Specific Salt Effect on the Solubility of *fac*-Tris(α-amino acidato)cobalt(III)

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The salt effect on *fac*-tris(aniono)cobalt(III) of α-amino acids (*fac*-[Co(amino acidato)$_3$]), such as D-proline and glycine, was examined by determining its solubility in various aqueous salt solutions. For a comparison, the solubilities of tris(2,4-pentanedionato)cobalt(III) ([Co(acac)$_3$]) and L-phenylalanine (L-phalaH) were also determined. The enthalpy (ΔH_s) and entropy of dissolution (ΔS_s) were estimated from the temperature dependence of the solubility. While NaCl and Na_2SO_4 cause a decrease in the solubilities (salting-out effect) of [Co(acac)$_3$] and L-phalaH, these salts result in an increase in the solubility (salting-in effect) of *fac*-[Co(amino acidato)$_3$]. The salting-out of [Co(acac)$_3$] is caused by an increase in ΔH_s, while the salting-out of L-phalaH results from a decrease in $T\Delta S_s$. On the other hand, the salting-in of *fac*-[Co(amino acidato)$_3$] is caused by a decrease in ΔH_s. These results suggest that the origin of the salt effect on *fac*-[Co(amino acidato)$_3$] and L-phalaH differs from that of the salt effect on [Co(acac)$_3$].

It has been extensively reported that the solubilities of nonelectrolytes decrease upon the addition of salts, such as NaCl and Na_2SO_4 (salting-out).[1—3] The author has also reported the salting-out effect of various salts on 1-phenyl-1,3-butanedione and its metal chelates.[4—6] However, in a preceding study, it was found that the solubility of *fac*-tris(glycinato)cobalt(III) (*fac*-[Co(gly)$_3$]) increases in the presence of Na_2SO_4 (salting-in).[7] In order to clarify whether this salting-in effect is characteristic of amino acid chelates or not, it is required to examine the effect of a wide variety of salts on the solubilities of the amino acid chelates.

In the present study, the solubilities of *fac*-(−)-tris(D-prolinato)cobalt(III) (*fac*-(−)-[Co(D-pro)$_3$]) in aqueous solutions of salts, such as NaCl, KCl, LiCl, NH_4Cl, $(NH_4)_2SO_4$, and tetraethylammonium bromide (Et_4NBr) were determined over the temperature range of 5 to 35 °C, and the thermodynamic parameters of dissolution at 25 °C were estimated from the temperature dependence of the solubilities. In this paper, (+) and (−) represent dextrorotatory and levorotatory at 589 nm, respectively. Furthermore, the solubilities of tris(2,4-pentanedionato)cobalt(III) ([Co(acac)$_3$]) in aqueous NaCl and Et_4NBr solutions were also determined, and the salt effect on *fac*-(−)-[Co(D-pro)$_3$] was compared with that on [Co(acac)$_3$].

In connection with the well-known salting-out effect on proteins, the salting-in effect on the amino acid chelates causes particular interest in the salt effect on amino acids, themselves. Thus, in this study the solubility of L-phenylalanine (L-phalaH) in aqueous NaCl solutions was also determined; the salt effect on L-phalaH is discussed based on a comparison with the salt effect on *fac*-(−)-[Co(D-pro)$_3$].

Experimental

The procedures used for the syntheses and separations of *fac*-(−)-[Co(D-pro)$_3$] and *fac*-(−)-tris(L-prolinato)cobalt(III) (*fac*-(−)-[Co(L-pro)$_3$]), and for the solubility measurement were previously reported.[8] The solubility in mol kg^{-1} (S_m) was obtained by calculating the number of chelate molecules or L-phalaH molecules in an aliquot of the saturated solution based on the concentration of the chelate or L-phalaH in a working solution prepared by diluting the above-mentioned aliquot. In this paper, S_m is defined as the moles of chelate molecules or L-phalaH molecules in 1 kg of an aqueous salt mixture. The above-mentioned concentration was determined spectrophotometrically by measuring the absorbances at 236, 217, 323, and 258 nm for *fac*-(−)-[Co(D- or L-pro)$_3$], *fac*-[Co(gly)$_3$], [Co(acac)$_3$], and L-phalaH, respectively. In a solubility measurement at 25 °C, the solubility in mol dm^{-3} (S_c) was also obtained by withdrawing an aliquot of the saturated solution with a measuring pipette.

Commercial NaCl, KCl, and Na_2SO_4 (reagent grade, Wako Chemical Industries Ltd.) were dried for 3 h at 120 °C. Commercial NH_4Cl, $(NH_4)_2SO_4$, and Et_4NBr (reagent grade, Wako Chemical Industries Ltd.) were dried in a vacuum desiccator over concd H_2SO_4 for several days. A stock solution of LiCl was prepared by neutralizing HCl with Li_2CO_3. The concentration of the stock solution was determined gravimetrically by evaporating an aliquot of the stock solution in a 50 cm^3 glass-stoppered bottle to dryness at 120 °C. The salt concentration in the working solution of each salt for the solubility measurement was calculated in both mol kg^{-1} (m_s) and mol dm^{-3} (c_s). Redistilled water was used.

Results

The S_m values in aqueous salt solutions are listed in Table 1 for *fac*-(−)-[Co(D-pro)$_3$], in Table 2 for *fac*-(−)-[Co(L-pro)$_3$] and *fac*-[Co(gly)$_3$], and in Table 3 for [Co(acac)$_3$]. The S_c values at 25 °C are tabulated in Table 4 for *fac*-(−)-[Co(D-pro)$_3$] and in Table 5 for *fac*-(−)-[Co(L-pro)$_3$], *fac*-[Co(gly)$_3$], and [Co(acac)$_3$]. The S_m and S_c values in aqueous NaCl solutions for L-phalaH are given in Table 6.

The solubility measurement was repeated at least four

Table 1. Solubilities (S_m) of *fac*-(−)-[Co(D-pro)$_3$] in Aqueous NaCl and (NH$_4$)$_2$SO$_4$ Solutions[a]

T/°C	NaCl Concentration m_s/mol kg^{-1}						
	0.202	0.528	1.000	1.550	2.632	3.820	5.641
	S_m/10^{-5} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}
5	6.32(0.09)	1.02(0.01)	1.38(0.01)	1.76(0.02)	1.98(0.01)	2.27(0.01)	2.46(0.02)
10	6.87(0.05)	1.07(0.02)	1.47(0.01)	1.85(0.02)	2.07(0.01)	2.32(0.02)	2.51(0.02)
15	7.42(0.03)	1.12(0.01)	1.56(0.01)	1.97(0.01)	2.20(0.01)	2.42(0.01)	2.60(0.02)
20	8.13(0.05)	1.21(0.01)	1.69(0.01)	2.07(0.02)	2.36(0.01)	2.56(0.02)	2.72(0.02)
25	9.08(0.11)	1.31(0.01)	1.87(0.01)	2.22(0.03)	2.54(0.01)	2.74(0.02)	2.94(0.01)
30	10.0(0.1)	1.43(0.01)	2.04(0.02)	2.39(0.03)	2.76(0.01)	2.97(0.02)	3.10(0.01)
35	11.0(0.1)	1.57(0.01)	2.30(0.03)	2.63(0.04)	3.03(0.01)	3.24(0.03)	3.39(0.01)

T/°C	(NH$_4$)$_2$SO$_4$ Concentration m_s/mol kg^{-1}						
	0.102	0.266	0.499	0.718	1.185	2.366	3.812
	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-4} mol kg^{-1}	S_m/10^{-5} mol kg^{-1}	S_m/10^{-5} mol kg^{-1}
5	1.24(0.01)	1.85(0.01)	2.14(0.02)	2.06(0.01)	1.57(0.01)	6.20(0.04)	1.78(0.02)
10	1.33(0.01)	1.96(0.01)	2.24(0.03)	2.17(0.02)	1.67(0.01)	6.74(0.02)	1.98(0.01)
15	1.41(0.02)	2.07(0.01)	2.40(0.01)	2.32(0.02)	1.81(0.01)	7.39(0.06)	2.22(0.01)
20	1.51(0.01)	2.24(0.01)	2.60(0.02)	2.50(0.02)	1.96(0.01)	8.16(0.11)	2.51(0.02)
25	1.66(0.02)	2.42(0.02)	2.81(0.03)	2.71(0.01)	2.14(0.01)	8.86(0.12)	2.81(0.02)
30	1.79(0.02)	2.67(0.02)	3.07(0.01)	2.92(0.02)	2.33(0.03)	9.58(0.23)	3.09(0.10)
35	1.96(0.01)	2.94(0.03)	3.37(0.04)	3.19(0.02)	2.54(0.05)	10.3(0.3)	

a) Errors defined as 95% confidence levels are given in parentheses.

times at each temperature in all cases. The solubilities given in these tables are the mean values of the individual experimental values. The errors given in parentheses denote the deviations at the 95% confidence levels, and are less than 2% in most cases.

An attempt to perform a solubility measurement of sparingly soluble *fac*-(+)-tris(L-alaninato)cobalt(III)[9] was unsuccessful, because the spectrophotometric determination, using the absorbance at 219 nm, was hindered by absorption of the salt. From this experimental restriction, *fac*-(−)-[Co(D-pro)$_3$], which has an absorption maximum at 236 nm, was selected to be the representative of *fac*-tris(α-amino acidato)cobalt(III) (*fac*-[Co(amino acidato)$_3$]). For the same reason, the solubility of *fac*-(−)-[Co(D-pro)$_3$] in an aqueous Et$_4$NBr solution could not be determined. Thus, the effect of Et$_4$NBr was examined by measuring the solubility of the more soluble *fac*-(−)-[Co(L-pro)$_3$].[8]

Since the solubilities of the chelates studied are relatively small (see Tables 1, 2, 3, 4, and 5), these saturated solutions may be regarded as being ideal dilute solutions with respect to the chelates. Thus, without an activity correction, the enthalpy (ΔH_s) and entropy of dissolution (ΔS_s) at 25 °C for the chelates were estimated based on the temperature dependence of $\ln S_m$ in the same manner as previously reported.[10]

Discussion

In general, the effect of salt on the solubility of a nonpolar nonelectrolyte can be expressed by

$$\log(S_c^\circ/S_c) = k_s c_s, \qquad (1)$$

where S_c° and k_s are the solubility in mol dm^{-3} of the nonelectrolyte in water and the salting coefficient, respectively.[2] A positive value of k_s indicates the salting-out effect, and a negative value is the salting-in effect.

The values for $\log(S_c^\circ/S_c)$ are plotted against c_s in Fig. 1 for *fac*-(−)-[Co(D-pro)$_3$] and *fac*-(−)-[Co(L-pro)$_3$], and in Fig. 2 for *fac*-[Co(gly)$_3$], [Co(acac)$_3$], and L-phalaH. In Fig. 2, the data for *fac*-[Co(gly)$_3$], [Co(acac)$_3$], and L-phalaH in aqueous Na$_2$SO$_4$ solutions reported in the preceding paper[7] are also plotted.

As shown in Fig. 2, the $\log(S_c^\circ/S_c)$ vs. c_s plots for [Co(acac)$_3$] in NaCl and Na$_2$SO$_4$ solutions practically satisfy Eq. 1. The k_s values for NaCl and Na$_2$SO$_4$, obtained by applying a least-squares method to Eq. 1, are 0.41 and 1.11 dm^3 mol^{-1}, respectively.

According to the McDevit and Long theory,[2] k_s is represented by

$$k_s = V_i^\circ(V_s - V_s^\circ)/2.3\beta_0 RT, \qquad (2)$$

where V_i°, V_s, V_s°, and β_0 are the partial molar volume of the nonelectrolyte at infinite dilution, the volume occupied by the salt as liquid, the partial molar volume of the salt at infinite dilution, and the isothermal compressibility of water, respectively. The term $(V_s - V_s^\circ)$ represents the extent of electrostriction by the salt; in this theory the salting-out effect is attributed to an increase in the internal pressure, resulting

Table 2. Solubilities (S_m) of *fac*-(−)-[Co(L-pro)$_3$] in Aqueous Et_4NBr Solutions and of *fac*-[Co(gly)$_3$] in Aqueous NaCl Solutions[a)]

T/°C	*fac*-(−)-[Co(L-pro)$_3$], Et_4NBr Concentration m_s/mol kg^{-1}					
	0.103	0.550	1.215	2.211	3.929	6.043
	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}
5	7.46(0.02)	1.52(0.01)	2.30(0.02)	2.81(0.01)	2.61(0.01)	1.95(0.01)
10	7.35(0.08)	1.46(0.02)	2.20(0.01)	2.72(0.01)	2.58(0.01)	1.99(0.02)
15	7.35(0.01)	1.44(0.01)	2.15(0.01)	2.65(0.02)	2.54(0.01)	2.02(0.02)
20	7.51(0.03)	1.42(0.01)	2.13(0.01)	2.64(0.01)	2.57(0.02)	2.12(0.02)
25	7.67(0.04)	1.42(0.01)	2.13(0.01)	2.61(0.01)	2.60(0.02)	2.20(0.01)
30	7.91(0.04)	1.45(0.01)	2.15(0.01)	2.70(0.01)	2.70(0.02)	2.31(0.03)
35	8.30(0.06)	1.49(0.01)	2.21(0.02)	2.77(0.01)	2.81(0.02)	2.42(0.01)
T/°C	*fac*-[Co(gly)$_3$], NaCl Concentration m_s/mol kg^{-1}					
	0.183	0.698	1.435	3.203	5.324	
	$S_m/10^{-4}$ mol kg^{-1}	$S_m/10^{-4}$ mol kg^{-1}	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}	
5	4.01(0.05)	7.55(0.06)	1.37(0.01)	3.79(0.02)	0.981(0.008)	
10	4.77(0.06)	8.91(0.04)	1.61(0.01)	4.23(0.06)	1.08(0.01)	
15	5.92(0.05)	10.7(0.1)	1.87(0.02)	4.88(0.09)	1.16(0.01)	
20	7.10(0.07)	12.8(0.2)	2.21(0.02)	5.43(0.01)	1.30(0.01)	
25	8.45(0.08)	15.2(0.1)	2.59(0.02)	6.14(0.10)	1.46(0.02)	
30	9.85(0.11)	17.9(0.2)	3.05(0.04)	7.18(0.15)	1.62(0.03)	
35	11.7(0.1)	20.9(0.1)	3.59(0.04)	8.24(0.04)	1.85(0.01)	

a) Errors defined as 95% confidence levels are given in parentheses.

Table 3. Solubilities (S_m) of [Co(acac)$_3$] in Aqueous NaCl and Et_4NBr Solutions[a)]

T/°C	NaCl Concentration m_s/mol kg^{-1}					
	0.621	1.457	2.227	3.257	4.381	5.609
	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-4}$ mol kg^{-1}	$S_m/10^{-4}$ mol kg^{-1}	$S_m/10^{-5}$ mol kg^{-1}	$S_m/10^{-5}$ mol kg^{-1}
5	4.20(0.04)	1.83(0.01)	9.14(0.05)	3.87(0.04)	11.5(0.2)	3.37(0.07)
10	3.76(0.02)	1.63(0.01)	8.32(0.09)	3.70(0.07)	10.5(0.1)	3.16(0.02)
15	3.21(0.03)	1.48(0.01)	7.83(0.10)	3.59(0.05)	9.83(0.07)	3.04(0.04)
20	2.93(0.03)	1.36(0.01)	7.50(0.03)	3.46(0.04)	9.38(0.02)	2.97(0.06)
25	2.69(0.02)	1.27(0.01)	7.24(0.03)	3.37(0.03)	9.70(0.09)	3.09(0.02)
30	2.53(0.01)	1.20(0.01)	7.04(0.02)	3.23(0.04)	9.64(0.13)	3.38(0.13)
35	2.42(0.02)	1.14(0.01)	6.79(0.07)	3.06(0.06)		3.31(0.05)
T/°C	Et_4NBr Concentration m_s/mol kg^{-1}					
	0.546	1.215	2.551	3.827	6.060	
	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-3}$ mol kg^{-1}	$S_m/10^{-4}$ mol kg^{-1}	
5	6.17(0.06)	5.19(0.03)	2.49(0.02)	1.38(0.01)	5.27(0.06)	
10	5.35(0.06)	4.80(0.02)	2.40(0.01)	1.37(0.01)	5.50(0.03)	
15	4.70(0.01)	4.51(0.02)	2.36(0.01)	1.39(0.01)	5.80(0.05)	
20	4.29(0.01)	4.30(0.01)	2.31(0.02)	1.48(0.02)	6.35(0.09)	
25	4.23(0.02)	4.15(0.01)	2.40(0.02)	1.55(0.01)	6.89(0.05)	
30	4.09(0.02)	4.03(0.01)	2.42(0.01)	1.63(0.01)	7.47(0.10)	
35	3.99(0.04)	3.97(0.02)	2.45(0.01)	1.70(0.01)	8.18(0.07)	

a) Errors defined as 95% confidence levels are given in parentheses.

from an ion–solvent interaction. Since the ($V_s-V_s^\circ$) values for Na_2SO_4 and NaCl are estimated to be 39.1 and 12.5 cm^3 mol^{-1}, respectively,[2)] it is reasonable that the salting-out effect of Na_2SO_4 is larger than the effect of NaCl. Thus, the salt effect found for [Co(acac)$_3$] is a popular effect for nonpolar nonelectrolytes.

On the other hand, all of the salts studied caused a salting-in of *fac*-[Co(amino acidato)$_3$] in relatively low-c_s regions. The extent of the salting-in effect was diminished with increasing c_s. In particular, the effects of Na_2SO_4 and $(NH_4)_2SO_4$ on *fac*-(−)-[Co(D-pro)$_3$] changed from salting-in to salting-out with increasing c_s. Thus, Eq. 1 is not valid for the log (S_c°/S_c) vs. c_s plots of *fac*-[Co(amino acidato)$_3$], and exact k_s values for *fac*-[Co(amino acidato)$_3$] could not be obtained using Eq. 1. However, when the experimental data for *fac*-[Co(amino acidato)$_3$] were tentatively fitted to a power series for the c_s of $\log(S_c^\circ/S_c)=A+k_sc_s+k_s'c_s^2+\cdots$, k_s estimated as limiting slopes of the curves at $c_s=0$ mol dm^{-3} is obviously negative for all of the salts (see Figs. 1 and 2).

The above-mentioned salting-in effect on *fac*-[Co(amino acidato)$_3$] is quite unexpected on the basis of Eq. 2, because these salts give positive ($V_s-V_s^\circ$) values.[2)] This result sug-

Table 4. Solubilities (S_c) at 25 °C of *fac*-(−)-[Co(D-pro)$_3$] in Some Aqueous Salt Solutions[a)]

Salt	c_s/mol dm^{-3}	S_c/10^{-4} mol dm^{-3}	Salt	c_s/mol dm^{-3}	S_c/10^{-4} mol dm^{-3}	Salt	c_s/mol dm^{-3}	S_c/10^{-4} mol dm^{-3}
NaCl	0.200	0.935(0.008)	LiCl	0.394	1.31(0.01)	KCl	0.204	1.00(0.01)
	0.521	1.36(0.01)		0.985	2.19(0.01)		0.605	1.66(0.02)
	0.978	1.99(0.01)		2.004	3.95(0.01)		1.012	2.15(0.03)
	1.500	2.38(0.03)		3.549	8.77(0.07)		2.215	3.21(0.03)
	2.489	2.85(0.02)		5.332	16.9(0.1)		3.511	3.38(0.04)
	3.530	3.19(0.03)						
	5.020	3.57(0.01)						
NH_4Cl	0.517	1.55(0.01)	$(NH_4)_2SO_4$	0.101	1.71(0.01)	Na_2SO_4	0.107	1.89(0.03)
	1.115	2.44(0.01)		0.261	2.53(0.02)		0.303	2.66(0.03)
	2.274	3.74(0.03)		0.483	2.99(0.03)		0.587	2.63(0.02)
	3.063	4.45(0.03)		0.686	2.92(0.01)		1.000	2.07(0.02)
	4.479	5.26(0.04)		1.101	2.36(0.02)		1.794	0.748(0.019)
	5.747	6.12(0.10)		2.039	1.03(0.01)			
				3.010	0.342(0.003)			

a) $S_c^\circ = 6.02(0.04)\times 10^{-5}$ mol dm^{-3}; errors defined as 95% confidence levels are given in parentheses.

Table 5. Solubilities (S_c) at 25 °C of *fac*-(−)-[Co(L-pro)$_3$], *fac*-[Co(gly)$_3$], and [Co(acac)$_3$] in Aqueous Salt Solutions[a)]

	fac-(−)-[Co(L-pro)$_3$][b)]			*fac*-[Co(gly)$_3$][c)]	
Salt	c_s/mol dm^{-3}	S_c/10^{-2} mol dm^{-3}	Salt	c_s/mol dm^{-3}	S_c/10^{-3} mol dm^{-3}
Et_4NBr	0.101	0.786(0.004)	NaCl	0.181	0.885(0.010)
	0.500	1.50(0.01)		0.686	1.57(0.03)
	1.001	2.28(0.01)		1.389	2.83(0.04)
	1.601	2.88(0.01)		2.991	7.07(0.17)
	2.355	2.95(0.02)		4.759	17.8(0.2)
	2.997	2.53(0.03)			
		[Co(acac)$_3$][d)]			
Salt	c_s/mol dm^{-3}	S_c/10^{-4} mol dm^{-3}	Salt	c_s/mol dm^{-3}	S_c/10^{-3} mol dm^{-3}
NaCl	0.611	28.0(0.2)	Et_4NBr	0.497	4.39(0.03)
	1.410	13.7(0.1)		1.001	4.40(0.01)
	2.123	8.03(0.05)		1.773	2.66(0.03)
	3.041	3.85(0.03)		2.317	1.75(0.01)
	4.004	1.12(0.01)		3.000	0.798(0.004)
	4.998	0.368(0.003)			

a) Errors defined as 95% confidence levels are given in parentheses. b) $S_c^\circ = 5.89(0.03)\times 10^{-3}$ mol dm^{-3}. c) $S_c^\circ = 6.78(0.07)\times 10^{-4}$ mol dm^{-3}. d) $S_c^\circ = 4.64(0.02)\times 10^{-3}$ mol dm^{-3}.

gests a specific interaction between *fac*-[Co(amino acidato)$_3$] and the salts.

A comparison of the effect of Na_2SO_4 on *fac*-(−)-[Co(D-pro)$_3$] with its effect on *fac*-[Co(gly)$_3$] exposes a distinction between the former and latter in a high c_s region; although the addition of Na_2SO_4 in the high concentration causes a decrease in the solubility of *fac*-(−)-[Co(D-pro)$_3$], the solubility of *fac*-[Co(gly)$_3$] is maintained nearly constant in the same c_s region. A similar tendency was also found for the effect of NaCl; an increase in the solubility of *fac*-(−)-[Co(D-pro)$_3$] is less remarkable than an increase in the solubility of *fac*-[Co(gly)$_3$] in high NaCl concentration region (see Figs. 1 and 2). The distinction is of interest in connection with the origin of the specific salting-in effect on *fac*-[Co(amino acidato)$_3$], but still cannot be explained at the present stage.

It has been reported that tetraalkylammonium salts bring about a salting-in effect.[11)] In connection with these reports, the effect of Et_4NBr on [Co(acac)$_3$] and *fac*-(−)-[Co(L-pro)$_3$] was examined. For [Co(acac)$_3$], Et_4NBr exhibits a slight salting-in effect at low c_s, but results in a salting-out at high c_s. For *fac*-(−)-[Co(L-pro)$_3$], the effect of Et_4NBr is nearly identical with the effect of chlorides on *fac*-(−)-[Co(D-pro)$_3$] (see Fig. 1).

In order to consider the salt effect from the thermodynamic parameters of dissolution, ΔH_s is plotted against $T\Delta S_s$ and m_s in Figs. 3 and 4, respectively. Figures 4 and 3 show that ΔH_s of [Co(acac)$_3$] in aqueous NaCl and Et_4NBr solutions increases with increasing m_s, and that linear correlations between ΔH_s and $T\Delta S_s$ are found in both the cases, respectively. These linear correlations for NaCl and Et_4NBr solutions are expressed by

$$\Delta H_s = 2.7T\Delta S_s + 58.7\ (\gamma = 0.937) \tag{3}$$

and

$$\Delta H_s = 1.2T\Delta S_s + 18.2\ (\gamma = 0.997), \tag{4}$$

Table 6. Solubilities (S_m and S_c) of L-PhalaH in Aqueous NaCl Solutions[a)]

T/°C	NaCl Concentration m_s/mol kg^{-1}					
	0.104	0.310	0.865	1.635	3.464	5.580
	$S_m/10^{-1}$ mol kg^{-1}	$S_m/10^{-1}$ mol kg^{-1}	$S_m/10^{-1}$ mol kg^{-1}	$S_m/10^{-1}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}	$S_m/10^{-2}$ mol kg^{-1}
5	1.21(0.01)	1.19(0.01)	1.09(0.01)	0.936(0.004)	6.40(0.01)	3.62(0.03)
10	1.29(0.01)	1.28(0.01)	1.17(0.01)	1.01(0.01)	6.80(0.01)	3.82(0.01)
15	1.39(0.01)	1.36(0.01)	1.25(0.01)	1.08(0.01)	7.18(0.01)	4.05(0.02)
20	1.50(0.01)	1.48(0.01)	1.35(0.01)	1.17(0.01)	7.57(0.01)	4.32(0.01)
25	1.63(0.01)	1.59(0.01)	1.46(0.01)	1.27(0.01)	7.91(0.01)	4.66(0.02)
30	1.78(0.01)	1.75(0.01)	1.59(0.01)	1.37(0.01)	8.41(0.01)	4.94(0.05)
35	1.96(0.01)	1.89(0.02)	1.69(0.01)	1.42(0.01)	8.93(0.01)	5.32(0.04)
T/°C	NaCl Concentration c_s/mol dm^{-3}					
	0.103	0.307	0.846	1.576	3.217	4.965
	$S_c/10^{-1}$ mol dm^{-3}	$S_c/10^{-1}$ mol dm^{-3}	$S_c/10^{-1}$ mol dm^{-3}	$S_c/10^{-1}$ mol dm^{-3}	$S_c/10^{-2}$ mol dm^{-3}	$S_c/10^{-2}$ mol dm^{-3}
25	1.65(0.01)	1.62(0.01)	1.52(0.01)	1.35(0.01)	9.02(0.01)	5.63(0.02)

a) $S_c^\circ = 1.65(0.01)\times10^{-1}$ mol dm^{-3}; errors defined as 95% confidence levels are given in parentheses.

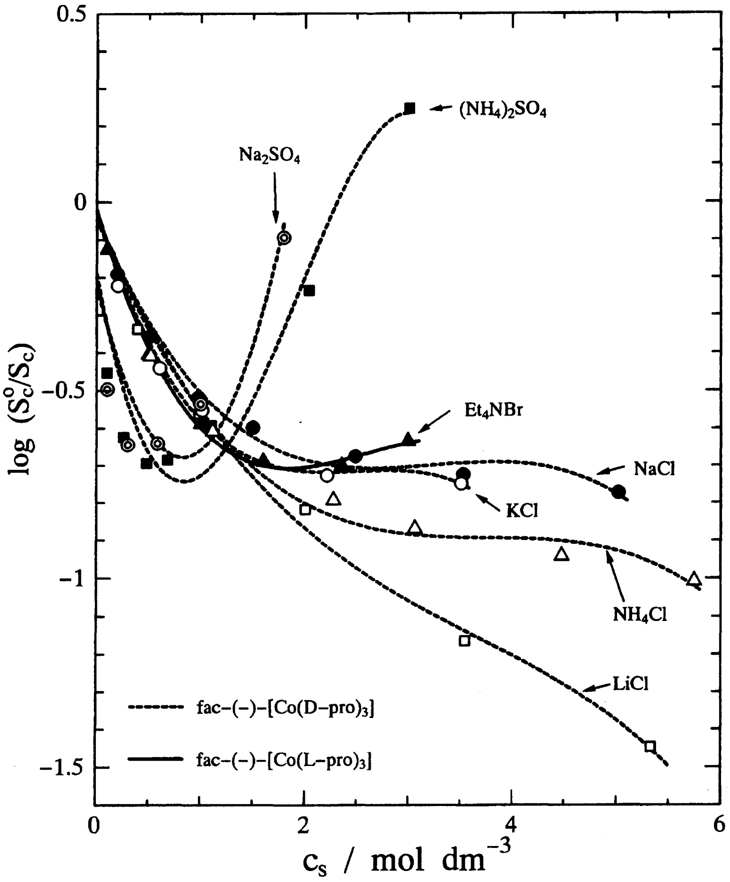

Fig. 1. Salt effect on *fac*-(−)-[Co(D-pro)$_3$] and *fac*-(−)-[Co(L-pro)$_3$] depicted by plotting log (S_c°/S_c) against c_s.

respectively, where γ is the correlation coefficient.

These findings indicate that the salting-out of [Co(acac)$_3$] by NaCl and Et_4NBr is caused by an extra increase in ΔH_s, which cannot be compensated by an increase in $T\Delta S_s$; also, the large extra increase in ΔH_s for NaCl results in a large salting-out effect relative to Et_4NBr. This thermodynamic feature for the salting-out of [Co(acac)$_3$] is consistent with the view that an increase in the internal pressure in the presence of salts brings about an increase in the energy for the formation of a cavity to accommodate [Co(acac)$_3$].

On the other hand, ΔH_s of L-phalaH in aqueous NaCl solutions decreases with increasing m_s up to about 3.5 mol kg^{-1} (see Fig. 4); in this m_s region the plot of ΔH_s against $T\Delta S_s$ gives a linear relation, expressed by

$$\Delta H_s = 0.7T\Delta S_s + 6.6\ (\gamma = 0.999). \qquad (5)$$

This result and Fig. 2, which shows that L-phalaH is subject

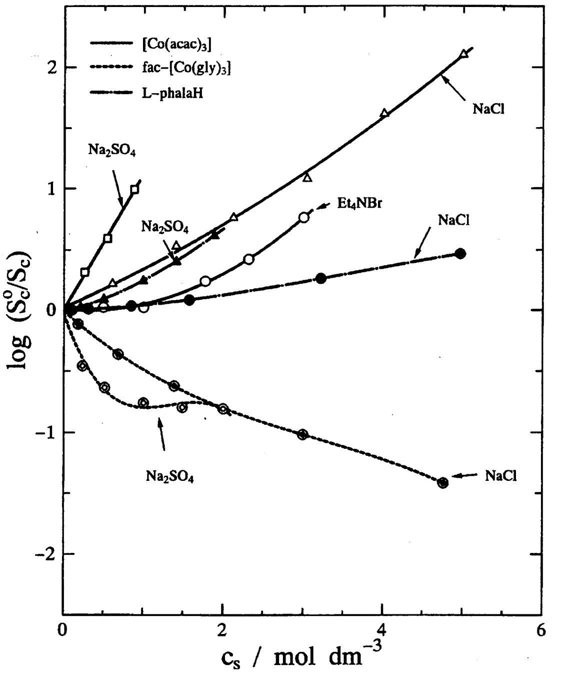

Fig. 2. Salt effect on *fac*-[Co(gly)$_3$], L-phalaH, and [Co(acac)$_3$] depicted by plotting log (S_c°/S_c) against c_s. The data for *fac*-[Co(gly)$_3$], L-phalaH, and [Co(acac)$_3$] in aqueous Na_2SO_4 solutions were taken from Ref. 7.

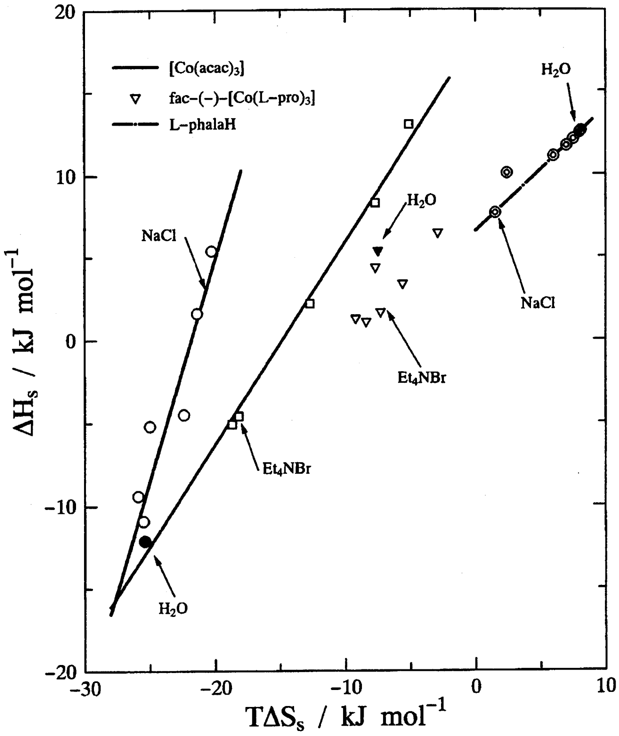

Fig. 3. Correlation between ΔH_s and $T\Delta S_s$ for *fac*-(−)-[Co(L-pro)$_3$], L-phalaH, and [Co(acac)$_3$].

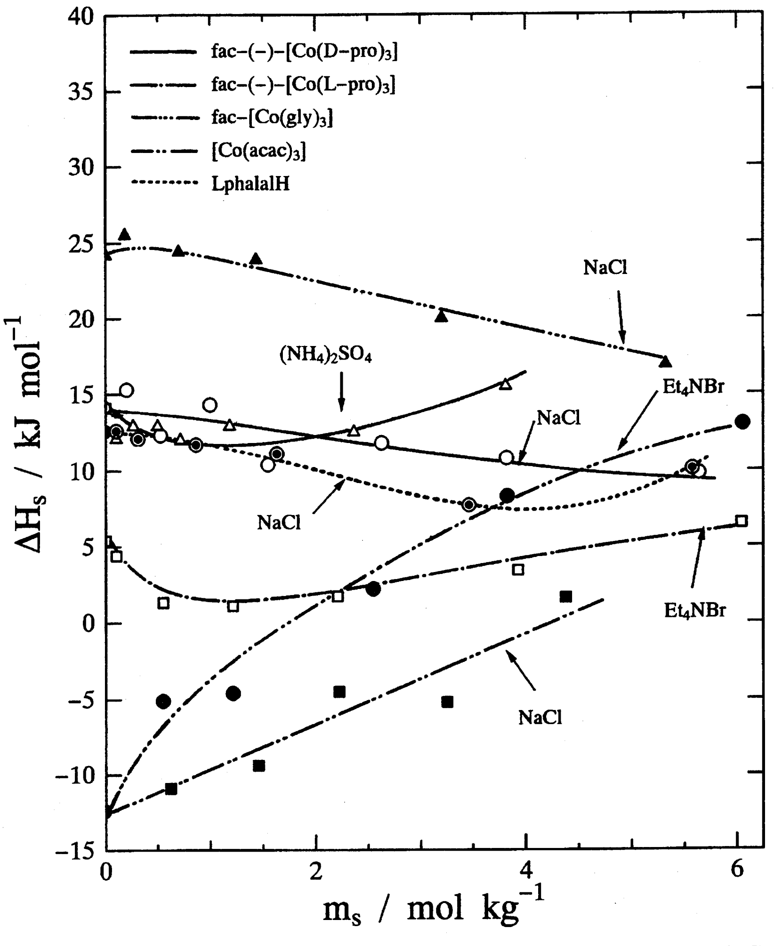

Fig. 4. Composition dependence of ΔH_s for *fac*-[Co(amino acidato)$_3$], L-phalaH, and [Co(acac)$_3$].

to the salting-out effect of NaCl and Na_2SO_4, indicate that despite the decrease in ΔH_s, a larger decrease in $T\Delta S_s$ results in the salting-out of L-phalaH. The comparison of the thermodynamic feature for the salting-out of L-phalaH with that of [Co(acac)$_3$] suggests that the origin of the salting-out of L-phalaH differs from the origin of the salting-out of [Co(acac)$_3$].

The composition profile of ΔH_s for *fac*-[Co(amino acidato)$_3$] is similar to that of ΔH_s for L-phalaH (see Fig. 4). The salting-in of *fac*-[Co(amino acidato)$_3$] is brought about predominantly by a decrease in ΔH_s; in the high m_s regions of $(NH_4)_2SO_4$ and Et_4NBr a decrease in the solubilities of *fac*-(−)-[Co(D-pro)$_3$] and *fac*-(−)-[Co(L-pro)$_3$] results from an increase in ΔH_s. In contrast to [Co(acac)$_3$], linear relations between ΔH_s and $T\Delta S_s$ were not found for *fac*-[Co(amino acidato)$_3$]. As a typical example, the plot for the data of *fac*-(−)-[Co(L-pro)$_3$] in aqueous Et_4NBr solutions is shown in Fig. 3. The finding that the extent of the salting-in of *fac*-[Co(amino acidato)$_3$] is diminished at c_s of about 1 mol dm^{-3} (see Figs. 1 and 2) and the above-mentioned lack of a linear relation between ΔH_s and $T\Delta S_s$ may suggest that the origin of the salt effect on *fac*-[Co(amino acidato)$_3$] varies in the vicinity of $c_s = 1$ mol dm^{-3}. A similar variation in the origin of the salt effect seems to occur for L-phalaH in the NaCl concentration region above 3.5 mol dm^{-3}.

Sugunan et al. have reported that KF and K_2SO_4 exhibit a large salting-in effect on nitrobenzoic acid, attributing it to the hydrogen-bond interaction of the proton of the carboxyl group in nitrobenzoic acid with F^- and $SO_4{}^{2-}$.(12) Nagashima et al. have found that L-phalaH forms sulfate salt in an aqueous H_2SO_4 solution through the hydrogen bond of the protons of the carboxyl and amino groups in L-phalaH with $SO_4{}^{2-}$.(13)

The above-mentioned finding supports the possibility of hydrogen-bond formation between the proton of the amino group in *fac*-[Co(amino acidato)$_3$] and $SO_4{}^{2-}$. However, in order to confirm the hydrogen-bond formation of the proton of the amino group in *fac*-[Co(amino acidato)$_3$], a detailed study, such as nuclear magnetic resonance, is necessary. Unfortunately, the low solubility of the sparingly soluble isomers of *fac*-[Co(amino acidato)$_3$] and the low yield of more soluble isomers of *fac*-[Co(amino acidato)$_3$](8,9) make any detailed study concerning hydrogen-bond formation difficult.

From the experimental standpoint that *mer*-tris(amino acidato)cobalt(III) (*mer*-[Co(amino acidato)$_3$]) is more soluble than *fac*-[Co(amino acidato)$_3$], a comparison of the salt effect on *mer*-[Co(amino acidato)$_3$] with the salt effect on *fac*-[Co(amino acidato)$_3$] may be expected to provide helpful information concerning the origin of the specific salt effect on *fac*-[Co(amino acidato)$_3$].

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