FORMATION CONSTANTS OF METAL-COMPLEXES
IN NON-AQUEOUS SOLVENTS* (PART III) (DMSO)

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* Part I – (Acetonitrile) – *Rev. Anal. Chem.* 5, 257 (1981).

Part II – (DMF) – *J. Scient. Ind. Res.* 41, 314 (1982).

SUMMARY

A review has been compiled of the formation constants of metal complexes in dimethylsulphoxide. The values of the overall stability constants and ion-pair association constants along with various other parameters, determined by different analytical techniques, have been given.

Dimethylsulphoxide (DMSO) has optical properties that are less favourable than dimethylformamide and acetonitrile, but can be used in the spectral region between 350 and 2200 nm /1/. Some of its physical properties are summarized in Table I. Its physical properties, purification procedures and choice of reference electrode and electrolytes in this medium have been described elsewhere /2-4/.

Table 1: Physical Properties of DMSO

Molecular weight	78.134
Freezing Point	18.54
Boiling Point (1 atm.)	189.0
Density (25°)	1.0958
Viscosity (25°)	1.996
Refractive Index (25°)	1.4773
Dielectric Constant (25°)	46.68
Dipole moment (25°)	3.9

The first voltametric studies in DMSO were conducted in 1959 by Cutmann and Schober /5/ in which they employed conventional and derivative polarographic methods for the study of alkali and alkaline earth metal ions using tetraethylammonium nitrate as the supporting electrolyte.

Matsuura *et al.* /6/ have studied the formation of halide complexes of lead and cadmium in DMSO, DMF and propylene carbonate using potentiometric methods. The formation of chloride, bromide, iodide and thiocyanate complexes of Cd in DMSO has been studied by Ahrland and Bjork /7, 8/ with the help of potentiometric and calorimetric titrations. They concluded that all the complexes formed are more stable in DMSO than in water. Samoilenko and coworkers /9/ have investigated potentiometrically the chloride, bromide, iodide and thiocyanate complexes of Cd and Hg(II). The halide complexes of Cd and bromide complexes of Hg(II) and Zn in DMSO have been studied by Ahrland *et al.* /10/ in 0.1 M ammonium perchlorate medium. The stability constants have been determined potentiometrically and in most

cases also calorimetrically. It has also been reported that the complexes are more stable in 0.1 M ammonium perchlorate than in 1 M ammonium perchlorate medium /7/. The complexes formed by Cd, Zn and Ag with n-butylamine and tri-n-butylphosphine in DMSO have been studied by Ahrlund *et al.* /11/. Ahrlund and coworkers /12,13/ have investigated the formation of halide and thiocyanate complexes of Zn and have evaluated their corresponding enthalpy changes in DMSO employing potentiometric and calorimetric data wherein they have found that all complexes formed are stabler in DMSO than in water /12/.

Suarez *et al.* /14/ have studied the chloro complexes of Cu(I) and Cu(II) in DMSO employing potentiometric and spectrophotometric techniques. The halide and thiocyanate complexes of Cu(I) as well as the chloride, bromide and thiocyanate complexes of Cu(II) have been studied potentiometrically by Foll and coworkers /15/ wherein they concluded that the halide complexes were more stable in DMSO than in aqueous solution. Sasaki *et al.* /16/ have investigated the halo and thiocyanato complexes of Cu(II) in DMSO, propylene carbonate and DFM employing potentiometric titrations. The stability constants and thermodynamic functions of Cu(I) halide and Cu(II) bromide complexes have been determined by Ahrlund and coworkers /17/. They have also studied /18/ the Cu(II) and Hg(II) complexes with ligands coordinating via N, P, As, Sb, or Bi employing a 0.1 M ammonium perchlorate medium. Stability constants have been determined potentiometrically by copper amalgam and mercury electrodes. The overall stability constants of the Hg(II) halide and thiocyanate complexes and their thermodynamic functions in DMSO have been investigated potentiometrically and calorimetrically by Ahrlund *et al.* /19/. The halide and thiocyanate complexes of Hg(II) have been studied by various other workers /20, 21/ in DMSO. Anodic dissolution of mercury and silver electrodes in the presence of polyamines /22/ has led to the study of formation of Hg(II) and Ag complexes with ethylenediamine, Symdimethylethylenediamine, NNN'N'-tetramethylethylenediamine, propane-1,3-diamine and triethylenetetramine. The electrode reaction orders, complexation steps and the stability constants of the complex species arising at the electrode surface have been studied by D.C. voltametry, cyclic voltametry and controlled potential coulometry.

Various workers /23-31/ have determined the solubility products and the overall formation constants of silver halides and acetate in DMSO and various other solvents using potentiometric and voltametric techniques; the formation of a polynuclear complex Ag_5I_7^- has

been reported /23/. The stability constants of Ag with triphenyl compounds Ph_3X (X = N, P, As, Sb or Bi) and their thermodynamic functions have been determined potentiometrically and calorimetrically in DMSO by Åhrland *et al.* /32/. Udovanko and Pomerant /33/ have investigated the complex formation of silver ions with ethanolamines (2-aminoethanol, 2,2'-iminobisethanol and 2,2'-nitrilotrisethanol) in DMSO and DMF employing potentiometric technique. The stability constants of cryptate complexes with Ag, Tl and K have been determined by Gutknecht and coworkers /34/ in DMSO, DMF, acetonitrile, propylene carbonate, hexamethylphosphortriamide and methanol at different temperatures with the help of potentiometric titration. The values of ion pair formation constants of Na with diethylfumarate and the benzil radical anion in DMSO, DMF and acetonitrile have been evaluated by Ryan and Evans /35, 36/. Ion association constants of Na^+ and K^+ with 1,4-naphthoquinone radical anions have been determined polarographically by Jaworski and Kalinowski /37/.

Suarez *et al.* /38/ have studied the chloro complexes of Au in DMSO using voltametric and potentiometric techniques. The Pt(II) chloro and bromo complexes in DMSO have been detected potentiometrically by Kukushkin *et al.* /39/ who have also calculated their overall stability constants. Samoilenko and Lyashenko /40/ have studied the halide and thiocyanate complexes of bismuth potentiometrically.

Conductance measurements of salt /41-47/ solutions (halides, perchlorate, nitrates and trifluoroacetates of alkali metal ions, Mn, Co, Ni, Cd and Cu) have yielded their ion pair association constants. Tanaka and Harada /48/ have determined the ion association constants of ion pairs formed between tris(ethylenediamine) Co (III) and the perchlorate, halide and thiocyanate ions in DMSO and DMF media. Association constants for *cis*- and *trans*-dichlorobisethylenediamine cobalt(III), *cis*-dichlorobis-ethylenediamine chromium(III) ions with chloride and bromide ions have been measured in DMSO employing spectrophotometric and conductometric techniques by Watts *et al.* /49-53/.

The formation constants for the 1:1 complexes of dibenzo-18-crown-6 with alkali metal ions in DMSO, DMF and propylene carbonate have been determined by Matsuura and coworkers /54/. Tusek-Bozik and Danse /55/ have measured the association constants for the formation of complexes between the macrocyclic polyethers bis(4-tert-butylbenzo)-18-crown-6 and bis(3,5-di-tert-butylbenzo)-18-crown-6 and alkali metal cations in DMSO, acetonitrile and methanol employing conductometric and potentiometric techniques.

The complexes of Co(II) with chloride and thiocyanate ions in DMSO have been investigated spectrophotometrically by Magnell and Reynolds /45/ and Schriver /56/. Employing IR spectroscopy Mieziš /57, 58/ has determined the stability constants of Co(II) and Ni-thiocyanate complexes in DMSO, propylene carbonate and acetonitrile and has concluded that there is N-coordination between the metal and thiocyanate ion. Skopenko and Spivak /59/ have studied spectrophotometrically the formation of selenocyanate complexes of Co(II) and Ni in DMSO and have concluded that Co(II) forms two complex species while Ni forms only one species. The stability constants of Co(II), Ni and Cu-dicyanamide and tricyanomethanide have been determined spectrophotometrically in DMSO, DMF, acetone, propylene carbonate and water by Skopenko and Bolely /60, 61/. Dulova and coworkers /63/ have investigated the complexes of Cu(II) formed with pyridine and primary aliphatic amines. The stability constants of mixed complexes formed between iodide ions and Co(III)-dimethylglyoxime, Co(III)-cyclohexane-1,2-dione-dioxime and Co(III)-furyl-dioxime in DMSO, DMF, acetone and acetonitrile have been determined by Burger *et al.* /63, 64/.

Luehrs and Abate /65/ have investigated the chloride, bromide, iodide and thiocyanate complexes of Ag in DMSO, acetone and acetonitrile employing solubility and spectrophotometric measurements. They have reported the formation of polynuclear complex species, Ag_2X^+ , Ag_3X^{2+} , and their stability constants have been determined and compared with parallel complex species in water. The chloride and bromide complexes of Te have been studied spectrophotometrically by Korewa *et al.* /66,67/. Wada and Reynolds /68,69/ have studied spectrophotometrically the Fe(III)-chloride complexes and have reported the formation of two complex species. The thiocyanate complex of Fe(III) has been investigated by Longford and Chung /70/. The binding of cyanide ion and imidazole to ferriprotoporphyrine has been studied by Wang and coworkers /71/ who have determined the stability constants of the complex species. The Fe(III) complexes with dihydrogen violurate have been investigated by Julve *et al.* /72/ employing spectrophotometry and potentiometry.

Bismuth thiocyanate complexes in DMSO, DMF acetone and acetonitrile have been investigated spectrophotometrically by Skopenko and Zhumobaev /73/. Yatsimirskaya and coworkers /74, 75/ have studied the complexes of Bi(III) with potassium diphenyldiselenophosphate in DMSO and some other organic solvents. They have reported that the

increased solvation ability shifts the maximum absorption band of the complex to longer wavelengths and that there is a correlation between the stability constants and the solvent donor strength.

Complexes of Cs with three crown ethers viz. 18-crown-6, dibenzo-18-crown-6 and dicyclohexyl-18-crown-6 in DMSO, DMF, acetone, pyridine, propylene carbonate and acetonitrile have been evaluated from their NMR spectra /76/. In all the solvents, 18-crown-6 formed both 1:1 and 2:1 (metal-ligand) complexes. The formation of 2:1 complexes with the other two crown ethers has also been indicated in most solvents. Popov and coworkers /77, 78/ have investigated the complexes of Cs with cryptand C222 over a wide range of temperature and K^+ complexes with Cryptands C222, C221 and C211 in various organic solvents including DMSO by NMR spectra. Employing PMR studies, Wang and Li /79/ have determined the stability constants of Zn with imidazole, purine & pyrimidine derivatives in DMSO.

The complexing of NaI with Zn, Cd and Hg(II) in DMSO, DMF, pyridine, acetonitrile, acetone and methyl alcohol has been studied using calorimetric titrations /80/. It was found that the composition of the complex depends on the nature of the solvents. Arnek and Poceva /81/ have determined the stability constants and enthalpy changes of Hg(II)-bromide and iodide complexes calorimetrically.

The overall stability constants and ion-pair formation constants of metal ions with respective ligands have been compiled in Tables 2 and 3 respectively. The metal ions have been arranged alphabetically.

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TABLE 2

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remark	Reference
Ag ⁺	Cl ⁻	p ^a (M ⁺)	25	$\beta_2 = 12.1$	$K_{sO} = 10^{-10.4}$	25
	Cl ⁻	Pot.	25	$\beta_2 = 11.7$	$K_{sO} = 10^{-10.4}$	26
	Cl ⁻	Pot.		$\beta_2 = 12.2$	$K_{sO} = 10^{-10.9}$	28
	Cl ⁻	Pot.	23	$\beta_2 = 11.2$	$K_{sO} = 10^{-10.4}$	29
	Cl ⁻	Volt.	23	$\beta_2 = 12.1$	I = 0.1 (TEAP)	29
	Cl ⁻	Pot.	25-75	$\beta_2 = 10.59(25^\circ); 10.23(45^\circ)$	I = 0.1 (NH ₄ NO ₃)	30
				9.92 (55°); 9.42 (75°)	$K_{sO} = 10^{-9.66}$	
	Cl ⁻	Sol.	24	$\beta_{12} = (Ag_2Cl_2^+) = 7.73$	I = 0.5 (TEAP)	12
				$\beta_{13} = (Ag_3Cl_2^+) = 7.32$		
	Br ⁻	Pot.	25	$\beta_2 = 11.4$	$K_{sO} = 10^{-10.6}$	26
	Br ⁻	Pot.	23	$\beta_2 = 11.7$	$K_{sO} = 10^{-10.6}$	29
		Volt.	23	$\beta_2 = 12.3$	I = 0.1 (TEAP)	29
	Br ⁻	Pot.	25-85	$\beta_2 = 10.59(25^\circ); 10.43(45^\circ)$	$K_{sO} = 10^{-10.04}$	30
				10.18 (65°), 10.1 (85°)	I = 0.1 (NH ₄ NO ₃)	30
	Br ⁻	Sol.	24	$\beta_{12} = (Ag_2Br_2^+) = 8.23$	I = 0.5 (TEAP)	65
	I ⁻	Pot.	25	$\beta_2 = 12.5$	$K_{sO} = 10^{-11.4}$	26
	I ⁻	Pot.	23	$\beta_2 = 13.1$	$K_{sO} = 10^{-12.0}$	29
		Volt.	23	$\beta_2 = 13.2$	I = 0.1 (TEAP)	
	I ⁻	Pot.	25-28	$\beta_{32}(Ag_3I_4) = 23.95(25^\circ)$	$K_{sO} = 10^{-11.47}$	30
				23.04 (45°),	I = 0.1 (NH ₄ NO ₃)	
				21.83 (65°),	I = 0.5 (TEAP)	
				20.83 (85°)		65

Table 2 / cont. ...

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remarks	References
I ⁻		Sol.	24	$\beta_{12}(\text{Ag}_2\text{I}^+) = 10.04$ $\beta_{13}(\text{Ag}_3\text{I}^{2+}) = 10.61$ $\beta_1 = 2.10; \beta_2 = 3.33;$ $\beta_1 = 9.28; \beta_2 = 15.91;$ $\beta_3 = 19.82$ $\beta_1 = 0.11$	I = 0.5 (TEAP)	65
Bu ₃ N		Pot.	25		I = 0.1 (NH ₄ CO ₃)	11
Bu ₃ P		Pot.	25		I = 0.1 (NH ₄ CO ₃)	11
Ph ₃ N		Pot.	25		I = 0.1 (NH ₄ CO ₃)	11
Fl ₃ P		Pot.	25		I = 0.1 (NH ₄ CO ₃)	32
Fl ₃ As		Pot.	25		I = 0.1 (NH ₄ CO ₃)	32
Fl ₃ Sb		Pot.	25		I = 0.1 (NH ₄ CO ₃)	32
Fl ₃ Bi		Pot.	25		I = 0.1 (NH ₄ CO ₃)	32
SCN ⁻		Sol.	24	$\beta_{12}(\text{Ag}_2\text{SCN}^+) = 6.40$ $\beta_2 = 8.6$	I = 0.5 (TEAP)	65
CH ₃ COO ⁻		Pot.	25		I = 0.5 (TEAP)	27
MEA		Pot.	25	$\beta_1 = 4.7; \beta_2 = 7.04$	I = 0.2 (LiNO ₃)	33
DEA		Pot.		$\beta_1 = 3.30; \beta_2 = 5.34$	I = 0.2 (LiNO ₃)	33
TEA		Pot.		$\beta_1 = 1.78; \beta_2 = 3.0$	I = 0.2 (LiNO ₃)	33
en		Volt.	25	$\beta_1 = 3.3$		22
dmien		Volt.	25	$\beta_1 = 2.0$		22
Pd		Volt.	25	$\beta_1 = 2.0$		22
trien		Volt.	25	$\beta_1 = 5.3$		34
					I = 0.1 (TEAP)	
					G = 40.8 kJ mol ⁻¹	
					H = 47.8 kJ mol ⁻¹	
					S = 21 J deg ⁻¹ mol ⁻¹	

Table 2 / cont. . . .

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remarks	Reference
Bi ³⁺	Cl ⁻	Pot.	25	$\beta_1 = 10.9; \beta_2 = 15.6$	I = 1 (LiClO ₄)	38
	Cl ⁻	Pot.		$\beta_1 = 4.5; \beta_2 = 8.84; \beta_3 = 12.0$		40
	Br ⁻	Pot.	25	$\beta_4 = 14.49$	I = 1 (LiClO ₄)	40
	Br ⁻	SP	25	$\beta_1 = 4.0; \beta_2 = 7.0$	I = 1 (LiClO ₄)	40
				$\beta_3 = 10.0; \beta_4 = 12.36$		
				$\beta_1 = 4.04; \beta_2 = 6.9$		
	I ⁻	Pot.	25	$\beta_3 = 10.0; \beta_4 = 12.46$	I = 1 (LiClO ₄)	40
				$\beta_1 = 2.0; \beta_2 = 5.78$		
				$\beta_3 = 8.5; \beta_4 = 12.0$		
				$\beta_5 = 15.6; \beta_6 = 17.48$		
Bi ³⁺	SCN ⁻	Pot.	25	$\beta_1 = 1.4$	I = 1 (LiClO ₄)	40
	Potassium Di-phenyl diseno-phosphate	SP	25	$\beta_3 = 2.22$	I = 1 (LiClO ₄)	53
Cd ²⁺	Cl ⁻	Pot.	25	$\beta_1 = 3.3; \beta_2 = 6.0$	I = 1 (NaClO ₄)	9
	Cl ⁻	Pot.	25	$\beta_3 = 8.59; \beta_4 = 10.84$	I = 1 (NH ₄ ClO ₄)	6
				$\beta_3 = 12.9; \beta_4 = 14.4$		
				$\beta_1 = 3.20; \beta_2 = 5.08$		
	Cl ⁻	Pot.	25	$\beta_3 = 7.71; \beta_4 = 9.43$	I = 1 (NH ₄ ClO ₄)	7
				$\beta_1 = 3.62; \beta_2 = 6.18$		
				$\beta_3 = 9.3; \beta_1 = 11.65$		
	Cl ⁻	Pot.	25	$\beta_1 = 4.36; \beta_1 = 7.38$	I = 1 (LiClO ₄ · 3H ₂ O)	7
				$\beta_3 = 10.76; \beta_4 = 13.18$	I = 0.1 (NH ₄ ClO ₄)	10

Table 2/ cont. . . .

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remarks	References
Co ²⁺	Br ⁻	Pot.	25	$\beta_1 = 3.3; \beta_2 = 5.84;$ $\beta_3 = 8.25; \beta_4 = 10.70$	I = 1 (NaClO ₄)	9
	Br ⁻	Pot.	25	$\beta_1 = 9.5; \beta_4 = 11.9$		6
	Br ⁻	Pot.	25	$\beta_1 = 2.93; \beta_2 = 4.70$		
	Br ⁻	Pot.	25	$\beta_1 = 7.56; \beta_4 = 9.20$	I = 1 (NH ₄ ClO ₄)	7
				$\beta_1 = 3.69; \beta_2 = 6.23;$ $\beta_1 = 9.46; \beta_4 = 11.29$	I = 0.1 (NH ₄ ClO ₄)	10
	I ⁻	Pot.	25	$\beta_1 = 2.58; \beta_2 = 4.27;$ $\beta_3 = 7.18; \beta_4 = 8.27$	I = 0.1 (NH ₄ ClO ₄)	10
	I ⁻	Pot.	25	$\beta_1 = 2.80; \beta_2 = 5.0$		
	I ⁻	Pot.	25	$\beta_1 = 7.11; \beta_4 = 8.15$	I = 1 (NaClO ₄)	9
				$\beta_3 = 5.9$		6
	I ⁻	Pot.	25	$\beta_1 = 2.19; \beta_2 = 3.61;$ $\beta_3 = 6.51; \beta_4 = 7.69$		
				$\beta_1 = 1.45$	I = 1 (NH ₄ ClO ₄)	7
	Bu ₃ N	Pot.	25	$\beta_1 = 0.76$	I = 0.1 (NH ₄ ClO ₄)	11
	Bu ₃ P	Pot.	25	$\beta_1 = 1.79; \beta_2 = 2.53; \beta_3 = 2.72$	I = 0.1 (NH ₄ ClO ₄)	11
	SCN ⁻	Pot.	25	$\beta_1 = 1.81; \beta_2 = 2.71; \beta_3 = 2.92$	I = 1 (NaClO ₄)	9
	SCN ⁻	Pot.	25	$\beta_1 = 8.62; \beta_4 = 9.04$	I = 1 (NH ₄ ClO ₄)	7
	Cl ⁻	SP	25	$\beta_1 = 7.20$	I = 1 (NH ₄ ClO ₄)	45
	Cl ⁻	SP	25	$\beta_1 = 2.67; \beta_2 = 4.71; \beta_4 = 6.76$		56
	SCN ⁻	SP	25	$\beta_1 = 1.64; \beta_2 = 2.50; \beta_4 = 3.40$		45
	SCN ⁻	SP	25	$\beta_1 = 2.18$		56
	SCN ⁻	SP	25	$\beta_1 = 1.74; \beta_2 = 2.85$		57
	SeCN ⁻	SP				59

Table 2 / cont. . . .

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remarks	References
Co(DMG) ₂ ⁺ Co ³⁺	I ⁻	SP	20	$\beta_1 = 1.23; \beta_2 = 1.86$		64
	bi(-phenyl) dioximate ⁻	SP	20	$\beta_2 = 1.16$		63
Ca ²⁺	bi(dioximate)- diiodo-	SP	20	$\beta_1 = 5.10; \beta_2 = 6.20$		63
	18C6	NMR	25	$\beta_1 = 3.04$		76
	DBC	NMR	25	$\beta_1 = 1.34$		76
	DCC	NMR	25	$\beta_1 = 2.20$		76
	Cl ⁻	Pot. SP	25	$\beta_1 = 6.0; \beta_2 = 12.2$		64
Cu ⁺	Cl ⁻	Pot.		$\beta_1 = 6.0; \beta_2 = 11.95$	I = 0.1(TEAP)	15
	Cl ⁻	Pot.	25	$\beta_1 = 4.37; \beta_2 = 8.87; \beta_3 = 9.45$	I = 1(NH ₄ ClO ₄)	17
	Br ⁻	Pot.		$\beta_1 = 5.0; \beta_2 = 9.6$	I = 0.1(TEAP)	15
	Br ⁻	Pot.	25	$\beta_1 = 4.19; \beta_2 = 7.94$	I = 1(NH ₄ ClO ₄)	17
	I ⁻	Pot.		$\beta_1 = 5.5; \beta_2 = 8.2$	I = 0.1(TEAP)	15
	I ⁻	Pot.	25	$\beta_1 = 4.71; \beta_2 = 7.67$	I = 1(NH ₄ ClO ₄)	17
	I ⁻	Pot.	25	$\beta_{21}(\text{Cu}_2\text{I}^+) = 6.5$		
				$\beta_{22}(\text{Cu}_2\text{I}_2) = 9.6$		
	SCN ⁻	Pot.		$\beta_1 = 4.3; \beta_2 = 9.3$	I = 1(NH ₄ ClO ₄)	17
	Ph ₃ P	Pot.	25	$\beta_1 = 6.57; \beta_2 = 10.43; \beta_3 = 11.83$	I = 0.1(TEAP)	17
	Ph ₃ As	Pot.	25	$\beta_1 = 2.65; \beta_2 = 4.14$	I = 0.1(NH ₄ ClO ₄)	18
	Ph ₃ Sb	Pot.	25	$\beta_1 = 1.26; \beta_2 = 1.79$	I = 0.1(NH ₄ ClO ₄)	18
Cu ²⁺	Cl ⁻	Pot.		$\beta_1 = 4.4; \beta_2 = 7.4$		
		SP		$\beta_3 = 9.0; \beta_4 = 11.0$		14
	Cl ⁻	Pot.		$\beta_1 = 4.5; \beta_2 = 7.5; \beta_3 = 9.1$		17

Table 2 / cont.

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remarks	Reference
	Cl ⁻	Pot.		$\beta_4 = 23.1$		16
	Br ⁻	Pot.		$\beta_4 = 17.9$		16
	I ⁻	Pot.		$\beta_4 = 15.4$		16
	SCN ⁻	Pot.	8	$\beta_4 = 17.6$		16
Fe ³⁺	Cl ⁻	SP	25	$\beta_1 = 3.72; \beta_2 = 5.76$	I = 0.1(NaClO ₄)	68
	Cl ⁻	SP	25	$\beta_1 = 3.62; \beta_2 = 5.72$	I = 0.1(NaClO ₄)	79
	CN ⁻	NMR	20	$\beta_1 = 4.28; \beta_2 = 7.30$		71
	SCN ⁻	SP	25	$\beta_1 = 3.07$	I = 0.24(NaNO ₃)	70
Hg ²⁺	Cl ⁻	Pot.	25	$\beta_1 = 10.87; \beta_2 = 17.97$		
	Cl ⁻	Pot.	25	$\beta_3 = 21.95; \beta_4 = 24.04$	I = 1(NH ₄ ClO ₄)	19
	Cl ⁻	Pot.	25	$\beta_2 = 21.2; \beta_3 = 26.9$	I = 0.1(TEAP)	20
	Cl ⁻	Pot.	25	$\beta_2 = 21.1; \beta_3 = 26.9; \beta_4 = 28.3$	I = 1(LiClO ₄)	9
	Cl ⁻	Pot.	25	$\beta_1 = 13.40$		21
	Br ⁻	Cal.	25	$K_3 = 5.6; K_4 = 2.65$	I = 1(NaClO ₄)	81
	Br ⁻	Pot.	25	$\beta_1 = 12.14; \beta_2 = 23$		
	Br ⁻	Pot.	25	$\beta_3 = 25.33; \beta_4 = 27.87$	I = 1(NH ₄ ClO ₄)	19
	Br ⁻	Pot.	25	$\beta_2 = 22.2; \beta_3 = 28; \beta_4 = 30.4$	I = 0.1(TEAP)	20
	Br ⁻	Pot.	25	$\beta_3 = 28.3; \beta_4 = 29.2$		9
	Br ⁻	Pot.	25	$\beta_1 = 14.60$		21
	Br ⁻	Pot.	25	$\beta_1 = 12.92; \beta_2 = 21.97;$ $\beta_3 = 27.63; \beta_4 = 30.23$		10

Table 2 / cont.

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remarks	References
	I ⁻	Pot.	25	$\beta_1 = 13.52; \beta_2 = 23.27;$ $\beta_3 = 29.28; \beta_4 = 31.91$	I = 1(NH ₄ ClO ₄)	19
	I ⁻	Pot.	25	$\beta_2 = 24.2; \beta_3 = 30.4; \beta_4 = 32.5$	I = 0.1 TEAP ₁	20
	I ⁻	Pot.		$\beta_3 = 30.4; \beta_4 = 32.3$	I = 1(NaClO ₄)	9
	I ⁻	Pot.		$\beta_1 = 16.0$		21
	I ⁻	Cal.	25	$K_3 = 6.1; K_4 = 2.55$	I = 1(NaClO ₄)	81
	SCN ⁻	Pot.	25	$\beta_1 = 9.33; \beta_2 = 14.99;$ $\beta_3 = 17.95; \beta_4 = 20.26$		19
	SCN ⁻	Pot.	25	$\beta_2 = 16.1; \beta_3 = 19.1; \beta_4 = 21.2$		20
	SCN ⁻	Pot.	25	$\beta_2 = 16.1; \beta_3 = 19.0; \beta_4 = 20.4$		9
	SCN ⁻	Pot.		$\beta_1 = 10.70$		21
Hg ²⁺	P ₁₃ P	Pot.	25	$\beta_1 = 11.06; \beta_2 = 17.62$	I = 0.1(NH ₄ ClO ₄)	18
	P ₁₃ A ₅	Pot.	25	$\beta_1 = 6.77; \beta_2 = 8.97$	I = 0.1(NH ₄ ClO ₄)	18
K ⁺	C222	Pot.	25	$\beta_1 = 6.92$	$-\Delta H = 39.5 \text{ kJ mol}^{-1}$ $-\Delta G = 60.8 \text{ kJ mol}^{-1}$ $-\Delta S = -71 \text{ J deg}^{-1} \text{ mol}^{-1}$	34
Ni ²⁺	SCN ⁻	SP		$\beta_1 = 2.63; \beta_2 = 3.66;$ $\beta_3 = 4.08; \beta_4 = 5.41$ (spectrophotically determined)		58
				$\beta_1 = 2.65; \beta_2 = 3.67;$ $\beta_3 = 2.84; \beta_4 = 5.41$ (from ionic determinations)		58
	SeCN ⁻	SP		$\beta_1 = 2.42$		59

Table 2 / cont. ...

Metal Species	Ligand	Method	Temp. °C	Log of formation constant	Remarks	References
Pb ²⁺	Cl ⁻	Pot.	25	$\beta_1 = 10.7$		62
Pt ²⁺	Cl ⁻	Pot.		$\beta_1 = 4.74$	I = .01	39
	Br ⁻	Pot.		$\beta_1 = 5.4$	I = .01	39
Te ⁴⁺	Cl ⁻	SP	20	$K_5 = 0.77$		66
	Br ⁻	SP		$K_2 = 0.85$		67
Tl ⁺	C ₂ O ₄ ²⁻	Pot.	25	$\beta_1 = 6.3$	$\Delta G = 35.6 \text{ kJ mol}^{-1}$	34
Zn ²⁺	Cl ⁻	Pot.	25	$\beta_1 = 1.93; \beta_2 = 5.83;$ $\beta_3 = 8.07; \beta_4 = 9.0$	I = 1(NH ₄ ClO ₄) $\Delta G = -33 \text{ kJ mol}^{-1}$	12
	Cl ⁻	Cal.	25	$\beta_1 = 1.95; \beta_2 = 5.86;$ $\beta_3 = 8.23; \beta_4 = 7.0$		13
	Br ⁻	Pot.	25	$\beta_1 = 0.34; \beta_2 = 3.73;$ $\beta_3 = 5.08; \beta_4 = 5$	I = 1(NH ₄ ClO ₄)	12
		Cal.	25	$\beta_1 = 0.3; \beta_2 = 3.70;$ $\beta_3 = 5.11; \beta_4 = 0$		13
	Br ⁻	Pot.	25	$\beta_1 = 1.37; \beta_2 = 5.17; \beta_3 = 7.17$	I = 0.1(NH ₄ ClO ₄)	10
	I ⁻	Pot.	25	$\beta_1 = 1.30; \beta_2 = 0.71; \beta_3 = 0.86$		12
	I ⁻	Cal.	25	$\beta_1 = 2.70; \beta_2 = 0.69; \beta_3 = 0.81$		13
	S ₂ N ⁻	Pot.	25	$\beta_1 = 1.38; \beta_2 = 2.80;$ $\beta_3 = 5.20; \beta_4 = 5.86$		12
	SCN ⁻	Cal.	25	$\beta_1 = 1.38; \beta_2 = 2.78;$ $\beta_3 = 5.23; \beta_4 = 5.98$		13
	Bu ₃ N	Pot.	25	$\beta_1 = 1.3; \beta_2 = 3.5$		11

TABLE 3

Metal Species	Ligand	Method	Temp.	Ion pair Association constant	Ref.
Co ²⁺	ClO ₄ ⁻	SP	25	K ₁ = 1.3	45
	CF ₃ COO ⁻	SP	25	K ₁ = 1.95	47
Co(en) ₂ Cl ₂ ⁺	Cl ⁻	SP	20-30	K ₁ = 2.50(20°) (<i>Cis</i>) 2.44(25°) 2.42(30°)	49
	Cl ⁻	SP	60	K ₁ = 2.60 (<i>Cis</i>)	51
	Cl ⁻	Cond.	25	K ₁ = 1.43 (<i>trans</i>) K ₁ = 2.60 (<i>Cis</i>) I → 0 K ₁ = 2.0 (<i>trans</i>)	52
Co(en) ₂ Cl ₂ ⁺	Br ⁻	Kin.	30-45	K ₁ = 1.70(31°) (<i>trans</i>) 2.45(45°) (<i>Cis</i>)	53
Co(en) ₂ BrCl ⁺	Cl ⁻	Cond.	25	K ₁ = 2.49 (<i>Cis</i>) I → 0	52
Co(en) ₃ Cl ₂ ⁺	Cl ⁻	Cond.	25	K ₁ = 2.53 (<i>Cis</i>) K ₁ = 2.71 (<i>Cis</i>)	52
Co(en) ₂ Br ₂ ⁺	Br ⁻	Cond.	25	K ₁ = 1.86 (<i>Cis</i>) I → 0	52
Co(en) ₂ ClBr ⁺	Br ⁻	Cond.	25	K ₁ = 2.10 (<i>Cis</i>) I → 0	52
Co(en) ₃ ³⁺	Cl ⁻	Cond.	25	K ₁ = 5.22	48
	Br ⁻	Cond.	25	K ₁ = 3.32	48
	I ⁻	Cond.	25	K ₁ = 2.53	48
	SCN ⁻	Cond.	25	K ₁ = 2.46	48
	ClO ₄ ⁻	Cond.	25	K ₁ = 1.72	48
Cr(en) ₂ Cl ₂ ⁺	Cl ⁻	Cond.	25-35	K ₁ = 2.48(25°) (<i>Cis</i>) 2.45(30°) 2.43(35°) I → 0 2.28(70°)	50
Cs ⁺	DBC	Cond.	25	K ₁ = 3.31	54
	mtb-DBC	Cond.	25	K ₁ = 3.31	55
	dtb-DBC	Cond.	25	K ₁ = 3.13	55
K ⁺	DBC	Cond.	25	K ₁ = 3.41	54
	mtb-DBC	Cond.	25	K ₁ = 3.42	55
	dtb-DBC	Cond.	25	K ₁ = 3.32	55
Mn ²⁺	ClF ₃ COO ⁻	SP	25	K ₁ = 2.1	47
Na ⁺	DBC	Cond.	25	K ₁ = 3.31	54
	mtb-DBC	Cond.	25	K ₁ = 3.30	55
	dtb-DBC	Cond.	25	K ₁ = 3.16	55
Ni ²⁺	CF ₃ COO ⁻	SP	25	K ₁ = 1.85	47
	I ⁻	PP	18	K ₁ = 0.64	42
	DBC	Cond.	25	K ₁ = 3.37	54
	mtb-DBC	Cond.	25	K ₁ = 3.35	55
	dtb-DBC	Cond.	25	K ₁ = 3.30	55

ABBREVIATIONS

Pot.	Potentiometry	DEA	2,2'-Iminobisethanol
Volt.	Voltammetry	TEA	2,2'-2''-Nitrilotrisethanol
Pol.	Polarography	Bu ₃ N	Tri-n-butylamine
SP	Spectrophotometry	Bu ₃ P	Tri-n-butylphosphine
Cal	Calorimetry	Ph ₃ X	triphenylderivatives
Cond.	Conductance measurement		(X = N, P, As, Sb, Bi)
Sol.	Solubility method		
PP	Freezing Point		
Km	Kinetic method		
β	Overall formation constant		
K	Stepwise formation constant		
K _o	Solubility product		
18C6	18-Crown-6		
DBC	Dibenzo-18-Crown-6		
DCC	Dicyclohexyl-18-Crown-6		
TEAP	Tetraethylammonium perchlorate		
en	Ethylenediamine		
dmen	Sym-dimethylethylenediamine		
Pd	Propane-1,3-diamine		
Trien	Triethylenetetramine		
DMG	Dimethylglyoxine		
mtb-DBC	Bis-(4-tert-butylbenzo)-18-Crown-6		
dtb-DBC	Bis-(3,5-tert-butylbenzo)-18-Crown-6		
MEA	2-Aminoethanol		

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