheless, some important variations in going from La to Lu.

As a result of lanthanide contraction, changes in coordination through the series La to Lu are to be expected.

In the solid state there may be a pronounced change in structural type at one or more points in the series; at such changeover points a compound may have two or more crystal forms. (Cotton and Wilkinson,1988)

1.5. Magnetic Properties of Heteronuclear Complexes

The synthesis of polynuclear mixed-copper lanthanoid complexes has attracted attention for several reasons. The nature of magnetic exchange interactions between rare-earth and transition-metals ions is not only theoretical interest but also relevant to the possible use of rare-earth orthoferrites and related metarials as magnetic bubble devices. Yttrium and rare-earth copper oxide compounds exhibit superconductivity with relatively high T_c values. It also of current interest to prepare high nuclearity metal complexes in an effort to make nanoscale magnetic materials. (Benelli et.al., 1990; Chen et. al., 1995)

Whenever two magnetic ions are brought into close proximity our naturel inclination is to assume that, like bar magnets, they will arange themselves so that they couple anti-ferromagnetically, and thus reduce overall magnetism of the dimer.

In 1985, Italian scientists, led by Gatteschi, observed that when copper (II) and gadolinium (III) were brought into close proximity the coupling between the ions was ferromagnetic. This was suprising as gadolinium (III) has unpairred electrons in all seven f-orbitals, and it might be expected that at least one of these orbitals would overlap with semi-occupied orbital on copper (II). Such an interaction between two half-occupied orbitals would be anti-ferromagnetic, as it would create a molecular orbital which could contain both electrons. Such an interaction is observed between Cu^{II} and the d^5-centre Mn^{II} where the coupling is always anti-ferromagnetic. The explanation cannot lie in the interaction between ground state confirugations. (Bencini et al., 1985, Kahn et al., 2000)

The 4f orbitals of the lanthanoids are small, internal orbitals and this leads between the Cu^{II} 3d and Gd^{III} 4f-orbitals being minimal, and hence the overlap which would lead to anti-ferromagnetic coupling is of little importance. The important interaction is between semi-occupied orbital, d_{x2-y2}, on Cu^{II} and empty orbital on the Gd^{III} centre. In such a charge transfer configurations on there are two possible orientations for the electron transferred from Cu^{II} to Gd^{III}. If it alings anti-parallel to the seven electrons in the f- orbitals this would be lead to on S=3 spin state, and would be equivalent to anti-ferromagnetic exchange. If the additional electron aligns parallel to the seven f electrons, this would given on S=4 spin state, and is equivalent to ferromagnetic exchange. Due to Hund's rule the latter will be lower in energy than the former, and hence this

excited state of the system favours ferromagnetic exchange. Intialy there was some debate about which gadolinium orbital was the electron acceptor, but it now seems clear that the 5d- orbitals are best suited to this role. It is the interaction of this charge transfer configuration with the ground state which leads to the ferromagnetic coupling that is always observed. (Brianese et al., 1998,1999)

At about the same time as this chemistry appeared, the high T_c superconductors containing copper-lanthanoid mixtures were also reported. (Winpenny, 1998)

Table 1.3. Various types of magnetic behaviour

TYPE	SIGN	Magnitude	Field Dependence of ?	Origin
Diamagnetism	-	10^{-6} emu units	Independent	Field induceded, paired electron circulations
Paramagnetism	+	0 to 10^{-4} emu units	Independent	Angular momentum of the electron
Ferromagnetism	+	10^{-4} to 10^{-2} emu units	Dependent	Spin aligment from dipole-dipole interaction of moments on adjacent atoms, ??
Antiferromagnetism	+	0 to 10^{-4} emu units	Dependent	Spin pairing, ??, from dipole-dipole interactions

1.6 Calculations of Magnetic Moments

The Sherwood Scientific Magnetic Susceptibility Balance is based on the Evans method which uses the same configuration as the traditional Gouy method, but, instead of measuring the force which a magnet exerts on the sample, the equal and opposite force which the sample exerts on a suspended permanent magnet is observed. (Sherwood Instruction Manual)

The sample should be in the form of a reasonably fine and uniform powder. A small amount of solid is introduced into the weighed sample tube, and the bottom of the tube gently tapped on a wooden bench a number of times to shake the solid down. This procedure is repeated until a sufficient length of sample is obtained. The sample length is then measured making sure that the top of the sample is horizontal. The length should be in the range 2,5 cm - 3,5 cm.

The mass susceptibility, X_g, is calculated using (the below eqution for powder samples the air-correction term is ignored).

$$X_g \; ? \; \frac{C_{Bal}\, l (R \; ? \; R_0)}{10^9 m}$$

l: Sample length (cm)

m: Sample mass (g)

R: Reading for tube plus sample

R_0: Empty tube redaing

C_{Bal}: Balance calibration constant

Since glass is diamagnetic R_0 wil be negative.

The calibration constant in the above equation is determined using a sealed-off sample of $MnCl_2$ solution given by the firm.

$$C_{Bal} ? \frac{C_{Tube}}{?R ? R_0?}$$

The temperature is read from a thermometer situated in the balance room.

Since the Curie-weiss law applies, the reading will be related to the tube temperature, t(°C), by the factor $\frac{1}{t ? 255}$

In CGS (or Gaussian) system, the three magnetic vectors are interrelated by the following equation.

$$\vec{B} ? \vec{H} ? 4? \vec{M}$$

$\vec{B}$: Magnetic induction

$\vec{H}$: Magnetic field strenght

$\vec{M}$: Magnetization

Diving by $\vec{H}$ (assuming $\vec{H}$ and $\vec{M}$ are coincident)

$$\frac{\vec{B}}{\vec{H}} ? 1 ? 4? \frac{\vec{M}}{\vec{H}}$$

$$\frac{\vec{B}}{\vec{H}} ? 1 ? 4?? _?$$

$\chi_\rho = \left(\frac{M}{H}\right)$ is referred to as the magnetic susceptibility per unit volume or simply the volume susceptibility.

Dividing χ_ρ by the density of the substance produces the gram susceptibility or the mass susceptibility

$$\chi_g = \frac{\chi_\rho}{d} \left(cm^3/g\right)$$

Multiplying X_g by the molecular weight produces a molar susceptibility,

$$\chi = \chi_g MW \left(cm^3/mole\right)$$

In principle χ is the algebraic sum of two contributions associated with different phenomena;

$$\chi = \chi_D + \chi_P$$

χ_D: Diamagnetic susceptibility

χ_P: Paramagnetic susceptibility

It is the assumed that diamagnetic susceptibility is essentially additive. χ_D(the molar diamagnetic susceptibility) of a molecule or complex ion can be obtained to a good approximation by summing the

diamagnetic contributions from all of the atoms, χ_A, and from all of the bonds in functional groups, χ_B:

$$\chi_D = \sum_i \chi_{A_i} + \sum_j \chi_{B_J}$$

The values for χ_A and χ_B are referred to as Pascal's constants. The values for χ_B are generally positive. They accounts fort he fact that a molecule with multiple or conjugated bonds is less diamagnetic than a rather similar molecule with only single bonds.

Both χ and M are macroscopic properties. In describing the magnetic properties of metal complexes, it is common to employ a microscopic quantity called the effective magnetic moment,

$$\mu_{eff} = \left(\frac{3k}{N\beta^2}\right)^{1/2} (\chi_P T)^{1/2} = 2.828 (\chi_P T)^{1/2}$$

The susceptibility employed in this equation is χ_P described above. In SI units

$$1\beta = 1\beta_e = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} J T^{-1}$$

Sample calculation for $Gd(SbH_2)_2(NO_3)_3$;

m_f: 0.9599 g m_i: 0.8269 g

l: 2.6 cm T: 21 °C

R: 1518 R_0: -35

Std: 1011/-34 Std (measured): 1022/-35

$$\chi_g = \frac{C_{Bal} \cdot l \cdot (R - R_0)}{10^9 m}$$

$$C_{Bal} = \frac{1011 - 34}{1022 - 35}$$

$$C_{Bal} = \frac{1045}{1057} = 0.989$$

Temperature correction;

$$C_{Bal} = 0.989 \times \frac{255 - 20}{255 - 21}$$

$$C_{Bal} = 0.985$$

$$\chi_g = \frac{(0.985) \times (2.6) \times (1518 - 35)}{10^9 \times (0.133)}$$

$$X_g = 2.99 \times 10^{-5} cm^3 / g$$

$$\chi_M = (X_g) \times (MW)$$

$$X_M = (2.99 \times 10^{-5}) \times (936 - 21)$$

$? _M ? 2.799 ? 10^{?2} cm^3 / mol$

$? _M ? X_D ? X_p$

Calculation of $? _D$ via Pascal constants;

$C : 2 ? 18 ? ?? 6.0 ? 10^{?6} ?? ? 216.0 ? 10^{?6}$
$H : 2 ? 20 ? ?? 2.9 ? 10^{?6} ?? ? 116 ? 10^{?6}$
$N : 2 ? 2 ? ?? 5.6 ? 10^{?6} ?? ? 22.4 ? 10^{?6}$
$O : 2 ? 2 ? ?? 4.6 ? 10^{?6} ?? ? 18.4 ? 10^{?6}$

ConstitutiveCorrections

$C(aromatic) : 2 ? 12 ? ?? 0.25 ? 10^{?6} ?? ? 6 ? 10^{?6}$
$C ? N : 2 ? 2 ? ?? 8.1 ? 10^{?6} ?? ? 32,4 ? 10^{?6}$
$Gd^{3?} : (? 20.0 ? 10^{?6})$
$NO_3^? : 3 ? ?? 18.9 ? 10^{?6} ?? ? 56.7 ? 10^{?6}$
$? _D ? ? 423.1 ? 10^{?6} cm^3 / mol$

$$\chi_M = 2.799 \cdot 10^{-2}\ cm^3/mol$$

$$\chi_M = \chi_D + \chi_P$$

$$\chi_P = \chi_M - \chi_D$$

$$X_p = 2.799 \cdot 10^{-2} - (-423.1 \cdot 10^{-6})$$

$$\chi_P = 2.799 \cdot 10^{-2} - 0.04231 \cdot 10^{-2}$$

$$X_p = 2.841 \cdot 10^{-2}\ cm^3/mol$$

$$\mu_{eff} = 2.828\sqrt{\chi_p \cdot T}\ BM$$

$$\mu_{eff} = 2.828\sqrt{2.841 \cdot 10^{-2} \cdot 294} = 8.17\ BM$$

The experimental values for Gd^{3+} are ± 8,0 BM, and the calculated value is 7,94 BM. (For Gd^{3+} the ground term is $^8S_{7/2}$, and the formula $\mu_{eff} = g\sqrt{J(J+1)}\ BM$ (where

$$g = 1 + \frac{S(S+1) + L(L+1) - J(J+1)}{2J(J+1)}\ )$$

gives $\mu_{eff} = 7.94\ BM$

(Kahn, O., 1993; Drago, R.S.,1977; Aguiori, A., 1997)

1.7. The Aim of The Study

Heterodinuclear complexes with extended ligand bridges are the subject of many recent studies. Interest in this area concerns attempts to mimic the active sites and functions of biological substances and to desing and synthesize molecular magnets. Assembly metal complexes exhibiting versatile magnetic behaviours such as light switchable magnets and single molecular magnets have attracted special attention in the last decade. The molecular-based magnetic materials consisting of

d-transition metal ions have been well developed, and the magneto-chemistry of d-f metal complexes will be one of the future targets in this field. Since Gattechi and co-workers discovered a ferromagnetic coupling between Cu^{II} and Gd^{III} ions in 1985, several 3d-4f polynuclear complexes including dinuclear $Cu^{II}Gd^{III}$, trinuclear $Cu^{II}_2Gd^{III}$, tetranuclear $Cu^{II}_2Gd^{III}_2$ and other 3d-4f metal complexes have been reported. (Bencini et al. 1986; Andruh et al., 1993) As most of the complexes presenting an isolated $Cu^{II}Gd^{III}$ couple shows a ferromagnetic character, a behaviour so general led some authors to propose it to be an intrinsic property of the copper(II)-gadolinium(III) couple. Transition metal-lanthanide heteronuclear compounds, reported in literature, are generally syntherized by reacting a transtition metal complex with a lanthanide salt. With the expectation that a different compound-maybe an isomer-could be obtained, we have reversed the sequence of preparation, that is we have reacted lanthanide complexes with a simple transition metal salt.

2. EXPERIMENTAL

1,4 diaminobutane, salicylaldhyde, metal nitrates and methanol were purchased from Merck Chemicals; acetone was purchased from BDH. All synthesizes were under air atmosphere.

Elemental analyses were performed by the Tübitak ATAL Laboratory, using with Elemental Analyzer Leco 932 CHNS-O equipment, in Ankara. X-Ray diffractcion were performed by Dokuz Eylul University, using with Rigaku D/Max-2200/PC XRD equipment, in Izmir. The mass spectroscopy were performed by the Tübitak ATAL Laboratory, using with Atmospheric Pressure Isonization Electrospray (API-ES) technique and Agilent 1100 LC-MS equip, in Ankara. Thermogravimetric analysis were performed by Hacettepe University

Chemistry Department, using with Perkin Elmer Pyriss6 Model, in Ankara. The magnetic susceptibility were performed by Ege University Chemistry Department, using with Sherwood Scientific Magnetic Susceptibility Balance, in Izmir.

2.1. Preparation of N,N'-1,4-butylenebis(salicylaldimine) (SbH_2)

1,4 diaminobutane (1 mmol) and salicylaldehyde (2 mmol) were placed in 40 ml methanol and stirred. The yellow crystals was obtained from cooling solution. They were collected by suction filtration and washed with cold acetone and finally dried in air.

2.2. Preparation of $Gd(SbH_2)_2(NO_3)_3$

N,N'-1,4-butylenebis(salicylaldimine) (2 mmol) was dissolved in 30 ml methanol. Gadolinium nitrate (1 mmol) was dissolved in 10 ml methanol. The second solution was then added dropwise into the first solution. Soon, yellow crystals began to precipitate. They were collected by suction filtration and washed with cold acetone and finally dried in air.

2.3. Preparation of $Nd(SbH_2)_2(NO_3)_3\ (H_2O).2H_2O$

N,N'-1,4-butylenebis(salicylaldimine) (2 mmol) was dissolved in 30ml methanol. Neodymium nitrate (1 mmol) was dissolved in 10 ml methanol. The second solution was then added dropwise into the first solution. Soon, yellow-orange crystals began to precipitate. They were collected by suction filtration and washed with cold acetone and finally dried in air.

2.4. Preparation of $Sm(SbH_2)_2(NO_3)_3.2H_2O$

N,N'-1,4-butylenebis(salicylaldimine) (2 mmol) was dissolved in 30 ml methanol. Samarium nitrate (1 mmol) was dissolved in 10 ml methanol. The second solution was then added dropwise into the first solution. Soon, yellow crystals began to precipitate. They were collected by suction filtration and washed with cold acetone and finally dried in air.

2.5. Preparation of $GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$

A methanol solution (10 ml) of copper (II) acetate monohydrate (2 mmol) was added to a suspension of gadolinium (III) complex, $Gd(SbH_2)_2(NO_3)_3$ (1mmol), in 50 ml methanol. Soon, the suspension became clear and changed in colour to a dark green. The resulting green solution was allowed to stand for several days to give green crystals. They were collected by suction filtration and washed with cold acetone and methanol and dried in air.

2.6. Preparation of $NdCu_2(Sb)_2(NO_3)_3$

A methanol solution (10 ml) of copper (II) acetate monohydrate (2 mmol) was added to a suspension of neodymium (III) complex, $Nd(SbH_2)_2(NO_3)_3(H_2O).2H_2O$ (1mmol), in 50 ml methanol. Soon, the suspension became clear and changed in colour to a dark green. The resulting green solution was allowed to stand for several days to give green crystals. They were collected by suction filtration and washed with cold acetone and methanol and dried in air.

2.7. Preparation of $SmCu_2(Sb)_2(NO_3)_3.2H_2O$

A methanol solution (10 ml) of copper (II) acetate monohydrate (2 mmol) was added to a suspension of samarium (III) complex, $Sm(SbH_2)_2(NO_3)_3.2H_2O$ (1mmol), in 50 ml methanol. Soon, the suspension became clear and changed in colour to a dark green. The resulting green solution was allowed to stand for several days to give green crystals. They were collected by suction filtration and washed with cold acetone and methanol and dried in air.

3. RESULTS AND DISCUSSION

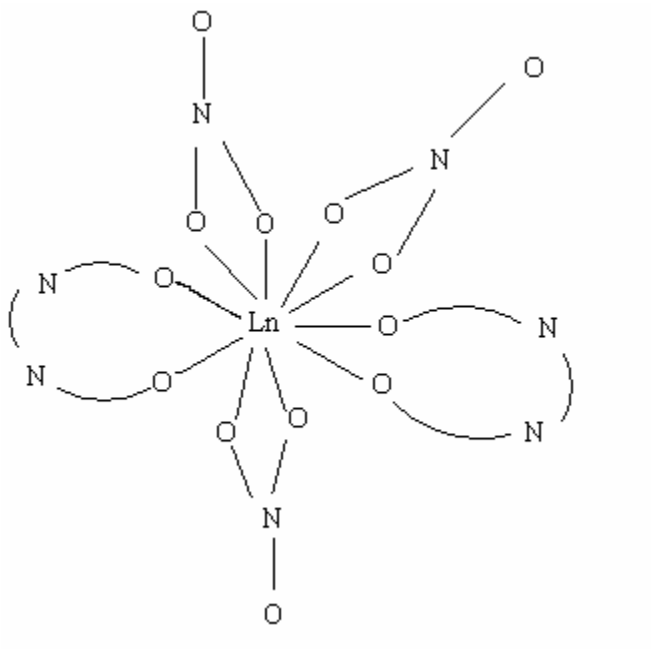
The schiff base, N,N'-1,4-butylenebis (salicylaldimine), (SbH_2), has been first prepared according to the usual procedure given in literature (**Schuetz, S.A., Day, V., Sommer, R.D., Rheingold, A.L., Belot, J.A.,** 2001). The complexes of three lighter lanthanides with schiff base (Nd, Sm and Gd) have been synthesized in methanol. Although the starting mole ratios have been initially set to L:M=1:1, the elemental analyses have shown that these complexes contain two SbH_2 ligands per mole of lanthanide (Table 3.2). TGA-DTA and IR along with elemental analyses suggest that gadolinium complex is anhydrous, that of samarium contains two moles of lattice water per mole of metal and that of neodymium has two moles of lattice water and one mole of coordinated water per mole of lanthanide. (Fig.3.8)

The IR spectra of Nd and Sm exhibit broad bands between 3300 cm^{-1} and 3600^{-1}, which is indicative of water(Nakamoto…..). In many transition metal complexes of schiff bases, ?(C=N) shifts to lower-energy region upon coordination, indicating that nitrogen atoms are involved in binding. (**Brianese N., Casellato U., Tamburini, S., Tomasin, P., Vigato, P. A.,** 1998.) In our complexes the reverse is the case,that is, ?(C=N), has shifted to higher energies upon complexation (1629 cm^{-1} in free ligand; around ~1650 cm^{-1} in the complexes) implying

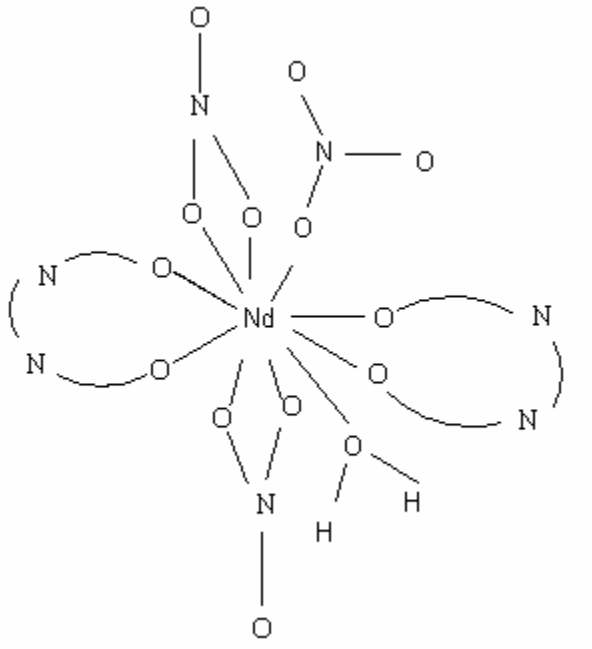
that nitrogens have been not involved in coordination. (Fig. 3.1, Fig. 3.2, Fig. 3.3, Fig. 3.4) (Tamburini et al., 2004.) The schiff base is coordinated to Ln^{3+} ion through oxygen atoms,that is, it behaves as a bidentate ligand instead of a tetradentade one, which is usually observed in transtion metal complexes. This situation seems to agree with the HSAB rule, which predicts that hard lanthanide ions prefer hard oxygens rather than the relatively softer nitrogens. As it is clear from the formulae of complexes the schiff base is in the neutral form, SbH_2, that is; phenolic hydrogens are preserved.

IR spectra of the complexes cast some light on the coordination modes of three nitrate ions. In general, the separation of the two highest frequency bands is larger for bidentate than for unidentate coordination. (Nakamoto……) In the spectrum of Gd complex, the strong peaks at 1287 cm^{-1} and 1484 cm^{-1} seem propable candidates for ?(N=O) and $?_a(NO_2)$. (Fig.3.2) This separation is sufficently great to make us think that nitrates act as chelating bidentate ligands. The situtation is very similiar for the samarium complex. However, the spectrum of neodymium complex exhibits a rather different situation. Whereas peaks at 1481 cm^{-1} and 1302 cm^{-1} correspond to chelating bidentate coordination, those at 1460 cm^{-1} and 1359 cm^{-1} stem from unidentate coordination. (Fig.3.3.)

The above findings have suggested that the coordination number around the lanthanide ions is 10. For Gd and Sm, 6 O atoms from three bidentate nitrates and 4 O atoms from two schiff bases occupy 10 coordination sites around the metal ion. As for the Nd complex, 10 coordination sites around the Nd^{3+} ion are accupied by 4 O atoms from two bidentate nitrates, 1 O atom from a unidentate nitrate, 1 O atom from a coordinated H_2O molecule, and 4 O atoms from two Schiff bases.



Ln=Sm or Gd



In a first approximation a rare earth ion a molecular compound behaves as a free ion. (**Drago, R.S.,** 1977) In a free ion, contributions to μ_{eff} is given by the following formula

$$\mu_{eff}=g[(j+1)]^{½} \text{ BM}$$

$$\text{where } g= 1+ \frac{S(S+1)-L(L+1)+J(J+1)}{2J(J+1)}$$

The simplest situation as far as the magnetism of the rare earth compounds is concered is offered by Gd (III) derrivatives (**Kahn, O.,** 1993, Molecular Magnetism, Wiley-VCH, USA). The ground state arising from the $4f^7$ configuration is $^8S_{7/2}$. Since L=0. There is no spin-orbit coupling. Then g=2.00 and the above equation reduces to the spin-only formula. For Gd^{3+} complexes ,the formula gives 7.94 BM; most experimental values are around ~8.0 BM. We have calculated μ_{eff} as 8.18 BM, which is sufficiently close to the above values.

For Nd^{3+} complex the calculated value according to the above equation is 3.62 BM; most experimental values are around ~3.5 BM and what we have found is 3.42 BM.

As for Sm^{3+} the situation is quite different owing to the presence of thermally populated excited states. The ^6H ground term for Sm(III) is split by spin-orbit coupling into six levels. The energies, E(J), are

$$E(J) = ? J(J+1) / 2$$

The energy of the ground state is taken as the origin. When calculated the energy separation between the ground state, $^6H_{5/2}$, and the first excited state, $^6H_{7/2}$, is found as 7/2 ?, ? being the spin-orbit coupling parameter. The energy separation is given as 1000 cm^{-1} in references. ? is calculated as 286 cm^{-1}. The excited states arising from ^6H can then be populated at room temperature and above. Taking into account this situation, $?_{eff}$ is calculated as 1.61 BM. What we have found is 1.64 BM

(the simple equation mentioned above gives 0.84 BM and most experimental values are around 1.50 BM).

The lanthanide complexes have been then reacted with copper (II) acetate monohydrate to obtain heteronuclear complexes. Elementel analyses have shown that, the resulting complexes contain two copper atoms per lanthanide atom. TGA-DTA and IR, in combination, suggest that neodymium-copper complex, $NdCu_2(Sb)_2(NO_3)_3$ has no water or solvent molecule; that of samarium has two molecules of lattice water and that of gadolinium contain two moles of lattice water along with two moles of coordinated water.

IR spectra have demonstrated that both kinds of coordination modes (chelating bidentate and unidentate) for nitrate ions are observed. (Fig. 3.1, Fig. 3.2, Fig. 3.3, Fig. 3.4)

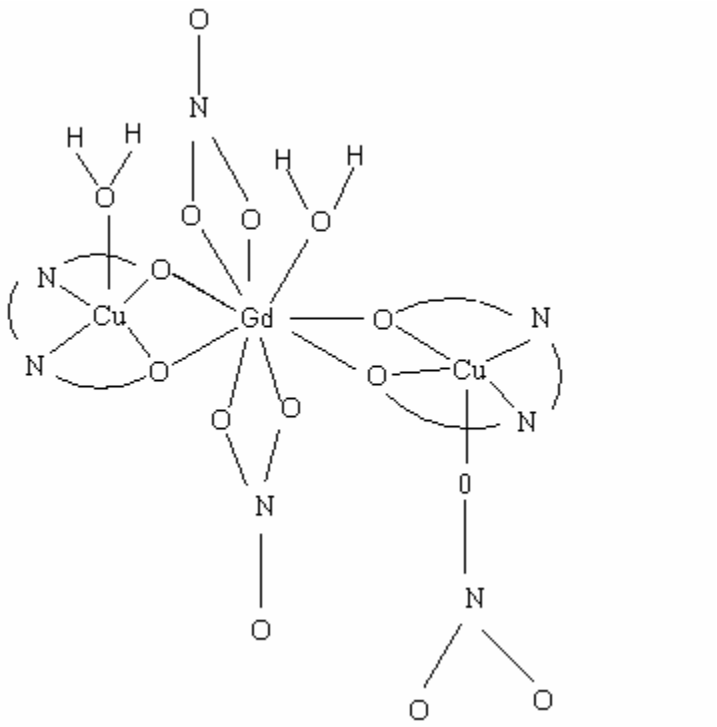
Each copper(II) ion in these heteronuclear complexes is coordinated to two nitrogen and two oxygen atoms of the ligand, which has been supported by the shift of ?(C=N) to lower-energy region (1629 cm^{-1} in free ligand; ~1650 cm^{-1} in lanthanide complexes and ~1620cm^{-1} in heteronuclear complexes.) (Fig. 3.5, Fig. 3.6, Fig. 3.7)

The Shiff base is in dianionic form in these heteronuclear complexes; that is, phenolic hydrogens are removed upon complexation.

LC-MS spectrum of gadolinium-copper complex has corroborated the formula and the molecular mass of the complex. Since gadolinium has seven isotopes (5 of them have comparable abundances) some peak groups are observed in the spectrum. The peak group around m/z=1067.3 seems to correspond to the complex which has lost a nitrate group.

IR and XRD spectra of complexes exhibit similar profiles, indicating that their main structures are essentially the same.

$GdCu_2(Sb)_2(H_2O)_2(NO_3)_3 \cdot 2H_2O$



This structure has been proposed for Gd-Cu complex due to the fact that a similar complex of N,N'-1,3-propylenebis(salicylaldimine), which has been synthesized in the reverse order, exhibits similar features. The unidendate nitrate is coordinated to one of the Cu (II) ions. Gadolinium (III) is nonacoordinate and copper (II) ions are pentacoordinate.

To decide which magnetic behavior a complex exhibits requires measurements of magnetic susceptibility at a temperature range (from

very low temperatures to room temperature). We have only measured magnetic susceptibility at room temperature. Therefore, what we can say about the magnetic behaviors of these complexes are very limited.

At room temperature, the magnetic ions present in a compound are generally considered to be isolated. The X_MT product of the complex is then assumed to be the sum of individual X_MT products of noninteracting ions (effective magnetic moments, μ_{eff}, are not additive).

The X_MT values calculated via the magnetic susceptibility measurements and those evaluated on the assumption that ions in question are magnetically isolated agree considerably well.

	Experimental	**Calculated**
$GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$	7.38 $cm^3mol^{-1}K$	8.63 $cm^3mol^{-1}K$
$SmCu_2(Sb)_2(NO_3)_3.2H_2O$	0.969 $cm^3mol^{-1}K$	1.03 $cm^3mol^{-1}K$
$NdCu_2(Sb)_2(NO_3)_3$	2.28 $cm^3mol^{-1}K$	2.39 $cm^3mol^{-1}K$

Table 3.1 The X_MT values of heteronuclear complexes

Table 3.2 Physical properties and analytical data of all the prepared complexes

	% C		% H		% N		μ_{eff} (BM)	d.p	Colour of Complexes
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.		
$Gd(SbH_2)_2(NO_3)_3$	45.02	46.19	3.68	4.31	10.72	10.47	8.18	218°C	Yellow
$Nd(SbH_2)_2(NO_3)_3(H_2O).2H_2O$	45.92	44.25	4.83	4.74	10.45	10.03	3.42	217°C	Yellow-orange
$Sm(SbH_2)_2(NO_3)_3.2H_2O$	46.00	44.79	5.13	4.59	10.68	10.16	1.66	229°C	Light yellow
$GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$	41.26	38.22	3.76	3.92	8.59	8.67	7.68	289°C	Dark green
$NdCu_2(Sb)_2(NO_3)_3$	43.58	41.33	2.86	3.47	8.62	9.37	4.27	309°C	Green
$SmCu_2(Sb)_2(NO_3)_3.2H_2O$	38.79	39.73	4.19	3.70	8.90	9.01	2.78	303°C	Light green

Note: % Yield of all syhthesized complexes is between %40 - %60.

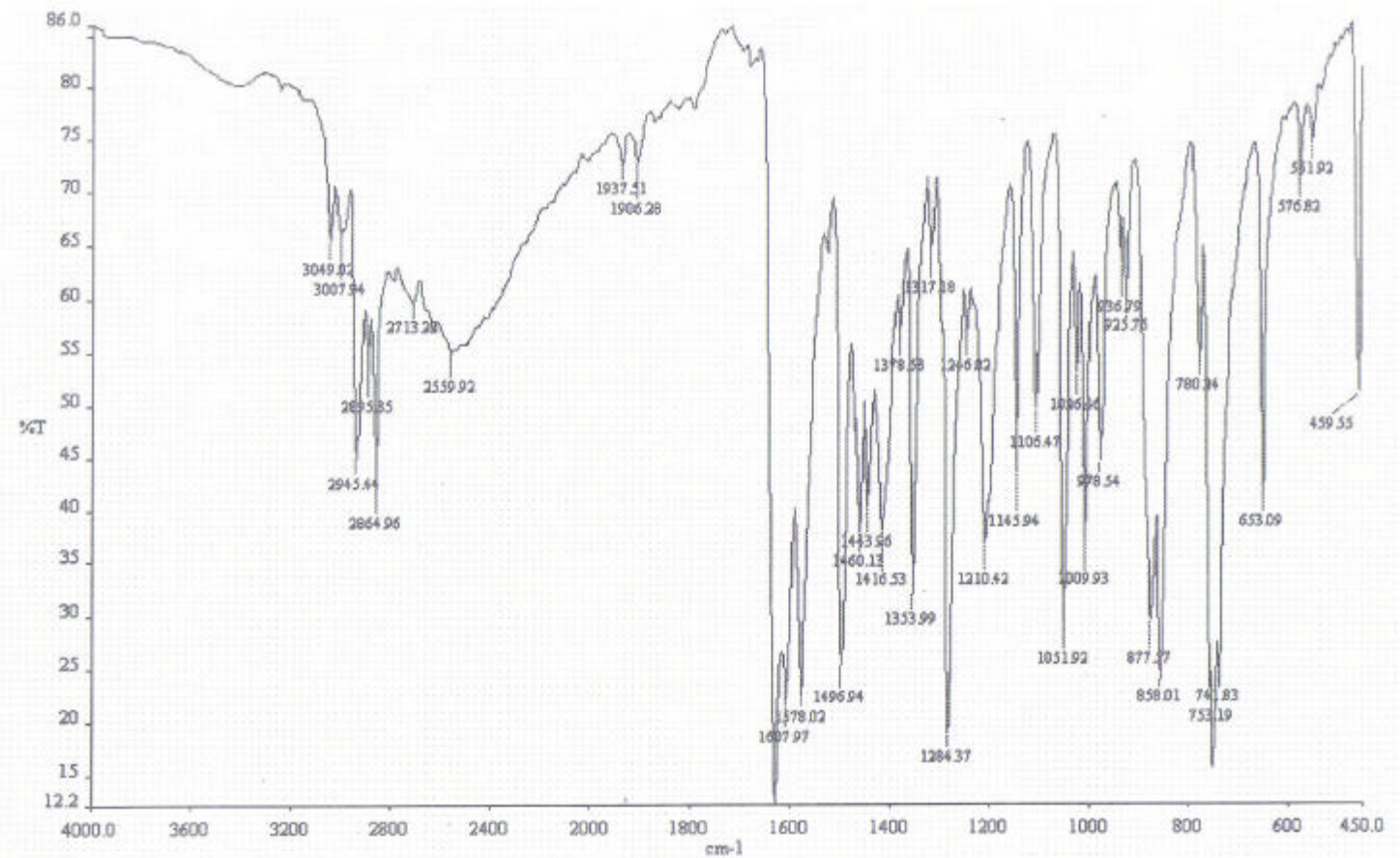


Figure-3.1. IR spectrum of N,N'-1,4-butylenebis(salicylaldimine)

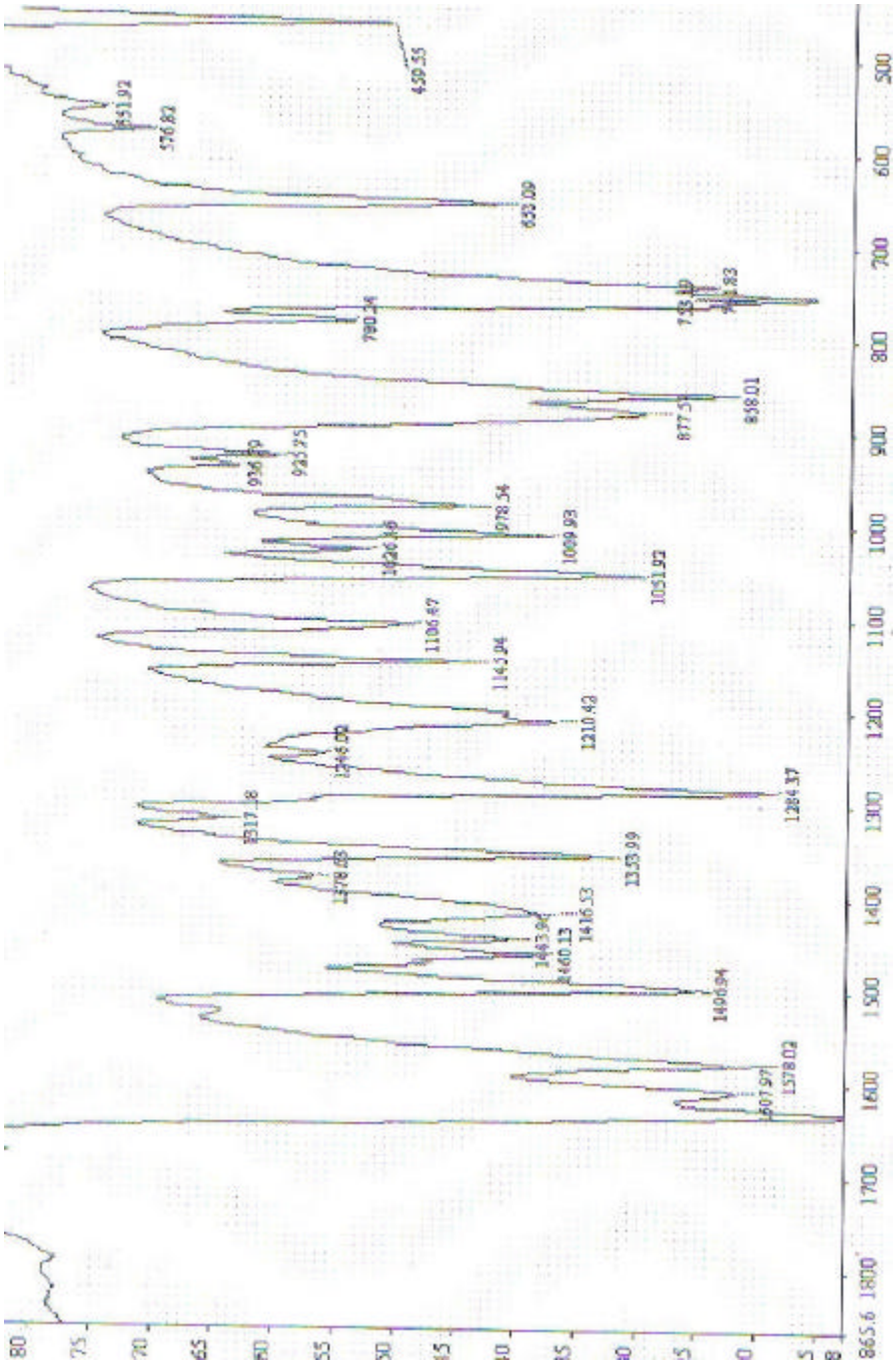


Figure-3.1. IR spectrum of N,N'-1,4-butylenebis(salicylaldimine)

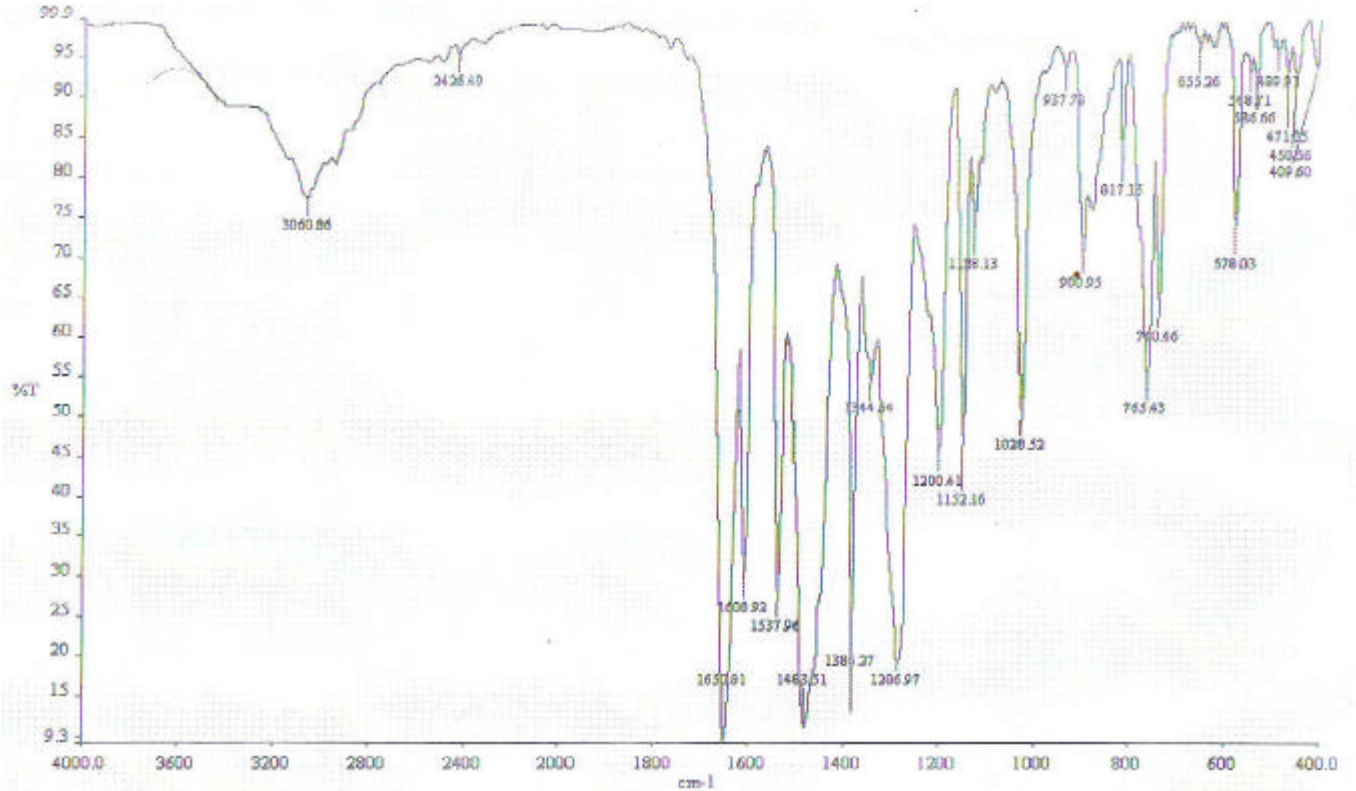


Figure-3.2. IR spectrum of $Gd(SbH_2)_2(NO_3)_3$

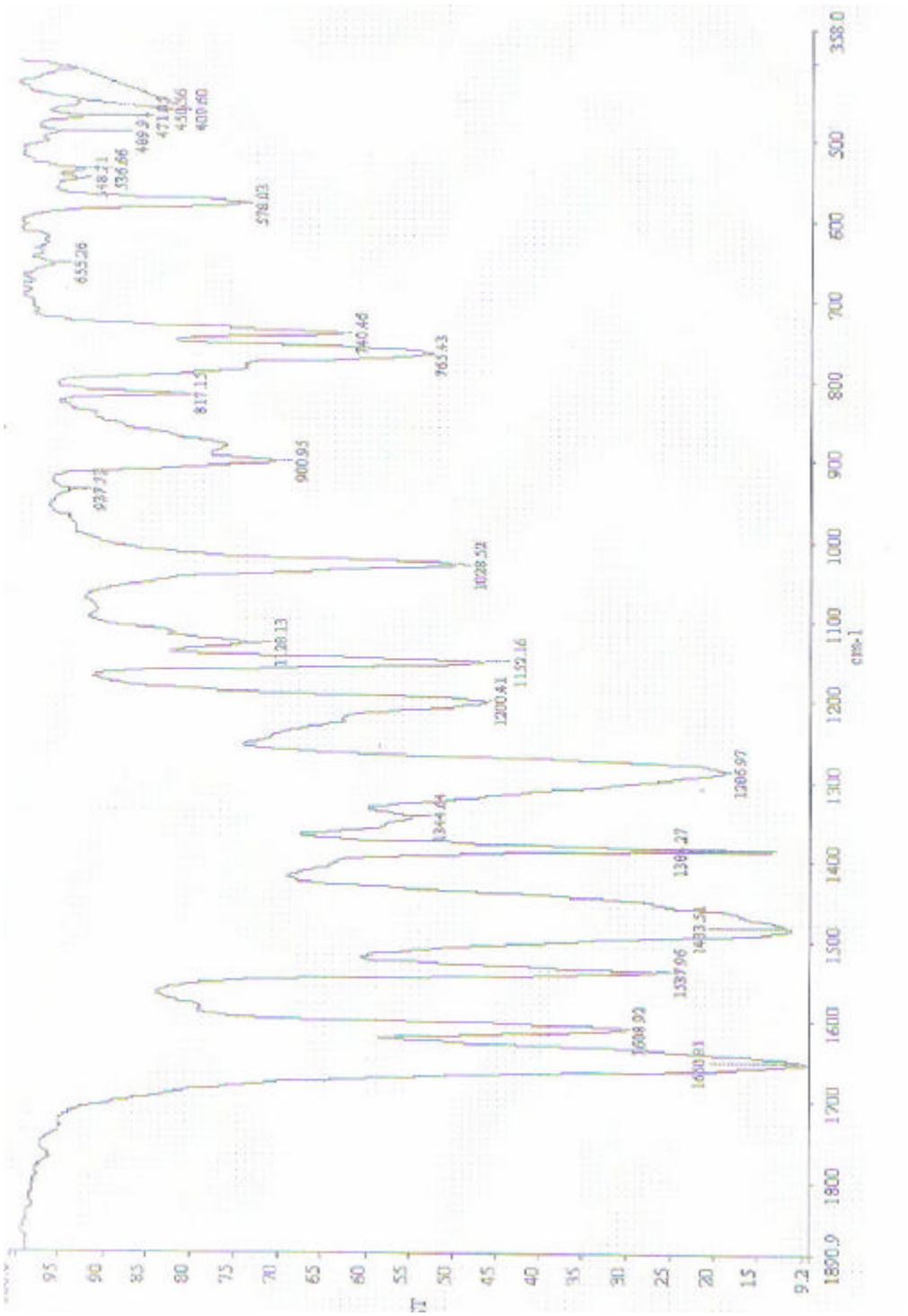


Figure-3.2. IR spectrum of $\mathbf{Gd(SbH_2)_2(NO_3)_3}$

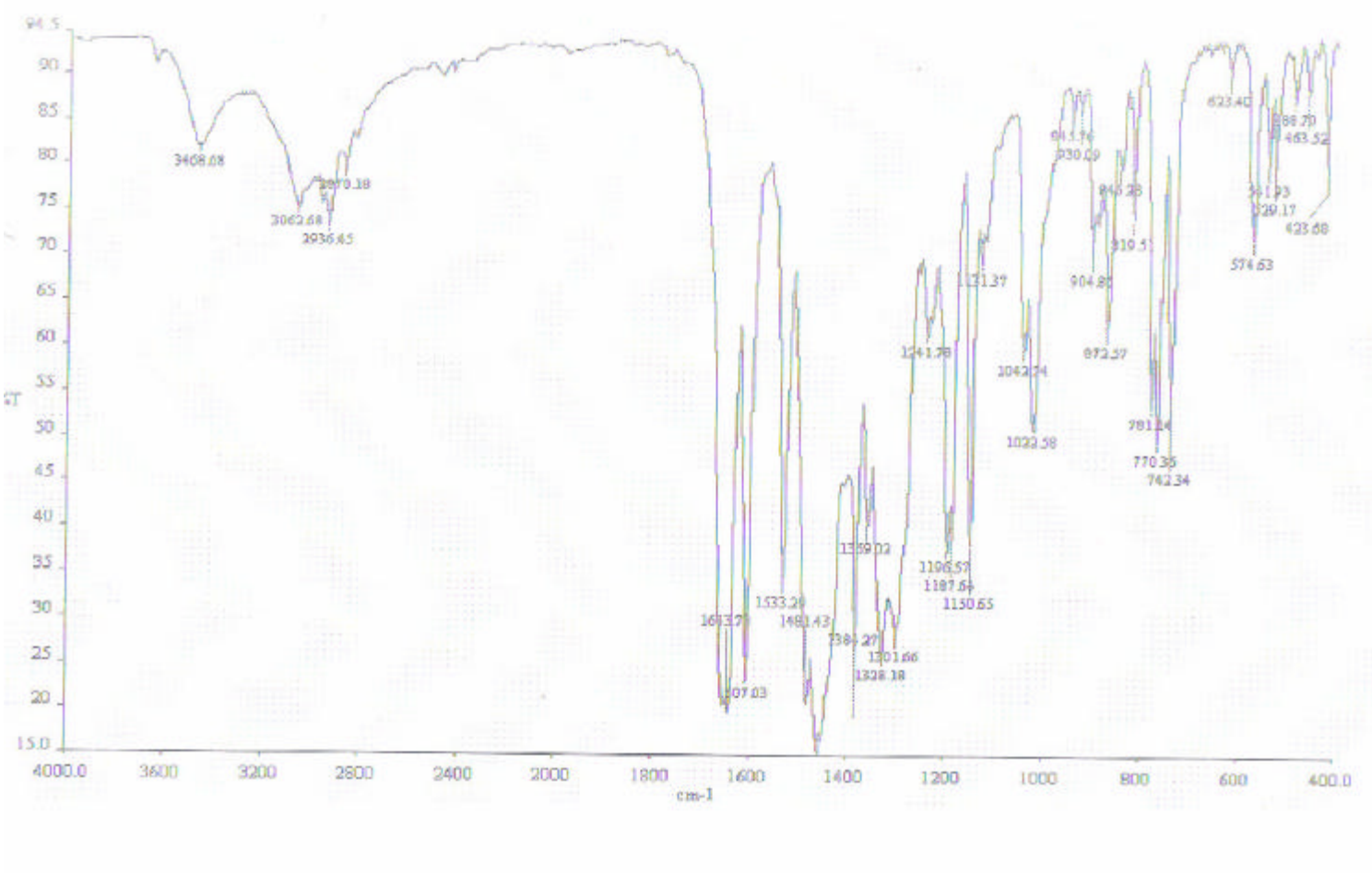


Figure-3.3. IR spectrum of **$Nd(SbH_2)_2(NO_3)_3\ (H_2O).2H_2O$**

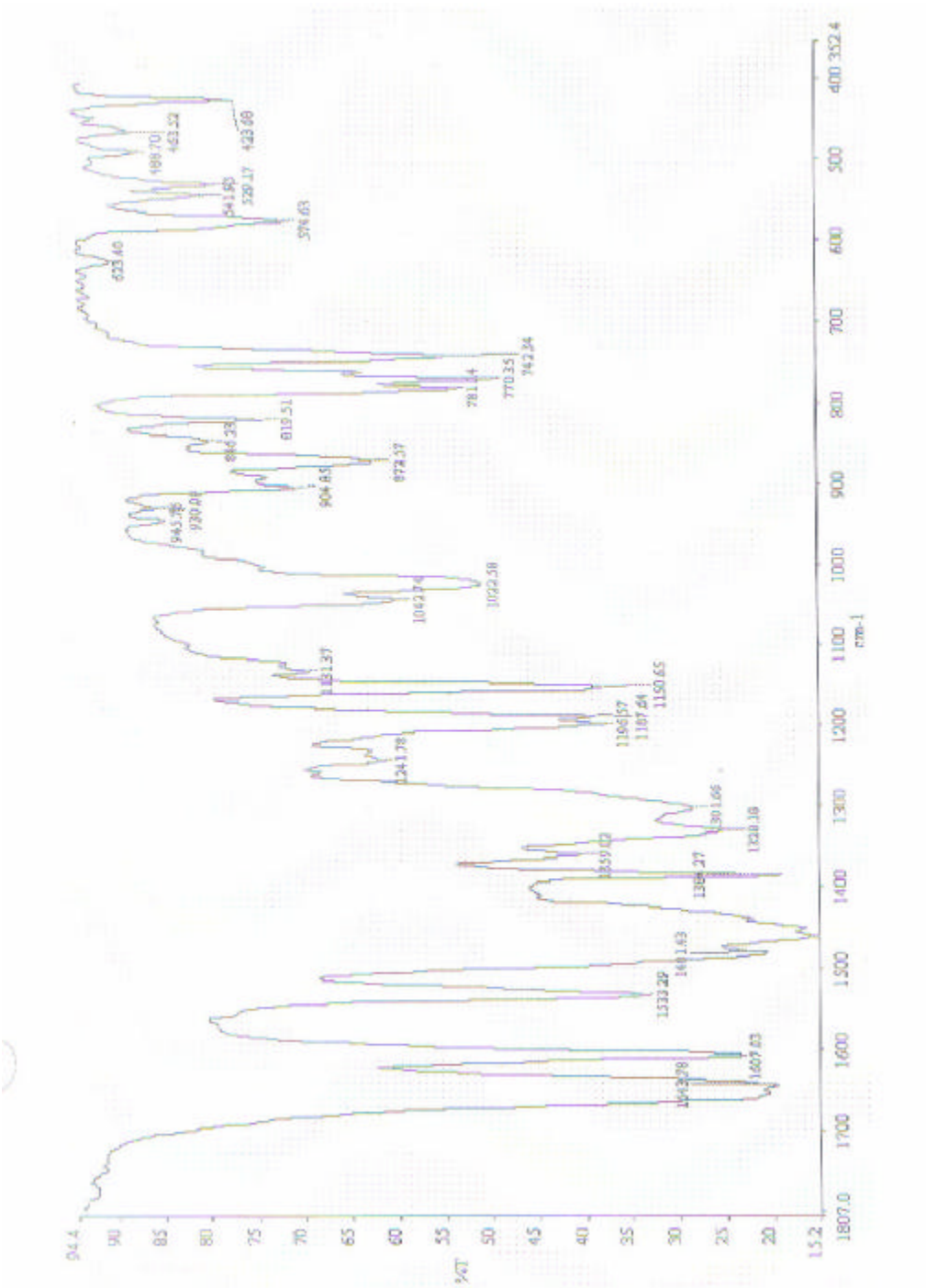


Figure-3.3. IR spectrum of **$Nd(SbH_2)_2(NO_3)_3\,(H_2O).2H_2O$**

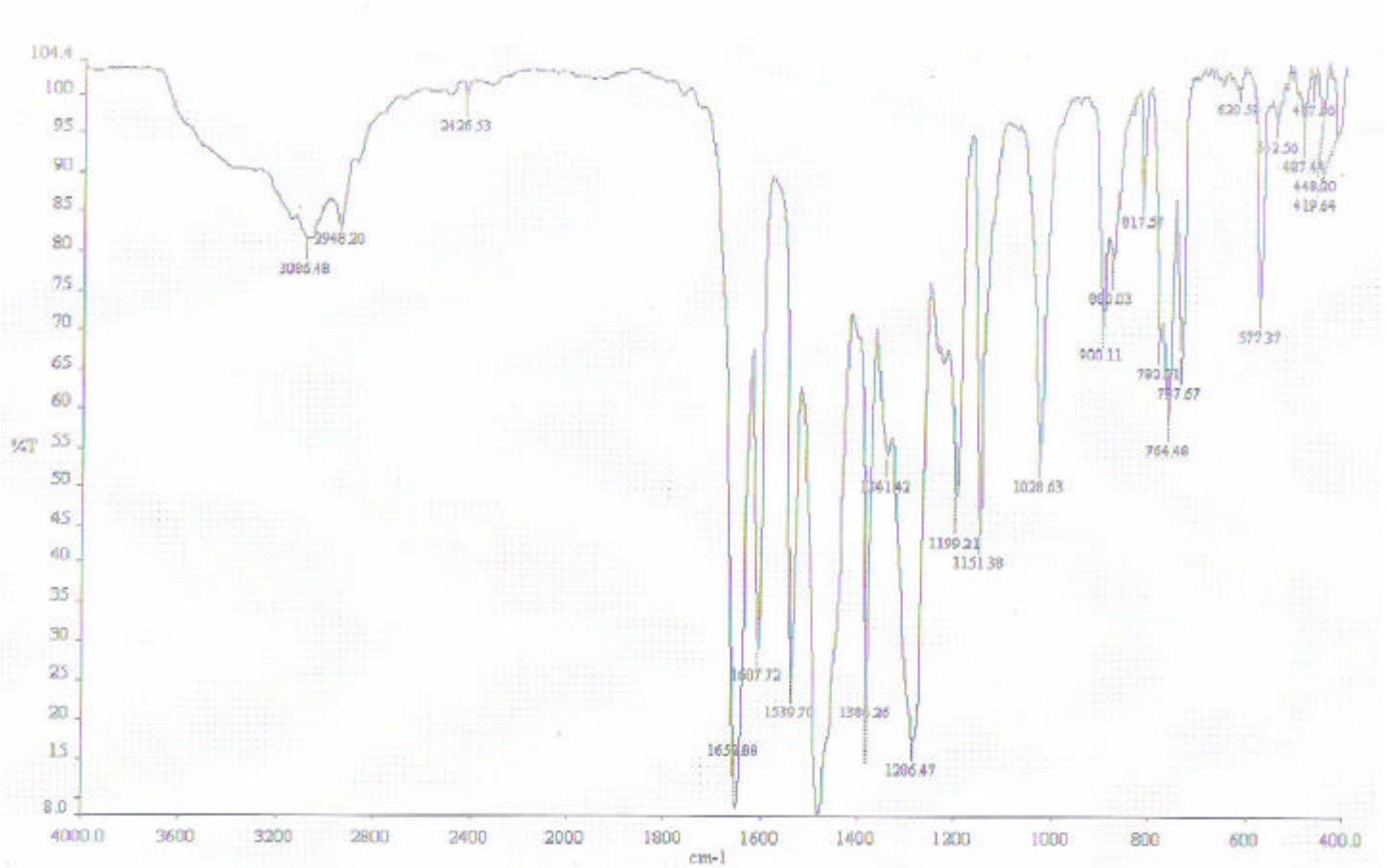


Figure-3.4. IR spectrum of $Sm(SbH_2)_2(NO_3)_3.2H_2O$

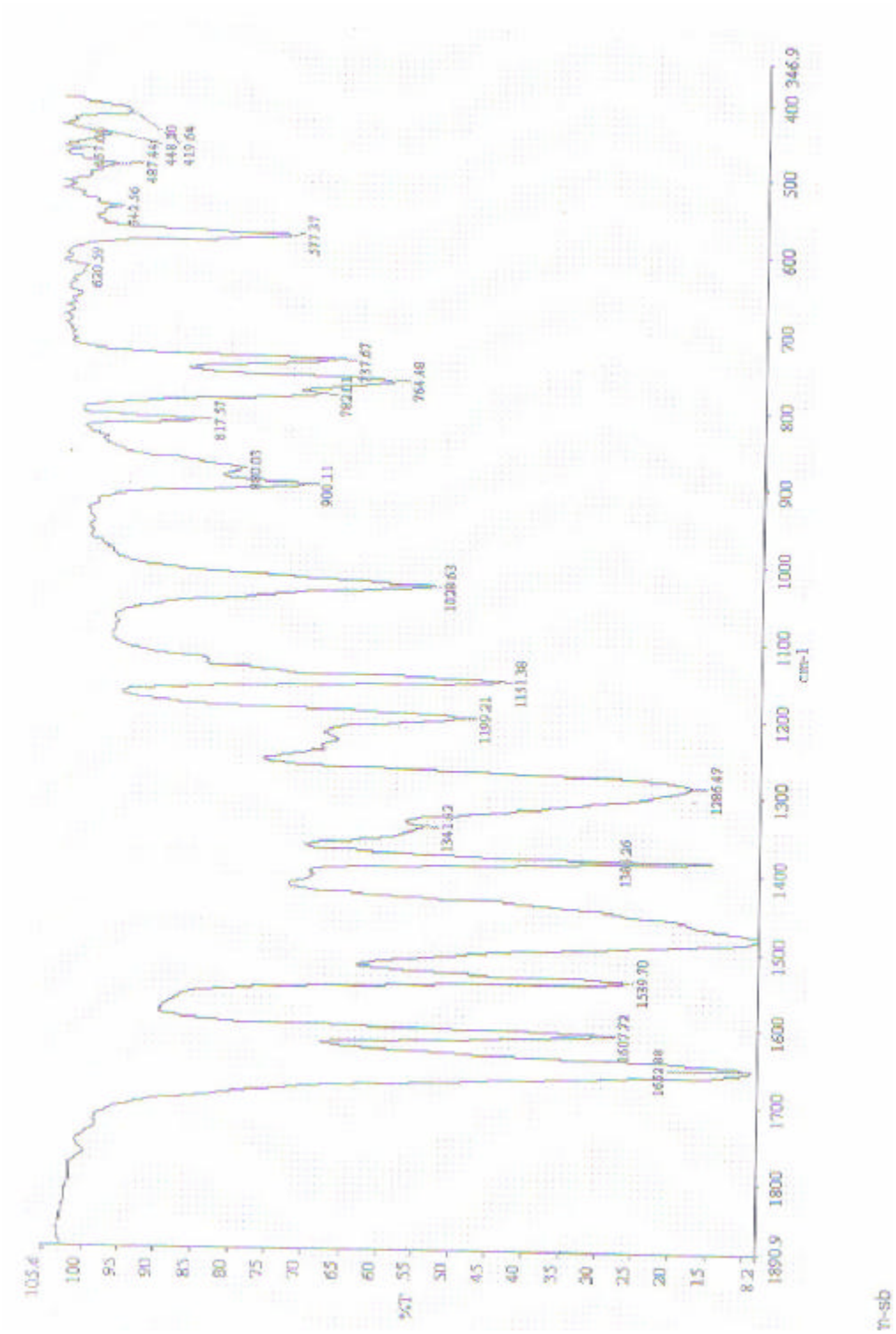


Figure-3.4. IR spectrum of **$Sm(SbH_2)_2(NO_3)_3.2H_2O$**

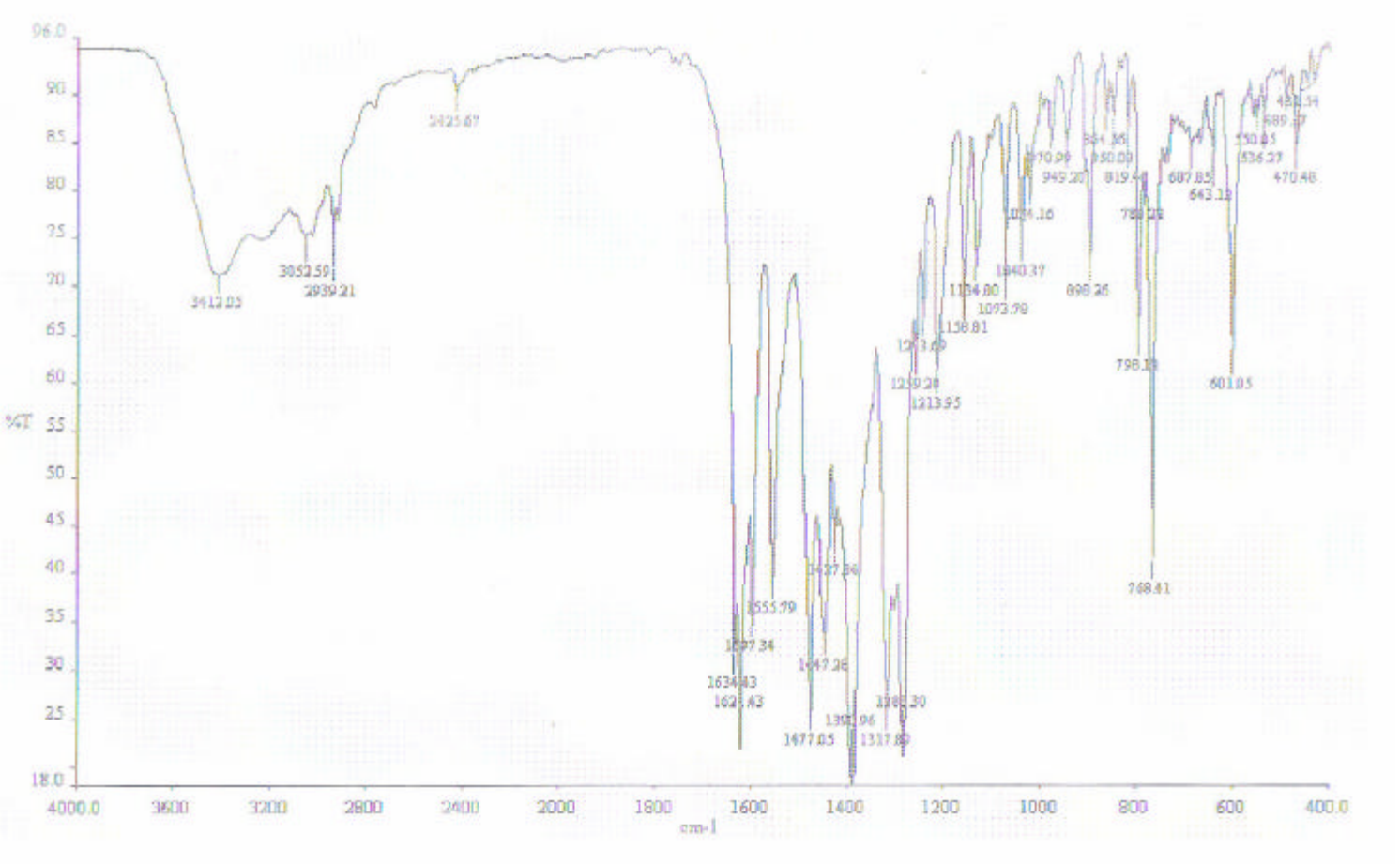


Figure-3.5. IR spectrum of $GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$

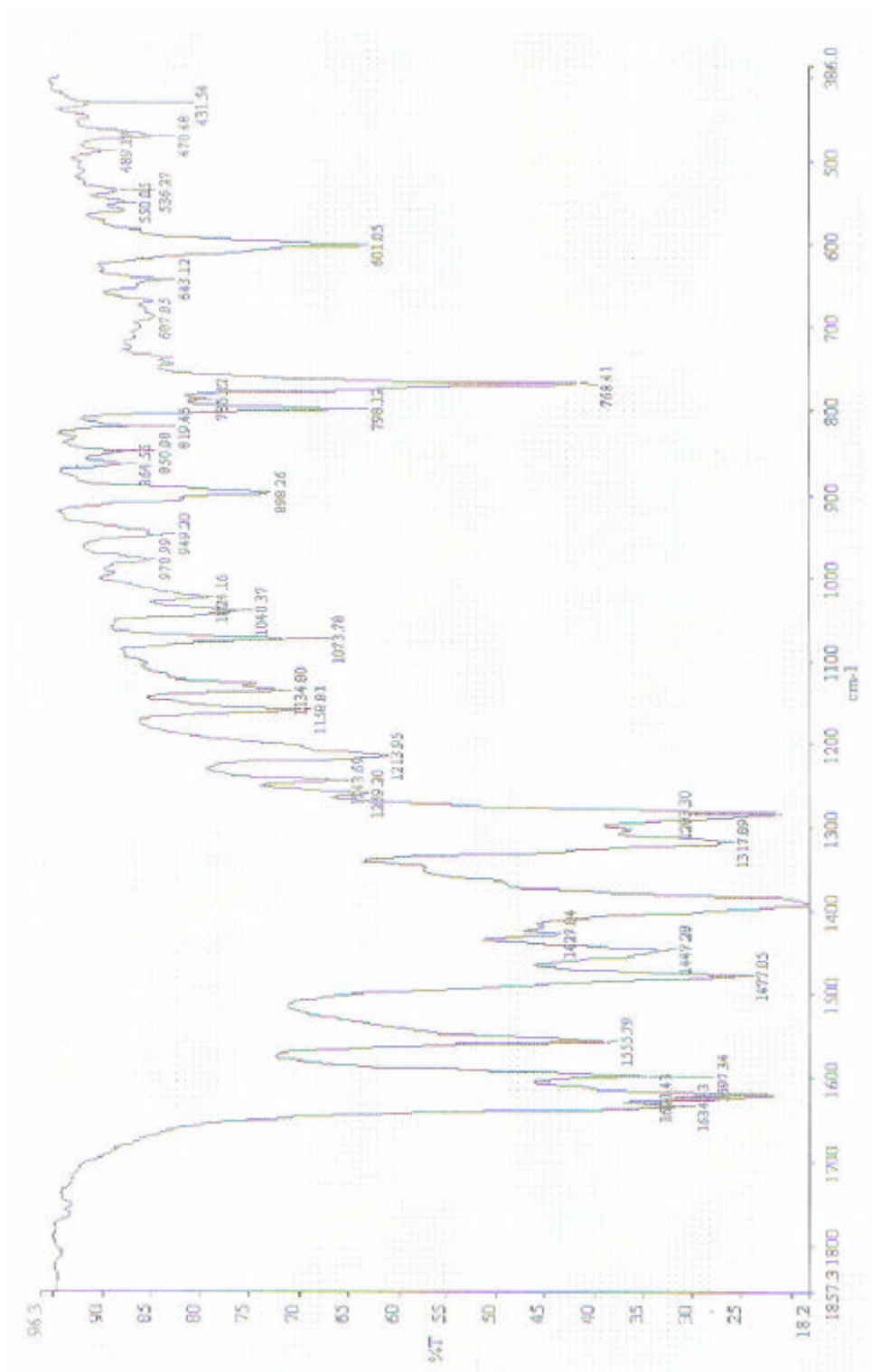


Figure-3.5. IR spectrum of $GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$

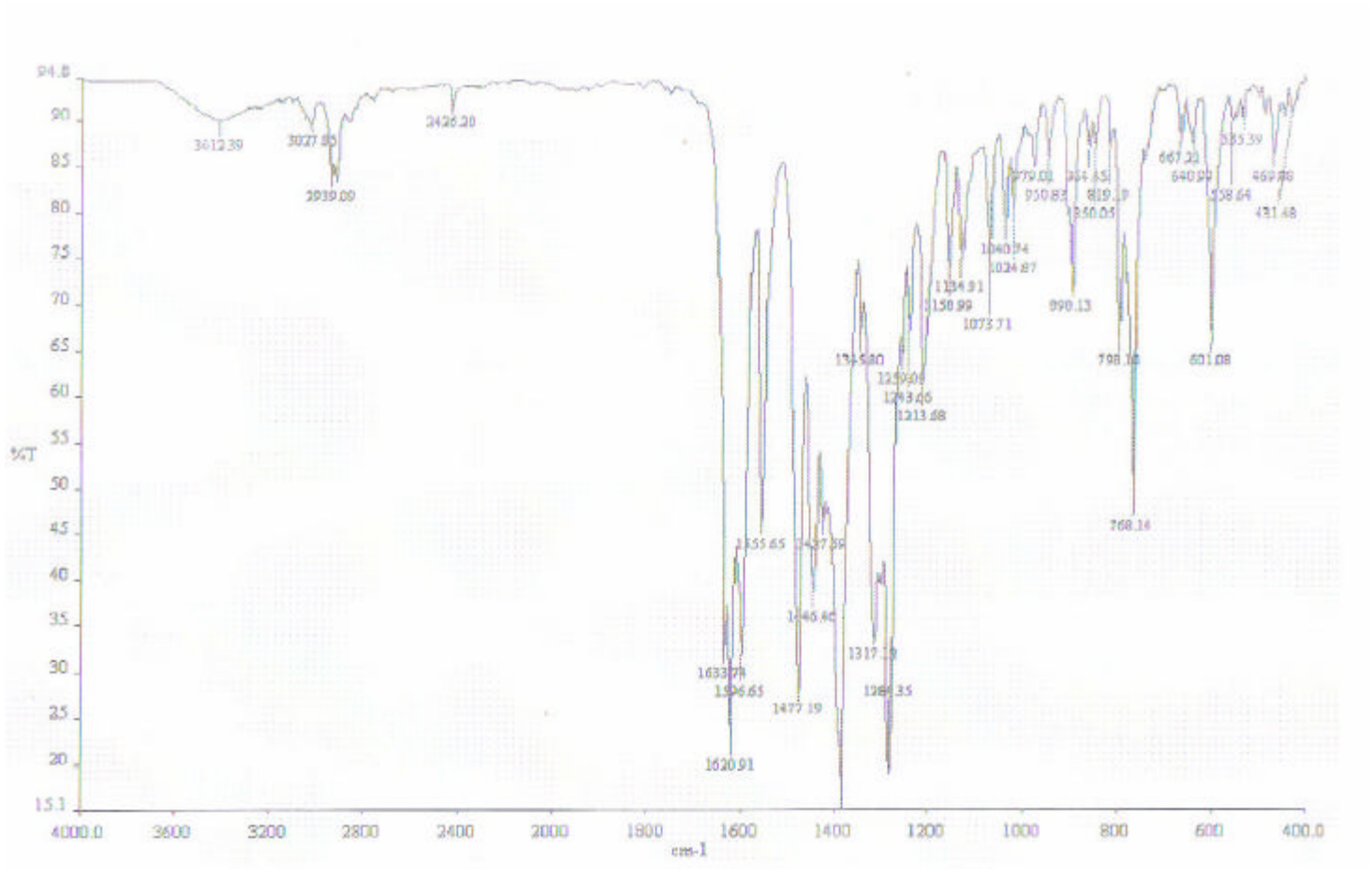


Figure-3.6. IR spectrum of **$NdCu_2(Sb)_2(NO_3)_3$**

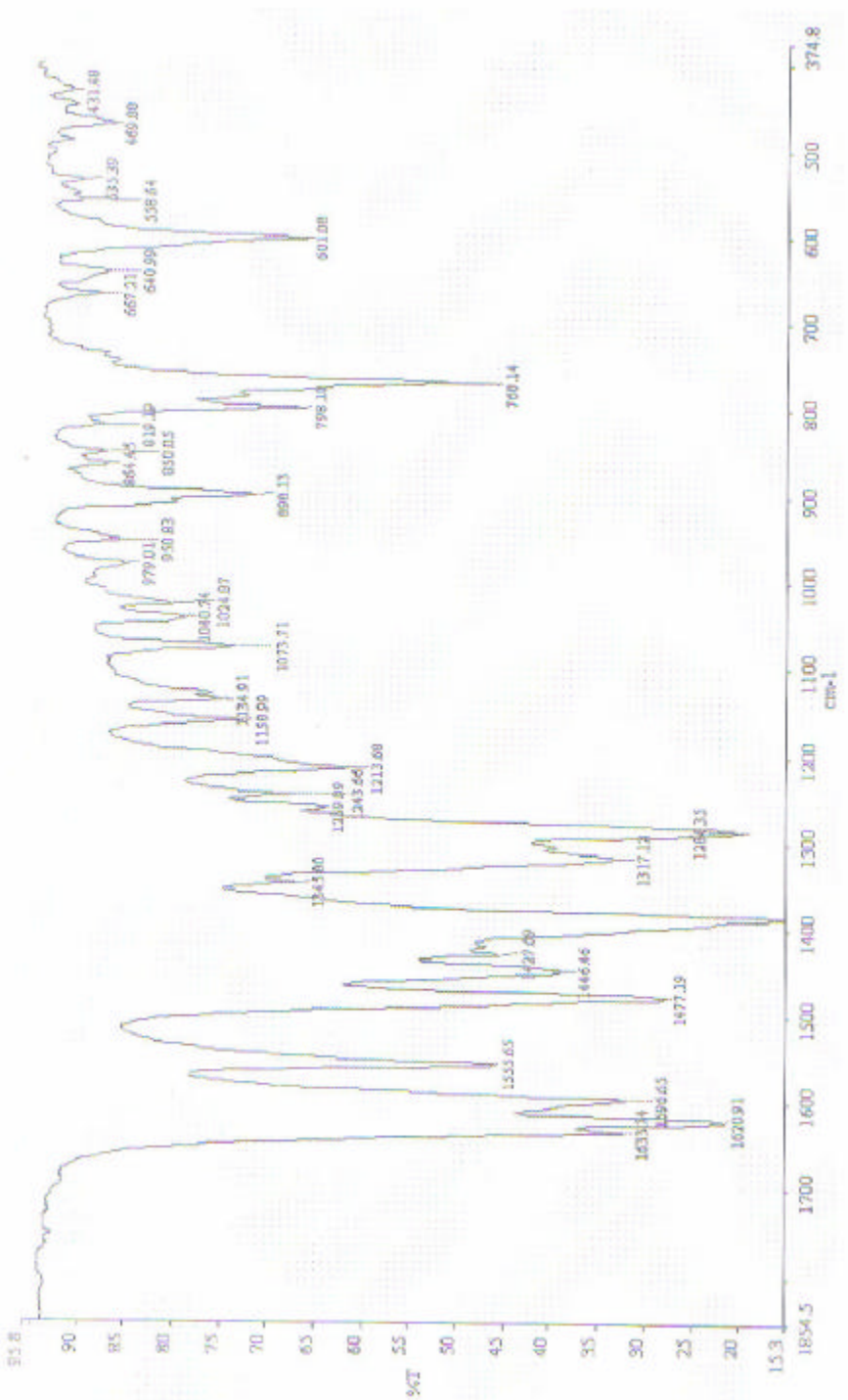


Figure-3.6. IR spectrum of $NdCu_2(Sb)_2(NO_3)_3$

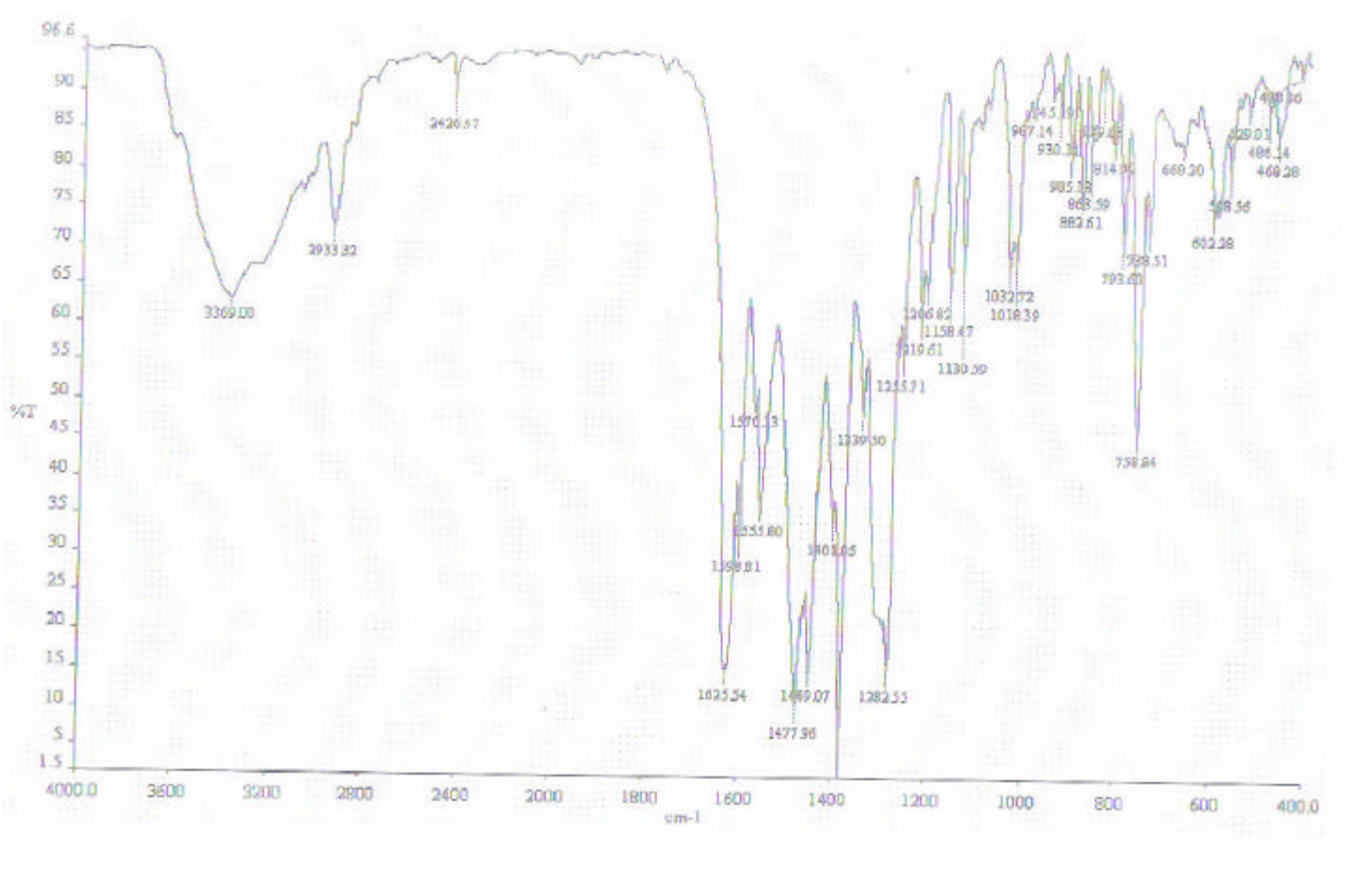


Figure-3.7. IR spectrum of **$SmCu_2(Sb)_2(NO_3)_3.2H_2O$**

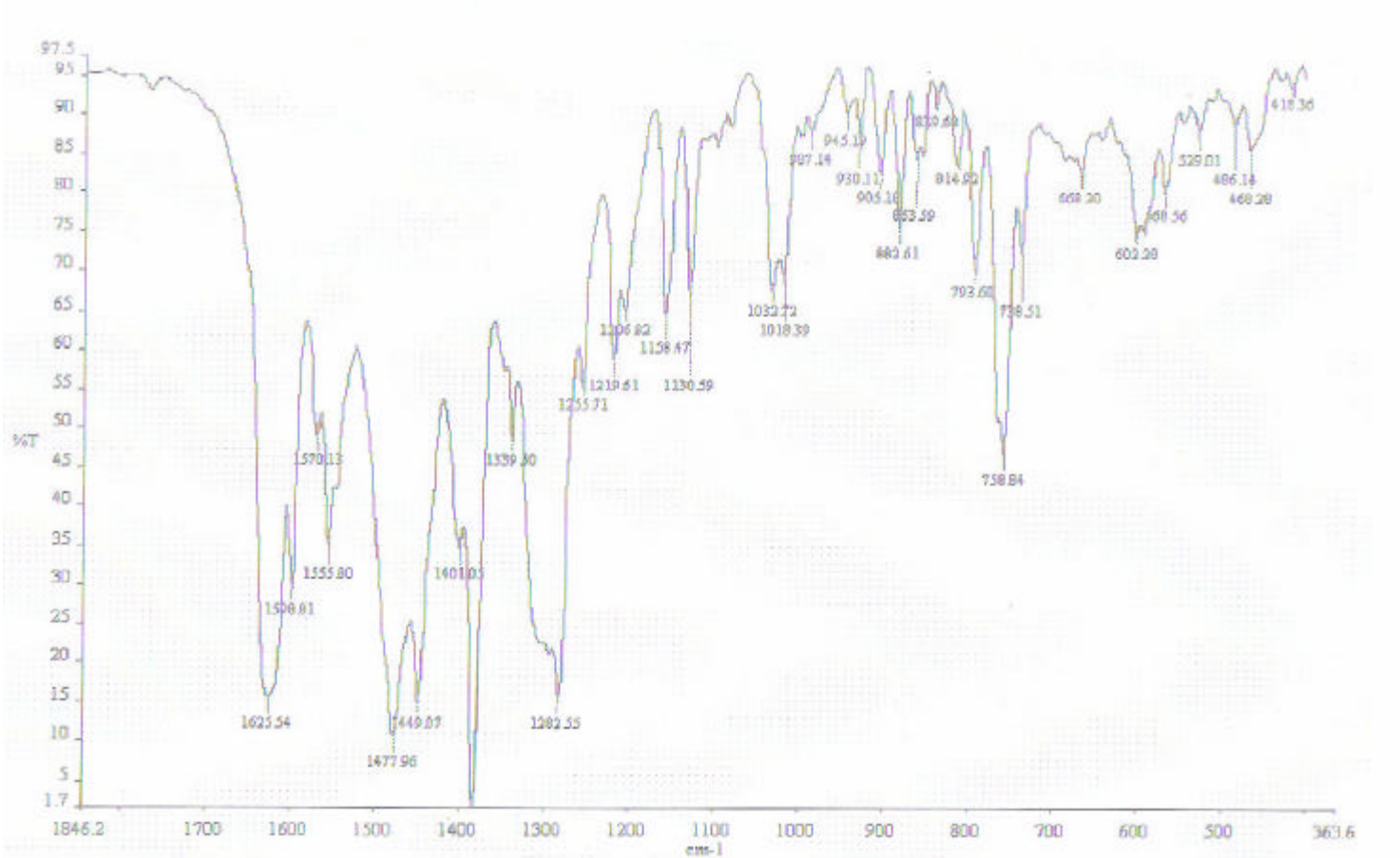


Figure-3.7. IR spectrum of $SmCu_2(Sb)_2(NO_3)_3.2H_2O$

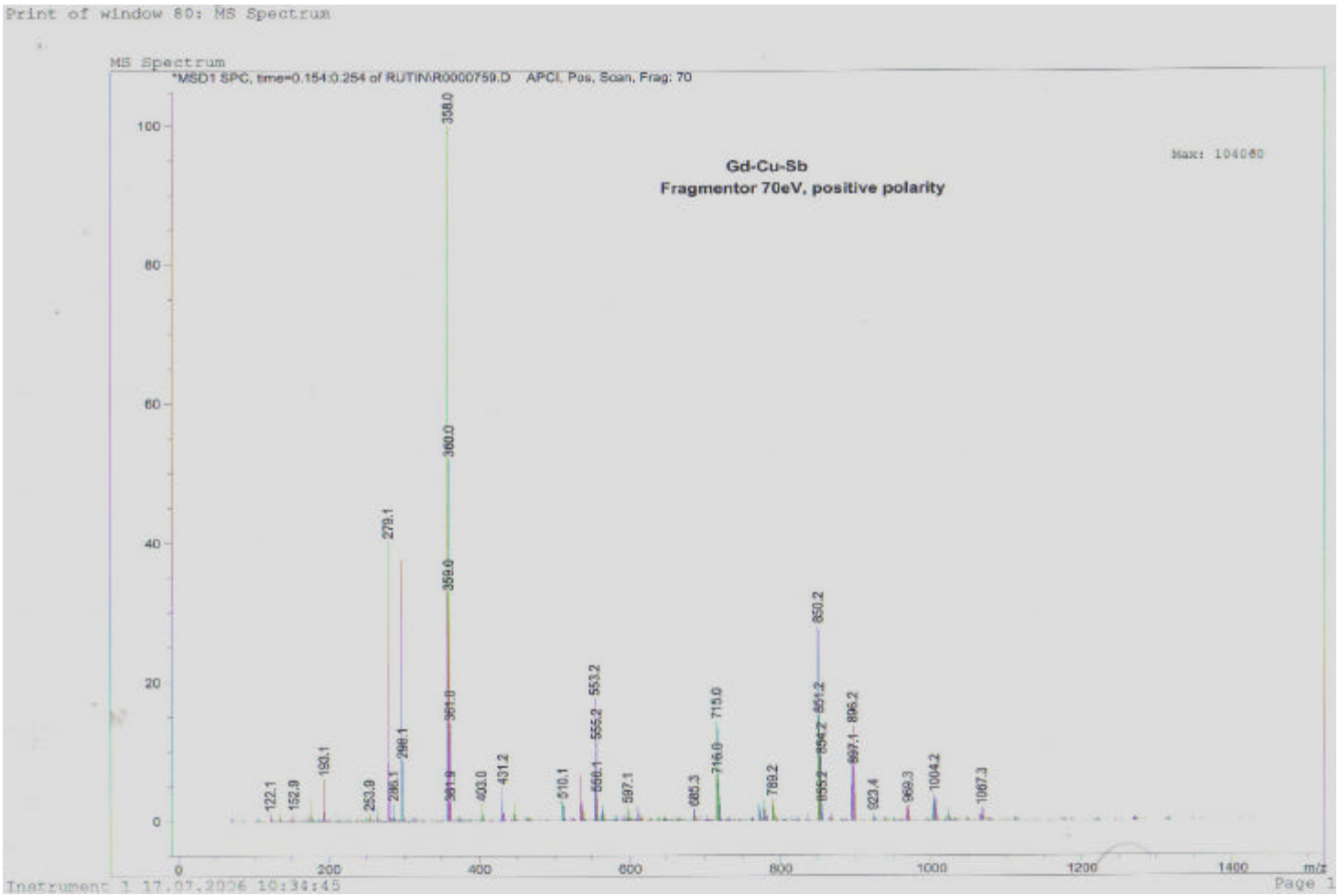


Figure-3.8. MS spectrum of $GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$

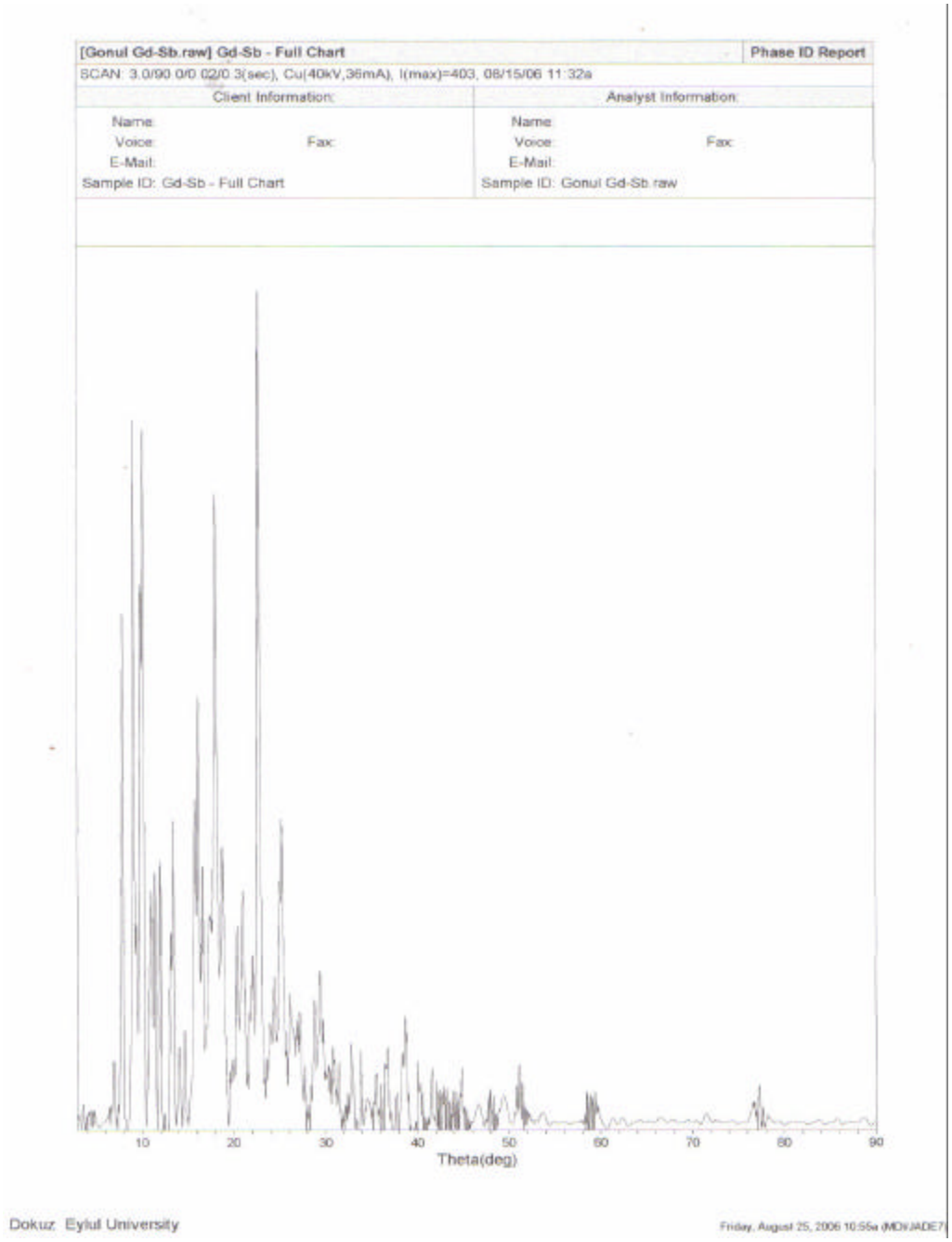


Figure-3.9. XRD spectrum of $Gd(SbH_2)_2(NO_3)_3$

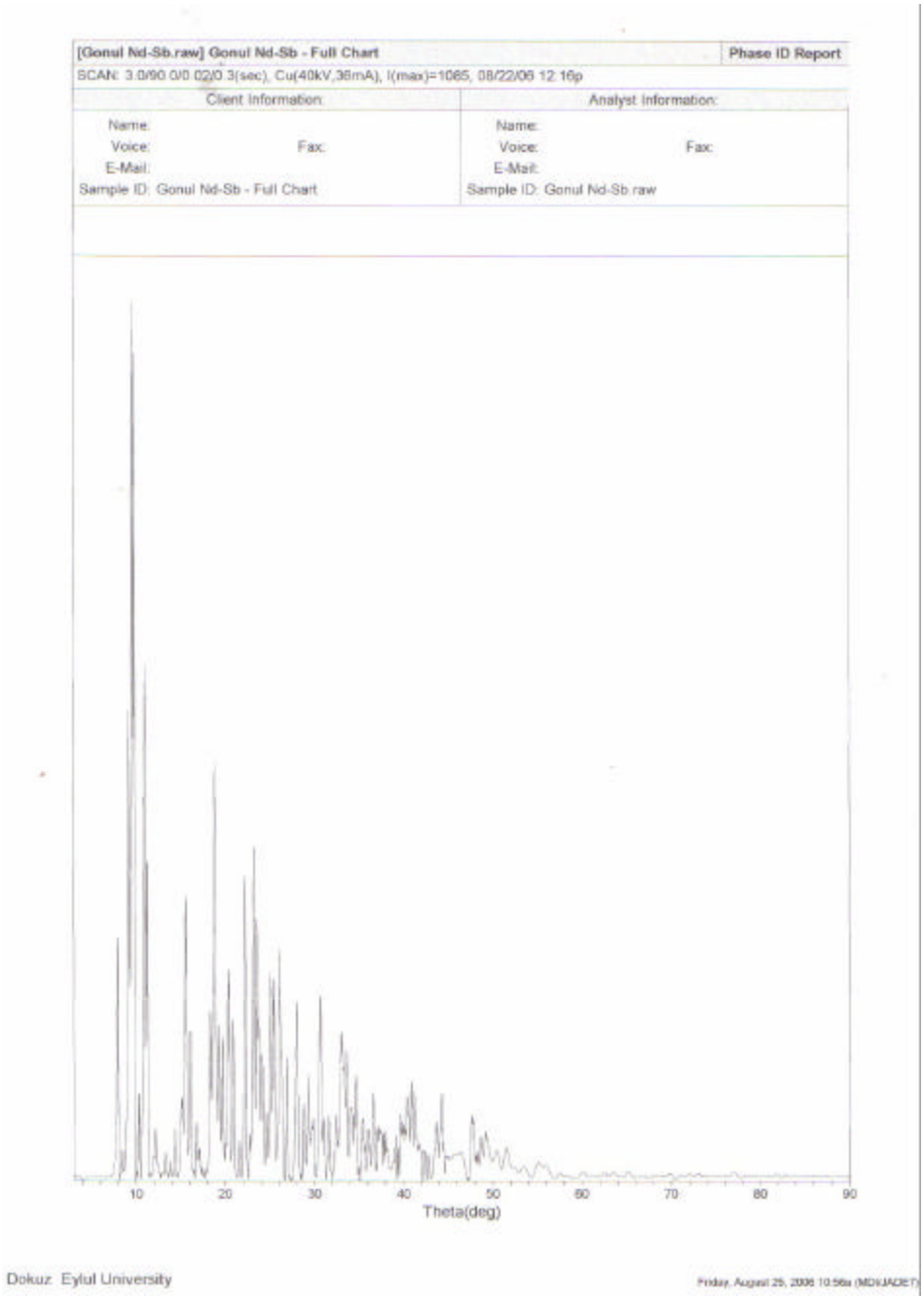


Figure-3.10. XRD spectrum of $Nd(SbH_2)_2(NO_3)_3\,(H_2O).2H_2O$

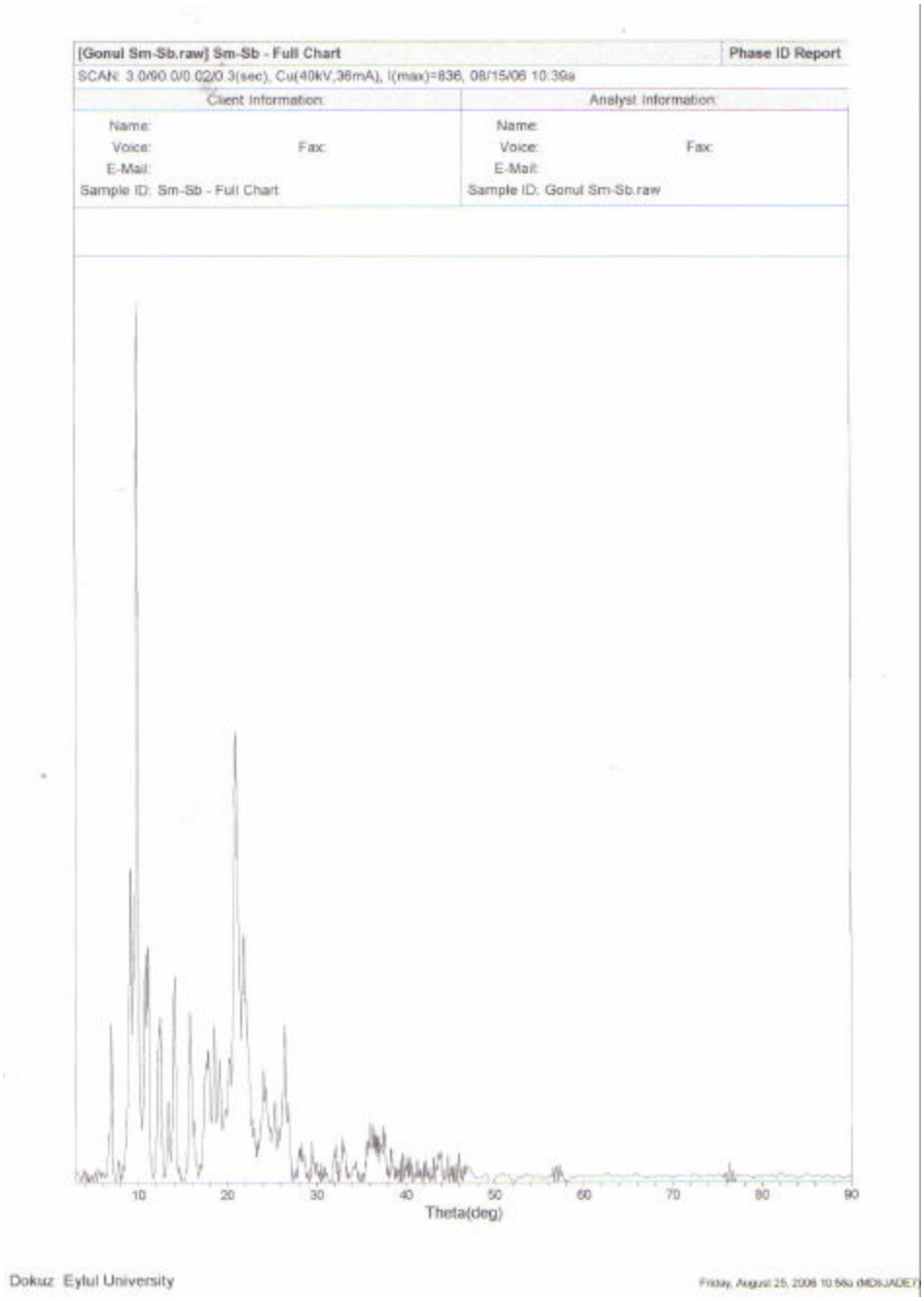


Figure-3.11. XRD spectrum of $Sm(SbH_2)_2(NO_3)_3.2H_2O$

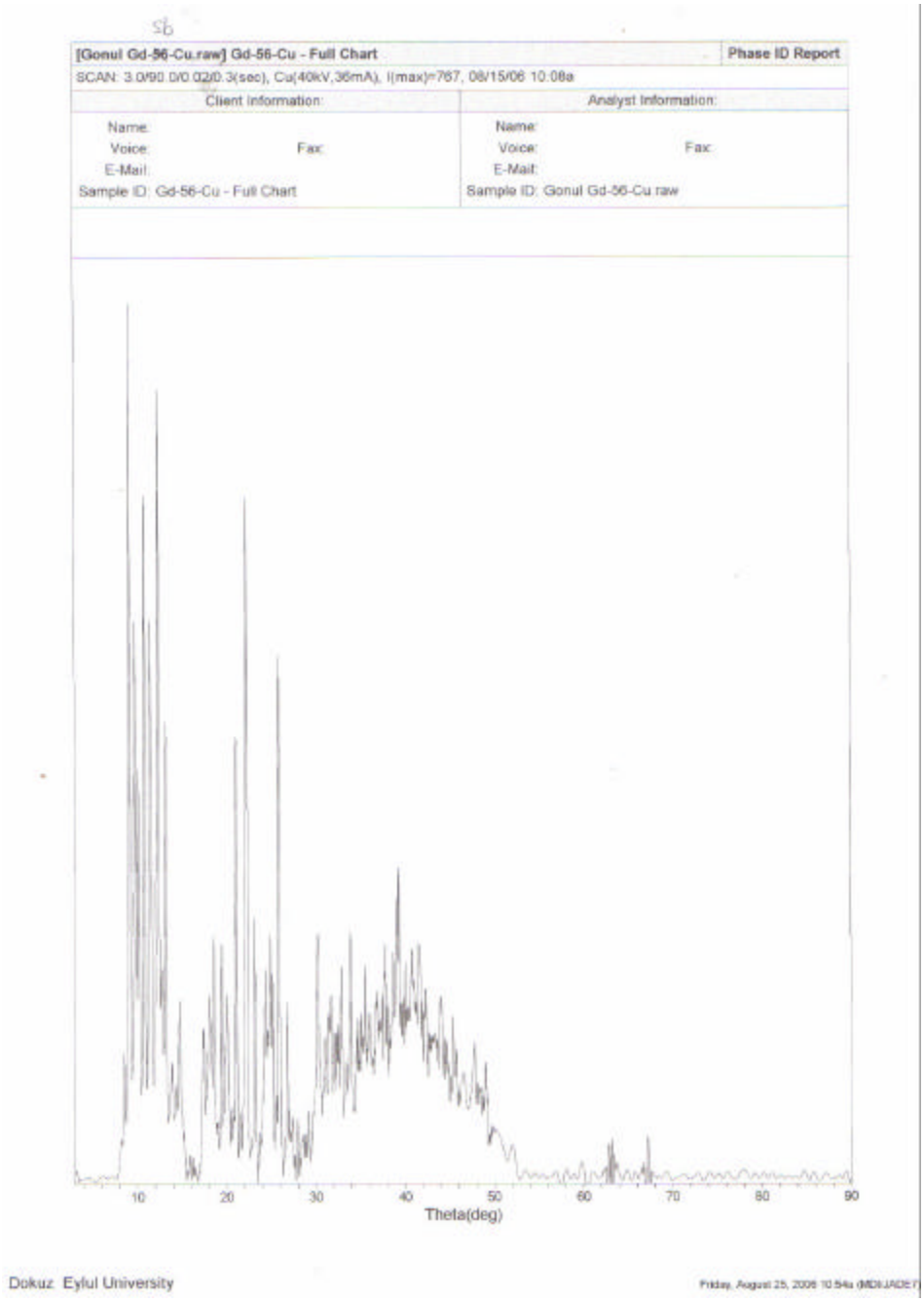


Figure-3.12. XRD spectrum of $GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$

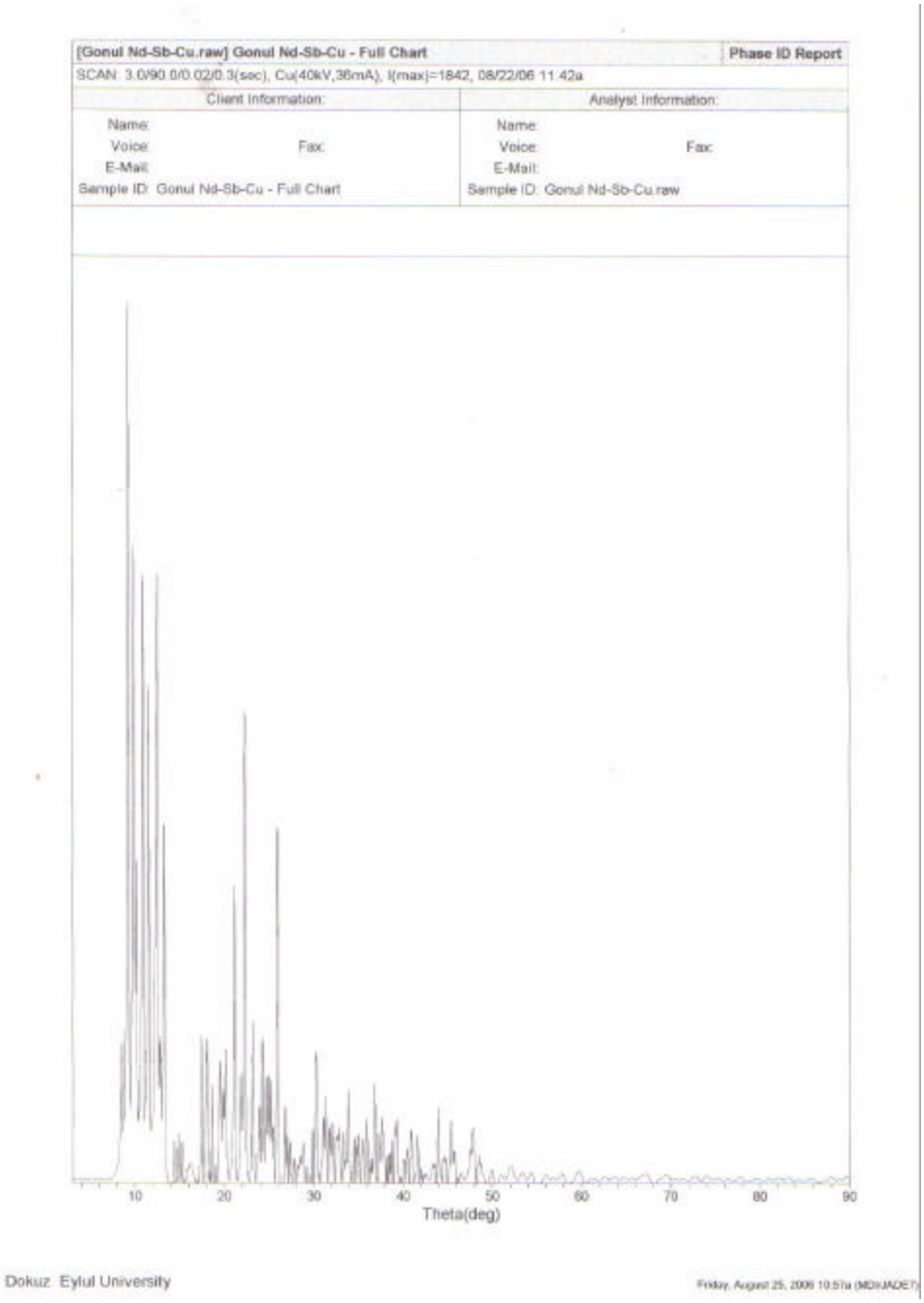


Figure-3.13. XRD spectrum of $NdCu_2(Sb)_2(NO_3)_3$

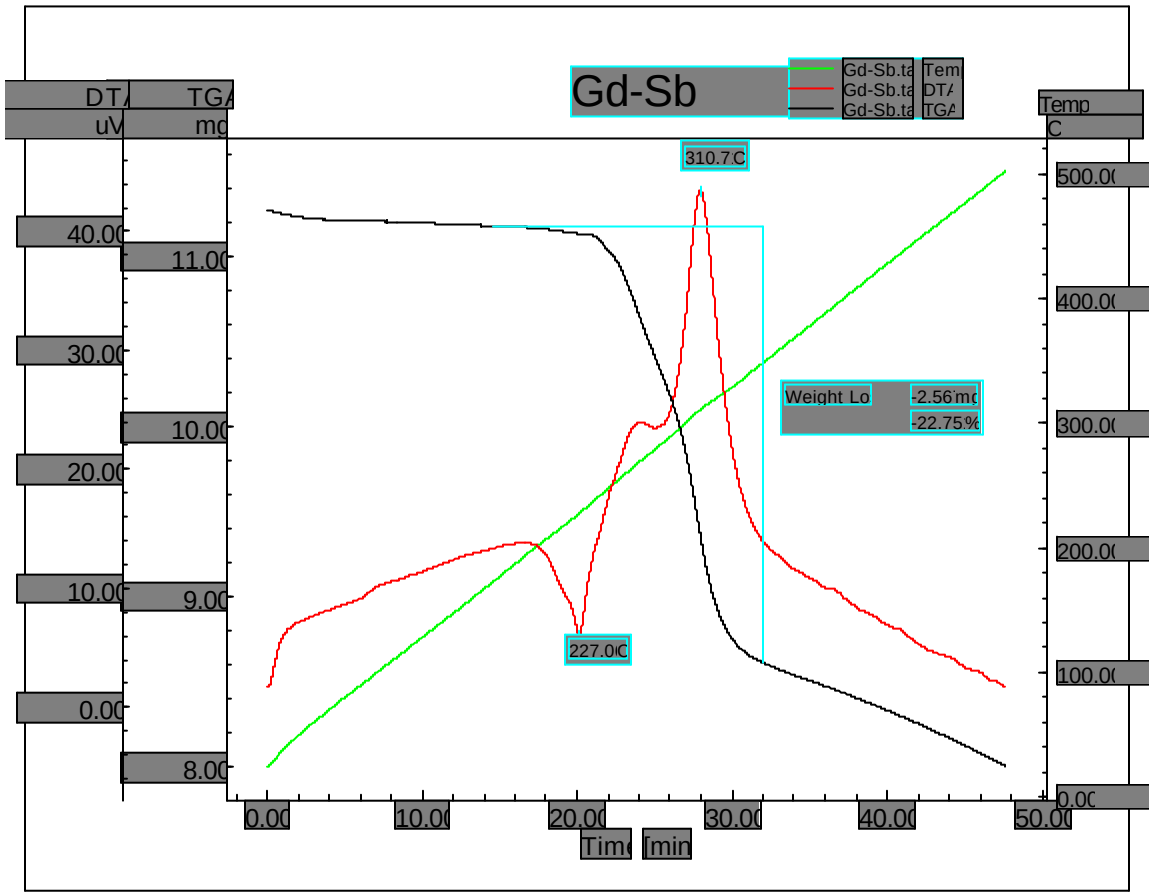


Figure-3.14. TGA of $Gd(SbH_2)_2(NO_3)_3$

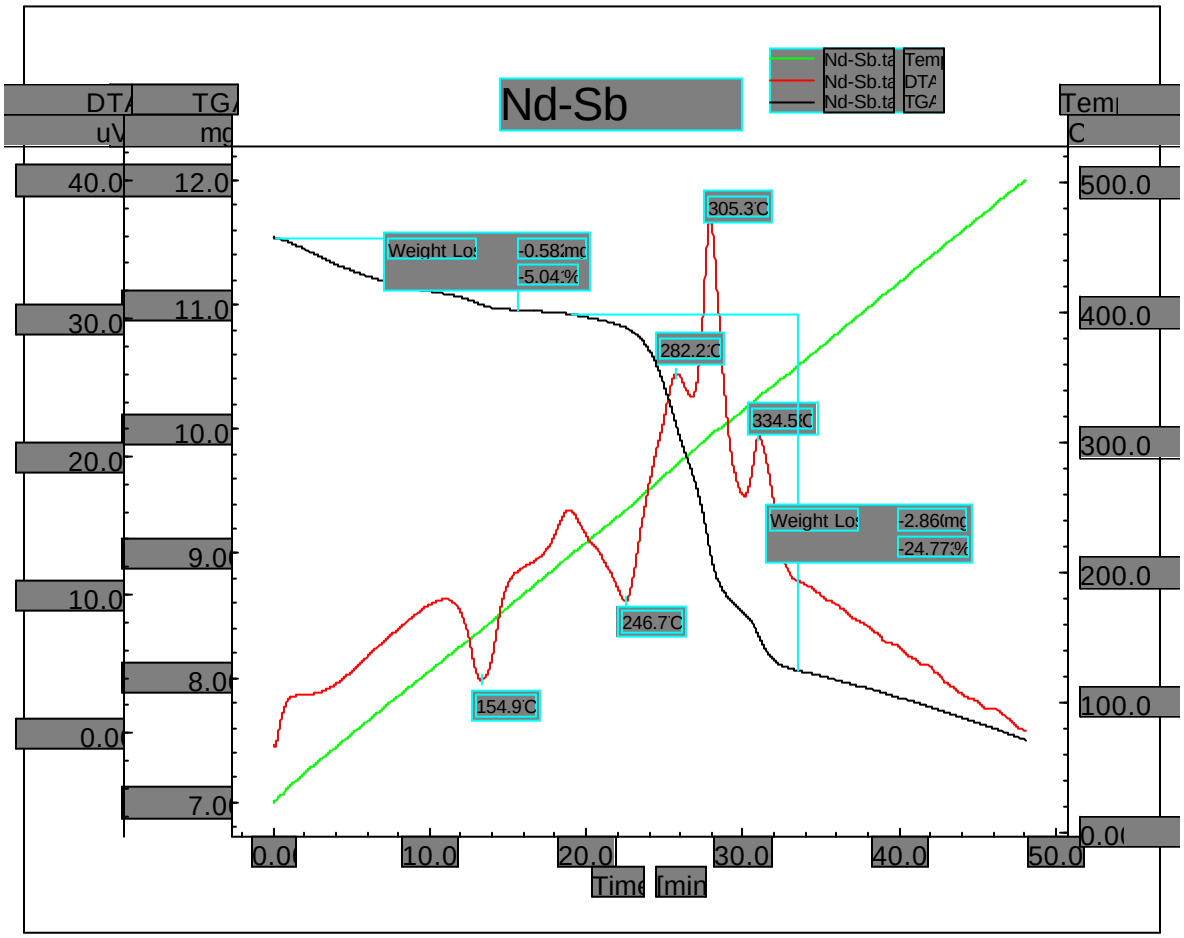


Figure-3.15. TGA of $Nd(SbH_2)_2(NO_3)_3\,(H_2O).2H_2O$

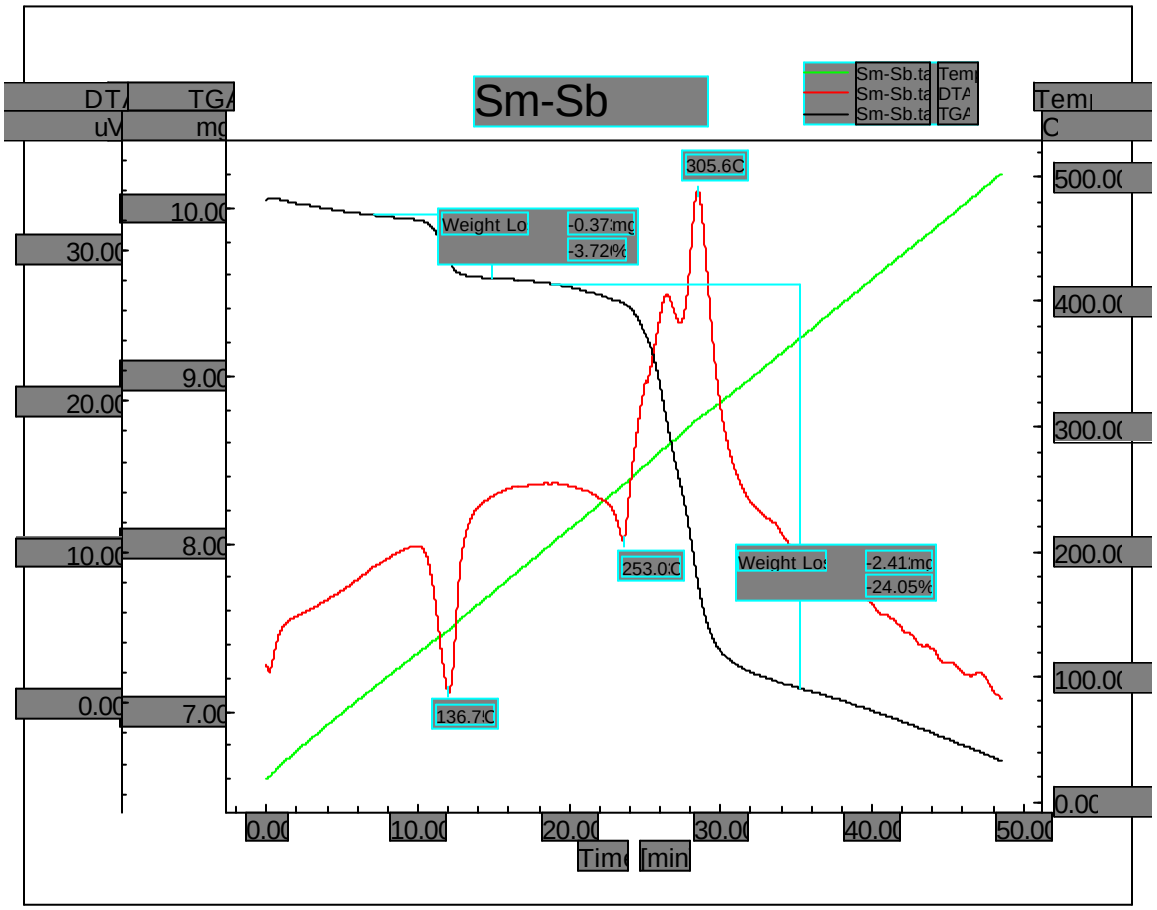


Figure-3.16. TGA of **$Sm(SbH_2)_2(NO_3)_3.2H_2O$**

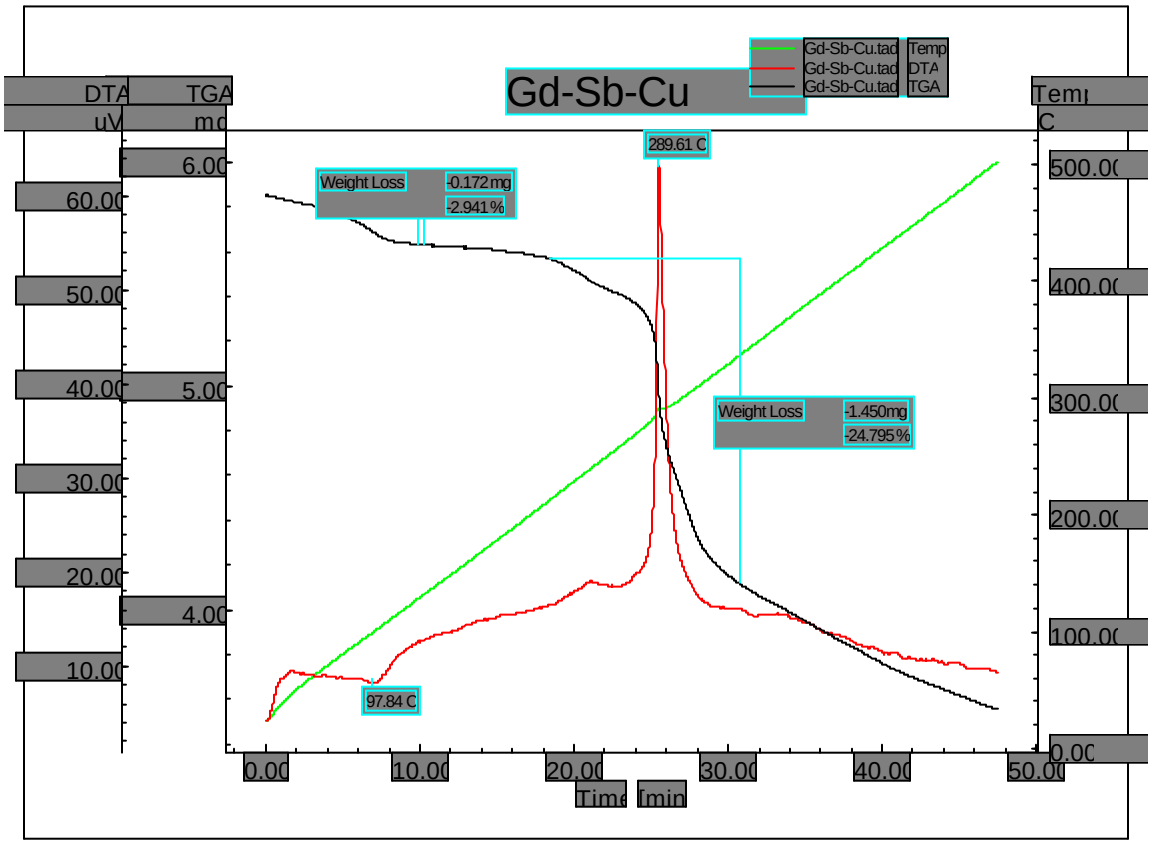


Figure-3.17. TGA of $GdCu_2(Sb)_2(NO_3)_3(H_2O)_2.2H_2O$

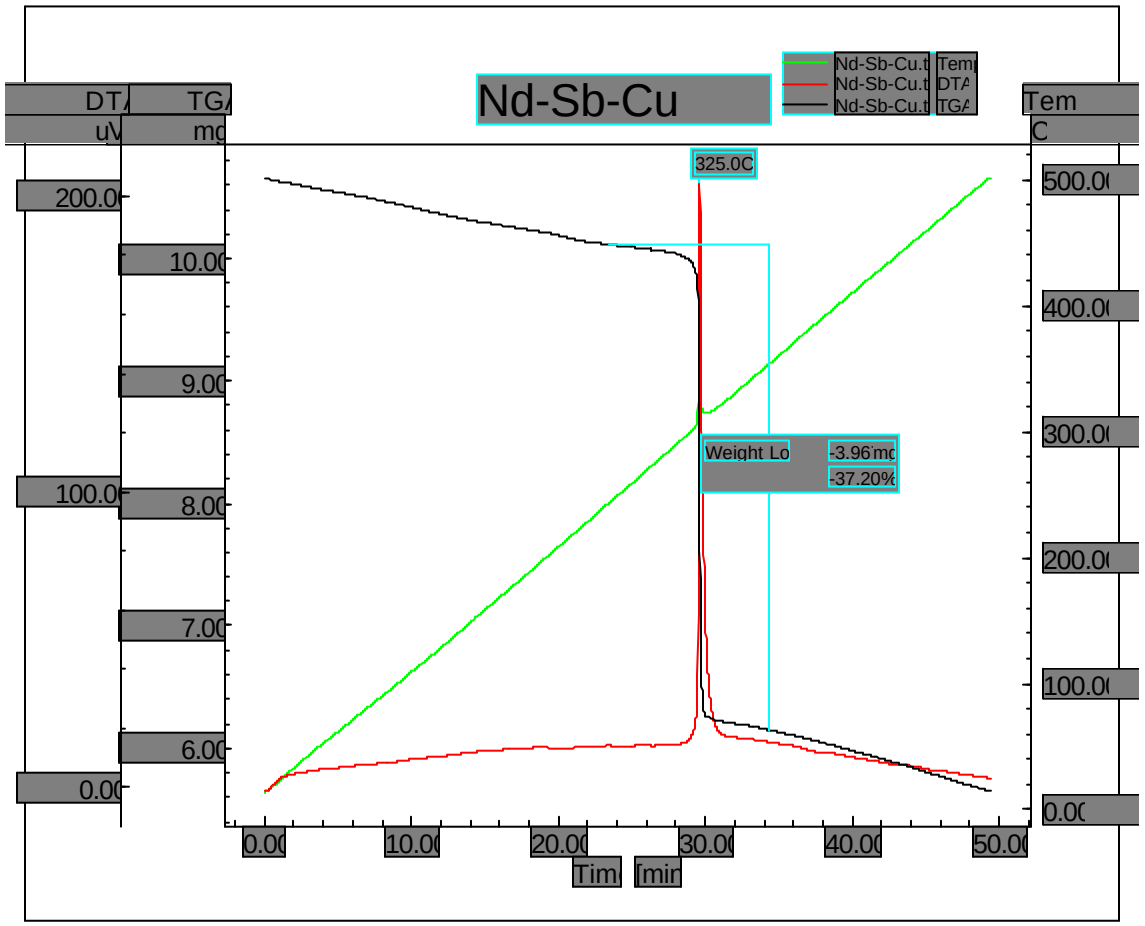


Figure-3.17. TGA of $NdCu_2(Sb)_2(NO_3)_3$

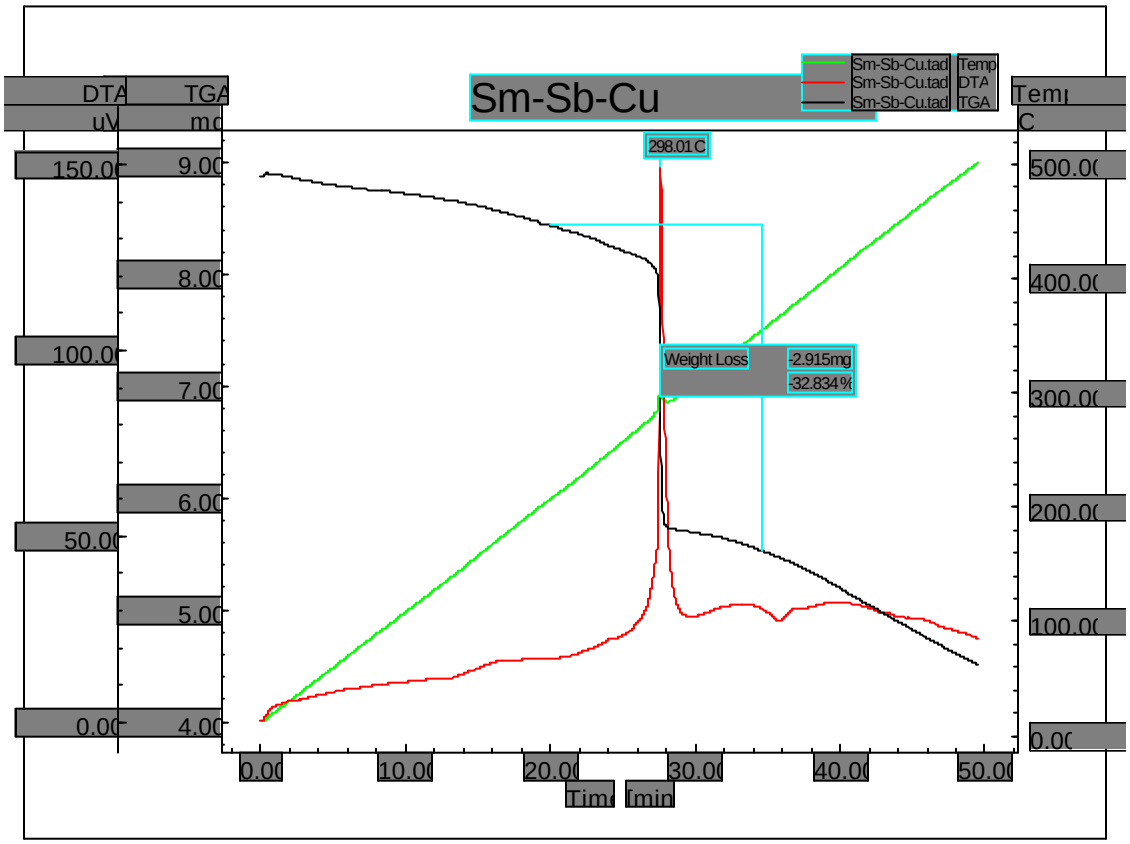


Figure-3.18. TGA of $SmCu_2(Sb)_2(NO_3)_3.2H_2O$

4.CONCLUSIONS

? It has been stated in literature that, Schiff base complexes of lanthanides are generally obtained as polynuclear compounds and in hydrated or solvated form. The complexes obtained in this study are all mononuclear and that of gadolinium is anhydrous.

? As expected, the results obtained by using the related simple equation for magnetic moments, agree well with those calculated through magnetic susceptibility measurements for neodymium and gadolinium complexes. They are also in close agreement with common experimental values. As for the samarium complex the magnetic moment calculated via the magnetic susceptibility measurement fits the literature values considerably well and in very close agreement with that evulated through the equation acconting for the populated excited states.

? Schiff base is coordinated to lanthanide (III) ions through oxygen atoms in accordance with HSAB rule.

? X_MT products of three heteronuclear complexes are approximately the same with those calculated on the assumption that two copper(II) ions and one lanthanide (III) ions are essentially noninteracting and magnetically isolated.

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