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Considerations on the Irving–Williams Series: Extension to Tetrahedral and Five-coordinated Geometries. Applications to the Macrocyclic Complexes of the 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane Ligand

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The stability constants of high-spin octahedral complexes formed by the series of dipositive metal ions from Mn(II) to Zn(II) follow the so called 'natural order' better known as the Irving–Williams series. Along this series the entropy contributions appear to be roughly constant so that the stability order is determined by the enthalpies of formation. The enthalpy profile can be rationalized in terms of CF, LF or MO theories [1].

Such considerations apply both to monodentate and polydentate ligands provided any solvent molecules in the coordination sphere are accounted for. As a consequence, if the stability constants follow the Irving–Williams order and the entropy term is roughly constant along a series of complexes formed by the same ligand and having the same stoichiometry, one can assume that the complexes are high-spin octahedral.

In this paper we intend to find analogous series of constants (and ΔH° changes) for complexes of different geometries from the octahedral. In fact the accepted theories for coordination compounds permit the prediction of the formation enthalpies for complexes of the dipositive metal ions from Mn(II) to Zn(II) with various geometries. Conversely, knowing the stability constants and/or the heats of formation for $3d^{5-10}$ complexes may provide valuable information on the structure of the complexes in solution.

Experimental

Materials

1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) (Strem Chemicals) was dissolved in anhydrous ether and precipitated as the tetrahydrochloride by passing a flux of gaseous hydrochloric acid through the solution. (Found: C, 41.7; H, 9.0; N, 13.9; Cl, 35.3%. $C_{14}H_{36}N_4Cl_4$ requires C, 41.80; H, 9.02; N, 13.93; Cl, 35.25%).

A solution of the ligand in 0.5 M dm^{-3} KNO_3 was prepared by dissolving the tetrahydrochloride in excess of standardized and CO_2-free NaOH solution so that the final pH was 11. In these conditions appreciable amounts of protonated forms of the ligand are not present. The calculated amount of solid KNO_3 (C. Erba RPE grade) was added by weighing. The $(NiTMC)(ClO_4)_2$ complex was prepared following the procedure reported in the literature [2]. (Found: C, 32.6; H, 6.3; N, 10.9%. $NiC_{14}H_{32}N_4Cl_2O_8$ requires C, 32.71; H, 6.27; N, 10.90).

Microcalorimetry

Heats of formation of the nickel and copper complexes with TMC in 0.5 M dm^{-3} KNO_3 solution were determined using an LKB 10700/2 batch microcalorimeter. The heat of formation of the nickel complex was obtained by determining the heat of decomposition of the complex using an alkaline solution of sodium cyanide and subtracting this value from the heat (42.8 kcal/mol) [3] of the reaction:

$$\mathrm{Ni^{2+}_{(aq)} + 4CN^{-}_{(aq)} \longrightarrow Ni(CN)^{2-}_{4(aq)}}$$

In a typical experiment, the solution of the complex (2.5×10^{-2} M dm^{-3}, 0.20 cm^3) was introduced by weight into one side of the calorimetric cell; the NaOH–NaCN solution (0.5 M dm^{-3} NaOH, 0.2 M dm^{-3} NaCN) (2 cm^3) was introduced into the other side using a precision pipette (Pipetman). The correction for the heat of dilution was obtained using 0.20 cm^3 of 0.5 M dm^{-3} KNO_3 solution and 2 cm^3 of NaOH–NaCN (0.5–0.2 M dm^{-3}) solution. Five determinations gave the average value $\Delta H^\circ_R = 0.0 \pm 0.2$ kcal/mol for the enthalpy of the reaction:

$$\mathrm{Ni^{2+}_{(aq)} + TMC_{(aq)} \longrightarrow Ni(MTC)^{2+}_{(aq)}}$$

The $Ni(TMC)^{2+}$ complex exists, in aqueous solution, as an equilibrium mixture of two forms: a yellow square-planar diamagnetic and a blue square-pyramidal paramagnetic form:

$$\mathrm{[Ni(TMC)]^{2+}_{(aq)} + H_2O \overset{K_{int}}{\rightleftarrows} [Ni(TMC)H_2O]^{2+}_{(aq)}}$$

The equilibrium constant is $K_{int} = 1.05$ [4] so that the amounts of species at equilibrium are 49% yellow and 51% blue. The enthalpy change for the interconversion is $\Delta H^\circ_{int} = -2.9$ kcal/mol [4]. By these values, the enthalpies of formation for the blue and the yellow species were obtained; they are reported in Table II. The heat of formation of the $[Cu(TMC)(H_2O)]^{2+}$ complex in 0.5 M dm^{-3} KNO_3 solution was determined directly. In a typical experi-

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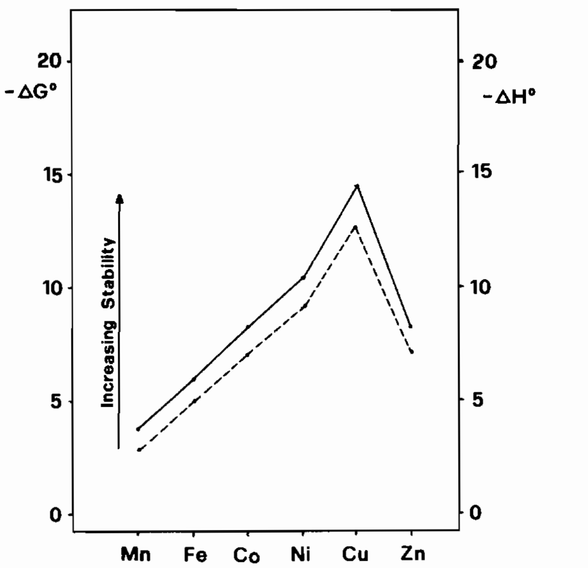
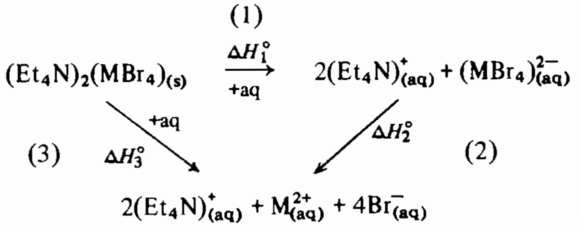


Fig. 1. Stability profile of high-spin octahedral complexes: mono ethylenediamine $[Men(H_2O)_4]^{2+}$ species. $\Delta G°$ (——) and $\Delta H°$ (– – –).

ment 0.35 cm^3 of 10^{-2} M dm^{-3} $CuCl_2$ solution (in 0.5 M dm^{-3} KNO_3) were introduced by weight into one side of the calorimetric cell and 2.0 cm^3 of solution of the ligand, prepared as described before, were introduced into the other side using a precision pipette (Pipetman). The heat of dilution was negligible. Five determinations gave the average value 13.4 ± 0.1 kcal/mol.

Results and Discussion

A plot of the $\Delta G°$ and $\Delta H°$ values for a complete series of high-spin octahedral complexes from Mn(II) to Zn(II) with one molecule of ethylenediamine [5] is shown in Fig. 1. It should be noted that: i) the two curves are, essentially, almost parallel, confirming that the $T\Delta S°$ term is approximately constant; ii) the ratio between the stability constants (logarithmic units) for the copper and nickel complexes ($\log K_{Cu}/\log K_{Ni}$) is close to 1.4. Analogous data for the complete series of tetrahedral complexes from Mn(II) to Zn(II) are not available in the literature. However the stability constant and the enthalpy and entropy of formation for the tetrahedral anion $(ZnBr_4)^{2-}$ in aqueous solution were obtained by a Raman spectroscopic technique [6]. Furthermore the heats of dissolution ($\Delta H_3°$ in scheme 1) of the solid complexes with the tetraethylammonium counterion of the tetrahedral anion $(MBr_4)^{2-}$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II)) were obtained calorimetrically [7]. The dissolution process (3) can ideally be separated into the two processes (1) and (2) shown in the following scheme:



Scheme 1

For the zinc complex, by combining the heat of dissolution ($\Delta H_3°$ = 3.46 kcal/mol) and the heat $\Delta H_2°$ = –0.9 kcal/mol, (Raman spectroscopically determined [6]), the $\Delta H_1°$ value (4.4 kcal/mol) was obtained. Assuming that this value is the same for the other metals considered, the enthalpies of formation in solution ($-\Delta H_2° = 4.4 - \Delta H_3°$ kcal/mol) of the tetrabromo complexes were obtained and are reported in Table I and in Fig. 2. The $T\Delta S°$ value ($T\Delta S°$ = –0.3 kcal/mol) determined for the $(ZnBr_4)^{2-}$ anion [6] was also used for the other metals and was combined with the enthalpy changes of Table I in order to calculate the $\Delta G°$ and $\log\beta_4$ reported in the same Table. These values, plotted in Fig. 2,

TABLE I. Thermodynamic Quantities[a] for the Reaction: $M^{2+}_{aq} + 4Br^-_{aq} \rightleftarrows (MBr_4)^{2-}_{aq}$ (at 25 °C).

	$\log\beta_4$	$\Delta G°$ kcal/mol	$\Delta H°$ kcal/mol	$T\Delta S°$ kcal/mol
$(MnBr_4)^{2-}$	–7.2	9.8	9.4	–0.4
$(FeBr_4)^{2-}$	–8.6	11.8	11.4	–0.4
$(CoBr_4)^{2-}$	–7.8	10.7	10.3	–0.4
$(NiBr_4)^{2-}$	–15.0	20.4	20.0	–0.4
$(CuBr_4)^{2-}$	–5.0(–4.55)[b]	6.8	6.4	–0.4
$(ZnBr_4)^{2-}$	–1.0[c]	1.3[c]	0.9[c]	–0.4[c]

[a] Estimated errors are ±0.3–0.5 kcal/mol. [b] Value obtained by kinetic methods [8]. [c] Value obtained by the Raman spectroscopy technique [6] at 20 °C.

TABLE II. Thermodynamic Quantities for the Reaction: $M^{2+}_{aq} + TMC_{aq} \rightleftarrows [MTMC(H_2O)]^{2+}_{aq}$, where TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, at 25 °C.

	$\log K$[a]	$\Delta G°$ [a] kcal/mol	$\Delta H°$ [e] kcal/mol	$T\Delta S°$ kcal/mol
$[CoTMC(H_2O)]^{2+}$	7.68	−10.5		
$[NiTMC)]^{2+}$ [c]	8.34[b,d]	−11.4	1.4[f]	12.8
$[Ni(TMC(H_2O)]^{2+}$	8.36[b,d]	−11.4	−1.5[f]	9.9
$Cu(TMC(H_2O)]^{2+}$	18.3	−25.0	−13.4[f]	11.6
$[ZnTMC(H_2O)]^{2+}$	10.35	−14.1		

[a] Values reported in ref. [10]. Other values, obtained by kinetic methods, are: 10.9 (Co), 11.8 (Ni), 17.7 (Cu), 12.2 (Zn) [11]. [b] The K value relative to the mixture blue + yellow was 8.65, an average value between 8.63 ± 0.04 (potentiometric) and 8.66 (spectrophotometric). $\log K_{yellow} = \log(0.49K_{mix})$ and $\log K_{blue} \equiv \log(0.51K_{mix})$. [c] Relative to the reaction: $Ni^{2+}_{aq} + TMC_{aq} \rightleftarrows (NiTMC)^{2+}_{aq}$ (yellow). [d] 0.1 mol dm^{-3} $NaNO_3$. [e] 0.5 mol dm^{-3} KNO_3. [f] This work. The values for Ni(II) were obtained using the formulas: $\Delta H°_{yellow} = \Delta H°_R - 0.51\Delta H°_{int}$ and $\Delta H°_{blue} = \Delta H°_R + 0.49\Delta H°_{int}$.

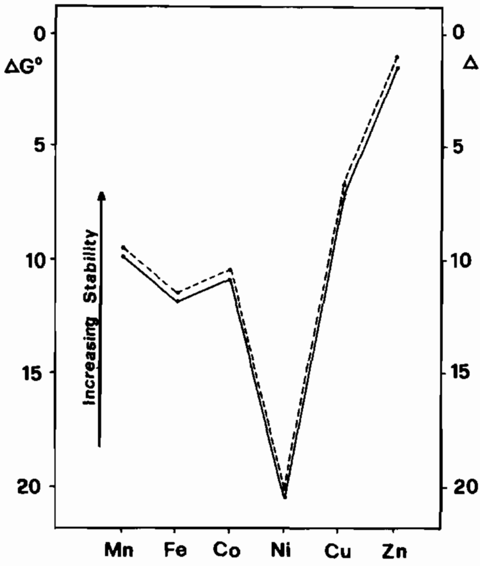


Fig. 2. Stability profile of tetrahedral complexes: tetrabromometallate(II) $[MBr_4]^{2-}$ ΔG° (———) and ΔH° (– – –).

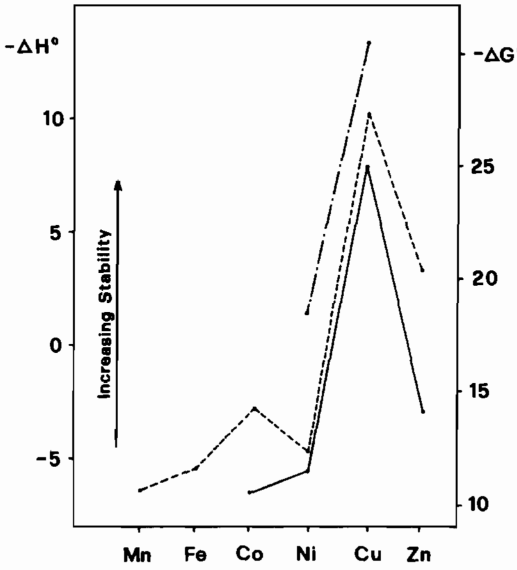


Fig. 3. Stability profile of five coordinated complexes: ΔH° (– – –) for $MMe_5dienBr_2$; ΔG° (———) and ΔH° (–·–) for $[MTMC(H_2O)]^{2+}$ complexes.

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yield a profile completely different from that shown in Fig. 1 for the high-spin octahedral complexes. It is noteworthy that the value of $\log\beta_4 = -4.55$ reported for the $(CuBr_4)^{2-}$ ion from kinetic measurements [8] is in good agreement with the value listed in Table I.

By following a procedure similar to that described above for the $\Delta H_3°$ values of the tetrahedral complexes we can assume that the trend of the stability constants parallels that of the heats determined calorimetrically [9] for the dissolution process:

$$(MBr_2Me_5dien)_{(s)} \rightleftarrows M^{2+}_{(aq)} + 2Br^-_{(aq)} + Me_5dien_{(aq)}$$

where Me_5dien is the tridentate ligand $CH_3N[CH_2CH_2N(CH_3)_2]_2$ and the complexes in the series Mn(II)–Zn(II) have a distorted square-pyramidal structure. These ΔH° values are plotted in Fig. 3 where they give a different profile from those of the octahedral (Fig. 1) and tetrahedral (Fig. 2) complexes. Particularly interesting is the comparison between the relative stabilities of the copper and nickel compounds. In the octahedral complexes the ratio between the stabilities of the copper(II) and nickel(II) compounds is about 1.4, as noted before, while in the five-coordinated compounds (Me_5dien series) the ratio is higher than 2.

A series of stability constants for the complexes of the metal ions from cobalt(II) to zinc(II), formed by the macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC), was recently reported [10]. These complexes are considered to be square-pyramidal with the apical position occupied by a molecule of water. The $\Delta G°$ values for the TMC complexes are also plotted in Fig. 3. The curves for the Me_5dien and TMC complexes are roughly parallel. The imperfect parallelism (in particular the point for cobalt is above that of nickel in the first curve and *vice versa* in the second curve) is probably due to a lesser or greater distortion with respect to a perfect geometry. The lack of values for the Mn(II)– and Fe(II)–TMC complexes means that more general conclusions cannot be drawn. In any case the ratio $\log K_{CuTMC(H_2O)}/\log K_{NiTMC(H_2O)}$ is 2.2 and the enthalpies of formation of these two complexes, reported in Fig. 3, exhibit the same trend as the corresponding $\Delta G°$ values.

In Table II the thermodynamic quantities relative to the formation of the square-planar yellow form of the $(NiMTC)^{2+}$ complex are reported. This reaction is endothermic but the complex is stabilized by a favourable entropy contribution.

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