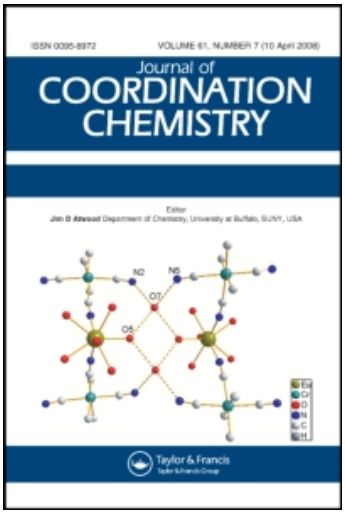

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Studies on Biologically Relevant Binary and Ternary Metal Complexes. IV. Stability of Binary and Ternary Metal Complexes Containing Bis(Imidazol-2-Yl)Methane and Amino Acids

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NOTE

STUDIES ON BIOLOGICALLY RELEVANT BINARY AND TERNARY METAL COMPLEXES. IV. STABILITY OF BINARY AND TERNARY METAL COMPLEXES CONTAINING BIS(IMIDAZOL-2-YL)METHANE AND AMINO ACIDS

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Formation constants for the interaction of bis(imidazol-2-yl) methane (BIM) with Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) are reported at t = 35°C, u = 0.2M (KNO_3). Stability constants for the ternary complexes (MLA) of Co(II), Ni(II), Zn(II) and Cd(II) with BIM as primary ligand (L) and various amino acids, ethylenediamine and pyrocatechol as secondary ligands (A) are also reported under similar experimental conditions. Factors contributing to the stability of the binary and ternary complexes are discussed.

Keywords: Bis(Imidazol-2-yl)methane, aminoacids, complexes, stability constants.

INTRODUCTION

Ternary complexes have been extensively investigated as biomimetic models of enzyme–metal ion–substrate complexes.[1–5] As a continuation of our earlier work[6–9] on ternary metal complexes containing imidazole or imidazole derivatives, we have determined the formation constants of ternary Co(II), Ni(II), Zn(II) and Cd(II) complexes (MLA) containing bis(imidazol-2-yl)methane (BIM) as the primary ligand (L) and glycine, alanine, valine, norvaline, leucine, norleucine, phenylalanine, tryptophan, serine, threonine, methionine, aspartic acid, histidine, pyrocatechol, 5-nitropyrocatechol and ethylenediamine as secondary ligands (A). The formation constants of the binary mono (ML) and bis (ML_2) complexes of BIM with Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) have also been determined potentiometrically at 35.0°C and μ = 0.2 M (KNO_3). The experimental details have been described in an earlier paper.[8] The formation constants of the binary and ternary metal complexes are reported in Tables I and II respectively.

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TABLE I

Formation constants[a] of the binary metal complexes: T = 35°C; μ = 0.2 M (KNO_3).

Ligand	Co(II)		Ni(II)		Zn(II)		Cd(II)		Mn(II)	Mg(II)	Ca(II)
	$\log K^{M}_{MA}$	$\log K^{M}_{MA_2}$	$\log K^{M}_{MA}$	$\log K^{MA}_{MA_2}$	$\log K^{M}_{MA}$	$\log K^{MA}_{MA_2}$	$\log K^{M}_{MA}$	$\log K^{MA}_{MA_2}$	$\log K^{M}_{MA}$	$\log K^{M}_{MA}$	$\log K^{M}_{MA}$
Bis(imidazol-2-yl) methane	5.40	4.48	6.85	5.93	5.13	4.67	4.94	4.39	3.18	1.63	1.80
Glycine	4.62	4.11	5.90	4.54	4.86	4.13	4.12	3.45			
Alanine	4.35	3.42	5.60	4.10	4.80	4.05	4.10	3.40			
Valine	4.24	3.56	5.70	4.29	4.70	4.02	3.91	3.32			
Norvaline	4.27	3.75	5.80	4.42	4.70	3.87	3.85	3.19			
Leucine	4.27	3.66	5.47	4.43	4.69	3.99	4.01	3.29			
Norleucine	4.21	3.69	5.40	4.40	4.55	3.91	3.99	3.22			
Serine	4.19	3.52	5.42	4.34	4.66	3.83	3.78	3.02			
Threonine	4.13	3.78	5.52	4.28	4.69	3.84	3.89	3.28			
Methionine	3.98	3.52	5.32	4.34	4.37	3.56	3.63	2.88			
Aspartic acid	5.78	4.72	7.17	5.99	5.23	4.09	4.31	3.29			
Histidine	8.11		8.35		6.34		5.86				
Ethylenediamine	5.81	4.69	7.46	6.25	5.62	4.55	5.34	4.35			
Phenylalanine	3.90	3.65	5.13	4.02	4.61	3.66	3.78	3.27			
Tryptophan	4.10	3.91	5.25	4.45	4.59	4.05	3.66	3.42			
Pyrocatechol	7.69	6.48	7.60	6.18	8.11	6.46	7.46	4.80			
5-Nitropyrocatechol	6.25	5.02	6.16	4.98	6.52	5.27	5.96	4.80			

Dissociation constants at 35°C; μ = 0.2 (KNO_3): bis(imidazol-2-yl)methane, $pK_1 = 4.38$; $pK_2 = 6.69$; ethylenediamine dihydrochloride, $pK_1 = 6.80$; $pK_2 = 9.88$; pyrocatechol, $pK_1 = 9.09$; $pK_2 = 12.88$; 5-nitropyrocatechol, $pK_1 = 6.54$; $pK_2 = 10.28$. [a] Errors in log K values are ±0.02.

TABLE II

Formation constants for the ternary complexes and corresponding Δlog K values;[a] T = 35°C; μ = 0.2 M (KNO_3).

	Co(II)		Ni(II)		Zn(II)		Cd(II)	
Secondary ligands (A)	log K^{ML}_{MLA}	Δlog K	log K^{ML}_{MLA}	Δlog K	log K^{ML}_{MLA}	Δlog K	log K^{ML}_{MLA}	Δlog K
Glycine	4.22	−0.40	5.40	−0.50	4.40	−0.46	3.56	−0.56
Alanine	3.89	−0.46	5.07	−0.53	4.33	−0.47	3.50	−0.60
Valine	3.81	−0.43	5.14	−0.56	4.21	−0.49	3.47	−0.44
Norvaline	3.86	−0.41	5.23	−0.57	4.29	−0.41	3.45	−0.40
Leucine	3.86	−0.41	4.87	−0.60	4.26	−0.43	3.62	−0.39
Norleucine	3.84	−0.37	5.01	−0.39	4.14	−0.41	3.58	−0.41
Serine	3.71	−0.48	4.88	−0.54	4.13	−0.53	3.21	−0.52
Threonine	3.64	−0.49	4.94	−0.58	4.21	−0.48	3.38	−0.51
Methionine	3.57	−0.41	4.72	−0.60	3.81	−0.56	3.09	−0.54
Aspartic acid	5.10	−0.68	6.46	−0.71	4.57	−0.66	3.62	−0.69
Histidine	7.32	−0.79	7.58	−0.77	5.57	−0.72	5.10	−0.76
Ethylenediamine	4.92	−0.89	6.63	−0.83	4.71	−0.91	4.53	−0.81
Phenylalanine	3.76	−0.14	4.88	−0.25	4.39	−0.22	3.59	−0.19
Tryptophan	4.22	+0.12	5.28	+0.03	4.66	+0.07	3.67	+0.01
Pyrocatechol	7.49	−0.20	7.42	−0.18	7.90	−0.21	7.31	−0.15
Nitropyrocatechol	5.81	−0.44	5.71	−0.45	6.09	−0.43	5.57	−0.39

[a] Δlog K calculated according to equation (*1*).

The formation constants for the binary BIM–metal complexes (Table I) follow the Irving–Williams order.[10] The higher affinity of BIM for Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) and the lower affinity for Mn(II), Mg(II) and Ca(II) may be rationalized in terms of Pearson's HSAB Principle.[11] In ternary complexes the influence of BIM in modifying the behaviour of the metal ion towards the secondary ligand has been quantitatively expressed in terms of the parameter Δlog K which is defined by equation (*1*).

$$\Delta\log K = \text{Log } K^{ML}_{MLA} - \log K^{M}_{MA} \qquad (1)$$

The Δlog K values for all the systems investigated in the present work are listed in Table II. In order to obtain precise Δlog K values, the binary and ternary constants have been determined under identical experimental conditions. For a regular octahedral metal ion and bidentate primary and secondary ligands the statistically expected Δlog K value[2] is −0.4.

The Δlog K values for the ternary complexes of Co(II), Ni(II), Zn(II) and Cd(II) with various amino acids, excepting tryptophan and phenylalanine, are of magnitude expected statistically. The enhanced stability of ternary complexes containing tryptophan and phenylalanine is attributed to intramolecular metal ion-bridged stacking interactions between the aromatic side chain of these amino acids and the imidazole groups of BIM. The corresponding Cu(II) ternary complexes[8] show stronger stacking interactions. The enhanced stability of ternary complexes containing pyrocatechol can be attributed to $d\pi \rightarrow p\pi$ back bonding, thus leading to a higher positive charge on the metal ion and a consequent stronger interaction with the negative oxygen atoms of pyrocatechol. Comparison of the Δlog K values for pyrocatechol, glycine and ethylenediamine show that the relative ability of the donor atoms in the secondary ligand to bind the [M(II)–BIM] complex decreases in the order $^{-}$O–O^{-} > N–O^{-} > N–N. When viewed in terms of the nature of the metal ion, Ni(II) seems to have a lower tendency to form ternary complexes. Stacking and related noncovalent interactions play an important role in the specificity, selectivity and reactivity of metalloenzyme catalysed reactions.[12]

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