

# Ternary Coordination Complexes of Chromium(III) with Glycine and Some Dicarboxylic Acids—Potentiometric, Spectral and Ion-Exchange Studies

\*K. VENKATACHALAPATHI<sup>a</sup>, M. SIVASANKARAN NAIR<sup>b</sup>, D. RAMASWAMY and M. SANTAPPA<sup>c</sup>

Central Leather Research Institute, Adyar, Madras-600 020

Reliable stability constants for the  $\text{CrAH}$ ,  $\text{CrA}$ ,  $\text{CrA}_2$ ,  $\text{CrA}_3$ ,  $\text{Cr(OH)}$  and  $\text{Cr}_2\text{A}_4\text{(OH)}_2$  have been obtained at  $50 \pm 0.1^\circ$  and  $I = 0.1 \text{ mol dm}^{-3}$  in the  $\text{Cr(III)}$ -glycine system by the computer based analysis of the potentiometric data. Ternary complexation of  $\text{Cr(III)}$  with glycine as the primary ligand (A) and malonic, maleic, or succinic acids as the secondary ligand (B) gives rise to  $\text{CrAB}$ ,  $\text{CrA}_2\text{B}$ , and  $\text{CrA}_3\text{B}$  (only in the systems with B = malonic or maleic acid) types of ternary complexes. The results suggest the marked stabilities of these ternary complexes over the corresponding binary analogues which may probably be accounted for by considering the charge neutralization and interligand interactions in the ternary systems. The results indicate the preferred formation of  $\text{Cr(III)}$  ternary chelates containing five and six membered rings rather than those with five and seven membered rings. The enhanced stability of the unsaturated mixed complexes,  $\text{CrAB}$ , over the saturated complexes of the type  $\text{CrA}_2\text{B}$  or  $\text{CrA}_3\text{B}$  is evident from the results. Ion exchange and spectroscopic evidence have been obtained to support the existence of  $\text{CrAB}$ ,  $\text{CrA}_2\text{B}$  and  $\text{CrA}_3\text{B}$  ternary species in the  $\text{Cr(III)}$ -glycine(A)-malonic acid(B) system.

It is well established that the ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances through biological membranes<sup>1,2</sup>. Thus, considerable attention has been paid in recent years on the study of binary and ternary complexes of transition metal ions with particular reference to their syntheses, kinetic behaviours, isomerism, and factors governing their formation and stability<sup>1-6</sup>. Much of the synthetic and characterization studies have been carried out on  $\text{Cr(III)}$  complexes towards a better understanding of their biological and technological importance<sup>9,10</sup>. Kida<sup>11</sup> predicted that ternary  $\text{Cr(III)}$  complexes must be more stable than their corresponding binary complexes and subsequently many equilibrium studies on the binary  $\text{Cr(III)}$  complexes alone have been reported<sup>12</sup>. A careful analysis of these data indicates that the kinetic inertness and polymerization behaviour of  $\text{Cr(III)}$  have not been taken into consideration and inadequate equilibrium conditions have been employed. Furthermore, various protonated, hydroxy- and polynuclear-complexes have not been accounted during the computation of the equilibrium constants.

Considering the above points, we have been investigating<sup>13-16</sup> the multiple equilibria present in some  $\text{Cr(III)}$  binary and ternary complex systems. The present paper deals with the detailed study of the formation equilibria of  $\text{Cr(III)}$ -glycine(A) binary

system and also some  $\text{Cr(III)}$ -glycine(A)-dicarboxylic acid(B) mixed systems at adequate equilibrium conditions in aqueous perchlorate media by the simulated type of potentiometric technique. Ion-exchange and spectral evidences have been obtained to support the existence of the ternary complex species detected by the computer based analysis of the potentiometric data. The dicarboxylic acids used were malonic, maleic and succinic acids.

## Experimental

Solutions of glycine (E. Merck ; pure), malonic acid (Riedel ; pure), maleic acid (Riedel ; pure) and succinic acid (E. Merck ; G.R.) were prepared immediately before use in double-distilled water from materials dried under vacuum over  $\text{P}_2\text{O}_5$ . Hexaaquachromium(III) perchlorate and other reagents were prepared and estimated as described earlier<sup>18</sup>.

Conventional potentiometric methods were employed at  $50 \pm 0.1^\circ$  and  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) for the determination of dissociation constant of glycine. A Radiometer pH-meter (pH M4d) with  $\pm 0.01$  millivolts accuracy was used with glass and calomel combination electrode (GK 2401C) for all pH measurements and titrations. The simulated type of potentiometric technique employed for the determination of the stability constants of

Present addresses: a Department of Environmental Chemistry, Sri Venkateswara University College of Engineering, Tirupati-517 502.

b Department of Chemistry, Madurai Kamaraj University P. G. Extension Centre, St. John's College Campus, Palayamkottai-627 002.

c Vice-Chancellor, University of Madras, Madras-600 005.

binary and mixed Cr(III) complexes in this study was described in detail in our earlier paper<sup>13</sup>. The ligand dissociation constants and the gross stability constants of binary and ternary complexes of Cr(III) were evaluated with the aid of SCOGS computer program<sup>16,17</sup> on IBM-370 computer. The protonation constants of malonic, maleic and succinic acids and stability constants of binary species of these ligands with Cr(III) (Table 1) were

TABLE 1—STABILITY CONSTANTS FOR THE PROTON AND Cr(III) COMPLEXES OF DICARBOXYLIC ACID(B) AT  $50 \pm 0.1^\circ$  AND  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ )

Standard deviations are given in parentheses, Ref. 15

Parameter	Dicarboxylic acid, B		
	Malonic	Maleic	Succinic
$\log \beta_{HB}$	5.324 (5)	6.05 (1)	5.325 (5)
$\log \beta_{H_2B}$	7.951 (8)	7.88 (1)	9.379 (5)
$\log \beta_{CrB}$	7.33 (2)	6.58 (13)	6.67 (6)
$\log \beta_{CrB_2}$	13.35 (3)	12.45 (8)	12.22 (4)
$\log \beta_{CrB_3}$	16.75 (7)	16.00 (9)	
$\log \beta_{Cr_2B_3}$		21.74 (8)	22.99 (10)
$\log \beta_{Cr_2BH}$			9.36 (10)

reported previously<sup>15</sup>. While calculating the stability constants of ternary complexes, the stability constants of ligand protonated species and also the binary complex species due to the ligands A and B with Cr(III) obtained under similar conditions were fixed without further refinement. The criteria employed for the selection of the best-fit model was as described earlier<sup>13-15</sup>. Pye Unicam SP-1800

TABLE 2—STABILITY CONSTANTS FOR THE PROTON AND Cr(III) COMPLEXES OF GLYCINE (A) CHOSEN BY THE BEST-FIT MODEL AT  $50 \pm 0.1^\circ$  AND  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ )

Standard deviations are given in parentheses

Parameter	Values obtained
$\log \beta_{HA}$	9.167 (9)
$\log \beta_{H_2A}$	11.48 (1)
$\log \beta_{CrA_2}$	11.14 (13)
$\log \beta_{CrA}$	8.70 (11)
$\log \beta_{CrA_3}$	16.33 (6)
$\log \beta_{CrA_4}$	23.07 (25)
$\log \beta_{CrOH}$	-3.53 (9)
$\log \beta_{Cr_2A_4(OH)_2}$	27.57 (14)
No. of data points	93
pH range	2.0-3.9
$\log K_{CrA}^{Cr}$	8.70
$\log K_{CrA_2}^{CrA}$	7.63
$\log K_{CrA_3}^{CrA_2}$	6.74
$pK_{NH_2}$	9.167
$pK_{COOH}$	2.31

Double Beam spectrophotometer was used for the spectral measurements. The results obtained are reported in Tables 2-4. The charges of all the complex species in this paper are omitted for clarity.

TABLE 3—STABILITY CONSTANTS FOR THE TERNARY SPECIES CHOSEN BY THE BEST-FIT MODEL FOR THE Cr(III)-GLYCINE (A)-DICARBOXYLIC ACID (B) SYSTEMS AT  $50 \pm 0.1^\circ$  AND  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ )

Standard deviations are given in parentheses

Parameter	Dicarboxylic acid, B		
	Malonic	Maleic	Succinic
$\log \beta_{CrAB}$	17.04 (4)	15.74 (4)	15.37 (4)
$\log \beta_{CrA_2B}$	22.60 (24)	22.35 (12)	
$\log \beta_{CrAB_2}$	21.05 (9)	20.42 (3)	18.98 (6)
$\log K_{CrA}^{CrAB}$	8.34	7.04	6.67
$\log K_{CrB}^{CrAB}$	9.71	9.16	8.70
$\log K_{CrA_2}^{CrAB}$	6.28	6.02	
$\log K_{CrB_2}^{CrAB}$	7.70	8.01	6.76
$\Delta \log K_{CrAB}$	1.01	0.46	-0.01
$\Delta \log K_{CrA_2B}$	-1.05	-0.56	
$\Delta \log K_{CrAB_2}$	-1.00	-0.69	-1.94
$\log X_{CrAB}$	4.40	2.70	2.19
$\log X_{CrA_2B}$	4.93	4.91	
$\log X_{CrAB_2}$	6.56	6.31	
$\Delta \log \beta_{CrAB}$	1.89	1.05	0.79
$\Delta \log \beta_{CrA_2B}$	1.16	1.16	
$\Delta \log \beta_{CrAB_2}$	1.73	1.62	
pH range	2.50 to 5.00	1.90 to 4.50	1.80 to 4.00
No. of data points	144	82	88
$10^3 \cdot \sigma_V$	4.73	1.30	1.48

TABLE 4—SPECTRAL DATA FOR VARIOUS COMPLEX SPECIES

Complex species	$\lambda_{max}$ nm.	$\epsilon_{max}$
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	260	5.50
	408	15.44
	575	13.80
$[\text{Cr}(\text{mal})(\text{H}_2\text{O})_4]^+$	416	25.98
	560	31.42
$[\text{Cr}(\text{mal})(\text{gly})(\text{H}_2\text{O})_3]^0$	406	33.00
	548	31.60
$cis\text{-}[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^{2-}$	418	40.03
	566	49.7
$[\text{Cr}(\text{mal})_3(\text{gly})]^{2-}$	408	34.84
	542	43.30

## Results and Discussion

### Chromium(III)-glycine(A) binary system :

The acid dissociation constants of glycine reported in Table 2 are in good agreement with the literature values<sup>12</sup> after taking into consideration the variations in the experimental conditions. The formation curves obtained by plotting  $\bar{n}$ , the average number of ligands bound per metal ion, vs  $pA$ , the negative logarithm of free ligand concentrations, for different metal to ligand ratio solutions for the

title system are not superimposable, indicating the presence of multi-complex equilibria involving hydroxo, protonated and polynuclear species. The  $\bar{n}$  hump at lower pH region similar to that reported by Williams *et al.*<sup>18</sup> suggests the possible formation of protonated metal complexes. These curves further exhibit considerable spread and greater divergency at  $\bar{n} > 1$  in the 1:1 metal-ligand solutions where concentration of free metal ion is high. Hence hydrolyzed complex species are expected to be present. The maximum value of  $\bar{n}$  reaches 2.0 indicating the possibility of  $\text{CrA}_2$  species formation under the present experimental conditions.

contribution was found to be insignificant under the present experimental conditions. The stability constants for the  $\text{Cr}_2\text{A}_4(\text{OH})_2$  and  $\text{CrAH}$  glycine complexes are reported here for the first time. The crystal structure of the former species has been well established recently<sup>20</sup> and Hisayaok and Kiyocotsuka<sup>21</sup> found that formation of this species is always accompanied during the process of preparing  $\text{CrA}_3$  glycine complex. The  $\text{CrAH}$  species has been previously isolated and characterised<sup>22</sup>. It is interesting that the metal hydrolysis constant (3.53) obtained in the best-fit model is comparable to the value of 3.47 reported in the literature<sup>12</sup> at 50°.

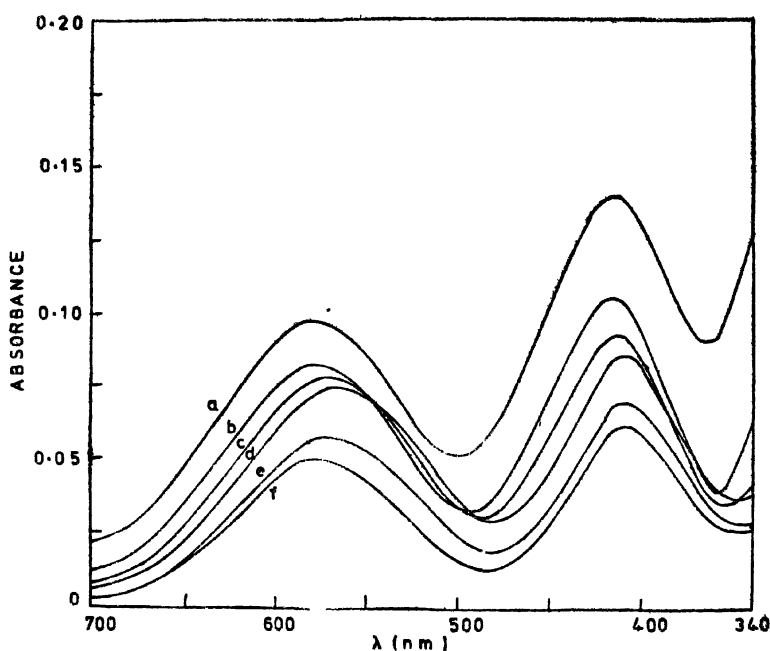


Fig. 1. pH dependence of the electronic spectra of Cr(III)-glycine (A) binary system with  $C_{\text{Cr}} = 3.0 \times 10^{-3}$  mol dm<sup>-3</sup> and  $C_{\text{A}} = 9.0 \times 10^{-3}$  mol dm<sup>-3</sup>. (a) pH 3.83; (b) pH 3.73; (c) pH 3.46; (d) pH 2.98; (e) pH 2.52; (f) pH 2.03 (metal alone).

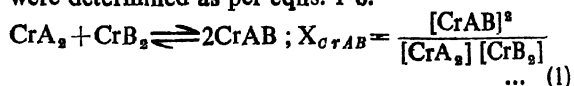
The pH dependence of the electronic spectra given in Fig. 1 is also in agreement with the above conclusions. The isobestic points seen in this figure clearly suggest the presence of more than one type of complex species. The  $\lambda_{\text{max}}$  values at 555 and 420 nm obtained in the present study are in agreement with the literature values for the  $\text{CrA}$  glycine species<sup>19</sup> involving a five-membered chelate ring of nitrogen and oxygen donor groups. The increased absorbance at 340 nm from pH 3.5 (Fig. 1) may be due to the possible presence of hydroxy complexes.

The computer-based analysis of the potentiometric data on the title binary system shows that the best-fit chemical model contains the complexes  $\text{CrAH}$ ,  $\text{CrA}$ ,  $\text{CrA}_2$ ,  $\text{CrA}_3$ ,  $\text{CrOH}$  and  $\text{Cr}_2\text{A}_4(\text{OH})_2$  in addition to the ligand protonated species  $\text{HA}$  and  $\text{H}_2\text{A}$ . Other species like  $\text{CrA}_2\text{H}$ ,  $\text{CrA}_2\text{H}_2$ ,  $\text{CrA}_2\text{OH}$ ,  $\text{CrAOH}$ ,  $\text{Cr}(\text{OH})_2$  and  $\text{Cr}_2\text{A}_3(\text{OH})_3$  have also been tested in different combination of models, but their

Slight discrepancies may be noted in the step-wise stability constants for the  $\text{CrA}$ ,  $\text{CrA}_2$  and  $\text{CrA}_3$  complexes between the presently obtained (Table 2) and literature values<sup>12</sup>. This may probably be due to the facts that inadequate equilibrium procedures had been employed in those studies and also all the relevant equilibria were not considered. Surprisingly, the ratio  $\log (K_{\text{CrA}_2}^{\text{CrA}}/K_{\text{CrA}_3}^{\text{CrA}_2}) = 1.07$  is higher than the statistically expected value of 0.68 log units. The difference can be attributed to the work done in bringing a second ligand from infinity to equilibrium position in  $\text{CrA}_2$  associate against the repulsive force exerted by the already bound ligand and to the rest effect which depends on the influence of bound ligands on the binding power of the metal ion<sup>23</sup>. The ratio,  $\log (K_{\text{CrA}_2}^{\text{CrA}}/K_{\text{CrA}_3}^{\text{CrA}_2}) = 0.89$ , is comparable to the statistical values of 0.94 log units.

The distribution of various species in terms of percentage bound Cr(III) as a function of pH was calculated for different metal to ligand ratio solution for the title system and one such pattern for the 1 : 5 solution of Cr(III) and glycine is given in Fig. 2. As anticipated from the formation curve analysis, the distribution pattern clearly shows that protonated metal complexes predominate in the lower pH region. The CrOH species was found to be favoured in the pH range of metal ion hydrolysis ( $pK_a=3.53$ ). As is evident from Fig. 2 the dihydroxy bridged complex is more favoured at high pH range.

In order to characterize the stability of various ternary complex species in relation to that of the parent complexes, the disproportionation constants were determined as per eqns. 1-6.



$$\log X_{\text{CrAB}} = 2 \log \beta_{\text{CrAB}} - (\log \beta_{\text{CrA}_2} + \log \beta_{\text{CrB}_2}) \quad \dots (2)$$

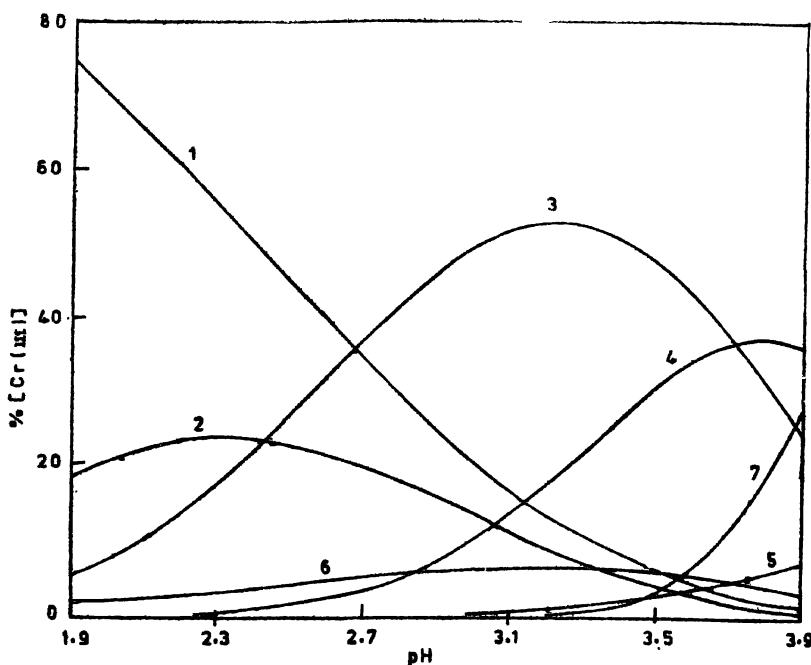
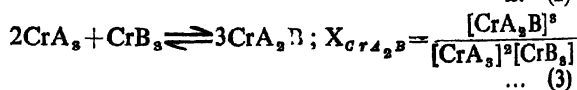
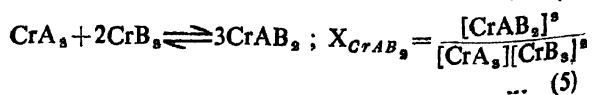


Fig. 2. Distribution of various species as a function of pH in the Cr(III)-glycine(A) binary system at Cr(III)-A ratio of 1 : 5. (1) unbound metal; (2) CrA; (3) CrA<sub>2</sub>; (4) CrA<sub>3</sub>; (5) CrA<sub>4</sub>; (6) CrOH and (7) Cr<sub>2</sub>A<sub>4</sub>(OH)<sub>2</sub>.

#### Ternary systems of chromium(III) :

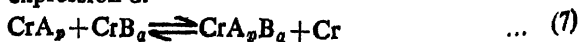
Three ternary systems viz., Cr(III)-glycine(A)-B where B=malonic, maleic or succinic acid were studied. In addition to the various binary species due to the ligands A and B (Tables 1 and 2), the best fit model chosen contains the complexes CrAB and CrAB<sub>2</sub> in all these systems. In the system with B=malonic or maleic acid, the CrA<sub>2</sub>B species was also found to be present when the experiments were carried out using large excess of glycine (A). However, the concentration of this species was found to be very low. It may be noted that the  $\sigma V$  values, the standard deviation in the titre obtained in the binary and ternary systems of Cr(III) reported in this paper, are comparable to the  $\sigma V$  values obtained while computing the ligand protonation constants. Hence the complex species obtained from the best fit models are valid under the experimental conditions investigated.

$$\log X_{\text{CrA}_2\text{B}} = 3 \log \beta_{\text{CrA}_2\text{B}} - (2 \log \beta_{\text{CrA}_2} + \log \beta_{\text{CrB}_2}) \quad \dots (4)$$



$$\log X_{\text{CrAB}_2} = 3 \log \beta_{\text{CrAB}_2} - (\log \beta_{\text{CrA}_2} + 2 \log \beta_{\text{CrB}_2}) \quad \dots (6)$$

The parameter,  $\Delta \log K_{\text{CrA}_2\text{B}_2}$ , the difference in stability of the binary complex with that of the ternary complex was derived from the general expression 8.



$$\Delta \log K_{\text{CrA}_2\text{B}_2} = \log \beta_{\text{CrA}_2\text{B}_2} - (\log \beta_{\text{CrA}_2} + \log \beta_{\text{CrB}_2}) \quad \dots (8)$$

The  $\Delta \log \beta_{CrA_2B_2}$ , the stabilization constants included in Table 3, result from the difference on their stabilities measured and those calculated on statistical grounds<sup>21,22</sup>. For statistical reasons<sup>23</sup>, values of  $\Delta \log K > -0.4$ ,  $\log X > 0.6$  and positive values of  $\Delta \log \beta$  indicate the enhanced stability of octahedral Cr(III) ternary complexes.

The  $\Delta \log K_{CrAB}$  values for all the three ternary systems in Table 2 are higher than the statistically expected value of  $-0.4$  suggesting their marked stabilities. The positive  $\Delta \log K_{CrAB}$  values in the systems with B=malonic or maleic acid show that these two ligands prefer to coordinate with the already coordinated CrA glycine complex rather than with the free aquated metal ion. The very small negative  $\Delta \log K$  value for the system with B=succinic acid indicates that the succinate dianion has equal tendency to add on to the CrA glycine complex and also to the hexa-aqua chromium(III) ion. The order of  $\Delta \log K_{CrAB}$  values in Table 3 suggests that the CrA glycine complex prefers dicarboxylate dianions in the order malonate>maleate>succinate. This order is more meaningful because the Cr(III) glycinate complex with five-membered ring prefers six-membered rings rather than the seven membered rings in the B ligand. Among the seven membered rings in the ternary systems with B=malonic or succinic acid, the maleate dianion is preferred due to the double bond in the ring. The stabilization of ternary complexes CrAB when compared to CrA or CrB can be best explained on the basis of charge neutralization in the ternary species. It may also be due to the inter-ligand interactions in the CrAB species through hydrogen bond formation between the amino group of glycine (A) and carboxylate group of the malonic, maleic or succinic acid (B) bound to Cr(III). The  $\Delta \log K$  values for the  $CrA_2B$  and  $CrAB_2$  complexes in Table 2 are negative in all the cases. This indicates that the dicarboxylate dianion prefers to add on to the aqueous metal ion rather than to the  $CrA_2$  glycine complex. The magnitude of the  $\Delta \log K$  values in Table 3 for  $CrAB$ ,  $CrA_2B$  and  $CrAB_2$  complexes clearly suggest that the unsaturated mixed complex of the type CrAB exhibits greater stabilization than the saturated complexes of the type  $CrA_2B$  or  $CrAB_2$ . This kind of dependency of stabilization of mixed ligand complex on the level of coordination has also been observed in the case of Cd(II) and Cu(II) ternary complexes<sup>24-26</sup>.

The disproportionation constant,  $\log X$ , values included in Table 3 for the  $CrAB$ ,  $CrA_2B$  and  $CrAB_2$  ternary complexes are far higher than the statistically expected value of 0.6 and their  $\Delta \log \beta$  values are all positive. Both these indicate the enhanced stability of the ternary complexes, the conclusion already arrived at from their  $\Delta \log K$  values. The  $\log X_{CrAB_2}$  value could not be computed for the Cr(III)-glycine(A)-succinic acid(B) system, since the stability constant data for the  $CrB_2$  is not known (Table 1). Comparison of the stepwise constants among the ternary systems also

suggests the same conclusions arrived at from the above statistical parameters. For e.g. the  $\log K_{CrAB}^{CrA_2B}$  values in Table 3 for the Cr(III)-glycine(A)-malonic, maleic or succinic acid(B) system decrease in the order B=malonic>maleic>succinic acids, demonstrating that the CrA glycine binary complex prefers the dicarboxylate anions (B) in the above order. The same order is in agreement with the order predicted from the  $\Delta \log K_{CrAB}$  and  $\log X_{CrAB}$  values. The  $\log K_{CrAB_2}^{CrA_2B}$  values in Table 3 for all the ternary systems under study are higher than the  $\log K_{CrA_2B}^{CrA_2B}$  values in Table 2, indicating that the glycinate anion is added to  $CrB_2$  to form  $CrAB_2$  preferably than its addition to  $CrA_2$  to form  $CrA_2B$ . Similarly, the preferential formation of  $CrA_2B$  complexes can easily be understood by comparing the  $\log K_{CrA_2B}^{CrA_2B}$  with the  $\log K_{CrAB_2}^{CrAB_2}$  (Tables 3 and 1).

The distribution of various species in terms of the percentage bound Cr(III) as a function of pH were calculated for all the ternary systems under study at different metal to ligands ratio solutions and one such pattern for the Cr(III)-glycine (A)-maleic acid(B) system in a 1:5:5 solution is given in Fig. 3. In all the systems, the concentration of the binary complexes due to glycine (A) ligand was found to be very low. The  $CrAB_2$  complexes were present in significant amounts in all the three systems and reached above 50% of the total metal near pH 4.5. The  $CrA_2B$  species is found to be present to a maximum of 20% even with excess of glycine (A) ligand as is the case with Cr(III)-glycine (A)-malonic acid(B) system in a 1:8:5:1.5 ratio solution. The  $CrAB$  species was found to be present in appreciable amounts (ca 40% of the total metal) in all the three ternary systems under study.

In order to confirm the existence of  $CrAB$ ,  $CrA_2B$  and  $CrAB_2$  ternary complexes, further studies on Cr(III)-glycine(A)-malonic acid(B) system were carried out as follows.

(i)  $CrAB_2$ : The solution, containing bis(malonato)chromium(III) complex (prepared by the method of Chang<sup>27</sup>) and glycine in 1:1 ratio was adjusted to pH 5.0 and thermostated at 50° for three days. The blank solution without glycine was also kept under similar conditions. The reaction was stopped by cooling the solution to 5° and the experimental and blank solutions were passed through two separate similar anion exchange resins DOWEX-1W, 1×8-400 (200-400 mesh). When both these columns were washed with 0.01 and 0.02 M *p*-toluenesulphonic acid, respectively, thick violet and pale pink coloured bands were separated and these were eluted and characterized as *cis* and *trans* isomers of bis(malonato)diaquachromium(III) complex. When the concentration of eluent was raised to 0.05 M, a thick pink coloured band got separated only in the experimental solution. This complex was eluted with 0.7 M eluent and characterised as bis(malonato)mono(glycinato)Cr(III) ternary complex. The nitrogen content was estimated by micro Kjeldahl method and chromium

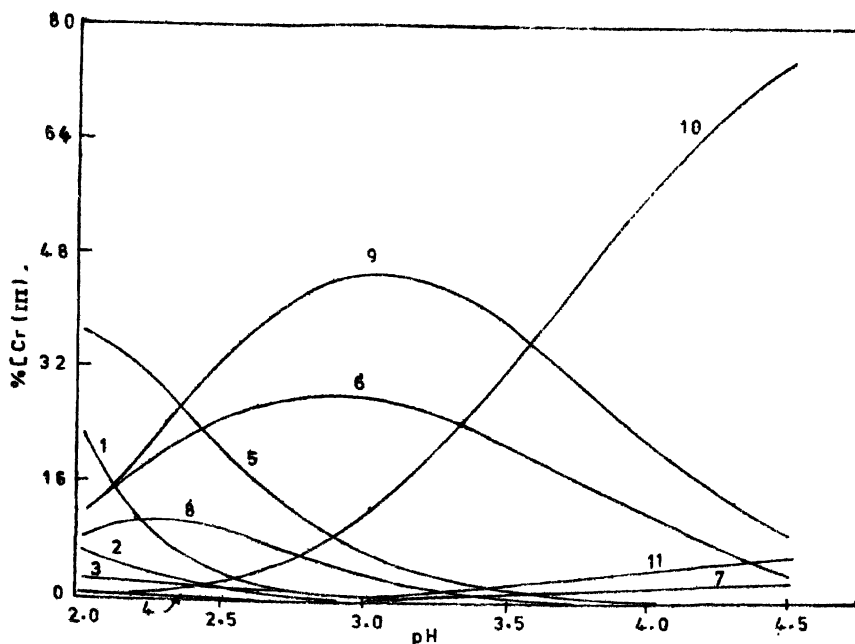


Fig. 3. Distribution of various species as a function of pH in the Cr(III)-glycine (A)-maleic acid (B) ternary system at a Cr(III)-A-B ratio of 1 : 5 : 5. (1) unbound metal; (2) CrAH; (3) CrA; (4) CrOH; (5) CrB; (6) CrB<sub>2</sub>; (7) CrB<sub>3</sub>; (8) Cr<sub>2</sub>B<sub>3</sub>; (9) CrAB; (10) CrAB<sub>2</sub> and (11) CrA<sub>2</sub>B. The species CrA<sub>3</sub>, CrA<sub>2</sub> and Cr<sub>2</sub>A<sub>4</sub>(OH)<sub>6</sub> are not represented in the figure because of their very low concentration.

by oxidising to Cr(VI) followed by spectrophotometry at 372 nm. The chromium to nitrogen ratio was found to be 1 : 1. The absorption spectra of this complex exhibited  $\lambda_{max}$  at 408 and 542, and  $\epsilon_{max}$  at 34.84 and 43.30 (Table 4). From the elution behaviour of this complex it is found to be more negative than the *bis*(malonato) complex. This is possible only if glycine enters into the coordination sphere of *bis*(malonato) complex. This was confirmed by the  $\lambda_{max}$  shift to lower frequencies by the ligand field contribution of nitrogen donor atom of glycine (Table 4).

(ii) **CrAB**: The mono(malonato)Cr(III) complex and glycine were mixed in 1 : 2 ratio, pH was adjusted to 4.0 and the solution was thermostated at 50° for 3 days. The solution was cooled, pH adjusted to 2.8 and passed through the cation exchange resin DOWEX-50W, 50×8-200(200-400 mesh). The mono(malonato) complex along with mono- and *bis*(glycinato) complexes and free glycine were retained in the column whereas the mono-(malonato)mono(glycinato)Cr(III) complex passed through the column. This effluent was passed through anion exchange resin DOWEX-1W, 1×8-400(200-400 mesh). The effluent was again passed through cation exchange resin at pH 2.8 to remove excess glycine if any. The complex was concentrated by rotary evaporation. The absorption spectra of this species showed  $\lambda_{max}$  at 406 and 548 nm and  $\epsilon_{max}$  at 33.0 and 31.60. Thus the elution pattern shows that the complex was without any charge. The chromium to nitrogen ratio was found to be

1 : 1. Analysis of the absorption spectra strongly suggested existence of  $[\text{Cr}(\text{mal})(\text{gly})(\text{H}_2\text{O})_2]^0$  by observing shifts in  $\lambda_{max}$  to lower frequency when compared to mono(malonato)Cr(III) complex (Table 4).

(iii) **CrA<sub>2</sub>B**: To the mono(malonato)Cr(III) complex, large excess of glycine was added and pH was adjusted to 4.0. After thermostating for three days at 50°, the solution was passed through cation exchange column DOWEX-50W, 50×8-200 (200-400 mesh) at pH 2.8. The non-cationic species passing through the column was again passed through the anion exchange resin in chloride form. Part of the complex was retained in anionic column. Preliminary studies of the eluted band indicated the presence of anionic mono(malonato)*bis*(glycinato)-Cr(III) complex.

#### References

1. "Inorganic Biochemistry", (Ed.) G. L. EICHORN, Elsevier, Amsterdam, 1973, Vols. 1 and 2.
2. "Metal Ions in Biological Systems", (Ed.) H. SIGEL, Marcel Dekker, New York, 1973-79, Vols. 1-7.
3. H. SIGEL, *Angew. Chem. Int. Ed. Engl.*, 1975, 14, 394.
4. "An Introduction to Bioinorganic Chemistry", (Ed.), D. R. WILLIAMS, Springfield 1976.
5. H. SIGEL, B. E. FISHER and B. PRIJS, *J. Amer. Chem. Soc.*, 1977, 99, 4489.
6. M. S. NAIR, P. NATARAJAN and M. SANTAPPA, *J. Chem. Soc., Dalton Trans.*, 1980, 1312; 1980, 2138; *Inorg. Chim. Acta*, 1980, 41, 7; *Indian J. Chem.*, 1980, 19A, 672, 1106.
7. M. S. NAIR, K. V. CHALAPATHI, M. SANTAPPA and P. K. MURUGAN, *J. Chem. Soc., Dalton Trans.*, 1982, 55; *Inorg. Chem.*, 1982, 21, 2418.

8. M. S. NAIR, K. V. CHALAPATHI and M. SANTAPPA, *J. Chem. Soc., Dalton Trans.*, 1982, 555.
9. W. Y. MERTZ, E. W. TOEPFFERY, E. E. ROGINSKY and M. M. POLANSKY, "Some Recent Advances in Human Nutrition Research", *Federation Proc.*, 1974, 33, No. 11.
10. C. L. ROLLINSON and ROSENBLUM in "Coordination Chemistry", (Ed.) S. KRISHNER, Plenum Press, 1969.
11. S. KIDA, *Bull. Chem. Soc. Japan*, 1961, 34, 962.
12. L. G. SILLEN and A. E. MARTELL, "Stability Constants of Metal-Ion Complexes", Spec. Publ., The Chemical Society, 1964, No. 17, 1971, Suppl. I, No. 25.
13. K. V. CHALAPATHI, M. S. NAIR, D. RAMASWAMY and M. SANTAPPA, *J. Chem. Soc., Dalton Trans.*, 1982, 291.
14. K. V. CHALAPATHI, M. S. NAIR, D. RAMASWAMY and M. SANTAPPA, *Indian J. Chem.* (communicated).
15. K. V. CHALAPATHI, T. RAMASAMI, D. RAMASWAMY and M. SANTAPPA, *Polyhedron* (communicated).
16. I. G. SAYCE, *Talanta*, 1968, 15, 1397; 1971, 18, 653.
17. I. G. SAYCE and V. S. SHARMA, *Talanta*, 1968, 19, 831.
18. A. M. CORRIE, G. K. R. MAKAR, M. L. D. TOUCHE and D. R. WILLIAMS, *J. Chem. Soc., Dalton Trans.*, 1975, 105.
19. R. H. LANE, A. F. SEDOR, M. J. GILBROY and L. E. BENNET, *Inorg. Chem.*, 1977, 16, 102.
20. R. D. GILLARD, S. H. LURIE, D. C. PRINCE, D. A. PHIPPS and C. F. WEICK, *J. Chem. Soc., Dalton Trans.*, 1974, 1385.
21. HISAYAOK and KIYOEOTSUKA, *Bull. Chem. Soc. Japan*, 1976, 49, 1841.
22. R. H. LANE, A. F. SEDOR, M. J. GILBROY and L. E. BENNET, *Inorg. Chem.*, 1977, 16, 102.
23. S. E. LIVINGSTON, *Quart. Rev.*, 1966, 14, 316.
24. W. B. SCHAAPE and D. L. MCMASTERS, *J. Amer. Chem. Soc.*, 1961, 83, 4699.
25. M. S. NAIR, M. SANTAPPA and P. K. MURUGAN, *Inorg. Chem.*, 1982, 21, 142.
26. M. S. NAIR and M. SANTAPPA, *Indian J. Chem.*, 1982, 21A, 58.
27. J. C. CHANG, *J. Inorg. Nuclear Chem.*, 1967, 29, 2387.