

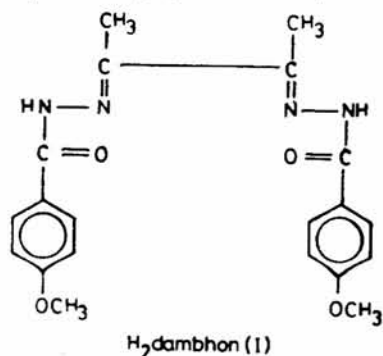
Synthesis and characterization of chromium(III) complexes of diacetyl bis(4-methoxybenzoyl hydrazone)

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A few chromium(III) complexes have been synthesized from reactions of diacetyl bis(4-methoxybenzoyl hydrazone) (H_2 dambhon) with $CrCl_3 \cdot 6H_2O$, $NH_4 [Cr(SCN)_4(NH_3)_2] \cdot H_2O$ and $K_3[Cr(SCN)_6] \cdot 4H_2O$. The complex $[Cr(dambhon)(Py)Cl] \cdot H_2O$ (**2**), reacts with acetylacetone, salicylaldehyde, glycine and N-phenylsalicylaldimine to yield chromium(III) heterochelates of the type $[Cr(dambhon)(L-L)] \cdot nH_2O$ [where L-L = anion of acetylacetone, $n = 1$ (**5**); anion of salicylaldehyde, $n = 1$, (**6**); anion of glycine, $n = 2$, (**7**) and anion of N-phenylsalicylaldimine, $n = 1$, (**8**)]. The complexes have been characterised by elemental analysis, molar conductance values, magnetic susceptibilities, molecular weights and spectroscopic (UV-vis and IR) data. It has been concluded that the formation of the complexes (**1**) to (**8**) involves quadridentate N_2O_2 donor ligand (H_2 dambhon) in the dibasic form ($dambhon^{2-}$).

Hydrazones have interesting ligational properties due to the presence of several potential coordinating sites, and both transition and non-transition metal complexes of these ligands have earlier been synthesized¹. However, no work on chromium(III) complexes of the hydrazones derived by the condensation of 4-methoxybenzoyl hydrazide with different ketones/aldehydes is available. As a part of our investigation on the transition and non-transition metal complexes with hydrazones²⁻⁷, we now report the reactions of diacetyl bis(4-methoxybenzoyl hydrazone) (Structure I) with different



chromium(III) salts under varied reaction conditions leading to the isolation of many new chromium(III) complexes. Further, the newly synthesized complex $[Cr(dambhon)(Py)Cl] \cdot H_2O$ (**2**) smoothly reacts with acetylacetone (Hacac), salicylaldehyde (Hsal), glycine(Hgly) and N-phenylsalicylaldimine (H-NPhsal) to yield new heterochelates of chromium(III).

Experimental

The solvents and chemicals were purified and dried before use by standard techniques. The elemental analysis was carried out at the RSIC, CDRI, Lucknow. The electronic spectra were recorded in ethanol on a Hitachi spectrophotometer, Model 200-20. The molar conductance measurements were made using an electrolytic conductivity bridge of Leeds and Northrup Co. Cat no. 4959. The magnetic susceptibilities were determined by the Gouy method. The IR spectra were recorded in KBr on a Perkin Elmer spectrophotometer, model 1330.

Preparation of the ligand (H_2 dambhon)

The ligand was synthesized by the procedure reported by us earlier⁸.

Preparation of chromium(III) complexes

$[Cr(dambhon)(H_2O)_2]Cl$ (**1**)

To a suspension of H_2 dambhon (3.83 gm, 0.01 mol) in ethanol (60 ml), a solution of $CrCl_3 \cdot 6H_2O$ (2.66 gm, 0.01 mol) in ethanol (50 ml), was added followed by immediate addition of anhydrous sodium acetate (1.64 gm, 0.02 mol) in hot ethanol (30 ml). The mixture was refluxed for ~ 2h on a water bath and then filtered while hot to remove the precipitated sodium chloride. The red brown filtrate on concentration and cooling to ~ 5°C overnight yielded a brown crystalline compound (**1**). It was filtered, washed with ethanol and dried over fused $CaCl_2$, yield 70%, m.p. dec. ~ 300°C.

The complex is soluble in water, ethanol, methanol, acetone, pyridine, DMSO, DMF, but insoluble in ether, benzene and chloroform. The compound is paramagnetic ($\mu_{eff} = 3.80$ BM at 30°C).

(a) The complex (**1**) could also be isolated by the reaction of H_2 dambhon with $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ in the presence of sodium acetate in boiling ethanol.

(b) A mixture of $CrCl_3 \cdot 6H_2O$ (0.26 gm, 0.001 mol), THF (70 ml) and 2,2-dimethoxypropane (30 ml) was

refluxed for 3 min and to this was added Na_2 dambhon (0.42 gm, 0.001 mol) (prepared *in situ* from stoichiometric amounts of H_2 dambhon and metallic sodium in ethanol) immediately followed by the addition of zinc dust (in excess) and the whole mixture refluxed for 7h and filtered while hot. The reddish brown filtrate was evaporated to dryness in a rotary evaporator and the remaining mass dissolved in a mixture of methanol and hexane (50 : 50, v/v) and filtered. The filtrate was again evaporated to dryness adopting the same procedure and finally the red-brown crystalline compound was separated out from the solution on standing in a refrigerator for 3 days. The compound (1) was collected on filtration and dried *in vacuo*, yield 60%, m.p. dec. above 300°C.

$[\text{Cr}(\text{dambhon})(\text{py})\text{Cl}]\cdot\text{H}_2\text{O}$ (2)

A mixture of $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ (2.66 gm, 0.01 mol) and H_2 dambhon (3.82 gm, 0.01 mol) was added to 50 ml of boiling pyridine (freshly distilled) immediately followed by the addition of ~ 1 g of zinc dust. The mixture was heated under gentle reflux for 30 min and filtered while hot. The brown filtrate, on treatment with few ml of water, gave brown solid (2), which was filtered, washed with water and ethanol and dried over fused CaCl_2 , yield 60%, m.p. dec. ~ 300°C.

The compound is soluble in hot py, DMSO and DMF but insoluble in water, ethanol, CCl_4 and benzene. The compound is paramagnetic ($\mu_{\text{eff}} = 3.77$ BM at 28°C).

$[\text{Cr}(\text{dambhon})(\text{NH}_3)_2]\text{SCN}$ (3)

Reinecke salt $\text{NH}_4[\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]\cdot\text{H}_2\text{O}$ (1.06 gm, 0.003 mol) was dissolved in ethanol (~ 50 ml). To it was added a suspension of H_2 dambhon (1.14 gm, 0.003 mol) in ethanol (40 ml). The mixture was heated under reflux for 3h and filtered. The brown filtrate, on concentration and cooling, yielded brown solid (3). This was filtered, washed with ethanol and dried *in vacuo*, yield 50%, m.p. dec. ~ 300°C.

The compound is soluble in water, ethanol and py, DMF and DMSO but insoluble in ether, CCl_4 , CHCl_3 , benzene. It is paramagnetic ($\mu_{\text{eff}} = 3.90$ BM at 27°C).

$\text{K}[\text{Cr}(\text{dambhon})(\text{NCS})_2]$ (4)

An ethanol suspension (50 ml) of H_2 dambhon (1.91 gm, 0.005 mol) was added to the hot solution of $\text{K}_3[\text{Cr}(\text{SCN})_6]\cdot 4\text{H}_2\text{O}$ (2.945 gm, 0.005 mol) in ethanol (50 ml). The mixture was then heated under reflux for 3h and filtered. The brown filtrate, on concentration in a rotary evaporator to half of its original volume and cooling to 5°C overnight, yielded a brown

compound. It was filtered, washed with ethanol and dried *in vacuo*, yield 60%, m.p. dec. ~ 295°C.

The compound is soluble in methanol, ethanol and py, DMF and DMSO, sparingly soluble in water, but insoluble in CHCl_3 and benzene. It is paramagnetic ($\mu_{\text{eff}} = 3.72$ BM at 30°C).

$[\text{Cr}(\text{dambhon})(\text{acac})]\text{H}_2\text{O}$ (5)

The complex $[\text{Cr}(\text{dambhon})(\text{Py})\text{Cl}]\text{H}_2\text{O}$ (2) (2.882 gm, 0.005 mol) was taken in ethanol (~ 150 ml). To it was added acetylacetone (Hacac) (0.5 gm, 0.005 mol) and heated under reflux for 4h and filtered while hot. The deep brown filtrate, on concentration and cooling, yielded a brown crystalline compound (5). It was filtered, washed with ethanol and dried *in vacuo*, yield 50%, m.p. 280°C (dec.).

The compound is soluble in methanol, ethanol py, DMF and DMSO, but insoluble in water, ether and benzene. It is paramagnetic ($\mu_{\text{eff}} = 3.82$ BM at 30°C).

$[\text{Cr}(\text{dambhon})(\text{sal})]\cdot\text{H}_2\text{O}$ (6);

$[\text{Cr}(\text{dambhon})(\text{gly})]\cdot 2\text{H}_2\text{O}$ (7);

$[\text{Cr}(\text{dambhon})(\text{N-phsal})]\text{H}_2\text{O}$ (8)

These three heterochelates of chromium(III) were synthesized following the method used for (5) using salicylaldehyde, glycine and N-phenylsalicylaldehyde in place of acetylacetone. The yield was found to be 50-60% and the complexes did not melt upto 300°C.

The complexes are soluble in methanol, ethanol and coordinating solvents (py, DMF and DMSO), but insoluble in water, ether and benzene. The magnetic moment (μ_{eff}) was found in the range 3.75-3.90 BM at 29°C.

Results and discussion

The isolated chromium(III) compounds are stable and the analytical data (Table 1) support their formulations.

The molar conductance data of the compounds are recorded in Table 1. The compounds (1) and (3) are found to be 1:1 electrolytes in water. On the other hand, the complexes (2) (in MeNO_2) and (5)-(8) (in MeOH) are non-electrolytes⁹. However, the Λ_M values of the complex (4) in ethanol (Λ_M of $10^{-3}M$ solution at room temperature in ethanol is found to be $68.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). These values are in conformity with the proposed formulations⁹, which is further supported by the molecular weights (Table 1).

Table 1— Characterization data of chromium(III) complexes

Complexes	Found (Calc.), %					μ_{eff} (B.M.)	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	Mol.wt.
	C	H	N	Cl	Cr			
[Cr(dambhon)(H ₂ O) ₂]Cl (1) (C ₂₀ H ₂₄ O ₆ N ₄ Cl Cr)	47.92 (47.67)	4.99 (4.36)	11.00 (11.12)	7.52 (7.04)	10.4 (10.32)	3.8	48.2 (EtOH)	495 (503.45)
[Cr(dambhon)(Py)(Cl)H ₂ O (2) (C ₂₅ H ₂₇ O ₅ N ₅ ClCr)	54.00 (53.14)	4.59 (4.78)	12.60 (12.40)	6.66 (6.28)	9.5 (9.21)	3.77	2.3 (MeNO ₂)	587 (564.45)
[Cr(dambhon)(NH ₃) ₂]SCN (3) (C ₂₁ H ₂₆ O ₄ N ₇ SCr)	47.99 (48.09)	5.11 (4.96)	18.38 (18.70)	—	10.11 (9.92)	3.90	66.7 (H ₂ O)	518 (524)
K[Cr(dambhon)(NCS) ₂] (4) (C ₂₂ H ₂₀ O ₄ N ₆ S ₂ KCr)	45.21 (44.96)	3.88 (3.40)	14.59 (14.30)	—	8.04 (8.85)	3.75	68.9 (EtOH)	592 (587)
[Cr(dambhon)(acac)]H ₂ O (5) (C ₂₅ H ₂₉ O ₇ N ₄ Cr)	54.98 (54.64)	5.33 (5.28)	10.68 (10.20)	—	9.88 (9.47)	3.82	17.8 (MeOH)	558 (549)
[Cr(dambhon)(sal)]H ₂ O (6) (C ₂₇ H ₂₇ O ₇ N ₄ Cr)	57.0 (56.74)	4.58 (4.72)	10.1 (9.80)	—	9.45 (9.10)	3.75	11.2 (MeOH)	595 (571)
[Cr(dambhon)(gly)]2H ₂ O (7) (C ₂₂ H ₂₈ O ₈ N ₅ Cr)	48.12 (48.70)	4.99 (5.16)	13.21 (12.91)	—	9.28 (9.59)	3.88	8.4 (MeOH)	568 (542)
[Cr(dambhon)(Nphsal)]H ₂ O (8) (C ₃₃ H ₃₂ O ₆ N ₅ Cr)	61.88 (61.30)	5.00 (4.95)	11.01 (10.83)	—	8.58 (8.04)	3.90	12.9 (MeOH)	— (646)

The room temperature magnetic moments are slightly lower than the spin-only value for a d^3 ion, and this aspect has been discussed thoroughly elsewhere^{10,11}.

The electronic absorption spectra of the chromium(III) complexes, (1) to (8) in solution show three absorption bands (in ethanol) in the range 17,850-20,650 cm^{-1} , 20,000-22,522 cm^{-1} and 25,000-27,000 cm^{-1} . 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 chromium(III) is almost the same in solid as well as in 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 ${}^4T_{1g}(O_h)$ 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 salicylaldimines¹², N-N¹-ethanylenebis(salicylaldimines)^{7,10,13,14} and N-N¹-ethanylenebis(acetylacetonate)¹⁴. If these are at $d-d$ bands, then the high molar extinction coefficients are possibly due to contributions from ligand transitions. However, according to Yamada *et al.*^{13,14}, the $d-d$ bands in such chelates might appear $\sim 15,000 \text{ cm}^{-1}$, which in the present case are masked by more intense bands.

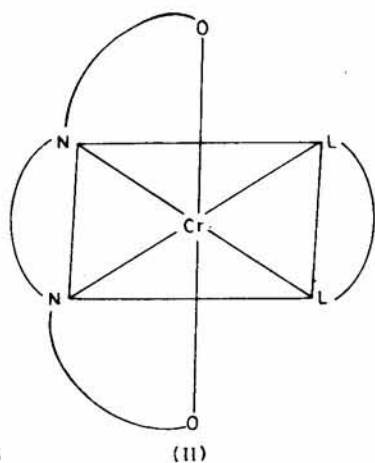
The infrared spectra of the complexes show some band shifts which reveal the coordination modes⁶ of the ligand H₂ dambhon with chromium(III) ion in the present complexes.

The free ligand shows band for $\nu\text{NH} \sim 3280\text{-}3310 \text{ cm}^{-1}$, which disappeared in the complexes (1) to (8) suggesting that the ligand acts in enol-form and binds with the chromium(III) ion after deprotonation⁸.

The uncomplexed ligands exhibit amide I ($\nu\text{C}=\text{N} + \nu\text{C}=\text{O}$), amide II and amide III bands (in the ranges 1630-1665, 1610-1620, 1565-1575, 1490-1495 & 1265 cm^{-1} respectively. The disappearance of these bands in the chromium(III) complexes (1) to (8) suggests enolization of the keto-groups of H₂ dambhon followed by the formation of complexes through deprotonation. However, the presence of strong and sharp band(s) $\sim 1598\text{-}1610 \text{ cm}^{-1}$ and $\sim 1040 \text{ cm}^{-1}$ is diagnostic of the azine chromophore ($\text{>C}=\text{N}-\text{N}=\text{C}<$)^{6,15}.

In addition, coordination of NH₃ in complex (3) is indicated by the appearance of bands at 3000-3400, 1550, 1290 and 850 cm^{-1} assignable to $\nu(\text{NH}_3)$, $\delta_d(\text{NH}_3)$, $\delta_s(\text{NH}_3)$ and $\rho_r(\text{NH}_3)$ ¹⁶⁻¹⁸ respectively. The pyridine ring vibrations are observed at $\sim 1450 \text{ cm}^{-1}$ (s) and 1075 cm^{-1} (m) for the complex (2). This observation also supports coordination of pyridine molecule.

In the complex (5), the oxygen bonded chelating acetylacetonato anion has been inferred from the vibrational spectra^{19,20}, which in the present case show $\nu\text{C}-\text{O}$ at 1550 cm^{-1} , and $\nu\text{C}=\text{C}$ is observed at 1540 cm^{-1} . It may be mentioned here that $\nu\text{C}=\text{O}$ for the carbon bound acetylacetonate occurs above 1650 cm^{-1} (ref. 21). Despite added complexities due to the presence of C=N and C=C stretching modes



(where $\begin{matrix} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{matrix}$ is the dianion dambhon²⁻ and $\begin{matrix} \text{L} \\ \diagup \quad \diagdown \\ \text{L} \end{matrix}$ is the monoanion of bidentate ligands].

of the present ligand, the IR spectral data clearly show the presence of oxygen bonded chelating acetylacetonato anion in the complex (5).

The infrared spectra of (4) shows bands $\sim 2070 \text{ cm}^{-1}$ (s), 760 cm^{-1} (m) due to $\text{C}\equiv\text{N}$ and $\text{C}-\text{S}$ stretching vibrations respectively^{18,22-24}. The bonding of thiocyanato group with chromium(III) ion occurs through nitrogen as evident from the band due to C-S stretching appearing at 760 cm^{-1} . Based on the data available in literature, it may be concluded that the thiocyanato group coordinates through nitrogen for first row transition metal and through sulphur for the second row transition metals. The non-bonding of SCN^- in the complex (3) is supported by the appearance of bands $\sim 2045 \text{ cm}^{-1}$ (νCN) and 735 cm^{-1} (νCS).

The presence of a band $\sim 1645 \text{ cm}^{-1}$ in the complex (1) indicates the presence of coordinated H_2O , which is further substantiated by the appearance of wagging modes of H_2O ~ 940 and 750 cm^{-1} , respectively¹⁸. The presence of water molecules in the complexes (1), (2) and (5)-(8), however, complicates the band assignments (see above). Heating of the complexes however at $115 \pm 5^\circ\text{C}$ indicated the presence of non-coordinated water in the complexes (2) and (5) to (8) as discussed above.

Finally it may be concluded that the ligand H_2 dambhon functions as a dibasic N_2O_2 quadridentate

ligand and N_2O_2 takes up the square plane (excepting in (5) to (8) and the other ligands attached to axial positions. In the complex (5)-(8), the dianion dambhon²⁻ possibly forced by the anion of the bidentate ligand (L-L) to attain a non-planar conformation (Structure II).

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