Unusual Thermodynamic Behaviour on Complexation of Cobalt(II) with Chloride, Bromide and Iodide Ions in Hexamethylphosphoric Triamide

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The complexation of cobalt(II) with chloride, bromide and iodide ions has been studied by spectrophotometry and calorimetry in hexamethylphosphoric triamide (HMPA) containing 0.1 mol dm⁻³ (n-C₄H₉)₄NClO₄ as a constant ionic medium at 25 °C. The formation of $[CoX_n]^{(2-n)+}$ (n = 1-4with X as Cl, n = 1-3 with X as Br and n = 1 and 2 with X as I) is proposed, and their formation constants, enthalpies and entropies are determined. Electronic spectra of individual cobalt(II) halogeno complexes are also extracted, indicating that the cobalt(II) ion is four-coordinated in HMPA (unlike other oxygen-donor solvents which show six-coordination), and four-coordinate tetrahedral $[CoX_n(HMPA)_{4-n}]^{(2-n)+}$ (n = 1-4) are formed stepwise. In spite of the remarkably strong donicity of HMPA compared to other aprotic donor solvents, the ΔH_1° values of formation of [CoX]⁺ are even smaller, or more negative, in HMPA than in the others. Indeed, for [CoCl]⁺ unusual exothermicity in HMPA is observed in contrast to endothermicity in N,N-dimethylformamide or dimethyl sulphoxide. This suggests that, although being sterically allowed, the four-coordination of $[Co(HMPA)_{4}]^{2+}$ is considerably crowded for bulky HMPA molecules, and Co-O(HMPA) bonds are thus elongated to some extent.

Hexamethylphosphoric triamide (HMPA) is a strong donor solvent (the donor number $D_{\rm N} = 38.8$),¹ with a medium dielectric constant of *ca*. 30,² and a dipole moment of 14.5 × 10⁻³⁰ C m in liquid HMPA,³ and dissolves various metal salts. Various $M(ClO_4)_2$ ·4HMPA crystals of transition metal(II) ions have been prepared,⁴ in which metal)(II) ions are four-coordinated to form $[M(HMPA)_{d}]^{2+}$, unlike in other solvate crystals of oxygen donor solvents, such as water, methanol, N-methylformamide (NMF), N,N-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) where there is six-coordination. The smaller coordination number within HMPA solvate crystals may be ascribed to steric hindrance of bulky HMPA molecules in the primary coordination sphere of metal(II) ions. Electronic spectra of some metal(II) perchlorate solutions in HMPA are practically the same as those in the metal(II) solvate crystals, suggesting similar coordination geometries of metal(II) ions in both crystal and solution.⁵⁻⁷ With regard to the cobalt(II) ion, its complexation with halide ions has been studied spectrophotometrically in HMPA,⁸ and the formation constants of $[CoCl_n]^{(2-n)+}$ (n = 1-4) have been reported.⁹ Furthermore, it has been pointed out that Co(ClO₄)₂. 4HMPA crystals dissolve to yield the [Co(HMPA)₄]²⁺ ion in nitromethane, and complexation equilibria of the $[Co(HMPA)_4]^{2+}$ ion with various donor solvent molecules have been discussed in terms of their basic and steric characteristics.^{10,11} However, no

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enthalpy and entropy values have been obtained so far for the formation of halogeno complexes of metal(II) ions in HMPA.

In this work we therefore aimed to determine the thermodynamic parameters of complexation of cobalt(II) with chloride, bromide and iodide ions in HMPA. The results are discussed in comparison with those in DMF.¹²

Experimental

Materials

All chemicals used were of reagent grade. The method for preparing $Co(ClO_4)_2 \cdot 4HMPA$ is described elsewhere.^{5, 6} Tetra-n-butylammonium perchlorate, tetra-n-butylammonium chloride, tetra-n-butylammonium bromide and tetra-n-butylammonium iodide were recrystallized once from a methanol-ether mixture and dried under vacuum over P_2O_5 at room temperature. Hexamethylphosphoric triamide was purified as described elsewhere.^{5, 6}

Measurements

All spectrophotometric and calorimetric measurements were carried out in a room maintained thermostatically at 25 °C by using computer-assisted titration systems developed at the Institute for Molecular Science in Okazaki. All test solutions involved 0.1 mol dm⁻³ (n-C₄H₉)₄NClO₄ as a constant ionic medium.

Electronic spectra were measured with an MPS-2000 spectrophotometer (Shimadzu) equipped with a PC-9800VM computer (NEC) which recorded absorbance data at 1 nm intervals over the wavelength range 300–850 nm. A flow cell with the pathlength of 0.5 cm was connected with a titration vessel through Teflon and glass tubes. A cobalt(II) perchlorate solution (25 cm³) was placed in a vessel under a dry nitrogen atmosphere, and titrated with a 0.05 or 0.1 mol dm⁻³ (n-C₄H₉)₄NX (with X as Cl, Br and I) titrant solution. Absorbance data at 50 selected wavelengths over the range 450–750 nm were employed for the least-squares calculation of formation constants.

In calorimetric measurements, a cobalt(II) perchlorate solution (40 cm³) was placed in a stainless steel vessel, the inside wall of which was coated with Teflon. The vessel, filled with dry nitrogen gas and isolated from moisture with a P_2O_5 drying tube, was inserted in an aluminium block kept thermostatically at 25 ± 0.0001 °C in an air bath. Cobalt(II) perchlorate solutions of varying concentrations over the range 4–29 mmol dm⁻³ were titrated with a 0.1 mol dm⁻³ (n-C₄H₉)₄NX (with X as Cl, Br and I) solution by using an autoburet (APB-118, Kyoto Electronics). Heats observed at each titration point were 0.1–2 J with a certainty ± 0.02 J. Heats of reaction were corrected for heat of dilution of the titrant, which was found to be small by separate experiments.

Data Analysis

The formation constants and enthalpies of formation of mononuclear $[CoX_n]^{(2-n)+}$ (with X as Cl, Br and I) complexes are optimized by a non-linear least-squares calculation of spectrophotometric and calorimetric data as used in previous work.¹²

Results and Discussion

Overall Formation Constants and Enthalpies

Fig. 1 shows typical electronic spectra observed for cobalt(II) chloride HMPA solutions. The data were analysed by assuming the formation of a set of $[CoX_n]^{(2-n)+}$ with various *n*'s. In the Co^{II}-Cl system, the measured spectra in solutions of high C_X/C_M ratios in fig. 1 differ significantly from the spectrum of the tetrahedral $[CoCl_4]^{2-}$ complex, suggesting

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Fig. 1. Measured electronic spectra of cobalt(II) chloride HMPA solutions in the range 450–700 nm at 25 °C. Intensities are normalized with the concentration of cobalt(II) ion. The total concentrations of cobalt(II) and chloride ions, $C_{\rm M}$ and $C_{\rm X}/{\rm mmol\ dm^{-3}}$, are: (1) 6.667, 0.000; (2) 6.329, 2.533; (3) 6.024, 4.821; (4) 5.747, 6.900; (5) 5.494, 8.795; (6) 5.263, 10.53; (7) 5.063, 12.03; (8) 4.706, 14.71; (9) 4.255, 18.09; (10) 3.773, 21.70; (11) 2.817, 28.88.

that the formation of $[CoCl_4]^{2-}$ must be very weak under the experimental conditions examined. However, set (1-3) assuming the formation of $[CoCl]^+$, $[CoCl_2]$ and $[CoCl_3]^$ only did not reduce sufficiently the Hamilton *R* factor (0.0218) in the non-linear leastsquares calculation. Therefore, we examined set (1-4), taking into account $[CoCl_4]^{2-}$ in addition to $[CoCl_n]^{(2-n)+}$ (n = 1-3), and in the course of the analysis the molar absorption coefficients of $[CoCl_4]^{2-}$ were fixed to those in DMF at the relevant wavelengths. It may be reasonable to expect that the electronic spectrum of $[CoCl_4]^{2-}$ is not appreciably changed in aprotic HMPA and DMF, as has been indeed established in DMF and DMSO,¹³ because the metal(II) ion is unsolvated in the primary coordination shell and ligating chloride ions interact weakly with the aprotic solvents. The set (1-4) gave a small *R* value of 0.0107, and the formation constants thus obtained are listed in table 1, together with those of the set (1-3) for comparison.

Spectrophotometric data obtained in the Co^{II} -Br and Co^{II} -I systems were analysed by a similar procedure to that used in the Co^{II} -Cl system. Among several sets examined, those giving relatively small *R* values are compared in table 2, for both Co^{II} -Br and Co^{II} -I systems. Set (1-3), assuming the formation of $[CoBr]^+$, $[CoBr_2]$ and $[CoBr_3]^-$, and set (1, 2), assuming the formation of $[CoI]^+$ and $[CoI_2]$ are finally proposed.

Fig. 2 shows calorimetric data obtained in the cobalt(II) halide systems in HMPA. The $-q/(\delta v C_{x, tit})$ values are plotted against the ratio of the total concentrations of ligand

Table 1. Least-squares refinement of overall formation constant, $\log(\beta_n/\text{mol}^{-n} \text{dm}^{3n})$, of $[\text{CoCl}_n]^{(2-n)+}$ in HMPA containing 0.1 mol dm⁻³ (n-C₄H₉)₄NClO₄ at 25 °C

	(1-3)	(1–4)
$\log \beta_1$	6.6 (0.4)	6.7 (0.2)
$\log \beta_{\rm s}$	10.7 (0.4)	10.9 (0.2)
$\log \beta_3$	13.2 (0.4)	13.7 (0.2)
$\log \beta_{\Lambda}$		14.5 (0.2)
$U^{\overline{a}}$	0.3093	0.0749
R^{b}	0.0218	0.0107

Values in parentheses refer to standard deviations. The total number of absorbance data is 4700. ^{*a*} Error-squares sum. ^{*b*} The Hamilton R factor.

Table 2. Least-squares refinement of overall formation constant, log $(\beta_n/\text{mol}^{-n} \text{ dm}^{3n})$, of $[\text{CoX}_n]^{(2-n)+}$ (for X as Br and I) in HMPA containing 0.1 mol dm⁻³ (n-C_4H_9)_4NClO_4 at 25 °C

	X as Br		X as I	
	(1, 2)	(1–3)	(1)	(1, 2)
$\log \beta_1$	5.4 (0.4)	5.53 (0.05)	2.40 (0.06)	2.69 (0.01)
$\log \beta_{\rm s}$	8.2 (0.4)	8.72 (0.05)	´	3.59 (0.08)
$\log \beta_3$		9.51 (0.07)		<u> </u>
U^{a}	1.88	0.0354	0.187	0.0104
R ^b	0.0335	0.0046	0.0579	0.00621
N^c	4450	4450	2100	2100

Values in parentheses refer to standard deviations. ^a Errorsquares sum. ^b The Hamilton R factor. ^c The number of absorbance data points.

to metal ion in solution, C_x/C_M , where q, δv and $C_{x, tit}$ denote the heat of reaction, the volume of an aliquot of titrant added, and the concentration of X^- ion in the titrant solution, respectively. The data were analysed on the basis of the formation constants determined by spectrophotometry as described in the preceding section. The overall enthalpies thus obtained are listed in table 3. As seen in fig. 2, the solid curves calculated using the formation constants and enthalpies finally obtained reproduce the experimental points well over the whole range of C_x/C_M examined.

Electronic Spectra of Individual Co¹¹ Halogeno Complexes

Electronic spectra of individual $[CoX_n]^{(2-n)+}$ extracted from the measured spectra are shown in fig. 3-5 for X as Cl, Br and I. The solvated cobalt(II) ion shows absorption bands of high molar absorptivities (100-2000 dm³ cm⁻¹ mol⁻¹) in the range 550-700 nm (curve 0 in fig. 3-5), arising from $v_3[{}^{4}A_2 \rightarrow {}^{4}T_1(P)]$ transitions,¹⁴ which gives evidence of a tetrahedral $[Co(HMPA)_4]^{2+}$ ion in solution.^{4,5} Electronic spectra of individual





Fig. 2. Calorimetric titration curves obtained for cobalt(II) halide HMPA solutions containing 0.1 mol dm⁻³ (n-C₄H₉)₄NClO₄ at 25 °C. Halide is (a) chloride, (b) bromide and (c) iodide. Concentrations of cobalt(II) ion, $C_{M, init}$ /mol dm⁻³, in initial test solutions are given. The solid lines show the curves calculated using the constants finally obtained.

25 °C					
	Cl	Br	I		
$\frac{\Delta H^{\circ}_{\beta_1}}{\Delta H^{\circ}_{\ell_2}}$	-15.2(0.3) -27.8(0.5)	-2.7(0.2) -2.5(0.2)	12.9 (0.1) 19.9 (2.5)		
$\Delta H_{\beta 3}^{\rho 2}$ $\Delta H_{\rho 4}^{\rho 2}$	-40.7(0.6) -48.4(3)	-0.4 (1.7)			
U^a R^b N^c	0.131 0.0465 118	0.0644 0.1408 61	0.0340 0.0246 73		

Table 3. Overall enthalpies, $\Delta H_{\beta n}^{\circ}/kJ \mod^{-1}$, of $[\operatorname{CoX}_{n}]^{(2-n)+}$ (for X as Cl, Br and I) in HMPA containing 0.1 mol dm⁻³ (n-C₄H₉)₄NClO₄ at 25 °C

Values in parentheses refer to standard deviations. ^a Error-squares sum. ^b The Hamilton R factor. ^c The number of calorimetric data points.

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Fig. 3. Extracted electronic spectra of individual cobalt(II) chloro complexes in HMPA. The number *n* represents $[CoCl_n]^{(2-n)+}$.



Fig. 4. Extracted electronic spectra of individual cobalt(II) bromo complexes in HMPA. The number *n* represents $[CoBr_n]^{(2-n)+}$.





Fig. 5. Extracted electronic spectra of individual cobalt(II) iodo complexes in HMPA. The number *n* represents $[CoI_n]^{(2-n)+}$.

Table 4. Thermodynamic parameters, $\log (K_n/\text{mol}^{-1} \text{dm}^3)$, $\Delta G_n^\circ/\text{kJ} \text{mol}^{-1}$, $\Delta H_n^\circ/\text{kJ} \text{mol}^{-1}$ and $\Delta S_n^\circ/\text{J} \text{K}^{-1} \text{mol}^{-1}$, for the stepwise formation of $[\text{CoX}_n]^{(2-n)+}$ (for X as Cl, Br and I) in HMPA and DMF at 25 °C

		НМРА		
	Cl	Br	I	Cl
$\log K_1$	6.7	5.55	2.69	3.43
$\log K_{s}$	4.2	3.19	0.89	3.42
$\log K_{2}$	2.7	0.79		4.99
$\log K_{\star}$	(0.8)			2.29
$\Delta \tilde{G}_1^\circ$	-38.4	-31.6	-15.4	-19.6
ΔG_{2}°	-24.0	-18.2	- 5.1	-19.5
ΔG_3°	-15.5	-4.5		-28.5
ΔG°_{A}	(-5)		—	-13.1
ΔH_1°	-15.2	-2.7	13.0	6.3
ΔH_{2}°	-12.6	0.3	6.9	52.2
ΔH_3°	-12.8	2.1		-24.8
ΔH_{4}°	(-8)			-6.2
ΔS_1°	78	97	95	87
ΔS_{2}°	38	62	40	241
ΔS_{2}°	9	22		12
ΔS_4°	(-10)	_		23

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Fig. 6. Distribution of (a) chloro, (b) bromo and (c) iodo complexes of cobalt(1) in HMPA at 25 °C. The number n represents $[CoX_n]^{(2-n)+}$

 $[CoX_n]^{(2-n)+}$ indicate also tetrahedral geometries of the complexes in HMPA. The absorption bands of $[Co(HMPA)_4]^{2+}$ shift systematically to longer wavelengths upon complexation with halide ions, and the magnitude of the shift increases with decreasing ligand field stabilization energies, $Cl^- > Br^- > l^-$.

Unusual Complexation in the Co^{II}-Cl System in HMPA

Stepwise formation constants, $\log(K_n/\text{mol}^{-1} \text{dm}^3)$, enthalpies, $\Delta H_n^\circ/\text{kJ} \text{mol}^{-1}$, and entropies, $\Delta S_n^\circ/\text{J} \text{K}^{-1} \text{mol}^{-1}$, of formation of $[\text{CoX}_n]^{(2-n)+}$ (for X as Cl, Br and I) in HMPA are summarized in table 4, together with those of $[\text{CoCl}_n]^{(2-n)+}$ in DMF for comparison. Fig. 6 shows the distribution of the complexes in HMPA, which demonstrates well that the formation of $[\text{CoX}_n]^{(2-n)+}$ is relatively favourable for X as Cl, less favourable for X as Br, and much less so for X as I. The formation of $[\text{CoBr}_4]^{2-}$, $[\text{CoI}_3]^-$ and $[\text{CoI}_4]^{2-}$ is very weak and practically negligible in solutions of $-\log([X^-]/\text{mol} \text{dm}^{-3}) > 1$ examined in the present work.

In the Co^{II}-Cl system, the log K_3 and log K_4 values are in good agreement with those obtained by Pilarczyk *et al.*,⁹ although the log K_1 and log K_2 values in this work are appreciably smaller than those in the literature.⁹ It is found that the log K_n and ΔS_n° values decrease monotonically with *n* in HMPA, which is expected because fourcoordinate [Co(HMPA)₄]²⁺ is formed, and thus no change in the coordination structure surrounding the cobalt(II) ion takes place upon its complexation with chloride ions in HMPA. In DMF where a six-coordinate [Co(DMF)₆]²⁺ is formed, the coordination

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geometry surrounding the cobalt(II) ion changes from octahedral to tetrahedral at a certain step of formation of $[\operatorname{CoCl}_n]^{(2-n)+}$.¹² The log K_n values vary irregularly, log $K_3 > \log K_1 \approx \log K_2 > \log K_4$, and the ΔS_2° value is especially large and positive in DMF, implying that the structure change occurs upon complexation of $[\operatorname{CoCl}_2]$.¹²

Interestingly, a remarkable difference was found in the log K_1 and ΔH_1° values for the formation of [CoCl]⁺ in HMPA, as compared with those in DMF.¹² The log K_1 value in HMPA is significantly larger than that in DMF, and especially water (0.07) and methanol (1.66).¹⁵ The ΔH_1° value is large and negative in HMPA, but large and positive in DMF. This result is surprising because HMPA is a much stronger electron-donor solvent (the donor number $D_N = 38.8$) than DMF ($D_N = 26.6$),¹ *i.e.* the metal(II)-solvent interaction is expected to be much stronger in HMPA than in DMF. It is emphasized that no change in the coordination geometry occurs upon complexation of [CoCl]⁺ in both solvents. This implies that the metal(II)-solvent interaction within $[Co(HMPA)_4]^{2+}$ is weakened in spite of strong donicity of HMPA molecules. It has been recognized that six-coordination of the cobalt(II) ion is avoided, because of strong steric hindrance of bulky HMPA molecules, to form [Co(HMPA)₄]²⁺ in HMPA. Furthermore, exothermicity observed for the formation of [CoCl]⁺ suggests that four-coordination of the Co^{II} ion is still crowded to a considerable extent within $[Co(HMPA)_4]^{2+}$. We therefore propose that, although having no direct structural evidence yet, the Co-O(HMPA) bond is elongated. The replacement of an HMPA molecule by a chloride ion to form $[CoCl(HMPA)_3]^+$ may lessen sharply the extent of steric hindrance, and thus lead to shortening of the remaining Co-O(HMPA) bonds within the complex, which can be the origin of strong exothermicity in HMPA. Such unusual behaviour of cobalt(II) ions in HMPA has also been suggested by Gutmann et al.¹⁶ on the basis of ¹H-n.m.r. spectra of the HMPA complexes.

It should be noted that HMPA behaves as a strong donor, if its coordination to metal(II) ions is not sterically hindered. Such evidence is also obtained. Considering the reaction, $[CoCl_3S]^- + Cl^- = [CoCl_4]^{2^-} + S$, in which both complexes have a tetrahedral four-coordination geometry, we expected that coordination of a solvent molecule S within $[CoCl_3S]^-$ is not sterically hindered. The log K_4 value for the reaction has been determined so far in several solvents such as acetonitrile (AN), acetone (Ac), *N*,*N*-dimethylacetamide (DMA), DMF and DMSO by spectrophotometry. The log K_4 value in fact decreases in the order of solvents, ¹⁵ AN (3.5) > Ac (2.8) > DMF (2.3) > DMA (1.5) > DMSO (1.2)^{17} > HMPA (0.8), *i.e.* the order of increasing solvent donicities, AN $(D_N = 14.1) < Ac (17.0) < DMF (26.6) < DMA (27.8) < DMSO (29.8) < HMPA (38.8).$

The Co¹¹-Br and Co¹¹-I Systems in HMPA

Electronic spectra of individual $[CoX_n]^{(2-n)+}$ (with X as Br and I) also gave evidence for the tetrahedral geometry of the complexes in HMPA as described in a previous section. In both Co^{II}-Br and Co^{II}-I systems in HMPA, the log K_n and ΔS_n° values (see table 4) decrease monotonically with *n*, as is the case for the Co^{II}-Cl system, which is consistent with four-coordination of $[CoBr_n]^{(2-n)+}$ and $[CoI_n]^{(2-n)+}$.

The log K_1 and log K_2 values decrease in the order, Cl > Br > I, as expected for a relatively hard cobalt(II) ion. The enthalpies play a dominant role in the variation trend of the log K_n values, *i.e.* the ΔH_1° value is large and negative for Cl^- , slightly negative for Br^- , and large and positive for I⁻. No systematic variation was found in the ΔS_n° values. In fact, the ΔS_n° (n = 1 or 2) values obtained in the Co^{II} -Br and Co^{II} -I systems are rather similar to the corresponding value in the Co^{II} -Cl system. The same has been found in other metal(II)-halide systems.¹⁸ Accordingly, the result obtained in the Co^{II} -Br and Co^{II} -I systems in HMPA is reasonably to be expected, considering the weaker Co^{II} -X interactions for larger X ions.

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