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Ion Association in the Na[CoEdta]–KI–Sucrose System

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Abstract—X-Ray diffraction study of Na[CoEdta] · $4H_2O$ was carried out. The stability constants of the $[CoEdta]^-$, I^- ion pairs in aqueous sucrose solutions were measured. The results were interpreted in terms of the "excluded volume effect".

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The ethylenediaminetetraacetatocobaltate ion $[CoEdta]^-$ is among the first objects used to investigate the anion–anion association in solutions [1–3]. A study of the $[CoEdta]^-$–I^- system has shown that in aqueous salt solutions, up to 40% of complex ions exist as anion pairs

$$[CoEdta]^- + I^- = [CoEdta]^-, I^- ; K_{ip}, \quad (1)$$

or associates Na^+_n, $[CoEdta]^-$, I^-. Our preliminary experiments have shown that the addition of sucrose to such systems increases the absorption of charge transfer bands.

$$[CoEdta]^-, I^- + h\nu = [CoEdta]^{2-}, I^{\bullet}. \quad (2)$$

The purpose of this work is to elucidate the cause of this phenomenon.

EXPERIMENTAL

Synthesis of sodium ethylenediaminetetraacetatecobaltate(III) tetrahydrate (I). A weighed portion of $CoSO_4 \cdot 7H_2O$ (3 g) was dissolved in 55 ml of water and $Na_2H_2Edta \cdot 2H_2O$ (4.27 g) was added. The evolved sulfuric acid was neutralized by 0.1 M solution of NaOH to pH 3. The solution thus formed was heated to 80°C, and a 30% solution of H_2O_2 (20 ml) was added. The hot solution was stirred for 30 min; during this period, the color changed from light lilac to dark violet. The resulting solution was filtered, cooled, and allowed to stand in air for a week. The large dark violet crystals were filtered off. The yield of I was 3.74 g (74%).

X-Ray diffraction analysis of I was carried out on a Siemens P4 diffractometer (MoK_α radiation, graphite monochromator, ω/2θ-scan mode). The structure was solved by the direct method. The water hydrogen atoms were located from the difference Fourier synthesis, the aliphatic hydrogen atoms of Edta were calculated from geometric considerations. The absence of a center of symmetry in the structure (space group $Pna2_1$) was unambiguously confirmed by the structure of the complex whose proper symmetry can be only 2 (apart from trivial 1), while space group *Pnma* has no rotation axes 2. The structure was refined by full-matrix least-squares method in the anisotropic approximation taking into account fixed hydrogen atoms of water molecules. The of atom Edta atoms were included using the riding model. All calculations were carried out by SHELXS-97 [4] and SHELXL-97 [5] program packages. Key crystal data and structure refinement details are presented in Table 1. Atom coordinates and other parameters of structure **I** are deposited with Cambridge Crystallographic Data Centre (no. 711544).

Solutions freshly prepared from reagent grade chemicals, sucrose (Merck), and distilled water were used. Specrophotometric studies of the solutions were carried out on a Specord 50PC spectrometer in the 300–700 nm range in 1-cm thick quartz cells at 25°C. To prevent the appearance of traces of triiodide ions (with strong UV absorption), sodium thiosulfate was added to iodide solutions in 1 : 100 molar ratio. The solution density was determined by measuring the weight of solutions in 50-ml volumetric flasks.

RESULTS AND DISCUSSION

Previously [7], crystal lattice parameters of **I** were reported; however, X-ray diffraction data were not published. The structure of the complex anion $[CoEdta]^-$ (Fig. 1a) is usual for this type of compound [8]. The sodium atom has an octahedral environment formed by six O atoms of water molecules four of which are bridg-

Table 1. Key crystal structure parameters and X-ray experiment details for Na[CoEdta] · $4H_2O$

Parameter	Value
Molecular formula	$C_{10}H_{20}CoN_2NaO_{12}$
T, K	296
System	Orthorhombic
Space group	$Pna2_1$
a, Å	6.4735(13)
b, Å	19.084(4)
c, Å	13.524(3)
V, Å^3	1670.7(6)
Z	4
ρ(calcd), g/cm^3	1.758
μ, mm^{-1}	1.121
Crystal size, mm	0.25 × 0.03 × 0.03
Data collection range for θ, deg	1.85–25.99
The number of measured reflections	4620
The number of independent reflections	2897
R_{int}	0.0835
The number of refined parameters	235
GOOF (F^2)	1.013
R_1, wR_2 ($I > 2\sigma(I)$)	0.0500, 0.1062
R_1, wR_2 (all reflections)	0.1846, 0.1425
Fleck parameter	0.00(4)

ing (Fig. 1b). The infinite chains $\{Na(H_2O)_4\}_n^{n+}$ directed along the *x* axis (Na···Na 3.575 Å) are surrounded by complex anions (Fig. 2). CCDC [6] contains data about only two compounds $\{Ru_2L_2X\}_n\{Na(H_2O)_4\}_{2n}$ (H_4L is (1-hydroxyethane-1,1-diyl)bis(phosphonic acid); X = Cl, Br) [9] containing such chains. In structure **I**, seven of the eight hydrogen atoms of water molecules participate in hydrogen bonds as donors (Table 2), while Edta oxygens are hydrogen bond acceptors. The joint action of hydrogen bonds combines the complex anions and cationic chains into a framework. The absence of coordination of sodium ions to Edta oxygen atoms in the solid phase casts doubt on the "extracoordination" of sodium cations to the complex anion in solutions [10].

The composition and properties of the solutions chosen to study the anion–anion association are presented in Table 3; the UV/Vis spectra of the anion pairs $[CoEdta]^-$, I^- in aqueous and aqueous sucrose solutions (recorded relative to the reference solution) are shown in Fig. 3. The absorption intensity of the anion pairs increases with increase in the sucrose concentration in solutions. Table 3 and Fig. 4 present the stability constants of the anion pairs $[CoEdta]^-$, I^- (K_{ip}) calculated using the extinction coefficients 1700–2000 l mol^{-1}cm^{-1} [3].

The constants calculated from the molal concentrations almost coincide, which suggests the "excluded volume" effect created by ions and sucrose molecules. Since the molar concentration of anions in these solutions is constant, their molal concentration is the higher the higher the sucrose concentration. This is responsible for the increase in absorption in all the studied systems.

ACKNOWLEDGMENT

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Table 2. Geometric parameters of hydrogen bonds in Na[CoEdta] · $4H_2O$

D–H···A contact	Distance, Å			DHA angle, deg	Coordinates of A atom
	D–H	H···A	D···A		
O(9)–H(1)···O(6)	0.83	2.19	2.864(9)	138	*x*, *y*, *z*
O(9)–H(2)···O(4)	1.09	1.85	2.806(9)	145	–*x* + 1, –*y* + 1, *z* + 1/2
O(10)–H(3)···O(8)	0.97	1.90	2.826(11)	157	–*x*, –*y* + 1, *z* – 1/2
O(11)–H(5)···O(6)	0.91	1.90	2.778(11)	162	*x*, *y*, *z*
O(11)–H(6)···O(5)	1.01	2.08	3.032(10)	156	*x* – 1, *y*, *z*
O(12)–H(7)···O(8)	0.93	2.20	3.036(13)	150	–*x* + 1, –*y* + 1, *z* – 1/2
O(12)–H(8)···O(2)	0.74	2.03	2.689(12)	149	*x* – 1, *y*, *z*

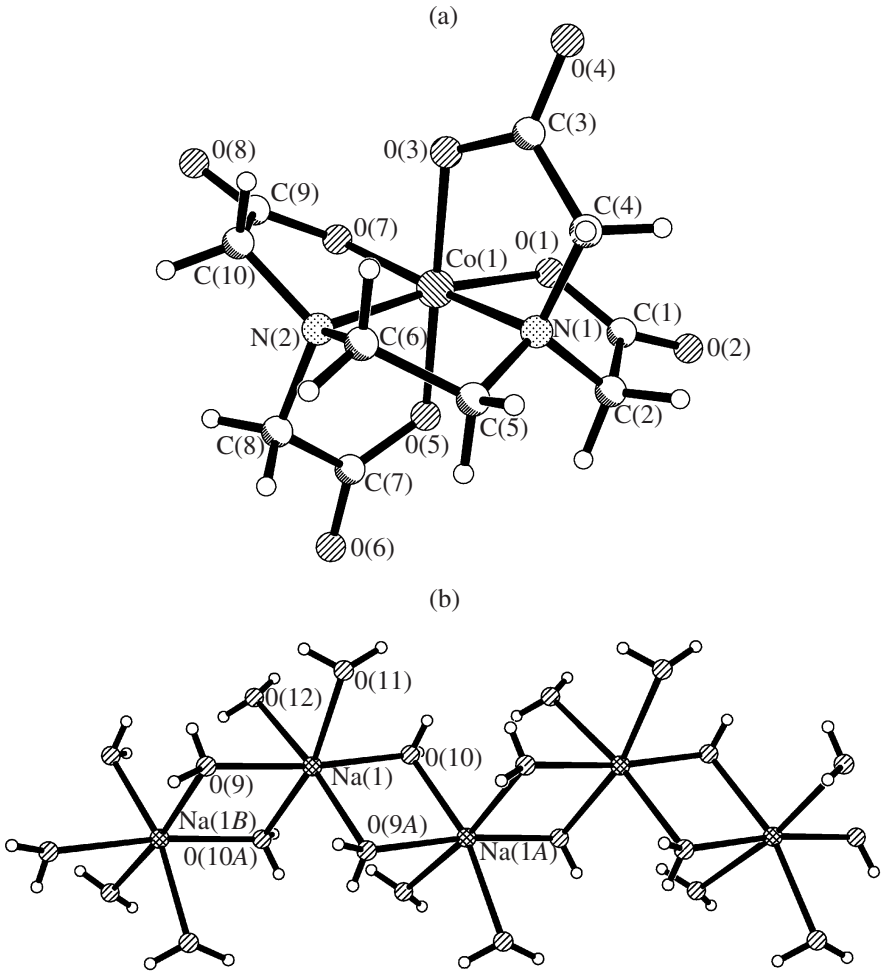

Fig. 1. Structure of (a) the complex anion $[CoEdta]^-$ and (b) the cationic chain $\{Na(H_2O)_4\}_n^{n+}$ in $Na[CoEdta] \cdot 4H_2O$.

Table 3. Composition and properties of solutions used to study the anion–anion association

Parameter \ Run	0	1	2	3	4
Concentration of Na[CoEdta], mol/l			10^{-3}		
Concentration of KI, mol/l	0	3	3	3	3
Concentration of sucrose, g/100 ml	0	0	20	40	60
Solution density, kg/l	0.996	1.346	1.419	1.494	1.561
Absorption maximum of the anion pair, cm^{-1}		32480	32720	32820	32850
K_{ip}^*, l/mol		0.200 (0.260)	0.261 (0.351)	0.307 (0.422)	0.347 (0.490)
K_{ip}^*, kg/mol		0.170 (0.221)	0.188 (0.253)	0.183 (0.252)	0.161 (0.227)

* Using the molar extinction coefficient of 2000 l mol^{-1} cm^{-1}; the values in parentheses were obtained using the molar extinction coefficient of 1700 l mol^{-1} cm^{-1}.

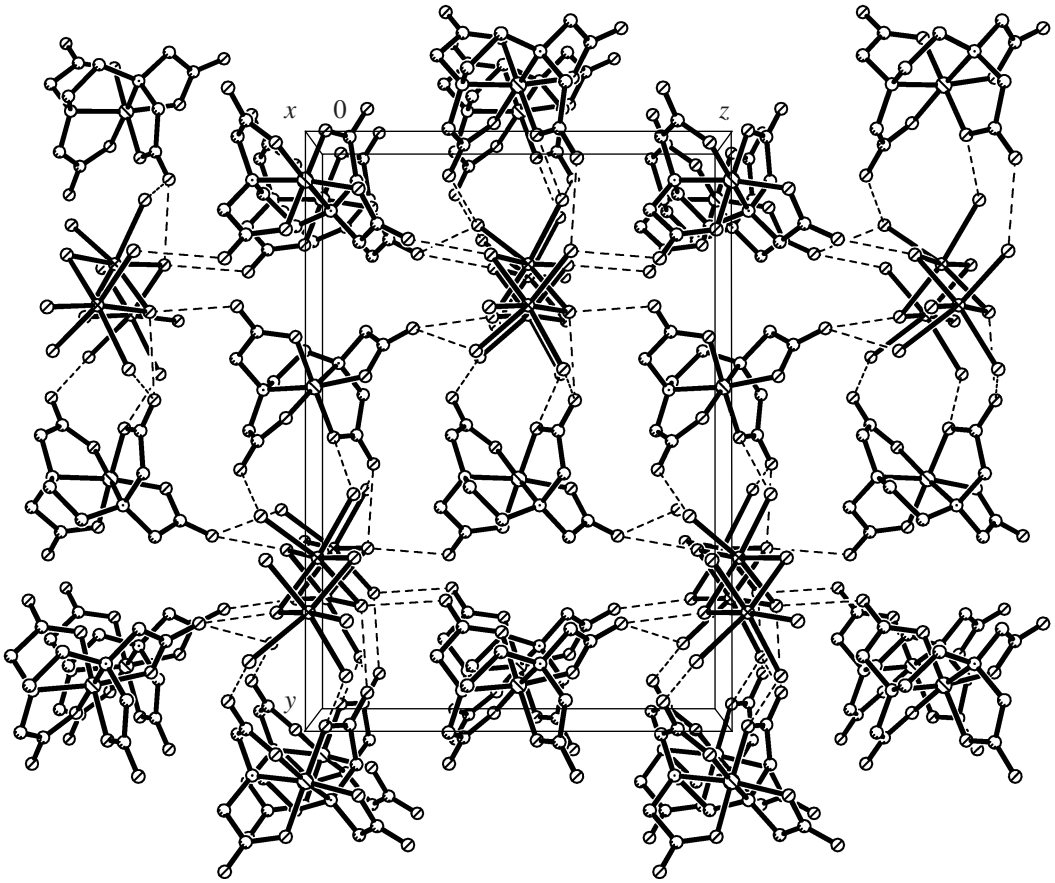

Fig. 2. Projection of the structure Na[CoEdta] · $4H_2O$ along the vector [1.0.0].

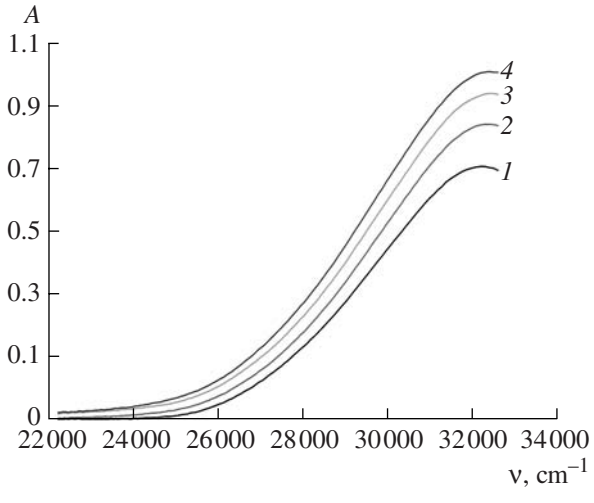

Fig. 3. UV/Vis spectrum of the ion pairs $[CoEdta]^-$, I^- in (*1*) aqueous and (*2*–*4*) aqueous sucrose solutions.

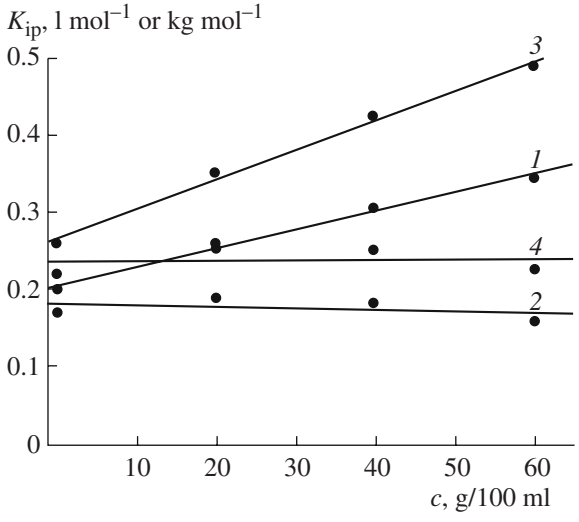

Fig. 4. Calculated stability constants of ion associates $[CoEdta]^-$, I^- vs. sucrose concentration (g/100 ml): (*1*, *3*) molar and (*2*, *4*) molal; ε = 2000 (*1*, *2*), 1700 l mol^{-1} cm^{-1}.

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