

Synthesis, characterization and thermal studies of transition metal complexes with O-, S-donor ligands

Abstract

Transition metal carboxylates have been synthesized with transition metal chlorides of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Ru(III). The binding ligands are 3-[(4-bromophenylamido)]propenoic acid (L) and diethyl dithiocarbamate. All these compounds have been characterized by elemental analyses, conductivity measurements, UV/Vis, FT-IR spectroscopy and thermal analysis. Semi empirical studies of three compounds have also been carried out for structural elucidation showing that the Cr and Co derivatives have a six coordinated octahedral geometry which is in accordance with the data obtained from elemental analysis, UV/visible and FTIR spectroscopy. Thermal studies of all synthesized derivatives were carried out in a temperature range of 50-1000°C under inert atmosphere. Their kinetic parameters, like activation energy, enthalpy, entropy and order of reaction, were also studied. All complexes decompose at a certain temperature leaving behind metal oxides as residual products. The synthesized complexes showed remarkable anti-bacterial activities with a few exceptions. Selected compounds were also investigated for DNAdamage assay. The interaction of selected metal derivatives with DNA and their binding strength were investigated by UV/vis spectroscopy. The increasing order is $[\text{CuL}(\text{H}_2\text{O})_2]\text{Cl} < [\text{RuLL}'(\text{H}_2\text{O})_2]\text{Cl} < [\text{FeL}(\text{H}_2\text{O})_4]\text{Cl}_2 < [\text{CuLL}' < 3\text{-}[(4\text{-bromophenylamido})]\text{propenoic acid}$.

Keywords: metal complexes, 3-[(4-bromophenylamido)]propenoic acid, diethyl dithiocarbamate, IR, UV, TG, biological activities

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Abbreviations: OC, open circular; SC, supercoiled; DNA: deoxyribonucleic acid; Cr, chromium; Mn, manganese; Fe: iron; Co, cobalt; Ni: nickel; Cu, copper; Ru: ruthenium; FTIR, fourier-transform infrared spectroscopy

Introduction

First row transition metal elements play important role in human life¹ and chemists are interested in co-ordination compounds for their application in industrial and synthetic processes, such as chemical, biological, environmental, ion-exchange catalysis, photochemistry, and biological applications. Moreover their thermal, spectral, microscopic and many other properties have also been examined.²⁻¹⁰

Metal carboxylates constitute an important class of compounds and receiving great attention due to their wide range of application in the field of biomedicine and catalysis in the recent years.¹¹ Literature shows that there are a wide variety of compounds of anions like dithiocarbamate, which have a corresponding mono thio analogue that is S,O bound.¹² Dithiocarbamates are usually made from sodium salts such as $\text{NaS}_2\text{CNMe}_2$ or by oxidations using thiram disulphides, they can also be made by insertion reactions of CS_2 with dialkyl amides. There is at present intense interest in the co-ordination of sulphur to metal ions, especially those of the *d*-transition series.¹³ Many of these complexes have unusual physical, chemical and structural properties. The *N,N*-diethyldithiocarbamate (dtc), has itself been widely used in the earlier transition metals¹⁴ in which, for example, the apparently simple complexes $M(\text{dtc})_2$ ($M(\text{II}) = \text{chromium, manganese, iron, copper and zinc}$) actually involve 5-co-ordination.¹⁵ They have been found to act as a uninegative bidentate ligand, coordinating through both sulfur atoms,¹⁶ and both four- and six-coordinated complexes of a number of transition metal ions have been isolated.¹⁷ Dithiocarbamates and their complexes with transition metals have been used as common pesticides, vulcanizing or analytical agents for decades.¹²

In continuation of our interest in the synthesis seven transition metals complexes of HL have been prepared and characterized for the first time. Further we intend to investigate the spectroscopic behavior and kinetics of these complexes.

Experimental

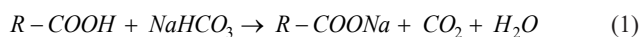
Materials and instrumentation

The organic solvents (ethanol, acetone, chloroform) were used of Merck, Germany origin and dried *in situ* using standard procedures.^{18,19} All chemicals were of analytical grade and used without further purification. All transition metal chlorides were procured from Aldrich or Fluka. 3-[(4-Bromophenylamido)]propenoic acid was prepared in laboratory as reported earlier.²⁰

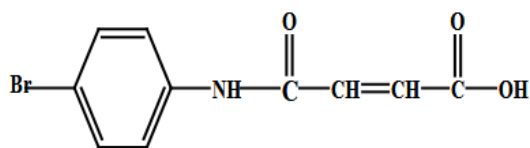
Melting points were obtained in a capillary tube using an electrothermal melting point apparatus Mitamura Rikero Kogyo, Japan. FT-IR spectra of the compounds were recorded as KBr discs in the range of $4000\text{-}250\text{cm}^{-1}$ on a Perkin-Elmer Spectrum; 1000 FT-IR Spectrophotometer. Atomic Absorption Spectra for transition metal estimations were recorded on an Analyst 300 of Perkin-Elmer. The conductance of the solutions of the complexes was determined from a 712 conductometer of Metrohm. Thermogravimetric analyses were carried out on a Perkin-Elmer, TGA-7 with computer interface. UV/visible spectra were recorded on a Lambda 2S of Perkin- Elmer.

Procedure for the synthesis of transition metal complexes

3-[(4-Bromophenylamido)]propenoic acid (1 mmol) was dissolved in anhydrous ethanol. Sodium bicarbonate (1 mmol) was dissolved in deionized water and was added drop wise to the ethanolic solution of the ligand acid with constant stirring, until a clear solution was obtained. The solvent was evaporated on rotary evaporator and dried over calcium chloride (anhydrous).



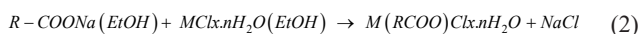
Where R =



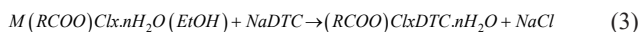
3-[(4-Bromophenylamido)]propenoic acid.

The sodium salt of the ligand acid (1mmol) was dissolved in anhydrous ethanol (250 mL) two-necked round bottom flask equipped with a water condenser and a magnetic stirrer bar. The transition metal chloride (1mmol) dissolved in ethanol was added drop by drop with constant stirring. The reaction mixture was refluxed for 3-4 hours in an inert atmosphere. The reaction mixture was allowed to stand overnight. Sodium chloride so formed was filtered off. The solvent was evaporated at room temperature. The solid mass left was recrystallized from a chloroform/*n*-hexane mixture (4:1). In the case of the Co complexes, 10 mL of 3% H₂O₂ was also added in the reaction mixture.

The solid compound obtained was dissolved with an equimolar amount of the sodium salt of diethyldithiocarbamate (NaDTC) in ethanol. The reaction mixture was firstly stirred and then refluxed for three hours. The sodium salt formed was filtered off and the solvent was evaporated at room temperature.

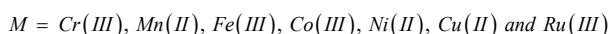


Reflux 3-4 hour.



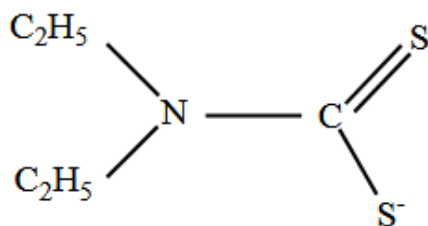
Reflux 3 hour.

Where



$x = 2, 3$ and $n = 2, 4, 6$.

DTC = Diethyldithiocarbamate



Results and discussion

3-[(4-Bromophenylamido)] propenoic acid is a brown odorless crystalline solid soluble in ethanol, methanol and acetone whereas insoluble in toluene and chloroform. It has the general formula C₁₀H₈NO₃Br and a melting point of 270°C. All newly synthesized compounds are semisolids. They are stable in air and are soluble in common organic solvents. The compounds have been characterized by IR and UV/Vis. spectroscopy to ascertain their structure and explore their properties. Selected complexes have also been screened for their biological activities and their interactions with DNA were

also studied. The physical data of the compounds are reported in the experimental part along with the syntheses of the individual compounds. The physical data of the synthesized complexes are given in Table 1. All the compounds show high melting points. Elemental (C, H and N) and metal analysis data show good agreement with the calculated and found values (Table 2).

UV/visible studies

The UV/Vis absorptions of the complexes have been examined in the region of 800-200nm with the object of ascertaining whether the spectra are compatible with those reported for the free ligand. The electronic spectra for the ligand and its metal derivatives were recorded in absolute ethanol and the results are described in Table 3. The sodium salt of 3-[(4-bromophenylamido)] propenoic acid does not show bands in the 400-800nm regions. The UV/Vis. spectra of the Cr and Co complexes exhibit octahedral geometry. The spectra of the manganese complexes suggest a tetrahedral structure whereas Ni complex exhibit a square planar geometry. The spectra of the Fe complexes show two absorption peaks that can be attributed to a distorted octahedral geometry. Copper complexes show one band which corresponds to the square planar stereochemistry of the complex. The ruthenium complexes show only the charge transfer bands of an octahedral geometry.

In almost all complexes, some bands are derived from inter ligand and charge transfer or $n \rightarrow \pi^*$ transitions with decreasing energies and intensities. The bands near 35087cm⁻¹ (285nm) and 37037cm⁻¹ (270nm) are assigned to inter ligand $\pi \rightarrow \pi^*$ transitions for the aromatic moiety of the ligand. Moreover, a few sharp absorption bands are observed in the region 41666cm⁻¹ (240nm) – 37037cm⁻¹ (270nm) in the spectra of the complexes which could be assigned to charge transfer L → M or $n \rightarrow \pi^*$ transitions.

Infrared spectroscopy

Infrared spectra of the investigated compounds, the ligand acid and the salt of the ligand acid have been recorded as KBr pellets in the range of 4000-250cm⁻¹. The IR spectra of the complexes were compared with the spectrum of free ligands to determine the changes that might have taken place during complexation. The important bands and assignments of ligands and their complexes are summarized in Table 4. In the 3500-2900cm⁻¹ region, ligand exhibit moderately intense bands typical of OH stretching vibrations, which were absent from the spectra of the complexes, indicating the coordination of a deprotonated COO⁻ group to the central metal atom. The C=O stretching vibrations of HL were observed at 1708cm⁻¹. The bands are intense and sharp. The difference between ν_{COO}^{asym} and ν_{COO}^{sym} is important in the prediction of the nature of the binding mode of the ligand.²¹⁻²³ The difference between the two vibration frequencies was in the range of 142-198cm⁻¹, suggesting a bidentate coordination mode of the COO⁻ in the complexes.²⁴ In all complexes, moderate to weak bands in the region of 425-495cm⁻¹ appear which are characteristic of M-O bond.

In the case of the diethyldithiocarbamate complexes with transition metals of 3-[(4-bromophenylamido)] propenoic acid, additional bands appear in the FT-IR spectra. A characteristic feature of the dialkyldithiocarbamate group is the C-N single bond stretching frequencies in amines in the region of 1250-1350cm⁻¹, close to the C-H deformation bands. A single sharp band of high intensity of C-S has been observed around 1000cm⁻¹, indicating the bidentate binding of the dithiocarbamate.²⁵ A band of medium intensity is characteristic for ν_{M-S} in the 505-445cm⁻¹ range indicating that the S atom has been coordinated to the metal atom.²⁶

Thermogravimetric assay

The thermal analysis of transition metal complexes was carried out by thermogravimetric technique. This technique also provides information about the kinetic parameters, such as order of reaction (n), activation energy (E*), enthalpy (ΔH^*) and entropy (ΔS^*) through the rate of decomposition of the reactants with the temperature as a function of time (20°Cmin^{-1}). The compounds were heated from ambient temperature to 1000 OC under inert atmosphere. The interpretation of the thermogram was done with the Horowitz and Metzger method [27,28] to find various kinetic parameters.

The ligand acid, 3-[(4-bromophenylamido)]propenoic acid (HL) decomposes in the temperature range of 190-310°C leaving traces of ash as residue with the order 0.92 and an activation energy of 10.43KJ/mole. The enthalpy of the reaction is 8.48KJ/mol and the entropy is -198.03J/molK. Most compounds show a single step decomposition behavior while in the case of mixed ligand, the decomposition pattern encompasses on two to three decomposition steps with different kinetic parameters. The results of the kinetic parameters are mentioned in Table 5.

Table 1 Physical data of Transition metal complexes of 3-[(4-Bromophenylamido)] propenoic acid and Diethyldithiocarbamate

Compound	Mol. Weight	Color	Yield (%)	Conductance $\mu\text{s/cm}$
HL	270	Dark brown	--	0.08
[CrL(H ₂ O) ₃ Cl]Cl	446.0	Green	93	53.3
[CrLL'(H ₂ O)Cl]	522.8	Green	71	32.6
[MnL(H ₂ O) ₂]Cl	395.5	Light yellow	96	64.1
[MnLL']	472.2	Brownish yellow	82	33.40
[FeL(H ₂ O) ₄]Cl ₂	467.9	Yellow	93	92.3
[FeLL'(H ₂ O) ₂]Cl	544.7	Dark yellow	80	42.90
[CoL(H ₂ O) ₂]Cl ₂	434.9	Purple	87	34.6
[CoLL'(H ₂ O)Cl]	529.7	Dark purple	77	24.50
[NiL(H ₂ O) ₂]Cl	399.2	Green	92	56.9
[NiLL']	476.0	Blackish green	73	33.84
[CuL(H ₂ O) ₂]Cl	404.1	Parrot green	92	52.3
[CuLL']	480.8	Blackish green	76	36.70
[RuL(H ₂ O) ₄]Cl ₂	513.1	Black	79	61.5
[RuLL'(H ₂ O) ₂]Cl	589.9	Black	68	45.5

L: 3-[(4-Bromophenylamido)]propenoic acid.

L': Diethyldithiocarbamate.

Table 2 Concentration of Metal, Carbon, Hydrogen and Nitrogen in Transition metal complexes of 3-[(4-Bromophenylamido)] propenoic acid and Diethyldithiocarbamate

Compound	Metal (%) Actual/Calc.	Carbon (%) Actual/Calc.	Hydrogen (%) Actual/Calc.	Nitrogen (%) Actual/Calc.
[CrL(H ₂ O) ₃ Cl]Cl	11.23/11.66	26.48/26.93	2.82/2.94	3.11/3.14
[CrLL'(H ₂ O)Cl]	10.01/9.95	33.38/34.46	3.82/3.66	4.91/5.36
[MnL(H ₂ O) ₂]Cl	15.01/13.89	31.48/30.37	2.12/2.80	3.82/3.54
[MnLL']	11.09/11.63	37.64/38.15	4.04/3.63	5.89/5.93
[FeL(H ₂ O) ₄]Cl ₂	11.52/11.94	25.17/25.67	2.91/3.23	2.68/2.99
[FeLL'(H ₂ O) ₂]Cl	10.34/10.25	33.06/33.08	3.63/3.89	5.29/5.14
[CoL(H ₂ O) ₂]Cl ₂	13.16/13.55	27.17/27.61	2.12/2.55	3.33/3.22
[CoLL'(H ₂ O)Cl]	10.96/11.12	33.45/34.01	3.19/3.62	5.22/5.29
[NiL(H ₂ O) ₂]Cl	14.39/14.70	29.52/30.08	2.27/2.78	3.53/3.51
[NiLL']	11.87/12.33	37.87/37.85	3.56/3.60	6.11/5.88
[CuL(H ₂ O) ₂]Cl	16.11/15.73	29.9/29.72	2.58/2.74	3.53/3.47
[CuLL']	13.91/13.21	38.02/37.46	3.65/3.56	5.70/5.83
[RuL(H ₂ O) ₄]Cl ₂	20.22/19.74	25.44/23.41	2.69/2.95	3.06/2.73
[RuLL'(H ₂ O) ₂]Cl	17.44/17.14	29.95/30.54	3.02/3.59	4.88/4.75

L: 3-[(4-Bromophenylamido)] propenoic acid.

L': Diethyldithiocarbamate.

Table 3 Absorption Pattern of Transition Metal Complexes of 3-[(4-Bromophenylamido)] propenoic acid and Diethyldithiocarbamate

Compound	λ cm ⁻¹ (nm)	Electronic Transition	Geometry
[CrL(H ₂ O) ₃ Cl]Cl	16452(608)	⁴ A _{2g} (F) → ⁴ T _{2g} (F)	Octahedral
	26984(371)	⁴ A _{2g} (F) → ⁴ T _{1g} (F)	
	34503(290)	⁴ A _{2g} (F) → ⁴ T _{1g} (P)	
[CrLL'(H ₂ O)Cl]	15921(628)	⁴ A _{2g} (F) → ⁴ T _{2g} (F)	Octahedral
	27818(360)	⁴ A _{2g} (F) → ⁴ T _{1g} (F)	
	29585(338)	⁴ A _{2g} (F) → ⁴ T _{1g} (P)	

Table Continued...

Compound	λ , cm ⁻¹ (nm)	Electronic Transition	Geometry
[MnL(H ₂ O) ₂]Cl	16129(620)	⁶ A _{1g} → ⁴ T _{1g}	Tetrahedral
	23310(429)	⁶ A _{1g} → ⁴ E _g ⁺ T _{1g}	
	31645(316)	⁶ A _{1g} → ⁴ E _g	
[MnLL']	15879(630)	⁶ A _{1g} → ⁴ T _{1g}	Tetrahedral
	24839(403)	⁶ A _{1g} → ⁴ E _g ⁺ T _{1g}	
	31435(318)	⁶ A _{1g} → ⁴ E _g	
[FeL(H ₂ O) ₄]Cl ₂	20325(492)	⁶ A _{1g} → ⁴ T _{1g} (G)	Octahedral
	24964(401)	⁶ A _{1g} → ⁴ T _{2g} (G)	
[FeLL'(H ₂ O) ₂]Cl	19527(512)	⁶ A _{1g} → ⁴ T _{1g} (G)	Octahedral
	25325(395)	⁶ A _{1g} → ⁴ T _{2g} (G)	
[CoL(H ₂ O) ₂]Cl ₂	16051(623)	¹ A _{1g} → ¹ T _{1g}	Octahedral
	23529(425)	¹ A _{1g} → ¹ T _{2g}	
[CoLL'(H ₂ O)]Cl	16260(615)	¹ A _{1g} → ¹ T _{1g}	Octahedral
	23041(434)	¹ A _{1g} → ¹ T _{2g}	
[NiL(H ₂ O) ₂]Cl	18734(534)	³ A _{2g} → ³ T _{1g} (F)	Square planner
	23809(420)	³ A _{2g} → ³ T _{1g} (P)	
[NiLL']	19834(504)	³ A _{2g} → ³ T _{1g} (F)	Square planner
	25189(397)	³ A _{2g} → ³ T _{1g} (P)	
[CuL(H ₂ O) ₂]Cl	25437(393)	² E _g → ² B _g	Square planner
[CuLL']	24890(402)	² E _g → ² B _g	Square planner
[RuL(H ₂ O) ₄]Cl ₂	43405(230)	CT	Octahedral
[RuLL'(H ₂ O) ₂]Cl	43925(228)	CT	Octahedral

L: 3-[(4-Bromophenylamido)]propenoic acid.

L': Diethyldithiocarbamate.

Table 4 IR spectral data (cm⁻¹) for the Transition Metal Complexes of 3-[(4-Bromophenylamido)]propenoic acid and Diethyldithiocarbamate

Compound	ν C=O	ν COO			ν N-H	ν C=S	ν C-N	ν M-O	ν M-S
		asym	sym	$\Delta\nu$					
HL	1708	1541	1389	152	3266	--	--	--	--
NaL'	1710	1587	1391	196	3258	--	--	--	--
[CrL(H ₂ O) ₃]Cl	1709	1597	1399	198	3257	--	--	482	--
[CrLL'(H ₂ O)]Cl	1711	1579	1394	185	3284	1007	1247	432	500
[MnL(H ₂ O) ₂]Cl	1739	1537	1353	184	3413	--	--	427	--
[MnLL']	1745	1580	1397	183	3264	1002	1270	428	505
[FeL(H ₂ O) ₄]Cl ₂	1710	1535	1393	143	3359	--	--	438	--
[FeLL'(H ₂ O) ₂]Cl	1716	1534	1392	142	3254	1012	1264	481	508
[CoL(H ₂ O) ₂]Cl ₂	1735	1544	1358	186	3257	--	--	448	--
[CoLL'(H ₂ O)]Cl	1712	1540	1395	145	3278	1008	1250	432	465
[NiL(H ₂ O) ₂]Cl	1741	1536	1355	181	3415	--	--	430	--
[NiLL']	1745	1542	1396	146	3324	1008	1247	431	445
[CuL(H ₂ O) ₂]Cl	1725	1536	1353	183	3413	--	--	425	--
[CuLL']	1711	1542	1392	150	3275	1009	1251	433	462
[RuL(H ₂ O) ₄]Cl ₂	1710	1536	1392	144	3254	--	--	495	--
[RuLL'(H ₂ O) ₂]Cl	1716	1544	1390	154	3250	1009	1249	450	489

L: 3-[(4-Bromophenylamido)] propenoic acid NaL': Sodium salt of diethyldithiocarbamate.

Table 5 Thermal Decomposition Pattern and Kinetic Parameters of Transition Metal Complexes of 3-[(4-Bromophenylamido)]propenoic acid and Diethyldithiocarbamate

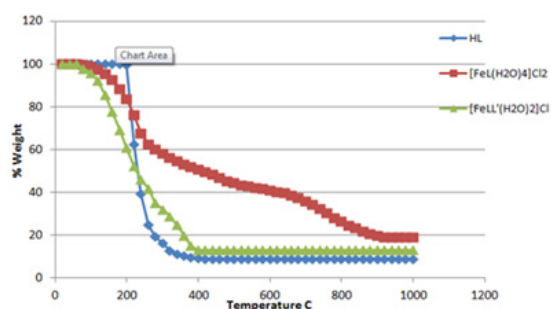
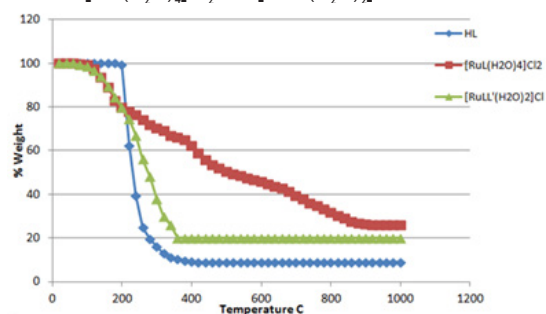
Compound	Temp. °C	Order (n)	E* kJ/mol	ΔH^* kJ/mol	ΔS^* J/molK	% wt. loss	
						cal.	obs.
HL	190-310	0.92	10.435	8.48	-198.03	--	973
[CrL(H ₂ O) ₃]Cl	90-900	1.13	10.15	7.70	-226.12	81.2	83.5
						18.8	16.5
[CrLL'(H ₂ O)]Cl	100-900	1.06	8.816	4.99	-272.37	83.9	84.8
						16.1	15.2
[MnL(H ₂ O) ₂]Cl	100-440	1.2	13.64	11.06	-199.4	48.5	46.5
						29.5	29.7
[MnLL']	700-900	0.95	139.3	132.3	107.05	22.0	23.8
						81.6	80.2
[FeL(H ₂ O) ₄]Cl ₂	100-900	1.01	6.01	4.35	-238.66	18.4	19.8
						39.2	40.0
[FeLL'(H ₂ O) ₂]Cl	90-280	1.06	12.91	11.09	-159.93	45.4	43.3
						300-900	1.06

Table Continued...

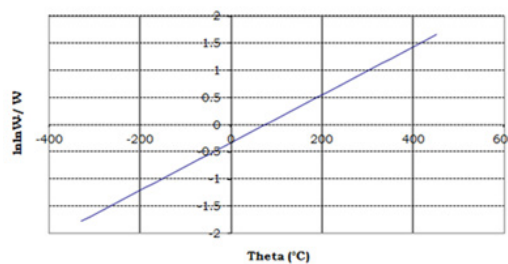
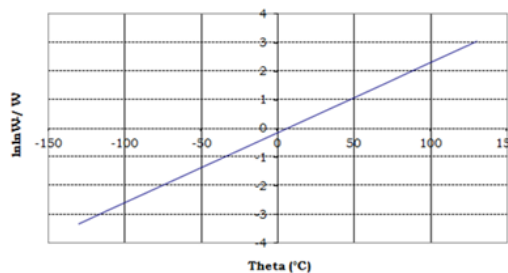
Compound	Temp. °C	Order (n)	E* kJ/mol	ΔH^* kJ/mol	ΔS^* J/molK	% wt. loss	
						cal.	obs.
[FeLL'(H ₂ O) ₂]Cl	100-900	1.02	6.86	5.16	-228.68	86.8 13.2	85.5 14.5
[CoL(H ₂ O) ₂ Cl ₂]	110-660	1.1	5.02	2.56	-279.7	80.4 17.2	81.7 18.3
[CoLL'(H ₂ O)Cl]	90-400	1.18	8.29	6.26	-227.7	45.4	44.4
	400-900	0.95	31.65	25.62	-200.09	40.5 14.1	39.2 16.4
[NiL(H ₂ O) ₂]Cl	90-700	1.18	6.64	3.89	-269.4	81.3 18.7	80.4 19.6
[NiLL']	60-550	1.01	5.65	3.48	-264	84.3 15.7	83.2 16.8
[CuL(H ₂ O) ₂]Cl	200-900	1.58	48.13	45.93	144.35	80.3 19.7	78.9 21.1
[CuLL']	100-500	1.07	6.17	4.09	-254.86	58.5	57.9
	700-900	0.92	126.47	119.49	69.82	25.0 16.5	24.8 17.3
[RuL(H ₂ O) ₄]Cl ₂	100-900	1.01	7.47	3.70	-281	73.4 22.8	76.1 23.9
[RuLL'(H ₂ O) ₂]Cl	90-340	1.22	10.80	8.88	-191.41	80.1 19.9	78.6 21.4

L: 3-[(4-Bromophenylamido)]propenoic acid.

L': Diethyldithiocarbamate.


Figure 1 Thermal decomposition pattern of 3-[(4-bromophenylamido)]propenoic acid, [FeL(H₂O)₄]Cl₂ and [FeLL'(H₂O)₂]Cl.

Figure 2 Thermal decomposition pattern of 3-[(4-bromophenylamido)]propenoic acid, [RuL(H₂O)₄]Cl₂ and [RuLL'(H₂O)₂]Cl.

All synthesized complexes decompose at higher temperature and left behind the oxides of the respective metals. The kinetic values described in Table 5 reflect the stability of the complexes against the given temperature. Figure 1 & 2 show the thermal behavior of compounds [FeL(H₂O)₄]Cl₂, [FeLL'(H₂O)₂]Cl and [RuL(H₂O)₄]Cl₂, [RuLL'(H₂O)₂]Cl respectively over the temperature range of 50-1000°C under inert atmosphere, whereas Figure 3 & 4 show the plots of θ vs. $\ln W^0/W$ for thermogravimetric analyses for decomposition of compounds [RuL(H₂O)₄]Cl₂, [RuLL'(H₂O)₂]Cl, respectively.


Figure 3 Plot of theta vs. $\ln W^0/W$ for thermogravimetric analysis for decomposition of [RuL(H₂O)₄]Cl₂.

Figure 4 Plot of theta vs. $\ln W^0/W$ for thermogravimetric analysis for decomposition of [RuLL'(H₂O)₂]Cl.

Biological activity

Antibacterial assay: 3-[(4-Bromophenylamido)]propenoic acid is capable of inhibiting bacterial growth and activity by interfering with the metabolic process in the bacteria. In the present work, the antibacterial activities of these complexes have been determined against four strains of bacteria (*Staphylococcus aureus* (ATCC 25923), *Bacillus subtilis* (DSM 3256), *Escherichia coli* (ATCC 25922), and *Pseudomonas aureginosa* (ATCC 10197)). Significant antibacterial activities were observed as compared to a standard drug. The metal complex [FeL(H₂O)₄]Cl₂ exhibited very good activity

against two bacteria *Staphylococcus aureus* and *Pseudomonas aureginosa* while it has relatively low activity against *Bacillus subtilis* and *Escherichia coli*. The metal complexes of [RuL(H₂O)₄]Cl₂ exhibited good activity against *Bacillus subtilis* and *Pseudomonas aureginosa*, while it showed moderate activity against *Staphylococcus aureus* and *Escherichia coli*. Compound [CuL(H₂O)₂]Cl showed good

activity against only *Staphylococcus aureus*, while it showed very low activities against all other three bacteria. The metal complexes [CuLL'] and [RuLL'(H₂O)₂]Cl showed moderate activity against all four bacteria, while [FeLL'(H₂O)₂]Cl are ineffective against all four bacteria. The results are described in Table 6 (Figure 5).

Table 6 Antibacterial Assay of Selected Transition Metal Complexes of 3-[(4-Bromophenylamido)]propenoic acid and Diethyldithiocarbamate

Std./ Compound	<i>S. aureus</i> ATCC 25923	<i>B. subtilis</i> DSM 3256	<i>E. coli</i> ATCC 25922	<i>P. aureginosa</i> ATCC 10197
	% Inhibition	% Inhibition	% Inhibition	% Inhibition
Imipenem	100(18 mm)	100(16 mm)	100 (18 mm)	100(21mm)
HL	24	11	31	22
[FeL(H ₂ O) ₄]Cl ₂	48	17	38	50
[FeLL'(H ₂ O) ₂]Cl	00	00	00	00
[CuL(H ₂ O) ₂]Cl	48	11	19	28
[CuLL']	24	28	25	33
[RuL(H ₂ O) ₄]Cl ₂	43	50	25	50
[RuLL'(H ₂ O) ₂]Cl	33	33	44	39

HL = L: 3-[(4-Bromophenylamido)]propenoic acid.

L': Diethyldithiocarbamate

Table 7 DNA Protection Activity of Transition Metal Complexes of 3-[(4-Bromophenylamido)]propenoic acid and Diethyldithiocarbamate

Compound	Concentration (ppm)	Protection	Damage
HL	1000	+++	-
	100	+++	-
	10	+++	-
[FeL(H ₂ O) ₄]Cl ₂	1000	-	+++
	100	-	+++
	10	+++	-
[FeLL'(H ₂ O) ₂]Cl	1000	+++	-
	100	+++	-
	10	+++	-
[CuL(H ₂ O) ₂]Cl	1000	-	+++
	100	+++	-
	10	+++	-
[CuLL']	1000	-	+++
	100	+++	-
	10	+++	-
[RuL(H ₂ O) ₄]Cl ₂	1000	-	++
	100	+++	-
	10	+++	-
[RuLL'(H ₂ O) ₂]Cl	1000	+++	-
	100	+++	-
	10	+++	-

L: 3-[(4-Bromophenylamido)]propenoic acid.

L': Diethyldithiocarbamate.

+: Weakly effective.

++: Moderately effective.

+++ : Strongly effective.

Table 8 Interaction of Transition Metal Complexes of 3-[(4-Bromophenylamido)]propenoic acid and Diethyldithiocarbamate with Different Concentrations of DNA

Compound	Absorbance of 1x10 ⁻³ M Compound at wavelength (nm)									
	Change in Absorbance and λ max of Compounds at Different Concentration of DNA									
	λ max (nm)	1.64 x 10 ⁻⁵ M (50μL of 1 x 10 ⁻³ M DNA)		3.23x10 ⁻⁵ M (100μL of 1x10 ⁻³ M DNA)		4.76x10 ⁻⁵ M (150μL of 1x10 ⁻³ M DNA)		6.25x 10 ⁻⁵ M (200μL of 1x10 ⁻³ M DNA)		
	λ _{max} (nm)	Abs.	λ _{max} (nm)	Abs.	λ _{max} (nm)	Abs.	λ _{max} (nm)	Abs.	λ _{max} (nm)	Abs.
HL	252	0.54003	252	0.50213	252	0.47504	252	0.45226	252	0.40847
	312	0.11095	312	0.10956	312	0.10752	312	0.10923	311	0.10562
[FeL(H ₂ O) ₄]Cl ₂	252	0.73363	252	0.68518	252	0.63952	252	0.60076	252	0.57015
[FeLL'(H ₂ O) ₂]Cl	252	0.74512	252	0.69617	252	0.64046	252	0.59320	252	0.54443
[CuL(H ₂ O) ₂]Cl	252	0.80019	252	0.750	252	0.70334	252	0.65667	252	0.61140
[CuLL']	252	0.64684	252	0.59471	252	0.55216	252	0.50975	252	0.46319
[RuL(H ₂ O) ₄]Cl ₂	252	0.57775	352	0.52640	252	0.48125	252	0.42849	252	0.39007
[RuLL'(H ₂ O) ₂]Cl	252	0.94813	252	0.88942	252	0.84698	251	0.79555	252	0.74472

L: 3-[(4-Bromophenylamido)]propenoic acid.

L': Diethyldithiocarbamate.

Table 9 The Association Constants and Gibbs Free Energies of Transition Metal Derivatives of 3-[(4-Bromophenylamido)]propenoic acid and Diethyldithiocarbamate

Compound	K/M ⁻¹	-ΔG/KJ mol ⁻¹
HL	127.4 × 10 ³	29.12
[FeL(H ₂ O) ₄]Cl ₂	26.31 × 10 ³	25.22
[FeLL'(H ₂ O) ₂]Cl	-18.22 × 10 ³	-
[CuL(H ₂ O) ₂]Cl	3.62 × 10 ³	20.30
[CuLL']	29.33 × 10 ³	25.49
[RuL(H ₂ O) ₄]Cl ₂	8.93 × 10 ³	22.54
[RuLL'(H ₂ O) ₂]Cl	25.87 × 10 ³	25.18

L: 3-[(4-Bromophenylamido)]propenoic acid.

L': Diethyldithiocarbamate.

Table 10 Bond angles (°) of [CrLL'(H₂O)Cl]

Atom1	Atom2	Atom3	Bond Angle (deg)	Atom1	Atom2	Atom3	Bond Angle (deg)
O2	Cr1	O23	63.2	O7	C6	C5	123.5
O2	Cr1	S24	104.8	N8	C6	C5	112.8
O2	Cr1	S26	161.9	C6	N8	C9	126.0
O2	Cr1	Cl42	86.7	C10	C9	N8	117.3
O2	Cr1	O43	90.5	C10	C9	C14	120.3
O23	Cr1	S24	161.7	N8	C9	C14	122.4
O23	Cr1	S26	105.4	C9	C10	C11	119.7
O23	Cr1	Cl42	86.4	C12	C11	C10	119.5
O23	Cr1	O43	90.7	C13	C12	C11	121.3
S24	Cr1	S26	82.3	C13	C12	Br17	119.4
S24	Cr1	Cl42	107.5	C11	C12	Br17	119.3
S24	Cr1	O43	75.0	C14	C13	C12	119.6
S26	Cr1	Cl42	107.4	C9	C14	C13	119.6
S26	Cr1	O43	75.0	C3	O23	Cr1	88.4
Cl42	Cr1	O43	176.6	Cr1	S24	C25	82.0
C3	O2	Cr1	88.5	S24	C25	S26	113.7
C4	C3	O23	121.8	S24	C25	N27	123.1
C4	C3	O2	120.0	S26	C25	N27	123.2
O23	C3	O2	118.2	Cr1	S26	C25	82.0
C5	C4	C3	121.5	C25	N27	C28	121.7
C6	C5	C4	123.2	C25	N27	C35	121.7
O7	C6	N8	123.7	C28	N27	C35	116.0
N27	C28	C29	111.7	N27	C35	C36	111.6

Table 11 Bond lengths (Å) of [CrLL'(H₂O)Cl]

Atom 1	Atom 2	Bond Length (Å)	Atom 1	Atom 2	Bond Length (Å)
O7	C6	1.21	Br17	C12	1.91
C6	N8	1.41	Cr1	O2	2.10
C6	C5	1.50	Cr1	O23	2.11
C5	C4	1.33	S24	Cr1	2.21
C4	C3	1.49	Cr1	S26	2.21
O23	C3	1.28	Cl42	Cr1	2.09
C3	O2	1.28	Cr1	O43	2.21
C10	C9	1.41	C25	S24	1.73
C9	N8	1.43	C25	S26	1.73
C9	C14	1.41	N27	C25	1.33
C14	C13	1.40	N27	C28	1.50
C13	C12	1.40	N27	C35	1.50
C12	C11	1.40	C35	C36	1.52
C11	C10	1.39	C28	C29	1.52

Table 12 Bond angles (°) of [CoL(H₂O)₂Cl₂]

Atom1	Atom2	Atom3	Bond Angle (°)	Atom1	Atom2	Atom3	Bond Angle (°)
O2	Co1	O23	62.2	N8	C6	C5	112.6
O2	Co1	Cl24	111.9	C6	N8	C9	126.1
O2	Co1	O25	166.4	C10	C9	N8	117.4
O2	Co1	Cl28	111.6	C10	C9	C14	120.1
O2	Co1	O29	66.5	N8	C9	C14	122.5
O23	Co1	Cl24	137.2	C9	C10	C11	119.8
O23	Co1	O25	105.2	C12	C11	C10	119.4
O23	Co1	Cl28	113.6	C13	C12	C11	121.4

Table Continued...

Atom1	Atom2	Atom3	Bond Angle (°)	Atom1	Atom2	Atom3	Bond Angle (°)
O23	Co1	O29	66.0	Cl3	Cl2	Br17	119.4
Cl24	Co1	O25	73.2	Cl1	Cl2	Br17	119.2
Cl24	Co1	Cl28	107.8	Cl4	Cl3	Cl2	119.6
Cl24	Co1	O29	73.0	C9	Cl4	Cl3	119.8
O25	Co1	Cl28	77.4	C3	O23	Co1	90.6
O25	Co1	O29	104.6	C5	C4	C3	121.4
Cl28	Co1	O29	178.1	C6	C5	C4	123.4
C3	O2	Co1	87.9	O7	C6	N8	123.1
C4	C3	O23	117.6	O7	C6	C5	124.3
C4	C3	O2	124.0	O23	C3	O2	118.4

Table 13 Bond lengths (Å) of [CoL(H₂O)₂Cl₂]

Atom 1	Atom 2	Bond Length (Å)	Atom 1	Atom 2	Bond Length (Å)
O7	C6	1.21	Cl2	Cl1	1.40
C6	N8	1.42	Cl1	Cl0	1.39
C6	C5	1.50	Br17	Cl2	1.91
C5	C4	1.33	Co1	O2	2.17
C4	C3	1.50	Co1	O23	2.09
O23	C3	1.30	Cl24	Co1	2.43
C3	O2	1.26	Co1	O25	2.14
Cl0	C9	1.41	Cl28	Co1	2.27
C9	N8	1.43	Co1	O29	2.15
C9	Cl4	1.41	Cl3	Cl2	1.40
Cl4	Cl3	1.39			

Table 14 Bond angles (°) of [CoLL'(H₂O)Cl]

Atom1	Atom2	Atom3	Bond Angle (°)	Atom1	Atom2	Atom3	Bond Angle (°)
O2	Co1	O23	64.3	N8	C6	C5	112.5
O2	Co1	S24	108.4	C6	N8	C9	126.3
O2	Co1	S26	171.7	Cl0	C9	N8	116.8
O2	Co1	Cl42	76.9	Cl0	C9	Cl4	119.0
O2	Co1	O43	103.7	N8	C9	Cl4	124.2
O23	Co1	S24	171.2	C9	Cl0	Cl1	119.6
O23	Co1	S26	109.0	Cl2	Cl1	Cl0	119.7
O23	Co1	Cl42	76.6	Cl3	Cl2	Cl1	121.7
O23	Co1	O43	103.9	Cl3	Cl2	Br17	118.2
S24	Co1	S26	77.7	Cl1	Cl2	Br17	120.1
S24	Co1	Cl42	107.3	Cl4	Cl3	Cl2	119.4
S24	Co1	O43	72.4	C9	Cl4	Cl3	120.6
S26	Co1	Cl42	107.0	C3	O23	Co1	87.9
S26	Co1	O43	72.5	Co1	S24	C25	87.9
Cl42	Co1	O43	179.3	S24	C25	S26	106.2
C3	O2	Co1	88.3	S24	C25	N27	126.9
C4	C3	O23	122.4	S26	C25	N27	126.9
C4	C3	O2	119.4	Co1	S26	C25	87.9
O23	C3	O2	118.2	C25	N27	C28	121.3
C5	C4	C3	121.8	C25	N27	C35	121.3
C6	C5	C4	123.5	C28	N27	C35	116.8
O7	C6	N8	122.6	N27	C28	C29	111.9
O7	C6	C5	125.0	N27	C35	C36	111.9

Table 15 Bond lengths (Å) of [CoLL'(H₂O)Cl]

Atom 1	Atom 2	Bond Length (Å)	Atom 1	Atom 2	Bond Length (Å)
O7	C6	1.21	Br17	Cl2	1.90
C6	N8	1.43	Co1	O2	2.06
C6	C5	1.49	Co1	O23	2.07
C5	C4	1.33	S24	Co1	2.19
C4	C3	1.50	Co1	S26	2.19
O23	C3	1.28	Cl42	Co1	2.47
C3	O2	1.28	Co1	O43	2.31
Cl0	C9	1.49	C25	S24	1.72
C9	N8	1.39	C25	S26	1.72
C9	Cl4	1.44	N27	C25	1.33
Cl4	Cl3	1.35	N27	C28	1.50
Cl3	Cl2	1.46	N27	C35	1.50
Cl2	Cl1	1.41	C35	C36	1.52
Cl1	Cl0	1.37	C28	C29	1.52

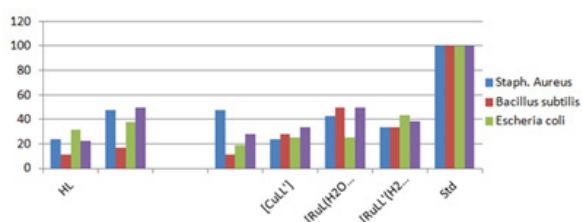


Figure 5 Graphical representation of antibacterial activity of selected compounds against four types of bacteria.

H₂O₂ induced DNA damage assay: Antioxidant and pro-oxidant effects of all synthesized compounds were investigated *in vitro* by using a DNA protection assay. With the attack of hydroxyl radicals generated in the Fenton reaction, if scission occurs on one strand (single stranded nicking) of plasmid DNA, the supercoiled (SC) form will be relaxed to generate a slower-moving open circular (OC) form. If both strands of the plasmid DNA are cleaved (double stranded nicking), a linear form that migrates between the open circular form and the supercoiled form will be generated. Thus, the ability of the test compounds to unwind or condense a supercoiling substrate such as a plasmid DNA was examined. In the present study, it was found that compounds [FeL(H₂O)₄]Cl₂, [CuL(H₂O)₂]Cl and [CuLL'] enhanced DNA damage and completely converted the supercoiled DNA into the linear and open circular forms.²⁹ Most compounds enhanced the DNA damage at 1000ppm concentrations as compared to lower concentrations (10, 100ppm) (Table 7). 3-[(4-Bromophenylamido)]propenoic acid protected the plasmid DNA at all concentrations (10, 100, 1000ppm). This conclusion was deduced by the disappearance or reduction in the initial quantity of DNA (Figure 6-8).

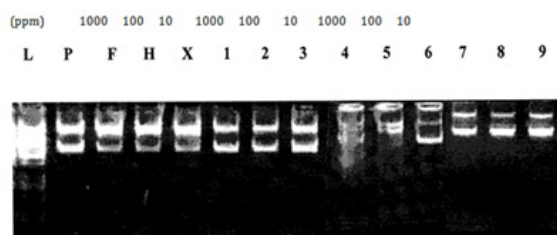


Figure 6 Effect of HL (1-3); compound [FeL(H₂O)₄]Cl₂ (4-6) and compound [FeLL'(H₂O)₂]Cl (7-9) on pBR322 plasmid DNA.

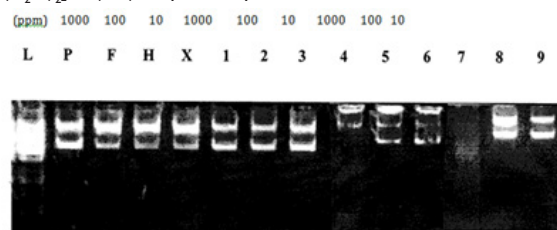


Figure 7 Effect of HL (1-3), compound [CuL(H₂O)₂]Cl (4-6) and compound [CuLL'] (7-9) on pBR322 plasmid DNA.

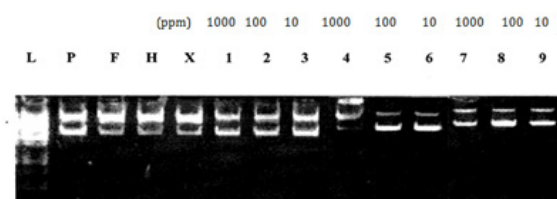


Figure 8 Effect of HL (1-3), compound [RuL(H₂O)₄]Cl₂ (4-6) and compound [RuL(H₂O)₄]Cl₂ (7-9) on pBR322 plasmid DNA.

L: IKB Ladder
 P: pBr 322 Plasmid
 F: pBr 322 Plasmid treated with FeSO₄
 H: pBr 322 Plasmid treated with H₂O₂
 X: pBr 322 Plasmid treated with FeSO₄ & H₂O

DNA interaction by UV/visible spectroscopy: The interactions of selected transition metal derivatives of 3-[(4-bromophenylamido)]propenoic acid and diethyldithiocarbamate were also examined by UV-Vis. spectroscopy in order to study the mode of binding with DNA. The hypochromic effect is observed in all cases, which is caused by the overlapping of electronic states of the chromophores of the complexes with DNA bases (Table 8). The binding constants were calculated according to the Benesi-Hildebrand equation.³⁰ The slope to intercept ratio of the plot between $A_0/(A - A_0)$ versus $1/[DNA]$ gives the binding constants. The plot between $A_0/(A - A_0)$ versus $1/[DNA]$ for the complex [CuL(H₂O)₂]Cl is shown in Figure 9 whereas the values of binding constants for the rest of the complexes is given in Table 9.

Constant of [CuL(H₂O)₂]Cl - DNA adduct

Semi empirical study: Semi empirical studies of selected compounds were conducted in which the molecules in the gas phase were modeled by a MOPAC 2007³¹ program using PM6 method.³² Selected parts of the complexes not containing the metal ion were pre optimized using molecular mechanics methods. Several cycles of energy minimizations had to be carried out for each of the molecules. The molecular mechanics correction was applied to the -Co-NH- barrier. The geometry was optimized using Eigen Vectors. The Root Mean Square Gradients for molecules were all less than one. Self Consistent Field was achieved in each case (Figure 10).

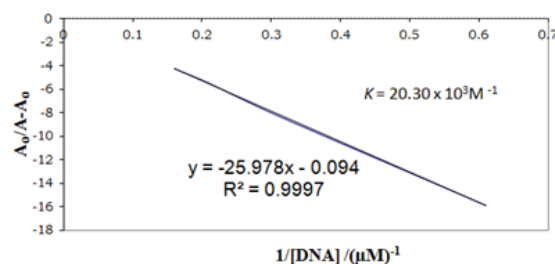


Figure 9 Plot of $A_0/(A - A_0)$ vs. $1/[DNA]$ for the determination of binding constant of [CuL(H₂O)₂]Cl - DNA adduct.

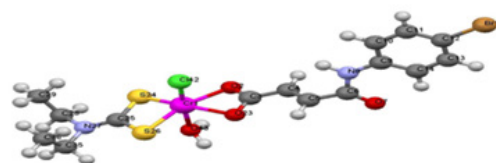


Figure 10 Optimized structure of [CrLL'(H₂O)Cl].

Semi Empirical Study of [CrLL'(H₂O)Cl]: The diethyldithiocarbamate and 3-[(4-bromophenylamido)]propionate ligands bind through the sulphur and oxygen atoms in the equatorial plane. The S-Cr-S angle is 82.3 deg while the O-Cr-O angle is 63.2 deg. The computed Cr-S distance is 2.21Å³³ and Cr-O (lig) distance is 2.10Å.³⁴ The apical position is occupied by a chloride ion and a water molecule occupies the other axial position and completes the coordination sphere of the chromium ion. The computed Cr-Cl distance is 2.09³⁵ while the Cr-O(H₂O) is 2.11Å.³⁶ In the dithiocarbamate

ligand the S-C bond length is 1.73 Å.³⁷ The Cl-Cr-O(H₂O) angle is 176.6 deg. The chromium ion is 0.29 Å above the mean plane of the S₂O₂ coordinating plane. The bond angles and bond lengths are given in the Tables 10 & 11 (Figure 11).

Semi empirical structure of [CoL(H₂O)₂Cl₂]: The diethyldithiocarbamate ligand binds to cobalt through the carboxylate oxygen atoms in the equatorial plane. The O-Co-O angle is 62.2°. The computed Co-O distances are 2.08 and 2.17 Å.³⁸ The other two equatorial sites are occupied by a water molecule and a Cl ion. The apical position is occupied by a chloride ion and a water molecule occupies the other axial position and completes the distorted octahedral coordination sphere of the cobalt ion. The computed Co-Cl distance is 2.27, 2.43 Å,³⁹ while the Co-O(H₂O) 2.14, 2.15 Å.³⁸ The Cl-Co-O(H₂O) angle is 178.1°. The cobalt ion is 0.5 Å above the mean plane equatorial plane. The bond angles and bond lengths are given in the Tables 12 & 13, respectively (Figure 12).

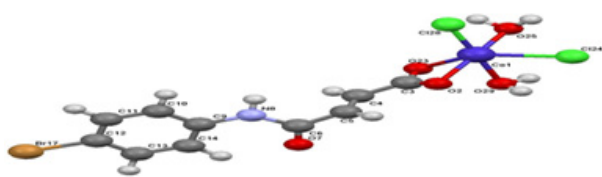


Figure 11 Optimized structure of [CoL(H₂O)₂Cl₂].

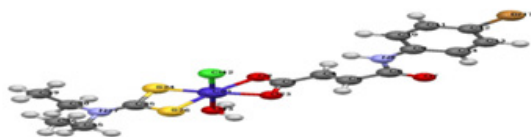


Figure 12 Optimized structure of [CoLL'(H₂O)Cl].

Semi Empirical Structure of [CoLL'(H₂O)Cl]: The diethyldithiocarbamate and 4-bromoanilinopropenoate ligands bind through the sulphur and oxygen atoms in the equatorial plane. The S-Co-S angle is 77.7°, while the O-Co-O angle is 64.3°. The Co-S distance is 2.19 Å⁴⁰ and the Co-O (lig) distance is 2.06 Å.³⁸ The apical position is occupied by a chloride ion and a water molecule occupies the trans axial position and completes the coordination sphere of the chromium ion. The Co-Cl distance is 2.47,³⁹ while the Co-O(H₂O) 2.31 Å.³⁸ The Cl-Co-O(H₂O) angle is 179.3°. The cobalt ion is 0.1 Å above the mean plane of the S₂O₂ coordinating plane. The bond angles and bond lengths are given in the Table 14 & 15 respectively.

Transition metal derivatives have been synthesized in quantitative yields by refluxing carboxylic acids and respective transition metal chlorides in dry ethanol. The FT-IR spectra clearly demonstrate that the [O,O] binding sites of the ligand coordinate to the metal and behave as bidentate ligands. Moreover, the appearance of new peaks in the region of 500-400 cm⁻¹ is due to M-O stretching mode which confirms that the metal has coordinated to the ligand. Semi empirical studies of complexes show that the Cr and Co derivatives are six coordinated, imparting octahedral geometry which is in accordance with the structure proposed by other spectroscopic results. Decomposition reactions of the complexes occur in one, two or three steps leaving only the metal oxide as residual product at 900-1000°C. Kinetic studies of all complexes indicate first order reactions. The activation energies for the first step is less compared with the second step. The same trend is valid for the enthalpy of the reactions. Biological activity data show that all complexes are biologically active with a few exceptions. Cu and Fe complexes of 3-[(4-bromophenylamido)]propenoic acid destroy DNA a little at

higher concentrations whereas the Ru complex protects it. It can be assumed that after testing against various other cancer models and at different doses these compounds may prove to be safer anticancer drugs for tomorrow. 4-Bromoanilinopropenoic acid showed more binding strength with DNA as compared to its metal derivatives. The increasing order is [CuL(H₂O)₂]Cl < [RuLL'(H₂O)₂]Cl < [FeL(H₂O)₄]Cl₂ < [CuLL' < 3-[(4-bromophenylamido)]propenoic acid.

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Conflicts of Interest

None.

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