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Chromium(III) Complexes of Schiff Bases

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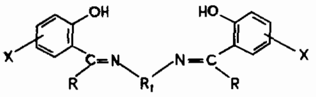
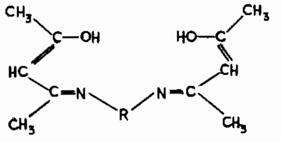
The preparation, electronic and infrared spectra, and magnetic moments of numerous solid complexes of chromium(III) of the type $[Cr(SB)L_2]X \cdot nH_2O$ $(L = NH_3$ *or* H_2O; $X = SCN$ *or* Cl; $n = 1$ *or* $0)$; $K[Cr(SB)L'_2]H_2O$ $(L' = CN$ *or* $ONO)$; $[Cr(SB)(py)(Cl)]$; $[Cr(SB)(L–L)]$ *(L–L = acetylacetonate anion);* $[Cr(SB)(L–L)]X \cdot nH_2O$ *(L–L = dipyridyl;* $X = ClO_4$; $n = 1$ *or* $0)$; $H[Cr(SB')_2]$; *and* $[Cr(SB'')_2]X$ $(X = ClO_4)$ *(SB = dianions of the tetradentate Schiff bases derived from salicylaldehyde, orthohydroxyacetophenone, and acetylacetone with ethylenediamine or orthophenylenediamine; SB' = dianions of the tridentate Schiff bases derived from salicylaldehyde with anthranilic acid, orthoaminophenol or glycine; and SB'' = monoanion of the Schiff base derived from salicylaldehyde and ethanolamine respectively) are reported. Bivalent quandridentate Schiff bases are presumably non planar in* $[Cr(SB)(L–L)]$ *species, while in other complexes they occupy square-planar configuration. The nitrite ion in* $K[Cr(SB)(ONO)_2]$ *is bound to the chromium(III) ion through the oxygen atom.*

Introduction

Although the metallic complexes of Schiff bases have been extensively studied,[1–3] relatively little work has been done on the corresponding chromium(III) complexes of Schiff bases.[4–9] As an extension of our previous study[10] on the six-coordinate complexes of chromium(III) of the type $[Cr(Lig)L_2]X$ and $[Cr(Lig)pyCl]$ (where Lig = a dianion of the quadridentate Schiff base derived from salicylaldehyde or substituted salicylaldehyde with various diamines; L = a monodentate ligand; X = monovalent anion; py = pyridine) we here report further six-coordinate complexes of chromium(III) with Schiff bases of the type (I), (II) and (III). The ligands will be abbreviated as follows: SALEN-H_2 for the ligand in (I; X = H, R = H, $R_1 = (CH_2)_2$), SALOPH-H_2 for that in (I; X = H, R = H, $R_1 = o\text{-}C_6H_4$), 7,7'-Me_2-SALEN-H_2 for that in (I; X = H, R = CH_3, $R_1 = (CH_2)_2$), ACACEN-H_2 for that in (II; R = $(CH_2)_2$), SALAA-H_2 for that in (III; $R_1 = o\text{-}C_6H_4CO_2H$), SALOAP-$H_2$ for in (III; $R_1 = o\text{-}C_6H_4OH$), SALGLY-H_2 for that in (III; $R_1 = -CH_2CO_2H$), SALENOL-H_2 for that in (III; $R = CH_2CH_2OH$), acac (acetylacetonate anion), dipy (dipyridyl), and py (pyridine).



(I)



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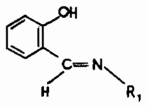

(III)

Experimental

Elemental analyses of Cr, N, and Cl were done in the laboratory by conventional methods. The microanalyses of C, H, and N were done by the Central Drug Research Institute, Lucknow, India through commercial service. Infrared spectra (KBr phase) were measured by the same Institute. Conductances were measured by Mullard conductivity bridge. Electronic absorption spectra were recorded in a Beckmann DU–2 spectrophotometer. Magnetic susceptibilities were recorded in a Gouy balance by usual methods. Solvents and chemicals were purified and dried by usual procedures.

Preparation of the Complexes

Chromium(III) complexes prepared in the present work are shown in Table I together with the elemental analyses.

$[Cr(SALEN)(NH_3)_2]SCN$ (I)

A mixture of Reinecke salt, $NH_4[Cr(NCS)_4(NH_3)_2]H_2O$ (0.001 mol) and SALEN-H_2 (0.001 mol) in ethanol (60 ml) was refluxed for about 2 hours, and

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TABLE I. Analytical Data of Chromium(III) Schiff Base Complexes.

Complex	Found %					Calcd. %					Λ_M[a] Ohm^{-1} cm^2 mole^{-1}
	C	H	N	Cl	Cr	C	H	N	Cl	Cr	
I. [Cr(SALEN)(NH$_3$)$_2$]SCN	50.02	4.24	16.68	–	12.88	49.75	4.88	17.07	–	12.69	65.8[b]
II. [Cr(SALOPH)(NH$_3$)$_2$]SCN · 1.5H$_2$O	51.82	4.58	14.02	–	10.08	51.96	4.74	14.45	–	10.74	60.7[b]
III. [Cr(7,7′-Me$_2$-SALEN)(NH$_3$)$_2$]SCN	52.34	5.51	16.62	–	12.08	52.05	5.48	15.99	–	11.87	78.5[b]
IV. [Cr(ACACEN)(H$_2$O)$_2$]Cl	41.81	6.08	8.11	10.54	15.12	41.62	6.35	8.09	10.40	15.03	96.5[b]
V. [Cr(ACACEN)(py)(Cl)]	52.67	6.00	11.24	9.69	13.50	52.45	5.91	10.80	9.24	13.37	C
VI. K[Cr(SALEN)(ONO)$_2$]H$_2$O	41.72	3.22	11.88	–	11.35	41.20	3.43	12.01	–	11.15	68[b]
VII. K[Cr(ACACEN)(ONO)$_2$]H$_2$O	34.38	5.20	13.08	–	12.33	34.05	4.73	13.24	–	12.29	71.5[b]
VIII. [Cr(ACACEN)(acac)]	54.71	6.88	7.78	–	14.08	54.69	6.70	7.50	–	13.94	C
IX. [Cr(ACACEN)(dipy)]ClO$_4$ · H$_2$O	48.40	4.98	10.31	–	9.52	48.17	5.10	10.22	–	9.48	52.7[b]
X. [Cr(SALEN)(acac)]	60.71	4.98	6.69	–	12.54	60.43	5.03	6.71	–	12.47	28[d]
XI. H[Cr(SALAA)$_2$]	63.21	4.01	5.60	–	10.04	63.27	3.58	5.27	–	9.79	49.7[d]
XII. H[Cr(SALOAP)$_2$]	65.00	4.61	5.76	–	10.33	65.69	4.00	5.89	–	10.95	50.1[d]
XIII. H[Cr(SALGLY)$_2$]	52.98	3.81	6.32	–	12.13	53.08	3.68	6.88	–	12.77	47.6[d]
XIV. [Cr(SALENOL-H)$_2$]ClO$_4$	45.33	4.02	5.70	–	11.21	45.01	4.16	5.83	–	10.83	60[b]

[a] 10^{-3} *M* Soln. [b] Aqueous soln.; the values of Λ_M changed with time. [c] Non-conducting in nitromethane. [d] In methanol.

filtered while hot. The brown filtrate gave brown crystalline compound on standing overnight in a refrigerator. This was filtered and recrystallized from ethanol and dried in a vacuum desiccator.

[Cr(SALOPH)(NH$_3$)$_2$]SCN · 1.5 H$_2$O (II)

This reddish–brown compound was prepared and purified as described above.

[Cr(7,7′-Me$_2$-SALEN)(NH$_3$)$_2$]SCN (III)

This reddish–brown crystalline complex was also isolated and purified by the above method.

[Cr(ACACEN)(H$_2$O)$_2$]Cl (IV)

A mixture of chromium(III) chloride hexahydrate (0.001 mol), THF (60 ml), and 2,2-dimethoxypropane (25 ml) was refluxed for 30 min, to which was then added ACACEN-Na$_2$ (0.001 mol) (prepared from stoichiometric amounts of ACACEN-H$_2$ and metallic sodium in alcohol) immediately followed by the addition of Zinc dust (in excess) and the whole mixture was refluxed for 5 hours and filtered while hot. The brown filtrate was evaporated to dryness under vacuum and the remaining mass was dissolved in a mixture of methanol and hexane (40:60 v/v) and filtered. This filtrate was again evaporated to dryness under vacuum. This procedure with the residue was repeated thrice, and finally a red-brown crystalline compound was separated out from the solution on standing in a refrigerator for 3 days. The compound was collected on filtration and dried under vacuum.

[Cr(ACACEN)pyCl] (V)

The Schiff base ACACEN-H$_2$ (0.001 mol) and chromium(III) chloride hexahydrate (0.001 mol) was taken in boiling pyridine (50 ml), immediately followed by the addition of Zinc dust (in excess). The mixture was refluxed for 2 hours and then filtered. The filtrate yielded brown crystalline complex on addition of few ml (~ 5 ml) of water. Recrystallized from methanol containing pyridine.

K[Cr(SALEN)(ONO)$_2$]H$_2$O (VI)

A suspension of [Cr(SALEN)(H$_2$O)$_2$]Cl[10] (0.01 mol) and potassium nitrite (0.05 mol) in 60 ml of methanol was refluxed on a water-bath for about two hours, and the solid KCl was filtered off. The filtrate, on concentration, gave the desired product as yellow–brown crystals, which were washed with ethanol and ether.

K[Cr(ACACEN)(ONO)$_2$]H$_2$O (VII)

This light brown compound was prepared following the method used for the preparation of (VI) above. The compound was purified by washing several times with methanol.

[Cr(ACACEN)(acac)] (VIII)

When an equimolar mixture of (V) and acac-Na was refluxed (1 hr) in methanol on a water-bath, a brown solution was obtained, which yielded a grey brown crystalline compound. It was recrystallized from methanol. Addition of acetone to the refluxed solution yielded better crystals.

[Cr(ACACEN)(dipy)]ClO$_4$ · H$_2$O (IX)

This brown compound was prepared by the above method using dipy instead of acac-Na and then adding sodium perchlorate (saturated aqueous solution) to the solution. It was recrystallized from aqueous alcohol.

[Cr(SALEN)(acac)] (X)

This brown compound was prepared following the method of (VIII) using [Cr(SALEN)pyCl][10] in place of [Cr(ACACEN)pyCl]. I.R. spectrum: 1645(s); 1630(vs); 1600(s); 1560(s); 1550(sh); 1540(m); 1525(m); 1508(s); 1470(m); 1440(s); 1400(w); 1380(s); 1340(m).

H[Cr(SALAA)$_2$] (XI)

$Cr_2(CH_3COO)_4 \cdot 2H_2O$ (0.001 mol) and SALAA-H_2 (0.004 mol) in methanol (60 ml) was refluxed on a water-bath for 3 hours and then filtered while hot. The volume of the filtrate was reduced to one-third of its original volume and ether was added to it, while a crystalline brown compound was separated, washed with ethanol, and dried under vacuum.

H[Cr(SALOAP)$_2$] (XII)

This reddish–brown compound was prepared following the method of (XI). Addition of ether was not necessary, volume reduction yielded this compound, which was washed with alcohol and ether and dried under vacuum.

H[Cr(SALGLY)$_2$] (XIII)

$Cr_2(CH_3COO)_4 \cdot 2H_2O$ (0.001 mol) was added to a boiling mixture of salicylaldehyde (0.001 mol) and glycine (0.001 mol) in water–ethanol mixture (1:4 v/v) followed by 2 hours reflux. The brown filtrate yielded crystalline brown compound on standing overnight. This was collected by filtration, washed with aqueous alcohol and dried under vacuum.

[Cr(SALENOLH)$_2$]ClO$_4$ (XIV)

A mixture of $Cr_2(CH_3COO)_4 \cdot 2H_2O$ (0.0005 mol) and SALENOL-H_2 (0.002 mol) was refluxed in ethanol (50 ml) for 2 hours and filtered. The volume of the filtrate was reduced to half and then a stoichiometric amount of sodium perchlorate solution was added. This, on standing in a refrigerator for 15 days, yielded brown crystals. These were filtered and washed with aqueous alcohol (2:3 v/v) and dried under vacuum.

Compounds I to IV, VI and VII, IX and XIV are soluble in water, alcohol and coordinating solvents, but insoluble in carbon tetrachloride, benzene, and ether. The crystals of V, VIII and X are soluble in methanol, coordinating solvents, but insoluble in water, ether and benzene. The complexes X to XIII are slightly soluble in water, highly so in coordinating solvents, fairly soluble in methanol and insoluble in chloroform, carbon tetrachloride, benzene, and ether.

Results and Discussion

Previously[10] we observed that the aerial oxidation of chromium(II) salts in presence of dibasic quadridentate Schiff bases of salicylaldehyde or substituted salicylaldehyde in suitable solvents is a good method for the synthesis of Schiff base complexes of chromium(III). In the present investigation, however, we observed that the reaction of chromium(II) chloride or chromium(II) acetate with ACACEN-H_2 in refluxing ethanol produce tris(acetylacetonato)chromium(III) instead of the desired complex [Cr(ACACEN)(H_2O)$_2$]X (X = Cl or CH_3COO). It has also been observed that when ACACEN-H_2 and [Cr(Urea)$_6$]$Cl_3 \cdot 3H_2O$ in equimolar proportions was refluxed (3 hr) in ethanol, followed by neutralization with saturated aqueous solution of sodium carbonate, tris(acetylacetonato) chromium(III) in about 50% yield was obtained. On the other hand, reaction (refluxing 2 hr) of SALEN-H_2 and [Cr(Urea)$_6$]$Cl_3 \cdot 3H_2O$ in equimolar proportions in ethanol and in presence of stoichiometric amounts of sodium acetate yielded (about 40%) [Cr(SALEN)(H_2O)$_2$]Cl.

We further observed that the reaction of Reinecke-salt, $NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$ with dibasic quadridentate Schiff bases SALEN-H_2, SALOPH-H_2 or 7,7′-Me$_2$-SALEN-H_2 (in equimolar proportions) in refluxing ethanol yields beautiful crystalline chelates (I) to (III) (Table I). In this connection mention may be made that Yamada and Iwasaki[8] recently reported the isolation of [Cr(SALEN)(H_2O)$_2$]NCS by the reaction of SALEN-H_2 (0.03 mol) and $NH_4[Cr(NCS)_4(NH_3)_2]$ H_2O (0.02 mol) in refluxing (3 hr) methanol. The chromium(III) complexes (V) to (X) (Table I) have been prepared by the methods which we have recently described[10–13] for the syntheses of analogous cobalt (III) complexes.

Since the dibasic quadridentate Schiff base SALEN-H_2, SALOPH-H_2, 7,7′-Me$_2$-SALEN-H_2 or ACACEN-H_2 usually (but not always[3,13]) demand a square-planar coordination, it is inferred that in the present chromium(III) complexes, (I) to (VII) each of them occupies a square-planar configuration and the two unidentate ligands occupy two *trans*-positions in an octahedral configuration. It may be mentioned here that a large number of cobalt(III) chelates of the type $[Co(Lig)(L{-}L)]^{0(\text{or } 1+)}$ (where L–L = neutral or monobasic bidentate ligands), with a strained non-planar quadridentate ligand (*i.e.*, Lig), have been isolated and characterized.[3,13,14] This non-planar structure is proven in the solid state for two compounds by X-ray analyses.[14a,b] It has also been demonstrated that the non-planar stereochemistry of "Lig" in some of these complexes of cobalt (III) is retained in non-donor solvents.[14] The structures of the chelates VIII to X of the present study, by analogy with that shown for the above type of cobalt(III) chelates, apparently involve SALEN or ACACEN bonding in a non-planar manner, determined by the chelating nature of the acac or dipy group.

The ionic nature of SCN^- in compounds (I) to (III)

TABLE II. Electronic Spectral Data (methanol)[a] and Magnetic Moments (at 298°K) of Chromiun(III) Schiff Base Complexes.

Complex	ν_{max} (log ε) cm^{-1}	μ_{eff}(B.M.)
$[Cr(SALEN)(NH_3)_2]SCN$	20,000(sh); 25,000(3.5); 31,711(3.9); 36,500(sh)	3.70
$[Cr(SALOPH)(NH_3)_2]SCN \cdot 1.5H_2O$	18,115(sh); 21,505(4.0); 29,850(5.0); 32,000(sh)	3.78
$[Cr(7,7'\text{-}Me_2\text{-}SALEN)]SCN$	19,679(sh); 25,974(3.3); 31,746(3.8); 37,000(4.5)	3.90
$[Cr(ACACEN)(H_2O)_2]Cl$	16,560(sh); 22,950(3.1); 27,500(3.9); 36,000(4.1)	3.78
[Cr(SALEN)(acac)]	20,650(sh); 22,000(sh); 25,850(3.7); 37,000(4.4)	3.81
$H[Cr(SALAA)_2]$	17,698(2.3); 24,096(3.7); 26,500(sh)	3.95
$H[Cr(SALOAP)_2]$	20,202(sh); 20,409(3.3); 23,256(sh); 26,666(sh)	3.5
$H[Cr(SALGLY)_2]$	19,667(1.9); 26,052(2.3)	3.6
Free ligand SALEN-H_2	25,980(3.1); 32,500(3.7); 36,900(sh); 39,500(4.3)	
Free ligand SALOPH-H_2	30,310(4.3); 37,400(sh); 39,220(4.7)	
Free ligand ACACEN-H_2	31,000(4.5); 33,000(4.4)	
Free ligand SALOAP-H_2	30,303(3.74); 35,087(3.70); 39,220(4.1)	

[a] Spectra in nujol mull are almost identical.

is demonstrated by the appearance of infrared bands at about 2068 cm^{-1} (strong) and 755 cm^{-1} (weak or medium) which may be considered as CN stretching and CS stretching vibrations respectively.[15] The complexes $K[Cr(SALEN)(ONO)_2]H_2O$ (VI) and $K[Cr(ACACEN)(ONO)_2]H_2O$ (VII) showed infrared absorption bands at about 1455 cm^{-1}, 1050 cm^{-1} and 830 cm^{-1} which may be ascribed to the oxygen-bonded nitrite ion.[16] Similarly, a strong and broad band around 1100 cm^{-1} observed for the complexes (IX) and (XIV) can be assigned to ν_3 mode of ClO_4 ion vibration (in T_d symmetry[17–19]). The NH stretching frequency[20,21] of NH_3 in (I) to (III) occurs around 3000 to 3400 cm^{-1}. For the complex [Cr(SALEN)(acac)] (X), the oxygen bonded chelating acetylacetonate anion has been inferred from the vibrational spectral data,[14,22,23] despite the added complexities due to the C=N and C=C stretching modes of the SALEN ligand. It may be mentioned here that the C=O stretch for carbon-bonded acetylacetone occurs above 1650 cm^{-1}.[24] The room temperature magnetic moment values (without TIP correction) are set out in Table II, which show octahedral stereochemistry for the present chromium (III) chelates. The marked deviation of the magnetic moments of $H[Cr(SALOAP)_2]$ (XII) and $H[Cr(SALGLY)_2]$ (XIII) from the room temperature spin-only values strongly suggest that there is antiferromagnetic exchange interactions in these systems.

The electronic absorption spectra of some of the chromium(III) complexes in solution are recorded in Table II. Some of the chelates, when taken in nujol mull give almost identical spectra, specially in the range 18,000–25,000 cm^{-1}. This suggests that the environment of the chromium(III) is substantially the same in both solid and solution. The bands observed in the range 18,000–25,000 cm^{-1} may be considered as the split components of the $^4T_{2g}$ (O_h) and $^4T_{1g}$ (F) (O_h) terms despite their high molar extinction coefficients. Similar high extinction coefficients were observed for band in this region in the chromium(III) complexes of N-substituted salicylaldimines,[6] N,N'-ethylenebis(salicylaldimines)[7,8,10] and N,N'-ethylenebis(acetylacetoneiminate)[9]. If they are at all d–d bands, then the high molar extinction coefficients are possibly due to contributions from ligand transitions. However, according to Yamada, *et al.*[8,9] the d–d bands in such chelates might appear around 15,000 cm^{-1}, which in the present case are hidden under much more intense bands.

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