Indian Journal of Chemistry
Vol. 64, February 2025, pp. 247-252
DOI: 10.56042/ijc.v64i2.11385

Note

Preparation and spectral characterization of Schiff base ligand and Cu(II), Co(II), Zn(II), Cd(II) metal complexes

S Manimalathi, J Priya & D Madheswari*

Government Arts College for Women, Salem 636 008,
Tamil Nadu, India

E-mail: smmalathislm@gmail.com,
priyaasstprofessor@gmail.com, drmadhu6666@gmail.com

Received 31 May 2024; accepted (revised) 22 January 2025

Schiff base ligand 2-((3,5-dibromo-2-hydroxybenzylidene) amino)acetic acid derived from 3,5-dibromosalicylaldehyde and glycine has been obtained in water and methanol. Complexes of this Schiff base ligand with Cu(II), Co(II), Zn(II), Cd(II) have been prepared with ligand-Metal ratio of 2:1. The structures of the prepared complexes have been elucidated on the basis of elemental analyses, electronic spectra, IR, ^{1}H NMR, mass spectra and TGA.

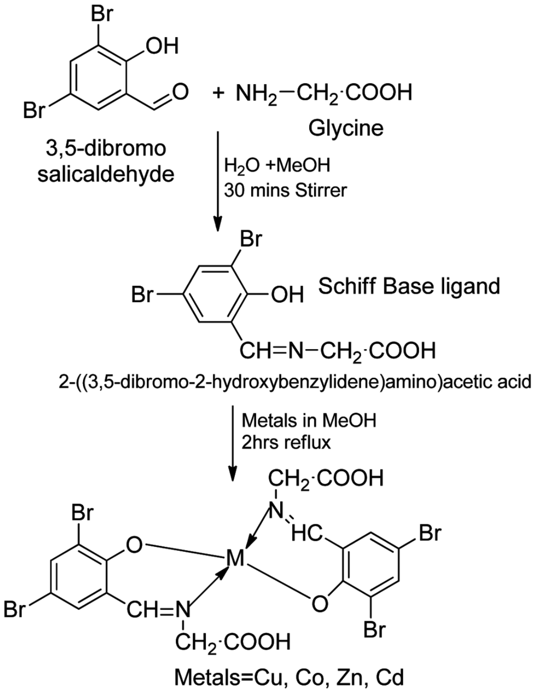
Keywords: Schiff base ligand, 3,5-Dibromosalicylaldehyde, Glycine, Metal complexes

An area of Bioinorganic Chemistry is still a strong-growing expanse for research which despite its designation it covers several disciplines of Chemistry and Biology. Recent Inorganic chemistry as it is nowadays in its empire has grown into a standard discipline due to the standard growth of Schiff base metal complexes. Currently many researcher and industry groups interested to Preparation of Schiff bases ligand and transition metal complexes with metal ions[1], The ligands, derived by condensation of a primary amine and an active carbonyl group contain the azomethine group. They form stable Schiff base ligand particularly if the amine and carbonyl compounds contain a second functional group sufficiently near the site of condensation to form a five or six-membered chelate ring upon chelation[2,3]. There are many publications dealing with metal chelates formed by Schiff bases. Because ligands containing O and N donor atoms are bonded to metal ions to have attracted significant attention due to variety of different applications in catalytic industrial and biological field such an antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and pharmacological[4,5]. The fact that transition metals is one of the essential metallic elements and that it possesses great biological activity when associated with certain metal-protein complexes which participate in the transport of oxygen and electronic transfer reactions of the storage of ions, has created enormous interest in the study of systems containing this metal[6-8]. Schiff bases and their complexes in aqueous solutions have been studied because of their interesting and important properties. This paper reports the preparation of the complexes formed between Schiff base ligands, we report the synthesis and characterization of a new Schiff base ligand and its complexes with Cu(II), Co(II), Zn(II), Cd(II). As far as we know, this is the first report of this ligand.

Experimental Section

Synthesis of Ligand

3,5-Dibromosalicylaldehyde (0.559 g, 2 mmol) and Glycine (0.1501 g, 2 mmol) were added successively to water and MeOH (50 mL). The resulting solution was stirred for 30 minutes. The residue was filtered at RT for slow evaporation was poured in the Schiff base ligand Scheme 1 formed as brown yellow Colour was filtered and recrystallized from ethanol.



Scheme 1 — Schiff base ligand and metal complexes

Synthesis of Metal Complexes

Cu(II), Co(II), Zn(II), Cd(II) complexes of the 2 mmol of Schiff base ligand were prepared by stirring the ligand with equimolar amounts of copper perchlorate hexahydrate, nickel perchlorate hexahydrate, Cadmium chloride and Zinc Chloride, respectively in 30 mL of ethanol and refluxed for 1 h [M= Cu(II), Co(II), Cd(II), Zn(II)] (Scheme 1). The solution was filtered and left in a petri dish to allow the solvent to evaporate slowly. The crystalline complexes formed were purified by recrystallization from ethanol.

Results and Discussion

The Table 1 describes the analytical data of the Schiff base ligand and their complexes.

Electronic spectra

The electronic spectra of the ligand and all the Metal complexes was recorded in DMSO at RT. The Schiff base ligand at 231.65 nm is attributed to $\pi \rightarrow \pi^*$ transition[6]. The band around 283.60 nm is due to the $n \rightarrow \pi^*$ transition of the non-bonding electrons presents on the nitrogen of the azomethine group in the Schiff base ligand. The complexes of Cu(II), Co(II), Zn(II), Cd(II) show less intense shoulders 382,256,234, 235. The spectra of all the complexes show an intense band at 380–420 nm which can be assigned to a charge-transfer transition for tetrahedral geometry[9]. The spectra are shown in the Fig. 1(a) to (e).

Table 1 — Analytical data of the Schiff base ligand and their complexes

Compd	Mol. Formula	Found (%)						Mol Wt.
		C	H	N	O	Br	M	
Ligand	$C_9H_7Br_2NO_3$	33.08	2.09	4.16	14.24	47.43	–	334.9
Cu	$C_{18}H_{12}Br_4CuN_2O_6$	29.40	1.64	3.81	13.05	43.46	8.64	730.7
Co	$C_{18}H_{12}Br_4CoN_2O_6$	29.58	1.65	3.83	13.13	43.73	8.06	726.7
Zn	$C_{18}H_{12}Br_4ZnN_2O_6$	29.32	1.64	3.80	13.02	43.65	8.87	731.7
Cd	$C_{18}H_{12}Br_4CdN_2O_6$	27.56	1.54	3.57	12.24	40.75	14.3	781.6

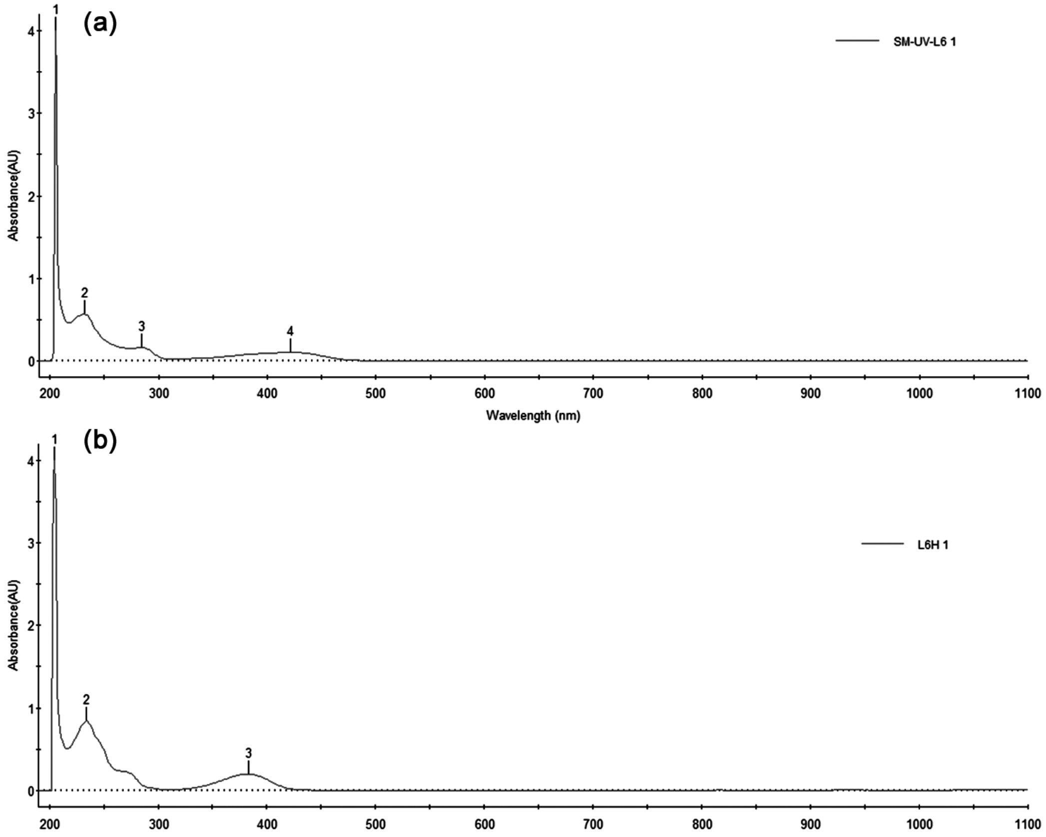


Fig. 1 — (a) UV-Vis spectrum of ligand, (b) UV-Vis spectrum of Cu (Contd.)

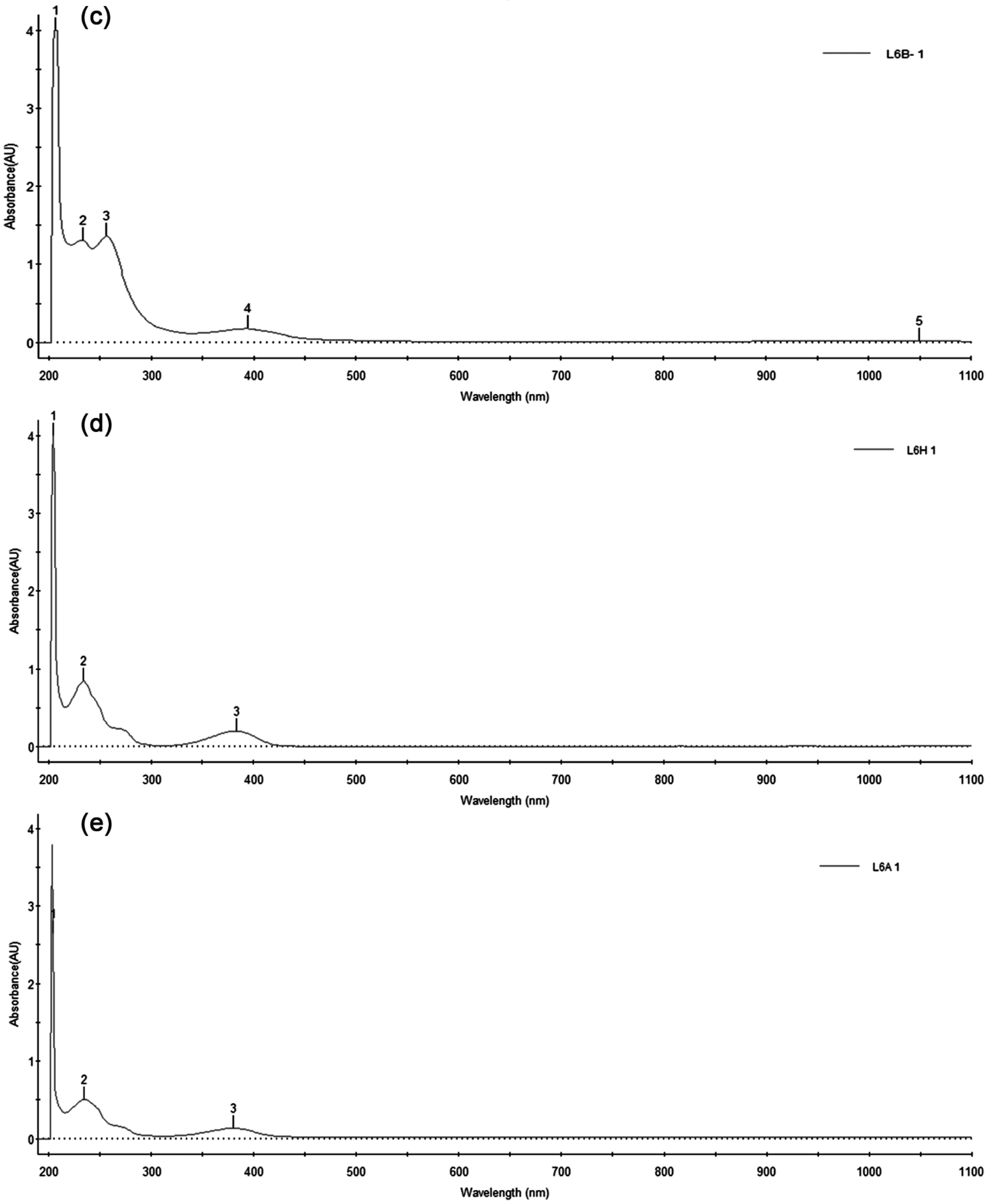


Fig. 1 — (c) UV-Vis spectrum of Co, (d) UV-Vis spectrum of Zn, (e) UV-Vis spectrum of Cd

Infrared spectra

In the IR spectra of the Schiff base ligand, the O–H, -C=N stretching vibrations were observed at 3437, 1650,cm^{-1},respectively. These values agree with those reported for similar compounds[10]. The azomethine vibration of the ligand at 1617 cm^{-1} was shifted to lower frequencies after complexation, appearing at 1606, 1603, 1600 and 1613 cm^{-1} for Cu(II), Co(II), Zn(II), Cd(II) complexes, respectively. Which means that the shifts are due to ligand-to-metal coordination by the azomethine nitrogen and oxygen[11,12]. The exceptional case is that the $\upsilon_{(C=N)}$ of complexes were found to be shifted to a lower wavelength number associated to the ligand, suggesting that the direction took place through the nitrogen atom of the ligand. In adding, the stretching of metal to oxygen and metal to nitrogen bands of the complexes seemed in the lower wavelength region in the range of 582–490 and 490–452 cm^{-1} also signifying the complexation through nitrogen and oxygen atoms from the ligand the spectra are shown in the Fig. 2(a) to (e).

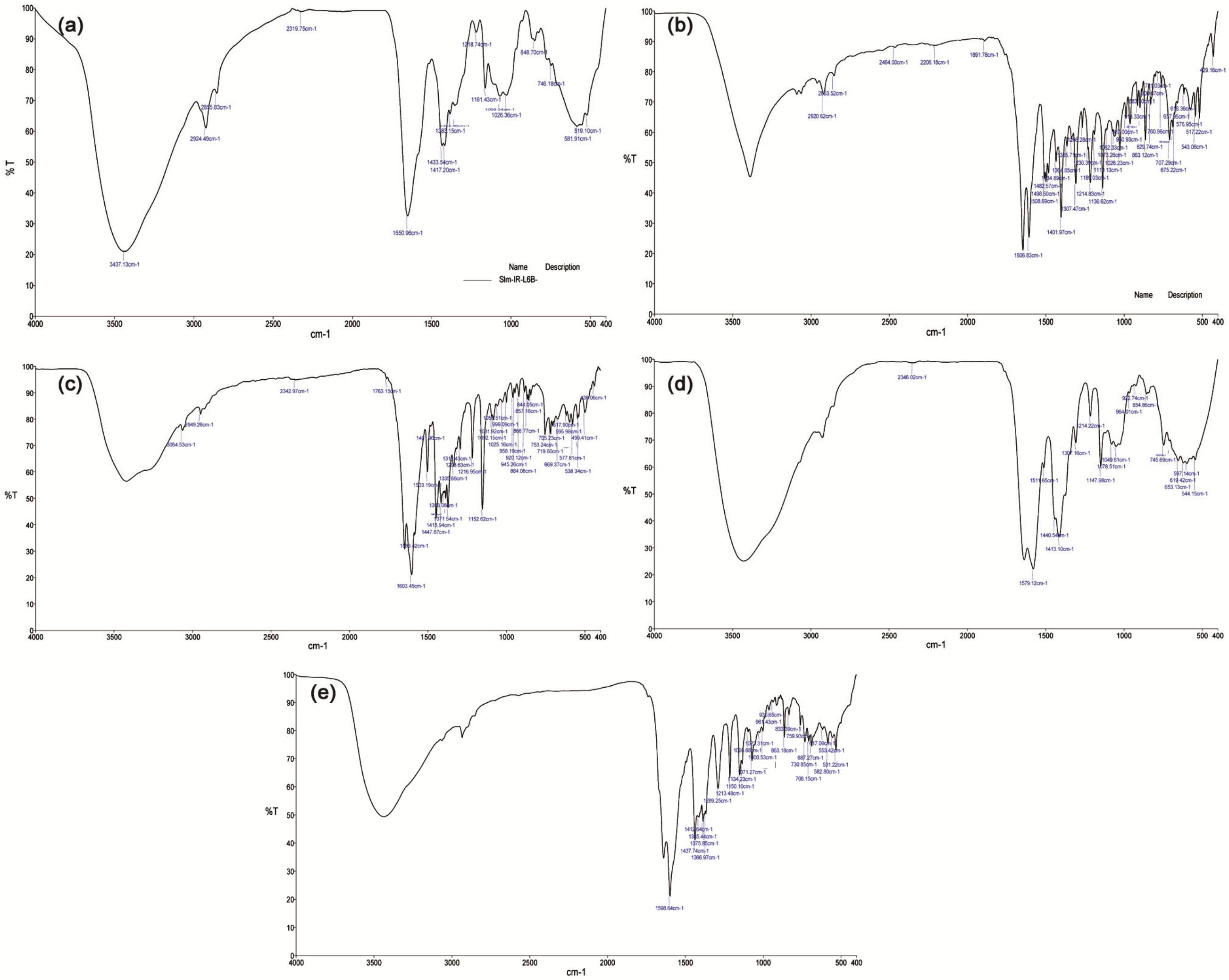


Fig. 2 — (a) IR spectrum of Schiff base ligand, (b) IR spectrum of Cu, (c) IR spectrum of Co, (d) IR spectrum of Zn, (e) IR spectrum of Cd

^{1}H NMR spectra

The ^{1}H NMR spectra of Schiff base with ligand showed different peaks (Fig. 3). 4.50 (2H, s, one of –COOH and other Phenolic –OH group), 7.75 -7.82 (4H, m, Ar-H atoms), 8.11 (1H, s, azomethine proton). Mass Spectrum of $C_9H_7Br_2$ NO_3 $[M+H]^+$: calculated = 334.9; found: 335.95 (Fig. 4).

Thermogravimetric Analysis

The decomposition temperature and weight losses of the Metal complexes were calculated from TGA data. The ligand is stable up to 228°C where its decomposition starts and is completed at 700°C. As can be seen in the TGA data all the complexes and the ligand decompose in two steps at different temperature ranges. All complexes undergo complete decomposition to the corresponding metal oxides, CuO, CoO, ZnO and CdO (Ref. 13). The thermal behaviour of the complexes is summarized in Table 2 and shown in Fig. 5a-d.

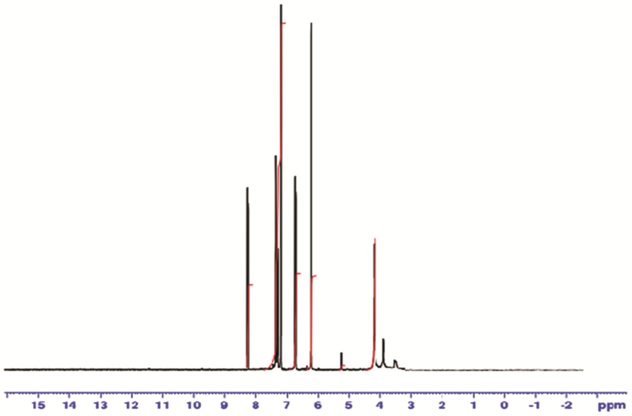


Fig. 3 — ^{1}H NMR spectrum of Schiff base ligand

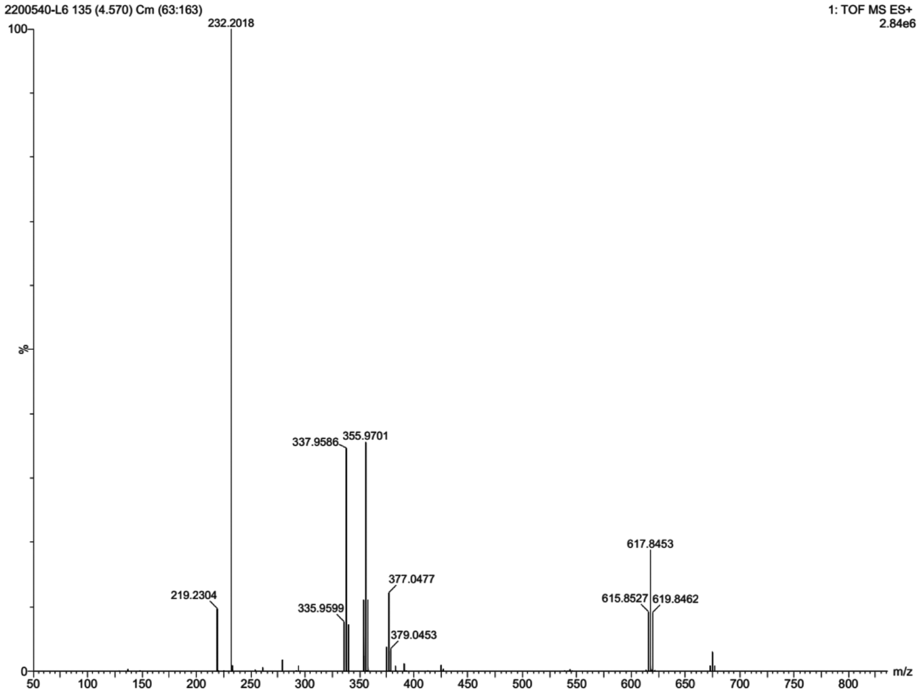


Fig. 4 — Mass spectrum of Schiff base ligand

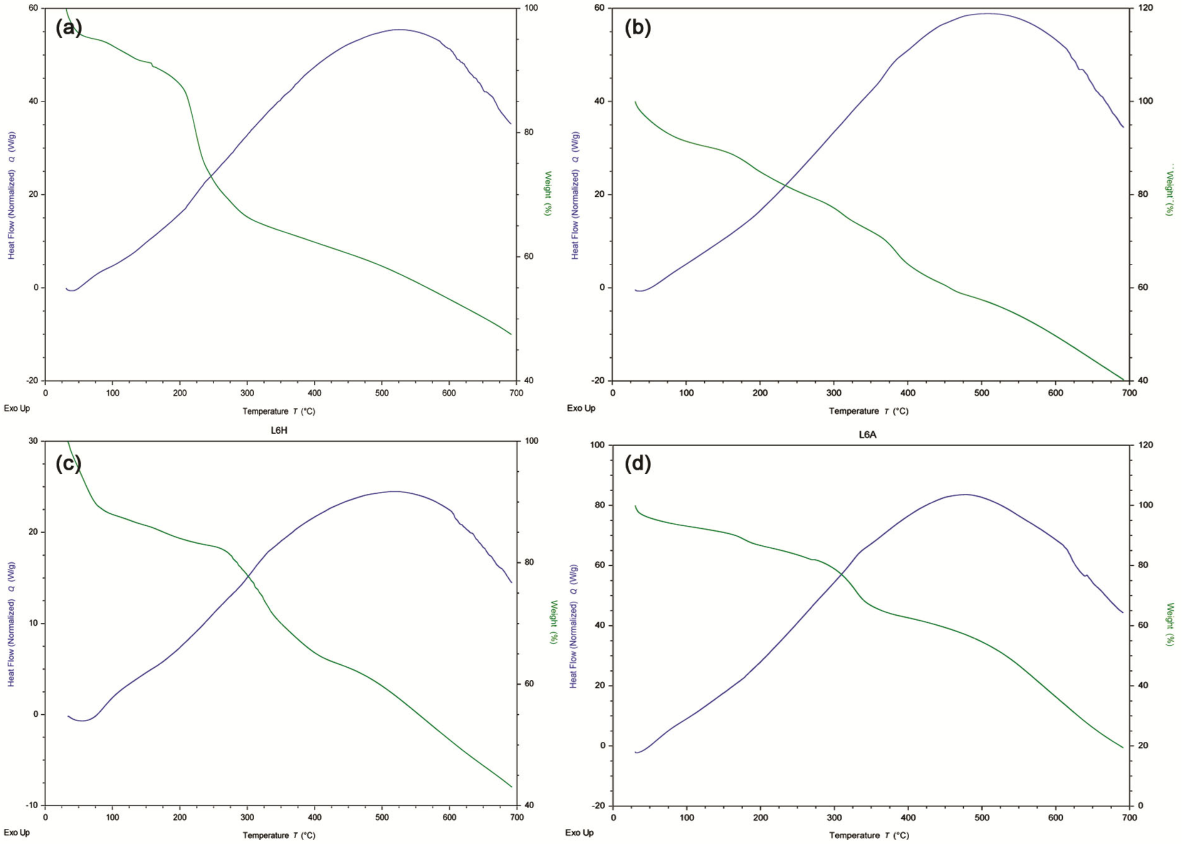


Fig. 5 — (a) TGA-Cu, (b) TGA–Co, (c) TGA- Zn, (d) TGA-Cd

Table 2 — Thermogravimetric analysis of the Schiff base ligand and metal complexes (M= Cu, Co, Zn, Cd)

Complex	Temperature range of decomposition (°C)	Wt. loss (%)	Assignment
Cu	110-450	35	Loss of 4 Br
	255-555	50.5	Formation of mixed metal oxide, CuO
Co	120-235, 250-670	25.55, 50.15	Loss of 4 Br with the formation of metal oxide CoO
Zn	70-200	35.53	Loss of Br
	290-600	45.30	Formation of mixed metal oxide, ZnO
Cd	170-300, 330-680	35.35, 45.10	Loss of Br and formation of CdO

Conclusion

In conclusion, we have reported the syntheses and structural characterizations of Schiff base ligand with N_2O_2 donor sites have been revealed as an excellent metal complexes of Cu(II), Co(II), Zn(II), Cd(II) mononuclear complexes. The spectral data of UV-Vis, IR, ^{1}H NMR and TGA have been obtained. On the basis of these data, tetrahedral geometry has been assigned to the complexes.

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