



Transition Metal Chelates of 2-[(2, 6-dichlorophenyl)-amino] Benzene Acetic Acid: Synthesis, Spectral Characterization and Antimicrobial Studies

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INTRODUCTION

Several aromatic carboxylic acids and metal Carboxylate complexes are known to have antibacterial and antifungal properties^{1,2}. Transition metal complexes of carboxylate anions can adopt a wide range of bonding modes including monodentate, symmetric and asymmetric chelating and bidentate and monodentate bridging³ and they are reported to play an important role in biochemistry⁴. Among these, acetates, benzoates and salicylates have attracted considerable interest from structural and biological viewpoints⁵⁻⁹. Structural diversity observed in metal carboxylates has significant influence of the preparation route on the structure of the final product¹⁰.

In view of the biochemical activity of transition metal carboxylates is influenced by the molecular structure and coordination status of the metal ion¹¹⁻¹², synthesis of transition metal chelates of 2-[(2,6-Dichlorophenyl)amino]benzene acetic acid (DAPA)(Fig. 1.) would be beneficial.

Synthesis of metal chelates

Calculated amounts of metal chlorides and ligand DAPA were separately dissolved in ethanol to obtain 0.1M solutions and then clear solutions were mixed in stoichiometric amounts. pH of the mixture was adjusted 6.0 to 7.0 by adding ammonia buffer and resultant mixtures were refluxed on water bath for about 1 to 2 and half hours and allowed to cool. Solid mass separated at the end was separated after digestion, washed with water and ethanol, dried and stored.

RESULTS AND DISCUSSION

Physico-chemical analysis

Complexes are sparingly soluble in DMSO/DMF, solvents, have high thermal stability at normal conditions¹⁴. Molar conductivity recorded in DMSO (Λ_m 6.3 to 7.2 $\Omega^{-1}\text{cm}^2$) is too low to account for dissociation reveals non electrolytic nature¹⁵. Magnetic moments (Table. 1) in the range 1.7 to 4.9 B.M. indicate square planar environment around copper and octahedral environment around cobalt and chromium complexes.

Electronic spectra

Ligand DAPA exhibits strong absorption band in the range of 48780 to 49751 cm^{-1} and a sharp peak at 32468 cm^{-1} because of intramolecular charge transfer $n \rightarrow \pi$, $\pi \rightarrow \pi^*$ within the ligand molecule. Electronic spectra of complexes under study exhibit new bands that do not resemble with free ligand support complex formation. In chromium complex, absorption bands at 25641 cm^{-1} and 15625 cm^{-1} and 17241 cm^{-1} are assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}$, ${}^4T_{2g} \rightarrow {}^4A_{2g}$ transitions¹⁶⁻¹⁷, in cobalt complex bands at 20833 cm^{-1} , 15625 cm^{-1} and 12500 cm^{-1} assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions¹⁵⁻¹⁹. In copper complex absorption at 14925 cm^{-1} is assignable to ${}^2B_{1g} \rightarrow {}^2A_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions^{20, 21}. Shifts in absorption bands, appearance of new bands and increase in molar absorptivity infer the involvement of metals in bonding with ligand.

Infra red spectra

ligand DAPA exhibits strong symmetric stretching at 3434 cm^{-1} due carboxylic, νOH asymmetric stretching at 3232 cm^{-1} for νNH , at 1629 cm^{-1} for $\nu\text{C}=\text{O}$, at 1287 cm^{-1} for $\nu\text{C}-\text{N}$ and at 1069 cm^{-1} $\nu\text{C}-\text{N}$ (ring)²⁵⁻²⁷. On complexation, νOH has been shifted to higher or lower wave number region and turned weak. δNH has disappeared, $\nu\text{C}=\text{O}$ and $\nu\text{C}-\text{N}$ have shifted to lower wave number. Deprotonation of-NH moiety due to involvement in coordination²⁸, bonding of acetate group via ketone²⁹⁻³¹ may be responsible for observed shifts. This has been supported by the appearance of new vibrations $\nu\text{M}-\text{O}$ and $\nu\text{M}-\text{N}$ that are absent in free ligand³⁵⁻³⁵. In copper complex bands at ($\nu\text{M}-\text{O}$) 528 cm^{-1} and ($\nu\text{M}-\text{N}$) 509 cm^{-1} have appeared. In cobalt complex shift in wave length can be

Table 1: physico-chemical parameter of DAPA metal complexes

Compound	%CCal(obs)	%HCal(obs)	%NCal(obs)	%MCal(obs)	Cl%	Magnetic moments $\mu\text{B.M.}$	Molar conductivity $\Lambda_m \Omega^{-1}\text{cm}^2$	Transitions observed
DAPA	56.78	3.74	4.73	-	-	-	-	$\pi \rightarrow \pi^*$ Transition
[Cr(DAPA)(H ₂ O) ₂ .Cl]Cl	40.17 (40.98)	3.37 (2.38)	3.35 (3.40)	12.42 (14.82)	-	3.91	6.3	Charge transfer ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}$ ${}^4T_{2g} \rightarrow {}^4A_{2g}$ transitions
[Co(DAPA)I(H ₂ O) ₂]	39.51 (40.7)	3.32 (3.18)	3.29 (3.40)	13.85 (13.80)	7.8	4.92	6.3	Charge transfer ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions
Cu(DAPA)Cl] 2H ₂ O	38.96 (39.88)	2.55 (2.08)	3.24 (4.17)	14.7 (13.83)	-	1.77	7.2	Charge transfer ${}^2B_{1g} \rightarrow {}^2A_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions

observed, the strong NH stretching at 3232cm^{-1} has disappeared in cobalt and chromium complexes suggesting that the ligand has coordinated to metal through secondary amine and carboxylic acid

Table 2: Significant IR wave numbers involved in coordination of DAPA complexes

Compound	VO-H (sym) cm^{-1}	VNH(asy) cm^{-1}	VC=O cm^{-1}	VC-N bend cm^{-1}	VC-N(ring) cm^{-1}	VM-O	VM-N
DAPA	3434	3232	1629	1287	1069	—	—
[Cr(DAPA)(H ₂ O) ₂ .Cl]Cl	3413	—	1631	1394	1111	518	466
[Co(DAPA) Cl(H ₂ O)]	3435	—	1577	1284	1047	544	510
[Cu(DAPA)Cl] 2H ₂ O	3536	3437	1577	1283	1093	528	509

Table 3: EPR parameters for ligand DAPA and metal complexes.

Complex	Gyrometric ratio	A (gauss)	Exchange interaction coupling constant G	Electrons per gram e/gm X 10 ²¹
[Cr(DAPA)(H ₂ O) ₂ .Cl]	g 1.844 g 1.850 g _{av} 1.848	A 150 A [⊥] 100 A _{iso} 116	1.040	1.41
[Co(DAPA) Cl(H ₂ O) ₂]	g 1.743	-	-	1.49
[Cu(DAPA)Cl]2H ₂ O	g 1.855	-	-	1.43

Table 4: Thermal decomposition and kinetic parameters of complexes

Complex	DTA peak °C	Temp Range °C	Order of reaction	Activation energy E _a KJ/Mole	Entropy change Δs J/K/Mole	Free energy of activation G KJ/Mole	Frequenc y factor Z/S
[Cr(DAPA)(H ₂ O) ₂ .Cl]Cl	341.15(+)	50 -625	1	9.36	-269.46	36.85	0.1494
[Co(DAPA) Cl(H ₂ O) ₂]	106.41(-)	30-110	2	22.88	-204.67	150.47	2.09
	200(+)	110-265	1	27.19	-221.72	39.82	25.826
	300 (+)	265-555	1	13.96	-254.07	32.84	0.3936
	815(-)	555-850	1	12.50	-296.11	51.42	0.0078
[Cu(DAPA)Cl] 2H ₂ O	110 (+)	50-155	2	11.15	-270.8	24.27	0.0605
	200(-)	155-250	2	38.35	-217.96	40.75	40.82
	530(-)	250-630	1	44.93	-330.67	74.48	8.33

groups. This has been evidenced by the appearance new bands ν_{M-O} and ν_{M-N} at 544cm^{-1} , 510cm^{-1} , in cobalt and at 518cm^{-1} and 466cm^{-1} , in chromium complex. Thus ligand DAPA exhibits binategative tridentate behavior and coordinates to the metal through secondary amine, chloride and carboxylic acid group. Significant changes of wave numbers involved in coordination of ligand DAPA and metal complexes are shown in Table 2.

¹HNMR spectra

¹HNMR spectrum of ligand shows peaks at δ 2.08 ppm corresponding to methyl proton, at δ 6.40 ppm due to Ar-C=O and at δ 4.0 ppm for Ar-NH. On complexation signals due to Ar-NH and methine proton have disappeared³⁵⁻³⁷ and peak corresponding to Ar-H has been shifted to deshielded region³⁵. Disappearance of peak for Ar-NH may be due to change in-NH moiety on involvement in bonding with metals to form complexes. Involvement of acetate group in bonding may be the reason for disappearance of methyl peak and shifting of Ar-H signal to the deshielded region. Besides this small peaks corresponding to coordinated water in chromium and cobalt complexes were observed at δ 2.0 ppm³⁹.

EPR Spectra

In chromium and cobalt complexes Sharp peaks indicate negligible distortion³⁶ where as broad signal in copper complex reveals distorted environment. Chromium complex (Fig. 2.) with a maximum at 3000 gauss suggests antistrophic nature, broadening of peak reveals distorted geometry of the complex. Presence of water

molecules in coordination can induce distortions and broadening of spectral lines are expected. Gyrometric ratio 'g' is a function of covalency, if it is greater than 2.3, metal is in ionic environment and if it is less than 2.3 metal ions will be predominantly in covalent atmosphere^{39,40}. g_{\parallel} and g_{\perp} (Table3) are found to be 1.844 and 1.850 and 'G' the exchange interaction coupling constant is 1.04 suggests strong exchange interactions. $g_{\parallel} > g_{\perp}$ and lower g_{av} values suggests covalent nature of the tetragonally elongated metal ligand bond and probability of unpaired electron being occupied in $d_{x^2-y^2}$ orbital^{37,38}. cobalt complex exhibits a peak around 3600 gauss on negative side having very low 'g' value. However this peak is not well resolved and isotropic or anisotropic nature can not be specified, Copper complex exhibits a sharp anisotropic peak at around 3350 Gauss on positive side with. 'g' = 1.855 and $e/gm = 1052 \times 10^{21}$.

Thermal analysis

In chromium complex (Fig 3) gradual and steady decomposition of the complex exothermically in the range of 50 to 625°C is observed. Decomposition seems to be activated at 341°C converting the complex into metal oxide residue at above 625°C. The amount of chromium observed in residue (14.82%) is in agreement with that of calculated (14.42%). Cobalt complex decomposed in four steps of which two are endothermic while other two are exothermic. Lattice water eliminated at around 110°C. Chlorides might be removed at above 200°C exothermically, while benzyl part seems to be expelled out from the complex at around 300°C. Decomposition

Table 5: Antibacterial activity of DAPA metal complexes

Sample	<i>E. Coli</i>		<i>S. typhi</i>		<i>S. aureus</i>		<i>B. subtilis</i>	
	Inhibition zone in mm	Activity index	inhibition zone in mm	Activity index	Inhibition Zone in mm	Activity index	Inhibition zone in mm	Activity index
DAPA	14	127	18	112	14	116	32	114
CuDAPA	20	181	20	125	18	150	34	121
CrDAPA	23	209	26	162	22	183	39	139
coDAPA	16	145	20	125	16	133	32	114
Control	11	-	16	-	12	-	28	-
Penicillin	-ve	-	-ve	-	-ve	-	-ve	-

completes at about 800°C leaving residue of cobalt oxide as end product. Mass of cobalt in residue as observed in TG (13.8%) is in close agreement with calculated value (13.85%). The Cu(DAPA) complex shows three peaks, first one is corresponding to exothermic removal of water molecules at 110°C and other two at 200°C and 530°C due to partial decomposition of ligand molecule. Complex is

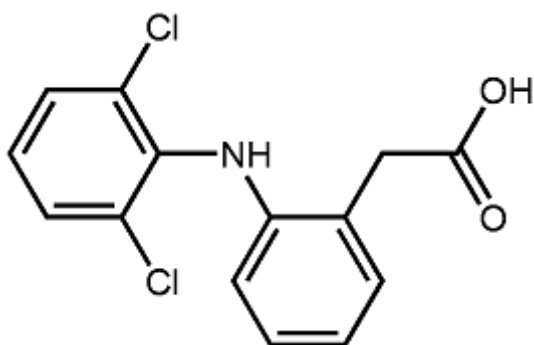


Fig. 1: 2-[(2,6-Dichlorophenyl) amino] benzene acetic acid (DAPA)

completely decomposed at a temperature of 630°C leaving the residue of copper oxide. Calculated mass of Cu (14.7%) is in resemblance with observed mass of Cu in residue observed (13.83%).

Thermal data of the complexes are subjected to analysis for non isothermal kinetic parameters (Table 4.) as per Coats Redfern

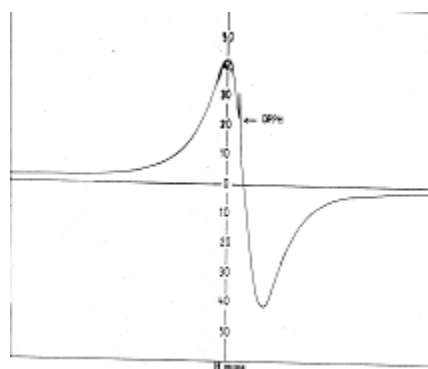


Fig. .2: EPR spectrum of complex $[\text{Cr}(\text{DAPA})(\text{H}_2\text{O})_2]\text{Cl}$

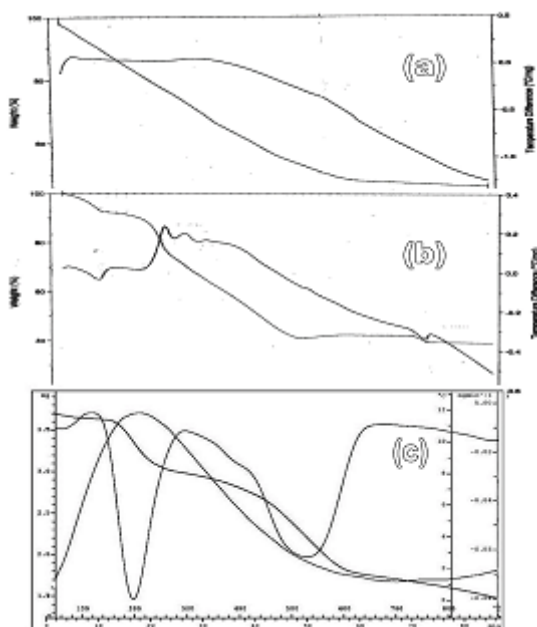


Fig. 3: TG/DTA scans of (a) $[\text{Cr}(\text{DAPA})(\text{H}_2\text{O})_2]\text{Cl}$, (b) $\text{Co}(\text{DAPA})\text{Cl}(\text{H}_2\text{O})_2$, (c) $[\text{Cu}(\text{DAPA})\text{Cl}] 2\text{H}_2\text{O}$

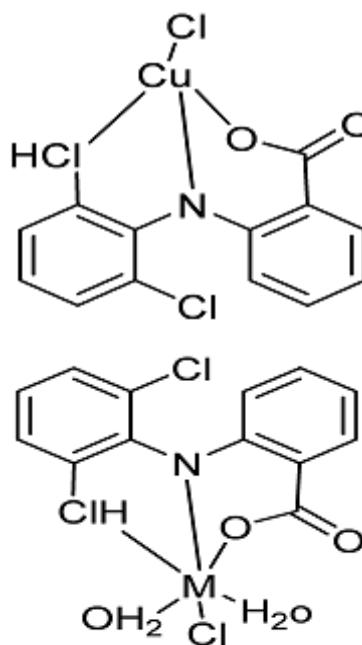


Fig. 4: proposed structures of complexes where M = Co(II) and Cr(III)

equation⁴³. In chromium complex first step differ from remaining three and in general, decomposition of complex followed first order kinetics while Cobalt and copper complexes reveal second order kinetics. Change in entropy and free energy values are nearly same in all the three steps suggesting that the activated complex has more ordered structure⁴⁷. Frequency factors are abnormal indicating that decomposition process is slow⁴⁸. Order of reaction suggests second order kinetics and decomposition of complexes at elevated temperature is a complex process⁴⁷. Energy of activation reveals stability of DAPA complexes in the order as Cu (II) > Co (II) > Cr (III)⁴⁷.

X-Ray analysis

Powder X-ray diffraction diffractions of the complexes are obtained from D₈ advance X-ray spectrophotometer using CuK α radiation source at a wavelength of 1.5407 Å within the 2 θ range of 10 to 90° at a room temperature. The interplanar distance 'd' is then obtained from major reflexes. Independent indexing, calculation of miller indices and evaluation of lattice parameters is followed by powder X computer programme. Unit cell volume and percent porosity of the complexes is then calculated by standard formulae⁵¹⁻⁵². Analysis revealed tetragonal crystal system for copper where as monoclinic lattice for cobalt and chromium complexes with 'p' type lattice.

Chromium complex reveals lattice parameters a = 18.10, b = 2.74 and c = 10.5 Å and $\alpha = \beta = 90^\circ$, $\gamma = 105.45^\circ$, unit cell volume and percent porosity are found to be 506.26 cm³ and 2.37. Cobalt complex exhibited maximum at 46.3 with 'd' equal to 1.946 Å having lattice parameters a = $\gamma = 90^\circ$ and $\beta = 100^\circ$ where as a = 12.61, b = 5.05 and c = 8.15 Å, values of unit cell volume and percent porosity calculated to be 511.73 cm³ and 5.946. In copper complex maxima is obtained at 55° with 'd' equal to 0.9327 Å. The lattice parameters $\alpha = \beta = \gamma = 90^\circ$ and a = b = 7.795 c = 5.401 Å. Unit cell volume and percent porosity are 328.63 cm³ and 6.632.

Microbial activity

Antimicrobial activity of the metal complexes increases compared to complexing ligands. This increase in antimicrobial activity of the

metal complexes is reported to be due to Overtone's concept and chelate effect⁵⁰. Bidentate ligands containing nitrogen donor atom have shown higher microbial activity compared to monodentate nitrogen donor ligands⁵¹. Antimicrobial activity also found to change with nature of ligands, total number of charges on the complex, (decrease in the order cationic > neutral > anionic complexes) nature of ion neutralizing complex ion, nuclearity of the metal centre in the complex⁵². Bimetallic complexes are usually seen to be more active as compared to monometallic complexes⁵³.

Lipid membrane that surrounds the cell micro-organisms favors the passage of only lipid soluble materials. Thus lipid solubility is an important factor to control antimicrobial activity. Movement of charged metal ions into the cell is hindered by non polar lipid membranes where as on chelation polarity of the metal ion is reduced which in turn increases lipid solubility. This increased lipid solubility will enhance the penetration of the metal chelates into membrane and interact with cellular compounds thereby blocking the normal cell process. Metal chelates that are lipid soluble and interact will cellular compounds exhibit antimicrobial activity⁵⁴. Ligands containing oxygen, nitrogen, and/or sulphur are reported to increase lipid solubility on complexation. Chloro complexes generally found to exhibit strong antimicrobial activity over other complexes⁵⁵. Results of the antibacterial study (Table 5) revealed that metal complexes exhibit strong inhibition activities. Inhibition zones produced by these complexes were found to be larger than that control and ligand.

CONCLUSION

The ligand DAPA forms thermally stable six member metal chelates with transition metals with distorted geometries, and behaves as a bidentate in nature. Electronic transitions support square planar geometry for copper and octahedral geometry for cobalt and chromium complexes. ¹H NMR spectra suggests involvement amine group and acetate group in coordination and also inferred by IR spectra. Further, appearance of ν M-O and ν M-N stretching vibrations confirms involvement of amine and acetate groups in coordination. ESR spectra indicated anisotropic

behavior suggesting that the line width are independent of temperature, Exchange interaction coupling constants support strong exchange interactions and local tetragonal axes are misaligned.

TG/DTA support presence of coordinated water and kinetic parameters indicate

decomposition process follow in general first or second order kinetics and activated complex has more ordered structure. Stability of the complexes decreases in the order as Cu (II) > Co (II) > Cr (III). Based on the results of elemental analysis, thermal results and spectroscopic studies following structures (Fig. 4.) are proposed to the complexes under study.

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