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Solubility Phase Diagram Containing Racemic Compound of Bis(ethylenediamine)oxalatocobalt(III) Oxalate

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Synopsis. Solubility of Δ- and *rac*-$[Co(ox)(en)_2](C_2O_4)_{0.5}$ was measured in water at 5—60 °C, the solubility isotherm of the ternary system, Λ-$[Co(ox)(en)_2](C_2O_4)_{0.5}$–$\Delta$-$[Co(ox)(en)_2](C_2O_4)_{0.5}$–$H_2O$, being determined at 25 °C. It was found that the oxalate is not spontaneously resolvable and forms the racemic compound, Λ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(ox)(en)_2](C_2O_4)\cdot nH_2O$.

In 1968 Yamasaki *et al.* reported the spontaneous resolution of bis(ethylenediamine)oxalatocobalt(III) oxalate, $[Co(ox)(en)_2]_2(C_2O_4)\cdot 8H_2O$, which shows hemihedral facets in the crystals.[1] However, the result seemed doubtful considering their method for preparing the oxalate, *i. e.* by the reaction, *trans*-$[CoCl_2(en)_2]Cl + 2H_2C_2O_4 \rightarrow [Co(ox)(en)_2]^+ + 3Cl^- + 4H^+ + C_2O_4^{2-}$. The crystals obtained seem to be chloride known to be spontaneously resolvable, since the solubility of *rac*-$[Co(ox)(en)_2](C_2O_4)_{0.5}$ ($m=0.369$ mol kg^{-1}) is larger than that of *rac*-$[Co(ox)(en)_2]Cl$ ($m=0.118$ mol kg^{-1}) at 25 °C and the molar ratio of counter ions, $Cl^-/(C_2O_4)_{0.5}^-$, is 3/2 even disregarding the association of H^+ and $C_2O_4^{2-}$. Chloride was obtained in our experiments. The hemihedrally distinguishable crystals obtained by Yamasaki *et al.* seem to be $[Co(ox)(en)_2]Cl\cdot 4H_2O$.

In order to confirm whether the spontaneous resolution of oxalate occurs or not, the optically active and the racemic oxalates were prepared and their solubilities in binary and ternary systems were measured.

Experimental

Materials. *$[Co(ox)(en)_2](C_2O_4)_{0.5}\cdot nH_2O$*: The Λ-, Δ-, and *rac*-$[Co(ox)(en)_2](C_2O_4)_{0.5}\cdot nH_2O$ were obtained from the corresponding chloride and $Ag_2(C_2O_4)$. Found: C, 21.20; H, 6.38; N, 14.09%. Calcd for Λ-$[Co(ox)(en)_2](C_2O_4)_{0.5}\cdot 4.5H_2O$: C, 21.44; H, 6.42; N, 14.28%. Found: C, 21.24; H, 6.44; N, 14.13%. Calcd for Δ-$[Co(ox)(en)_2](C_2O_4)_{0.5}\cdot 4.5H_2O$: C, 21.44; H, 6.42; N, 14.28%. Found: C, 23.01; H, 5.93; N, 15.33%. Calcd for *rac*-$[Co(ox)(en)_2](C_2O_4)_{0.5}\cdot 3H_2O$: C, 23.02; H, 6.07; N, 15.34%.

Measurements. Solubility in water was determined in molality.[2] The solid phases were identified from elemental analysis, absorption and CD spectra. Optical densities were measured with a JASCO UVIDEC-1 spectrophotometer and CD with a JASCO MOE-1 spectropolarimeter.

Results and Discussion

Binary System. The solubility of Δ- and *rac*-$[Co(ox)(en)_2](C_2O_4)_{0.5}$ is given in Table 1. The solubility ratio of racemate/Δ-salt is 0.720(5 °C) or 0.340(60 °C). If spontaneous resolution takes place, the ratio should exceed *ca.* $2^{2/3}=1.59$ expected in this type of electrolyte.[3] Thus, the present salt is not spontaneously resolvable. The solubility curve of Δ-salt shows an inflection at *ca.* 38 °C, at which the solid phase changes from (4.5—5)-hydrate(below 38 °C) to monohydrate(above 38 °C). However, the trihydrated racemic salt shows no solid phase change at 5—60 °C. This also confirms that the racemic salt exists as a racemic compound.

Table 1. Solubility of $[Co(ox)(en)_2](C_2O_4)_{0.5}$ in water (molality m/mol kg^{-1} of anhydrous salt)

T/°C	No. of salt[a) (1)	(2)-α	(2)-β
5	0.170	0.236	
10	0.209	0.342	
15	0.250	0.501	
20	0.302	0.736	
25	0.369	1.07	
30	0.444	1.50	
35	0.537	2.05	
40	0.645		2.56
45	0.769		2.76
50	0.918		3.02
55	1.10		3.38
60	1.29		3.79

a) (1): *rac*-$[Co(ox)(en)_2](C_2O_4)_{0.5}\cdot nH_2O$, $n\simeq 3$, (2): Δ-$[Co(ox)(en)_2](C_2O_4)_{0.5}\cdot nH_2O$, $n=4.5$—5(α) and $n\simeq 1$(β).

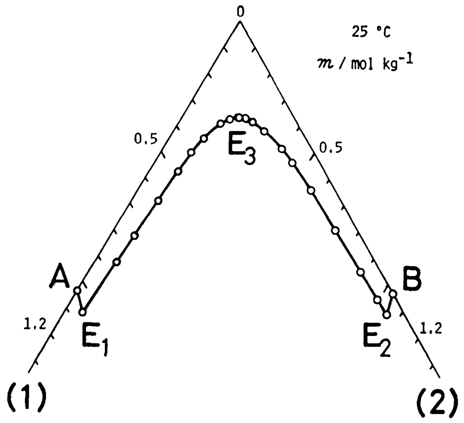

Fig. 1. Solubility isotherm of the ternary system, Λ-$[Co(ox)(en)_2](C_2O_4)_{0.5}$ (1)–Δ-$[Co(ox)(en)_2](C_2O_4)_{0.5}$ (2)–H_2O, at 25 °C. Solubility is presented in molality m of anhydrous salt.

Ternary System. Figure 1 and Table 2 show the solubility isotherm of the ternary system, Λ-$[Co(ox)(en)_2](C_2O_4)_{0.5}$–$\Delta$-$[Co(ox)(en)_2](C_2O_4)_{0.5}$–$H_2O$, at 25 °C. As is expected, the isotherm shows the formation of racemic compound, Λ-$[Co(ox)(en)_2]\cdot\Delta$-$[Co(ox)(en)_2]$-

Table 2. Equilibrium of the system, Λ-[Co(ox)(en)$_2$]-(C$_2$O$_4$)$_{0.5}$–Δ-[Co(ox)(en)$_2$](C$_2$O$_4$)$_{0.5}$–H$_2$O, at 25 °C

In liquid phases, solubility is presented in molality m of anhydrous salt. Abbreviations: Λ-[Co(ox)(en)$_2$]-(C$_2$O$_4$)$_{0.5}\cdot n$H$_2$O(n=4.5—5)=Λ, Δ-[Co(ox)(en)$_2$](C$_2$O$_4$)$_{0.5}\cdot n$H$_2$O(n=4.5—5)=Δ, and Λ-[Co(ox)(en)$_2$]$\cdot$$\Delta$-[Co(ox)(en)$_2$](C$_2O_4$)$_{0.5}\cdot nH_2$O($n\simeq 6$)=*rac*.

Positions of points (Fig. 1)	Liquid phase[a] m/mol kg^{-1}		Solid phase
	Λ	Δ	
A	1.07 (±0.01)		Λ
E_1	1.11 (±0.01)	0.06 (±0.01)	Λ+*rac*
E_1 ↕ E_3	0.851	0.071	*rac*
	0.745	0.077	
	0.604	0.082	
	0.486	0.091	
	0.402	0.098	
	0.337	0.110	
	0.252	0.136	
	0.216	0.157	
	0.192	0.176	
E_3	0.184 (±0.001)	0.184 (±0.001)	*rac*
E_3 ↕ E_2	0.163	0.206	*rac*
	0.144	0.239	
	0.120	0.297	
	0.098	0.388	
	0.090	0.448	
	0.078	0.562	
	0.073	0.721	
	0.067	0.885	
	0.061	0.994	
E_2	0.06 (±0.01)	1.11 (±0.01)	Δ+*rac*
B		1.07 (±0.01)	Δ

a) Values in parentheses are estimated errors and calculated from twice the standard deviations of measurements repeated 5—11 times.

(C$_2$O$_4$)$\cdot$6H$_2$O=*rac*-[Co(ox)(en)$_2$](C$_2$O$_4$)$_{0.5}\cdot$3H$_2$O, whose region spreads widely ($E_1E_3E_2$). It is evident that no spontaneous resolution occurs.[4] Points E_1 and E_2 are the invariant points where two solids (active and racemic salts) coexist.

DTA Analyses. Differential thermal analysis (DTA) of the optically active and the racemic oxalate was carried out under suspended conditions in water at *ca.* 0—100 °C,[5] providing one peak in heating process for each salt. The peak for the optically active salt (38 °C) corresponds to the transition observed in the binary solubility. The racemic salt shows a peak at *ca.* 74 °C at which the solid phase changes from trihydrate-(below 74 °C) to 0.5-hydrate(above 74 °C). However, the transition of racemate does not correspond to the change from the racemic compound to a racemic mixture, because the extrapolated solubility ratio at 74 °C (*ca.* 0.37) in Table 1 does not exceed 1.59, and the active and the racemic salts have different numbers of water of crystallization.

Thus, the optically active oxalate can not be obtained from the racemic solution of [Co(ox)(en)$_2$](C$_2$O$_4$)$_{0.5}$ in equilibrium, *viz.*, the salt is not spontaneously resolvable.

References

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