Inorganica Chimica Acta, *133* (187) 211–215

Chromium(III) Complexes of *N*-Salicylideneamino Acid

R. SHANTHI, K. S. NAGARAJA* and M. R. UDUPA**

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

(Received December 10, 1986)

Abstract

N-Salicylideneamino acid complexes of chromium(III), K[Cr(sal:aa)$_2$]·nH$_2$O ($n = 2$, aa = glycine, DL-serine, DL- or L-methionine; $n = 1$, aa = DL- or L-leucine, DL- or L-phenylalanine, DL-tryptophan; $n = 0$, aa = α-DL-alanine) were prepared and characterized. The conductivity values (~80 ohm^{-1} cm^2 mol^{-1}) in methanol inferred a 1:1 electrolyte nature of the complexes. TG data indicated that the end residue is a mixture of K_2CO_3 and Cr_2O_3. The octahedral geometry around chromium(III) was suggested from the magnetic and UV–Vis spectral data. The absolute configuration of the complexes is assigned as Δ from the CD spectra. The dibasic tridenticity of the ligand was inferred from the IR and far-IR spectral studies. An octahedral geometry around chromium(III) is completed by the two tridentate Schiff base chelates.

Introduction

The metal complexes of Schiff base ligands derived from salicylaldehyde and amino acids are important because they act as models [1–3] for the more complicated N-pyridoxylindeneamino acid systems which are the intermediates in the transamination reaction. Iron(III) [4, 5], cobalt(III) [4, 5], nickel(II) [6] and copper(II) [7–9] complexes have been reported with this class of ligands. We hereby report the synthesis and characterization of chromium(III) complexes with *N*-salicylideneamino acids.

Experimental

Materials

$CrCl_3·6H_2O$ (Baker) and amino acids were of laboratory grade and used as such. Salicylaldehyde was distilled prior to use.

General Preparation of the Complexes

A methanolic solution (20 ml) of salicylaldehyde (10 mmol) was added to an aqueous solution (20 ml) of an amino acid (10 mmol). To this solution KOH (20 mmol, 20 ml) was added with constant stirring for 10 min. The bright yellow solution obtained was refluxed with a methanolic solution (20 ml) of $CrCl_3·6H_2O$ (5 mmol) for 3 h on a water bath. On slow evaporation of the solvent the precipitated orange–brown product was filtered, washed with acetone and dried over fused $CaCl_2$. Yield 70–80%.

Measurements

The elemental analyses of the complexes were conducted on a Hewlett-Packard CHN 185 analyzer. Chromium was estimated spectrophotometrically using diphenylcarbazide reagent [10]. Conductivity measurements were carried out in methanol on Mod. WBR precision conductivity meter. Thermal analysis was carried out on a Stanton 781 simultaneous thermal analyser employing a heating rate of 10 °C min^{-1}. The UV–Vis, circular dichroism, EPR, IR and far-IR spectra were recorded on Cary-2300, Jobin-Yuon, Varian E-4, Perkin-Elmer 257 and Polytech IR 30 spectrometers respectively.

Results and Discussion

The compositions of the complexes are suggested from the chemical analyses (Table I). The complexes are soluble in MeOH, Me$_2$CO, CHCl$_3$, DMF and DMSO. The solubility in non-polar solvents increased with increase in the side chain of the amino acid. The complexes derived from sal:DL-aa have less solubility when compared to those derived from sal:L-aa. This behaviour is similar to that of iron(III) complexes reported by Burrows and Bailar [5]. The molar conductivity values (~80 ohm^{-1} cm^2 mol^{-1}) of the complexes in methanol indicated a 1:1 electrolyte behaviour.

The complexes undergo thermal decomposition (Table II) in two steps. The first step is the dehydration occurring between 60–145 °C. The decomposition of the ligand occurs between 220–450 °C

---

*Present address: Department of Chemistry, Loyola College (autonomous), Madras-600 034, India.

**Author to whom correspondence should be addressed.

0020-1693/87/$3.50

TABLE I. Analytical[a], Conductivity, Magnetic Moment and EPR Spectral Data of Chromium(III) Complexes

Complex	C(%)	H(%)	N(%)	Cr(%)	$\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$	μ_{eff}	g_{av}
$K[Cr(sal{:}gly)_2]\cdot 2H_2O$	44.51 (44.89)	3.05 (3.14)	6.00 (5.81)	10.85 (10.80)	85.3	3.82	1.950
$K[Cr(sal{:}DL\text{-}ala)_2]$	50.80 (50.62)	3.62 (3.82)	5.60 (5.91)	10.21 (10.98)	82.0	3.79	2.141
$K[Cr(sal{:}DL\text{-}leu)_2]\cdot H_2O$	55.00 (54.44)	5.62 (5.60)	4.93 (4.90)	9.00 (9.03)	80.1	3.85	1.975
$K[Cr(sal{:}L\text{-}leu)_2]\cdot H_2O$	55.15 (54.74)	5.70 (5.60)	4.92 (4.90)	9.05 (9.03)	79.8	3.86	1.982
$K[Cr(sal{:}DL\text{-}phe)_2]\cdot H_2O$	59.82 (59.70)	4.75 (4.70)	4.30 (4.35)	8.30 (8.08)	87.1	3.80	1.974
$K[Cr(sal{:}L\text{-}phe)_2]\cdot H_2O$	59.80 (59.70)	4.74 (4.70)	4.30 (4.35)	8.28 (8.08)	88.3	3.83	1.972
$K[Cr(sal{:}DL\text{-}ser)_2)_2]\cdot 2H_2O$	44.81 (44.35)	4.12 (4.09)	5.18 (5.17)	9.20 (9.60)	83.2	3.81	2.090
$K[Cr(sal{:}DL\text{-}trypt)_2]\cdot H_2O$	59.98 (59.90)	3.95 (3.91)	3.61 (3.88)	7.00 (7.20)	79.3	3.84	1.992
$K[Cr(sal{:}DL\text{-}met)_2]\cdot 2H_2O$	45.60 (45.35)	4.50 (4.43)	4.20 (4.44)	8.18 (8.25)	91.5	3.82	1.993
$K[Cr(sal{:}L\text{-}met)_2]\cdot 2H_2O$	45.65 (45.25)	4.80 (4.43)	4.22 (4.44)	8.15 (8.25)	89.3	3.83	1.970

[a] Calculated values are given in parentheses. gly = glycine, ala = alanine, leu = leucine, phe = phenylalanine, ser = serine, trypt = tryptophan and met = methionine.

TABLE II. Thermal Decomposition Data of Chromium(III) Complexes

Complex	Temperature range (°C)	Loss of H_2O (%) found(calc.)	Temperature range (°C)	Formation of $K_2CO_3 + Cr_2O_3$ (%) found (calc.)	DTA peak temperature[a] (°C)	
$K[Cr(sal{:}gly)_2]\cdot 2H_2O$	60–180	7.2 (7.4)	215–484	68.0 (69.8)	107 258, 350, 399, 456 460	endo exo
$K[Cr(sal{:}DL\text{-}ala)_2]$			200–447	70.5 (69.4)	300, 380, 404	exo
$K[Cr(sal{:}DL\text{-}leu)_2]\cdot H_2O$	60–170	3.8 (3.1)	170–330	76.5 (75.0)	80 180, 204, 290, 310	endo exo
$K[Cr(sal{:}DL\text{-}phe)_2]\cdot H_2O$	80–145	3.0 (2.8)	215–409	77.3 (77.5)	66 360, 380, 400	endo exo
$K[Cr(sal{:}DL\text{-}ser)_2)]\cdot 2H_2O$	75–170	5.3 (6.6)	220–575	75.1 (73.2)	80 331, 460, 575	endo exo
$K[Cr(sal{:}DL\text{-}trypt)_2]\cdot H_2O$	66–181	2.7 (2.5)	215–535	80.1 (80.0)	80 268, 404, 475	endo exo
$K[Cr(sal{:}DL\text{-}met)_2]\cdot 2H_2O$	66–180	4.2 (5.7)	190–456	77.2 (77.0)	85 325, 341	endo exo

[a] exo = exothermic; endo = endothermic.

yielding a mixture of K_2CO_3 and Cr_2O_3 which was characterized by chemical and spectral analyses. The dehydration is observed as an endothermic peak and the decomposition of the ligand as exothermic peaks in DTA curves.

The μ_{eff} values indicate that the complexes are paramagnetic corresponding to three unpaired electrons. EPR spectra of the powder samples show a single broad signal with $g_{iso} \sim 1.90$ as expected for chromium(III) complexes [11]. The complexes showed absorption maxima (Table III) around 500, 375, 300, 270 and 255 nm. The first two bands are assigned [12] to ${}^4A_{2g} \rightarrow {}^4T_{2g}(\nu_1)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (ν_2) respectively. The energy of ν_1 is taken as the crystal field stabilization energy (10 *Dq*) for chromium(III) complexes. The *Dq* value ~2000 cm^{-1}, is higher than

TABLE III. UV–Vis and IR Spectral Data of Chromium(III) Complexes

Complex	λ_{max} (log ϵ) (nm)	*Dq* (cm^{-1})	*B* (cm^{-1})	β	ν(OH)	ν(C=N)	$\nu(COO^-)_{asym}$	$\nu(COO^-)_{sym}$	ν(C–O) (phenolic)	ν(M–O) (phenolic)	ν(M–O) (carboxylic)	ν(M–N)
$K[Cr(sal{:}gly)_2]\cdot 2H_2O$	500(1.82), 392(3.62), 300(2.50), 270(3.56), 253(3.60)	2000	507	0.55	3400m,br	1625s	1610s	1400m	1330m	545m	470s	395m
$K[Cr(sal{:}DL\text{-}ala)_2]$	500(1.91), 390(3.60), 310(3.30), 272(3.80), 258(3.50)	2000	520	0.57		1610s	1595s	1395m	1330m	540s	455m	405s
$K[Cr(sal{:}DL\text{-}leu)_2]\cdot H_2O$	500(1.90), 375(3.51), 350(3.50), 288(3.73), 255(3.61)	2000	634	0.69	3400m,br	1625s	1605s	1390m	1340m	564s	465s	375s
$K[Cr(sal{:}L\text{-}leu)_2]\cdot H_2O$	500(1.95), 375(3.60), 350(3.52), 270(3.70), 255(3.60)	2000	634	0.69	3400m,br	1625s	1610s	1390m	1340m	560s	465c	393s
$K[Cr(sal{:}DL\text{-}phe)_2]\cdot H_2O$	500(1.95), 375(3.62), 310(3.80), 270(3.65), 248(3.81)	2000	634	0.69	3400m,br	1620s	1595s	1390m	1345m	555s	470s	400s
$K[Cr(sal{:}L\text{-}phe)_2]\cdot H_2O$	500(1.89), 375(3.60), 315(3.83), 270(3.60), 250(3.80)	2000	634	0.69	3400m,br	1620s	1590s	1390m	1340m	550s	470s	495s
$K[Cr(sal{:}DL\text{-}ser)_2)_2]\cdot 2H_2O$	520(1.94), 395(3.60), 310(3.61), 268(3.70), 245(3.85)	1923	573	0.62	3400m,br	1620s	1595s	1390m	1340m	555s	470s	400s
$K[Cr(sal{:}DL\text{-}trypt)_2]\cdot H_2O$	525(1.95), 395(3.65), 320(3.30), 290(3.90), 265(3.92)	1905	594	0.64	3400m,br	1620s	1590s	1390m	1340w	540s	460m	415s
$K[Cr(sal{:}DL\text{-}met)_2]\cdot 2H_2O$	520(1.50), 480(1.49), 350(2.81), 295(2.73), 270(3.85), 242(3.90)	2083	756	0.82	3420m,br	1625s	1600s	1390m	1345w	565s	460m	400s
$K[Cr(sal{:}L\text{-}met)_2]\cdot 2H_2O$	510(1.50), 375(3.33), 300(2.80), 270(3.80), 242(3.85)	1961	685	0.74	3400m,br	1625s	1600s	1385m	1340w	560s	460m	400s

that of tris(aminoacidato)–chromium(III) (1900 cm^{-1}) [13] and tris(salicylaldiminato)–chromium(III) (1770 cm^{-1}) [14] complexes. The Racah parameter (B) and covalency factor (β) of the complexes are calculated using the reported [15] equations. The B and β values (Table III) decrease as gly $<$ ala $<$ ser $<$ Trypt $<$ Phe $<$ Leu $<$ Met.

The complexes can exist in *fac* (1, 2, 3) and *mer* (1, 2, 6) geometric forms. The *fac* (orange) and *mer* (brown) isomers are observed in the solid state [4]. Attempts to separate the isomers by crystallization and TLC methods have failed. In methanolic or DMF solution a homogeneous brown colour is observed. The *mer* form which is lower in symmetry than the *fac* isomer is expected to show splitting in the first absorption band. The splitting of the ν_1 band (Fig. 1) at least in the case of K[Cr(sal:DL-met)$_2$]·2H$_2$O is observed, indicating the *mer* form of the complex. The non-observance of the splitting in the other complexes is due to the broadening of the absorption band. Model construction further revealed that the *mer* isomer is more stable than the *fac* isomer. The intensity of the ν_2 band is much more than that of ν_1 due to overlapping of the $\pi \rightarrow \pi^*$ internal ligand transition [16]. The high energy bands at 300 and 250 nm are assigned to internal ligand transitions.

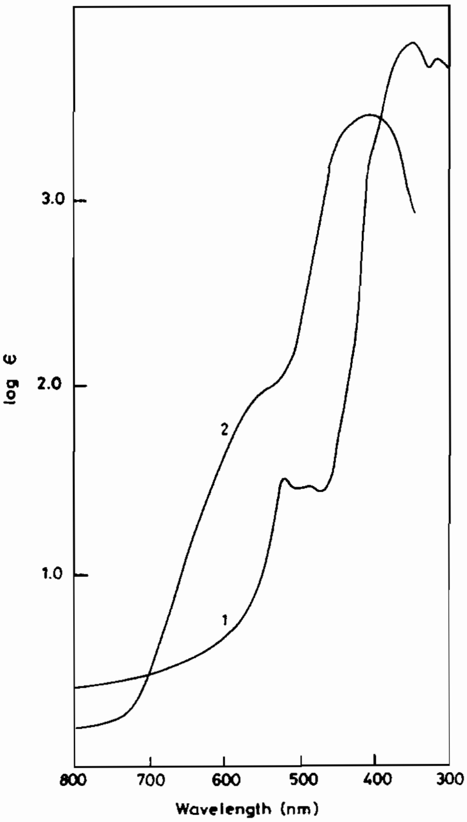

Fig. 1. Absorption spectra of (1) K[Cr(sal:DL-met)$_2$]·2H$_2$O and (2) K[Cr(sal:DL-leu)$_2$]·H$_2$O in methanol.

The assignments are made on comparison with the spectra of the free ligand in MeOH.

The CD spectra of K[Cr(sal:L-phe)$_2$]·H$_2$O and K[Cr(sal:L-met)$_2$]·2H$_2$O show negative and positive CD peaks in the first absorption band region (*ca.* 550 and 440 nm) and a negative CD peak in the second absorption band region (*ca.* 380 nm). In chromium(III) complexes the CD peak due to the magnetic-dipole allowed transition $^4A_{2g} \rightarrow {}^4T_{2g}$ indicates the absolute configuration [17] of the complex. The negative cotton effect observed at 550 nm due to $^4A_2 \rightarrow {}^4E_a$ indicates Δ configuration of the complexes. The positive CD peak observed at 440 nm is assigned [18] to $^4A_2 \rightarrow {}^4A$ and the negative CD peak at 380 nm is attributed to $^4A_2 \rightarrow {}^4E_b$. K[Cr(sal:DL-aa)$_2$] are found to be optically inactive as they exist in racemic mixtures.

The IR spectra of the ligands taken in CHCl$_3$ show absorptions at 1640, 1590 and 1400 cm^{-1} attributable to C=N, antisymmetric and symmetric COO$^-$ stretching frequencies respectively.

The IR spectra of the complexes except K[Cr(sal:DL-ala)$_2$] showed a road band at 3400 cm^{-1} due to lattice water. The coordination through the imine nitrogen is inferred form the shift [19] of ν(C=N) from 1640 to 1620 cm^{-1}. The $\nu(\mathrm{COO^-})_{\mathrm{asym}}$ is increased from 1590 to 1610 cm^{-1} in the complexes whereas $\nu(\mathrm{COO^-})_{\mathrm{sym}}$ decreases from 1400 to 1385 cm^{-1} indicating the unidenticity [20] of the carboxylate group ($\Delta\nu$(COO$^-$) ~200 cm^{-1}). The ν(C–O)(phenolic) at 1330 cm^{-1} observed in the ligand is shifted to 1340 cm^{-1} in the complexes and the intensity of the band has decreased [4, 19] showing the involvement of phenolic oxygen in coordination. The stretching frequencies of –SCH$_3$ and C–S of methionine [20, 21] at 1320 and 780 cm^{-1} respectively are not shifted in K[Cr(sal:met)$_2$]·2H$_2$O indicating that sulfur is not involved in bonding. The IR bands observed around 540, 450 and 420 cm^{-1} are assigned [19] to ν(Cr–O)(phenolic), ν(Cr–O)(carboxylic) and ν(Cr–N).

The studies infer that the octahedral geometry around chromium(III) is completed by the tridentate Schiff base chelate.

References

1 E. E. Snell, *J. Biol. Chem., 154,* 313 (1944).
2 E. E. Snell, *J. Am. Chem. Soc., 67,* 194 (1945).
3 D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc., 74,* 979 (1952).
4 R. C. Burrows and J. C. Bailar, *J. Am. Chem. Soc., 88,* 4150 (1966).
5 R. C. Burrows and J. C. Bailar, *J. Inorg. Nucl. Chem., 29,* 709 (1967).
6 L. J. Theriot, G. O. Carlistle and H. J. Hu, *J. Inorg. Nucl. Chem., 31,* 2891 (1969).
7 M. Kishita, A. Nakahara and M. Kubo, *Aust. J. Chem., 17,* 810 (1964).

8 Y. Nakao, K. Sakurai and A. Nakahara, *Bull. Chem. Soc. Jpn., 40,* 1536 (1967).
9 L. Casella, A. Pasini and U. Rento, *J. Chem. Soc., Dalton Trans.,* 1655 (1980).
10 E. B. Sandell, 'Colorimetric Determination of Trace Metals', Vol. 3, Interscience, New York, 1959, p. 392.
11 B. R. McGarvey, in R. L. Carlin (ed.), 'Transition Metal Chemistry', Vol. 3, Marcel Dekker, New York, 1966, p. 163.
12 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam, 1984, p. 414.
13 H. Oki and Y. Takahashi, *Bull. Chem Soc. Jpn., 50,* 2288 (1977).
14 M. J. O. Connor and B. O. West, *Aust. J. Chem., 21,* 368 (1968).
15 J. R. Peruma Reddi, *Z. Naturforsch., 22,* 908 (1967).
16 Y. Matsushima and A. E. Martell, *J. Am. Chem. Soc., 89,* 1322 (1967).
17 R. D. Gillard, *J. Inorg. Nucl. Chem., 26,* 657 (1964).
18 J. H. Dunlop and R. D. Gillard, *J. Inorg. Nucl. Chem., 27,* 361 (1965).
19 G. C. Percy, *J. Inorg. Nucl. Chem., 37,* 2071 (1975).
20 C. A. McAuliffe, T. V. Quagliano and L. M. Vallarino, *Inorg. Chem., 5,* 1997 (1966).
21 J. Maskowska and L. Chruscinski, *J. Inorg. Nucl. Chem., 43,* 3398 (1981).