Comparison of the Formation Constants of some Chromium(II) and Copper(II) Complexes

Károly Micskei and István Nagypál *
Institute of Inorganic and Analytical Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary

The stability constants of the complexes formed in the Cr^{2+}–tartronate (taro), –L-tartrate (tart), –phthalate (phtal), –diethylenetriamine (dien), –triethylenetetramine (trien), –L-aspartate (asp), –L-glutamate (glu), –*N*-methyliminodiacetate(mimda), –ethylenediamine-*N*,*N*′-diacetate (edda), and –glycylglycine (glygly) systems in aqueous solution of 1 mol dm^{-3} KCl at 25 °C, determined pH-metrically, are as follows: log K_1^{taro} = 3.86, log K_2^{taro} = 2.08, log K_1^{tart} = 2.04, log K_1^{phtal} = 2.48, log K_1^{dien} = 6.67, log K_2^{dien} = 2.68, log K_1^{trien} = 7.33, log K_1^{asp} = 4.67, log K_2^{asp} = 3.46, log K_1^{glu} = 4.53, log K_2^{glu} = 2.96, log K_1^{mimda} = 5.42, log K_2^{mimda} = 3.28, log K_1^{edda} = 7.86, log K_2^{edda} = 2.18, log K_1^{glygly} = 2.15. Protonated complexes are formed in the Cr^{2+}–tartronate, –tartrate, –aspartate, –glutamate, and –glycylglycine systems. The formation constants of the Cr^{2+} and Cu^{2+} complexes are compared and the effects of the different ionic radii and ligand structures are discussed. The significant similarity in the co-ordination properties of these two metal ions can be explained if it is assumed that the Jahn-Teller distortion affects their co-ordination behaviour in the same way.

The complexes formed in the Cr^{2+}–ethylenediamine (en), –malonate (mal), –glycinate (glyO), –β-alaninate (alaO), –iminodiacetate (imda), –nitrilotriacetate (nta), and –ethylenediaminetetra-acetate (edta) systems have been reported previously.[1] The 'excess' stabilities, proportional to ligand-field stability values, were calculated and compared for Cr^{2+} and Cu^{2+} complexes (on the basis of the work of Cannon[2]), demonstrating the similarity in the co-ordination of these two metal ions. The differences between the excess stabilities were interpreted as the effect of fused chelate rings. The detailed study of Cr^{2+} complexes can lead to a better understanding of the effects of the Jahn-Teller distortion on the co-ordination of both metal ions. These studies are in progress in our laboratory.[3,4]

In this paper examinations are extended to Cr^{2+}–tartronate (taro), –L-tartrate (tart), –phthalate (phtal), –diethylenetriamine (dien), –triethylenetetramine (trien), –L-aspartate (asp), –L-glutamate (glu), –*N*-methyliminodiacetate (mimda), –ethylenediamine-*N*,*N*′-diacetate (edda), and –glycylglycine (glygly) systems to study the effects of substituted ligands, chelate ring size, and number of fused chelate rings on complex formation. So far only the Cr^{2+}–dien and –trien systems have been studied.[5]

Experimental

The preparation and analysis of the $CrCl_2$ stock solution and the experiments in the oxygen-free medium were reported in our earlier paper.[1]

A Radiometer PHM-52 pH-meter and GK 2301 B electrode used for pH measurements were calibrated for $-\log [H^+]$ according to Irving *et al.*[6] The ionic strength of all the solutions was adjusted to 1 mol dm^{-3} (KCl) at 25 °C.

The liquid ligands (dien and trien) were purified by vacuum distillation, the solid ligands by recrystallization from water. The protonation constants for all the ligands and the formation constants for the Ba^{2+}–taro, –tart, –phtal, –mimda, –edda, –asp, and –glu systems were determined because of the Ba^{2+} contamination of the $CrCl_2$ stock solution. The initial total concentrations used for pH-titrations are collected in Table 1. After the evaluation of the formation curves the calculations were carried out with the program PSEQUAD.[7]

Results and Discussion

The protonation constants of all the ligands and the formation constants of Ba^{2+} complexes obtained agreed well with literature data.[8]

The analysis of the formation curves showed disturbing equilibrium processes in the case of the Cr^{2+}–tart, –taro, –asp, –glu, and –glygly systems in the lower pH range (tart, taro 2.0—3.5; asp, glu 3.5—5.5; glygly 4.5—5.5). The stability constants of the protonated complexes were calculated. Formation constants of the Cr^{2+} complexes after the final calculations are collected in Table 2.

The stability constants for the [Cr(taro)] and [Cr(mimda)] complexes were a little larger than for [Cr(mal)] and [Cr(imda)] because of the higher electron density on the donor atoms caused by hydroxyl and methyl substituents. These are similar to those of Cu^{2+} complexes formed with the same ligands. The trend of the stability values log $K_1^{[Cr(asp)]}$ > log $K_1^{[Cr(glu)]}$ > log $K_1^{[Cr(glyO)]^+}$ being different from log $K_1^{[Cu(asp)]}$ > log $K_2^{[Cu(glyO)]^+}$ > log $K_1^{[Cu(glu)]}$ can be explained by the greater ionic radius of Cr^{2+} (Cu^{2+}, 69 pm; Cr^{2+}, 82 pm). The [Cu(glu)] complex cannot be stabilized by the second, longer carboxyl group of the ligand. This is only possible with the larger Cr^{2+} (see data in ref. 1). The dissociation process of the peptide nitrogen proton, which is characteristic of the Cu^{2+}–glygly system could not be found in the Cr^{2+} system; only protonated and mono complexes formed because of the hydrolysis of the less stable complexes.

The value of log (K_1/K_2) (Table 3) increases significantly for

the fused chelate-ring ligands (mimda, dien, trien). The higher values for Cu^{2+} complexes can be attributed to the smaller ionic radius of the Cu^{2+} ion. The values for non-fused multidentate chelate ligands (asp, glu) are similar to those for bidentate ligands published previously[1] because of their glycine-type co-ordination.

The $\Delta\log K_{Cr}/\Delta\log K_{Cu}$ values, ratios of excess stabilities (r.e.s.), are collected in Table 4, together with our earlier data.[1] For the five- and six-membered bidentate chelate-ring ligands the r.e.s. values are the same (taro, mal, glyO, alaO, en) and independent of the nature of the donor groups. They are similar for asp and glu ligands also, because of their glycine-type co-ordination. Significant increase in the r.e.s. values was found only in the case of the seven-membered bidentate chelate-ring ligands (tart, phtal), a consequence of the size of Cr^{2+} Increasing the number of fused chelate rings decreases the r.e.s. values uniformly only for the same donor groups and chelate ring size (en > dien > trien). However, this tendency remains valid for the substituted amine (glyO > imda > nta) and ethylenediamine ligands (en > edda > edta) also. This tendency has been explained by the unfavourable placing of the five-membered fused chelate rings on the larger Cr^{2+} ion. The differences between chelate rings of the same size are related to the dissimilarity of excess stabilities caused by the ligands containing different numbers of oxygen- and nitrogen-donor groups.

Considering this and our earlier results,[1] significant similarities have been found in the co-ordination properties of Cr^{2+} and Cu^{2+} complexes, related to their analogous electron structures (d^4 and d^9 respectively). All the differences can be explained by the relative ion sizes and ligand structures. Co-ordination of the second multidentate ligands is more favourable in the co-ordination spheres of Cr^{2+} than in the case of Cu^{2+} because of the lower steric hindrance.

On increasing the number of fused chelate rings, the difference in the effect of ligand structures on excess stabilities between the Cu^{2+} and Cr^{2+} complexes increases, because of the hindered positions of the fused chelate rings on the larger Cr^{2+} ion. The Jahn-Teller distortion, which is generally used to explain the co-ordination of these two metal ions, is really the same, as the interpretation of our data suggests.

Table 1. Initial total concentrations of solutions used for pH-metric titrations

Ligand	T_H^0	T_L^0	T_{Cr}^0
Tartronate	0.029 64	0.013 45	0.004 87
	0.059 28	0.026 90	0.009 75
	0.075 47	0.033 63	0.014 62
	0.078 21	0.033 63	0.019 50
	0.107 85	0.047 08	0.024 37
Tartrate	0.085 48	0.040 00	0.009 75
	0.072 22	0.032 00	0.014 62
	0.090 96	0.040 00	0.019 50
	0.109 70	0.048 00	0.024 37
Phthalate	0.048 22	0.040 00	0.014 62
	0.093 70	0.080 00	0.024 37
	0.053 48	0.048 00	0.009 75
	0.034 74	0.032 00	0.004 88
N-Methylimino-diacetate	0.034 74	0.160 00	0.004 88
	0.069 48	0.032 00	0.009 70
	0.072 22	0.032 00	0.014 62
	0.090 96	0.040 00	0.019 50
	0.125 70	0.056 00	0.024 37
Ethylenediamine-*N,N'*-diacetate	0.039 51	0.016 00	0.004 87
	0.021 99	0.024 00	0.009 75
	0.024 73	0.024 00	0.014 62
	0.077 62	0.040 00	0.019 50
	0.130 52	0.056 00	0.024 37
Aspartate	0.098 21	0.096 00	0.014 62
	0.102 97	0.104 00	0.009 75
	0.125 10	0.080 00	0.019 50
	0.161 52	0.080 00	0.014 62
	0.120 34	0.072 00	0.024 37
Glutamate	0.088 22	0.040 00	0.004 87
	0.084 52	0.040 00	0.009 75
	0.141 55	0.080 00	0.014 62
	0.138 79	0.072 00	0.019 50
	0.136 03	0.064 00	0.024 37
Diethylenetriamine	0.077 13	0.027 30	0.004 87
	0.117 07	0.040 95	0.009 75
	0.157 00	0.054 61	0.014 62
	0.196 94	0.068 26	0.019 50
	0.274 07	0.095 55	0.024 37
Triethylenetetramine	0.064 57	0.015 26	0.004 87
	0.098 23	0.022 88	0.009 75
	0.131 89	0.030 51	0.014 62
	0.103 71	0.022 88	0.024 37
	0.137 37	0.030 51	0.024 37
Glycylglycine	0.088 22	0.080 00	0.014 62
	0.376 44	0.360 00	0.029 25
	0.413 70	0.400 00	0.024 37
	0.223 58	0.200 00	0.019 05
	0.119 57	0.100 00	0.004 87

Table 3. Comparison of $\log(K_1/K_2)$ values for Cu^{2+} and Cr^{2+} complexes

	$\log(K_1/K_2)$	
Ligand	Cu^{2+}	Cr^{2+}
Tartronate		1.78
Aspartate	1.79	1.21
Glutamate	1.30	1.57
N-Methyliminodiacetate	5.07	2.14
Diethylenetriamine	11.16	3.99
Ethylenediamine-*N,N'*-diacetate		5.68

Table 2. Stability constants of the Cr^{2+} complexes*

Ligand (L)	$\log\beta(CrLH)$	$\log\beta(CrL)$	$\log\beta(CrL_2)$
Tartronate	6.17 ± 0.04	3.86 ± 0.02	5.94 ± 0.03
Tartrate	5.55 ± 0.03	2.04 ± 0.02	
Phthalate		2.48 ± 0.02	
N-Methyliminodiacetate		5.42 ± 0.03	8.70 ± 0.04
Ethylenediamine-*N,N'*-diacetate		7.86 ± 0.01	10.04 ± 0.03
Aspartate	10.63 ± 0.03	4.67 ± 0.03	8.13 ± 0.04
Glutamate	11.02 ± 0.03	4.53 ± 0.02	7.49 ± 0.04
Diethylenetriamine		6.67 ± 0.02 (6.78)	9.35 ± 0.03
Triethylenetetramine		7.33 ± 0.04 (8.00)	
Glycylglycine	10.09 ± 0.02	2.15 ± 0.05	

* Data in parentheses from ref. 5.

Table 4. Logarithms of the stability constants of Mn^{2+}, Zn^{2+}, Cu^{2+}, and Cr^{2+} mono complexes; excess stabilities of Cr^{2+} and Cu^{2+} complexes and their ratios[a]

Ligand	Mn^{2+} [b]	Zn^{2+} [b]	Cu^{2+} [b]	Cr^{2+}	$\Delta\log K^{Cr}$	$\Delta\log K^{Cu}$	$\Delta\log K^{Cr}/\Delta\log K^{Cu}$
Tartronate	2.37	2.92	5.34	3.86	1.60	2.53	0.63
Tartrate	1.44	2.69	3.25	2.04	0.85	0.81	1.05
Phthalate	2.04	2.74	3.14	2.48	0.58	0.54	1.07
Aspartate	3.74	5.84	8.57	4.67	1.35	3.15	0.43
Glutamate	3.30	5.45	7.85	4.53	1.66	2.83	0.59
Diethylenetriamine	3.89	9.10	16.02	6.67	3.82	7.96	0.48
Triethylenetetramine	5.43	11.90	20.40	7.33	3.20	9.79	0.33
N-Methyliminodiacetate	5.40	7.66	11.90	5.42	0.48	4.69	0.10
Ethylenediamine-*N*,*N*′-diacetate	7.71	11.90	15.90	7.86	0.99	4.84	0.20

[a] $\Delta\log K^{Cu} = \log K^{Cu} - (\log K^{Mn} + 4 \log K^{Zn})/5$, $\Delta\log K^{Cr} = \log K^{Cr} - (6 \log K^{Mn} - \log K^{Zn})/5$. R.e.s. (ref. 1): en, 0.61; mal, 0.59; glyO, 0.54; alaO, 0.48; imda, 0.01; nta, −0.10; edta, −0.21. [b] Data from ref. 8.

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