which has less electron density if it is protonated.

The decay of the proposed radical cation VIII is an *intramolecular* electron-transfer process. The small negative activation entropy (−5.4 cal K^{-1} mol^{-1}) can be regarded as further evidence that the large negative values of the entropy of activation which are observed for inner-sphere redox reactions of Cr(H$_2$O)$_6^{2+}$ with mononuclear[14] and binuclear[15] carboxylatocobalt(III)–ammine complexes are the result of concentrating the charge (2+, 2+ or 2+, 3+) in the dielectric medium as has been pointed out by Taube et al.[16]

The intrinsic reducibility of the aromatic, heterocyclic carboxylic acid appears to be the driving force for the rapid formation of relatively stable radical species, since they are generated when the unbound ligand as well as complexes A and B are reacted with Cr^{2+}. The stability of the Co(III)–Cr(III) radical cations II and VIII may at least in part be due to a low "electron permeability" of the carboxylato group.[18] This has been discussed previously for the relative stable radical cation formed by the reaction of Co$^{\text{III}}$(NH$_3$)$_5$(O$_2$C–C$_6$H$_4$–NO$_2$-*p*)$^{2+}$ with the hydrated electron.[17]

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Registry No. Cr, 7440-47-3; pyrazinecarboxylic acid, 98-97-5; A, 37112-48-4; B, 62126-12-9; Cr(H$_2$O)$_6^{2+}$, 20574-26-9; tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate, 22445-08-5.

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Crystal Circular Dichroism Spectra of the Tris(ethylenediamine)cobalt(III) Chromophore. Direct Measurement of Transitions to Both E and A$_2$ Excited Levels

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Crystal circular dichroism spectra of the $\Lambda(+)_D$-tris(ethylenediamine)cobalt(III) chromophore diluted in a host crystal of racemic 2[Ir(en)$_3$]Cl$_3$·NaCl·6H$_2$O were measured with light propagating both parallel and perpendicular to the threefold axis of the chromophore. The validity of the theoretical prediction that the trigonal components of the $A_{1g} \rightarrow T_{1g}$ octahedral transition ($A_1 \rightarrow E$ and $A_1 \rightarrow A_2$) contribute to the rotatory strength with approximately the same absolute value, but opposite signs, is demonstrated experimentally, thus supporting the interpretation of the solution spectra as being residual wing absorptions arising from extensive cancelation of the rotatory strengths of these two transitions.

Introduction

Optically active tris(diamine)cobalt(III) complexes usually exhibit two circular dichroism (CD) bands of opposite signs in the absorption region around 21 000 cm^{-1}. These bands are normally considered to correspond to transitions to the E(D_3) and A$_2$(D_3) excited levels of T$_{1g}$(O_h) parentage in a D_3 environment, although there has been some disagreement in the literature about these assignments. McCaffery and Mason,[4] Schäffer,[5] and Kuroda and Saito[6] consider the solution spectra of the $\Lambda(+)_D$–[Co(en)$_3$]$^{3+}$ chromophore to correspond to residual wing absorptions resulting from extensive cancelation of the rotatory strengths of the two transitions, since the trigonal splitting is small. This argument is based on the assumption that solid-state and solution CD have the same physical cause, i.e., derive from a molecular property which is not greatly affected by the environment of the complex ion. Support for this assumption was provided several years ago by McCaffery et al.,[7] who compared solution and microcrystalline (KBr disks) CD spectra. Woldbye[8] and Dingle and Ballhausen,[9] however, have argued that in contrast to the situation in the crystal, the complex ion may exist in two conformers in solution, so that the negative component in the solution spectrum of $\Lambda(+)_D$–[Co(en)$_3$]$^{3+}$ could be due to the presence of conformations of the chelate rings in solution which differ from those occurring in the crystal. However, the discussion given by Hawkins,[10] the results of Piper and Karipides,[11] Sudmeier et al.,[12] and Harnung et al.,[13] and the calculations of Stickland and Richardson[14] provide good grounds for regarding the solution CD spectra of [Co(1,2-diamine)$_3$]$^{3+}$ in general as being due to residual wing absorptions. It was demonstrated by these authors that there are only minor differences between the CD spectra of the lel$_3$ and lel$_2$ob conformers which occur in solution and that lel$_3$, the crystal conformer, shows two components in the CD spectrum. This means that results obtained for the solid phase may be directly related to solution and vice versa.

One of the difficulties encountered in attempts to resolve the controversy outlined above has been the fact that until very

Table I. Unit Cell Dimensions[a]

No.	Compd	a, Å	c, Å	$10^{24}V$, cm^3	d_{calcd}, g/cm^3	d_{obsd}, g/cm^3
I	Mixed crystal	11.55	15.60	1802	1.97[b]	1.95
II	$2[Ir(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$	11.58	15.62	1815	2.06[b]	2.05
III	$2[Co(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$[c]	11.42	15.66	1770	1.61[b]	1.61
IV	$2\Lambda(+)_D$-$[Co(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$	11.43	$^1/_2 \times 16.10$	$^1/_2 \times 1820$	1.56	1.56[d]
V	$[Co(en)_3]Cl_3\cdot 3H_2O$	11.44[f]	15.48[f]	1756	1.51	1.50[e]

[a] Determined from x-ray powder photographs taken at 25 °C with Cu K_α radiation using a focusing camera of the Guinier type, calibrated with silicon. All crystals belong to the hexagonal crystal system and the indexing of all powder photographs is very similar (see Table II). [b] The density is calculated on the basis of two $2[M(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$ units, i.e., four metal atoms per unit cell. [c] Space group $P\bar{3}c1$, $Z = 2$.[22] [d] Space group $P3$, $Z = 1$.[19] [e] Space group $P\bar{3}c1$, $Z = 4$.[21] [f] Reference 23.

recently measurements of CD were restricted to solutions, glasses, and uniaxial crystals with light propagating along the optical axis, since the signal was otherwise distorted by interference from linear birefringence and linear dichroism. However, this problem was solved by Hofrichter and Schellman with the construction of a phase modulation spectrophotometer[15] and the technique was subsequently applied in measurements on an anisotropic crystal of an optically active copper(II) complex.[16] A discussion of the theoretical and practical aspects of the phase modulation technique in polarized spectroscopy is to be found in ref 16 and 17.

In the present work we provide evidence, based on measurements of CD parallel and perpendicular to the c axis of hexagonal mixed crystals of $2\Lambda(+)_D$-$[Co(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$ diluted in racemic $2[Ir(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$, to support the interpretation of the CD of microcrystals as being residual wing absorptions resulting from extensive cancelation of the rotatory strengths of the two first D_3 spin-allowed absorption bands of the $\Lambda(+)_D$-$[Co(en)_3]^{3+}$ chromophore.

Experimental Section

The mixed crystals were prepared in the following way: 9.0 g (ca. 17 mmol) of $[Ir(en)_3]Cl_3$·aq, 3.0 g (51 mmol) of NaCl, and 1.0 g (1.17 mmol) of $2\Lambda(+)_D$-$[Co(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$ were dissolved in 30 mL of water by heating, and the solution was allowed to stand at room temperature for spontaneous crystallization. The best developed crystals were removed and wiped with tissue paper. The remaining crystals were dissolved by heating, and the solution was again allowed to stand for spontaneous crystallization. By repeating this procedure several times it was possible to harvest crystals developed preferentially with faces either parallel or perpendicular to the c axis of the hexagonal crystals. Investigation of a crystal with an electron microprobe showed that the surfaces are homogeneous, but because of deterioration of the crystal, the cobalt content could not be estimated reliably in this way. Atomic absorption spectroscopy of solutions of four crystals, precipitated at different stages, showed the crystals to contain 2.18, 2.14, 2.18, and 2.19% Co, respectively, corresponding to 19.8 mol % of the cobalt complex. Anal. Calcd for $Ir_{1.6}Co_{0.4}NaC_{12}H_{60}N_{12}Cl_7O_6$: C, 13.46; H, 5.65; N, 15.70; Cl, 23.17. Found: C, 13.55; H, 5.77; N, 15.88; Cl, 23.20; giving C:H:N:Cl = 12.00:60.9:12.06:6.96. A cobalt content in the mixed crystals of 23 mol % is calculated from the absorption spectrum of a solution of the latter. From the CD spectrum of the same solution a cobalt content of 22 mol % is calculated. We consider the atomic absorption measurements to be the most accurate and have therefore used a value of 20 mol % in calculating molar absorptivities. The CD spectrum of a solution of the mixed crystals exhibits a negative band with maximum at 268 nm, showing that the mixed crystals contain an excess of $\Delta(+)$-$[Ir(en)_3]^{3+}$ (having[18] $\Delta\epsilon_{max} = -0.9$ at 272 nm); i.e., some Λ-$[Ir(en)_3]^{3+}$ in the racemic $2[Ir(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$ lattice has been replaced in the mixed crystals by Λ-$[Co(en)_3]^{3+}$. This is supported by x-ray powder photographs of the compounds listed in Table I.

For compounds IV[19,20] and V[21] in Table I a complete x-ray structure analysis has been carried out by Nakatsu et al., who pointed out[19] that these structures are closely related; their close similarity is illustrated in Figure 1. Both unit cells have nearly the same a-axis dimensions and the length of the c axis for the optically active double salt is about half that for the racemic $[Co(en)_3]Cl_3\cdot 3H_2O$; i.e., the basic structure of the optically active compound can be derived from that of the racemic compound by replacing the Δ configurations by Λ configurations. From these observations and from the similarities of the relevant powder diagrams[18] we conclude that all of the compounds listed in Table I are closely related in structure. An example of this similarity is shown in Table II, and Table I summarizes the unit cell dimensions derived from the indexing of the powder diagrams for the compounds. Table I also shows the agreement between the densities observed for compounds I–III and those calculated assuming two formula units in the hexagonal cell.

In the above described manner we have thus achieved a solid-phase dilution of the cobalt complex which does not give rise to spectral interferences in the ligand field absorption region, since the iridium complex has very low absorption above 330 nm.[18] Crystals with

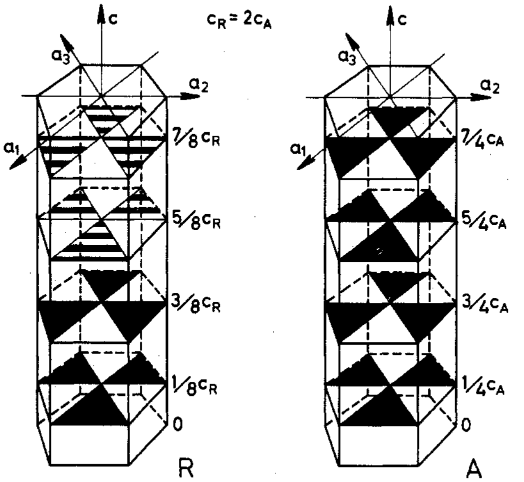

Figure 1. Resemblance of the structures of *rac*-$[Co(en)_3]Cl_3\cdot 3H_2O$[21] (R) and $2\Lambda(+)_D$-$[Co(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$[19] (A). The C_3 axes of the $[Co(en)_3\ (lel_3)]^{3+}$ units are parallel to the c axis of the crystal. The cobalt atoms of Λ-$[Co(en)_3]^{3+}$ are situated at the center of the shaded triangles. The cobalt atoms of the Δ-$[Co(en)_3]^{3+}$ are situated at the center of the striped triangles.

Table II. Indexing of the Lines of the Powder Photographs of Compounds II and V of Table I

	$2[Ir(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$			$[Co(en)_3]Cl_3\cdot 3H_2O$		
hkil	I_{obsd}	d_{obsd}, Å	d_{calcd}, Å	I_{obsd}	d_{obsd}, Å	d_{calcd}, Å
$10\bar{1}0$	vs	10.043	10.032	s	9.917	9.915
$10\bar{1}2$	vs	6.171	6.162	s	6.100	6.099
$11\bar{2}0$	vs	5.800	5.792	ms	5.736	5.724
$11\bar{2}1$	vvw	5.439	5.430			
$20\bar{2}0$	w	5.019	5.016			
$11\bar{2}2$	vvw	4.656	4.652			
$20\bar{2}2$	vs	4.221	4.220	vw	4.179	4.174
0004	s	3.902	3.904	m	3.872	3.868
$11\bar{2}3$	vvw	3.871	3.872	vw	3.832	3.832
$21\bar{3}0$	vvw	3.792	3.792			
$21\bar{3}1$	w	3.684	3.685	w	3.642	3.642
$10\bar{1}4$	s	3.637	3.638	mw	3.601	3.604
$21\bar{3}2$	vs	3.411	3.411	m	3.373	3.373
$30\bar{3}0$	vw	3.344	3.344			
$11\bar{2}4$	ms	3.238	3.237			

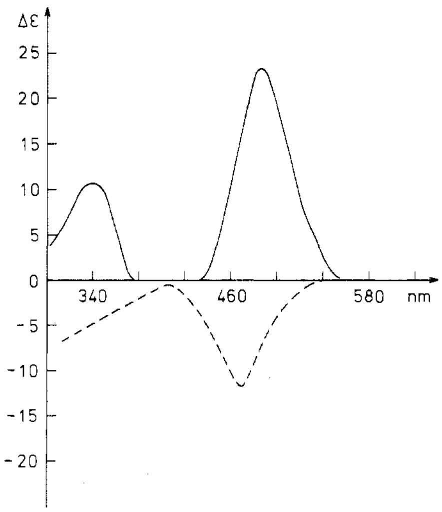

Figure 2. Experimental single-crystal circular dichroism spectra of $2\Lambda(+)_D$-[Co(en)$_3$]Cl$_3\cdot$NaCl$\cdot$6H$_2$O diluted in *rac*-2[Ir(en)$_3$]Cl$_3\cdot$NaCl$\cdot$6H$_2$O measured parallel (—) and perpendicular (- - -) to the molecular C_3 axis. Parallel maxima at 488 and ~335 nm; perpendicular maximum at 470 nm.

developed {0001} and {10$\bar{1}$0}, i.e., the faces containing the a_1, a_2 and a, c crystallographic axes, respectively, were polished down to an appropriate thickness (ca. 0.01 cm, giving rise to an absorbance of ca. 1 at 466 nm) using filter paper moistened with water. The crystals (two for each of the two orientations) were mounted on microscope slides and centered in the light beam of a microscope built into a phase modulation spectrophotometer as described elsewhere.[15,16] The results shown in Figure 2 are corrected for linear dichroism according to the expressions given in ref 16. The signs and the scaling of the spectra were established by the use of a pseudoisocyanin-*N*,*N*′-diethyl iodide standard in a stretched PVA film,[24] measured both in a conventional dichrograph (Cary Model 6001 CD accessory) and in the phase modulation spectrophotometer.

The cobalt concentration (in mol/L) in the crystal is

$$c = \frac{Zn}{NV} \times 10^3 p \times 10^{-2}$$

i.e. the molar absorptivity (in L/(mol cm)) in the mixed crystal is given by

$$\Delta\epsilon = \frac{\Delta A}{cl} = \frac{\Delta ANV}{Zn(10)pl} \quad \left(= \frac{\Delta AM}{nd(10)pl} \text{ cf. ref 9} \right)$$

where Z is the number of formula units *per* unit cell, n the number of chromophores *per* formula unit, N Avogadro's number, V the volume of the unit cell in cm^3, p the cobalt content of the mixed crystal in mol %, ΔA the measured circular dichroism, l the thickness of the crystal in cm, M the molecular weight of the mixed crystal, and d the density of the mixed crystal in g/cm^3. Rotatory strengths are evaluated from the expression[25]

$$R = 2.45 \times 10^{-39} \Delta\epsilon_{\max} \frac{\Delta\nu_{1/2}}{\nu_0} \quad \text{(cgsu)}$$

Discussion

The crystal CD spectra of $\Lambda(+)_D$-[Co(en)$_3$]$^{3+}$ measured parallel and perpendicular to the molecular C_3 axis, i.e., with light propagating into {0001} and {10$\bar{1}$0}, the faces containing the a_1, a_2 and a, c crystallographic axes, respectively, are shown in Figure 2. The perpendicular spectrum is corrected for linear dichroism, $A_c - A_a$, which was measurable directly since the orientation of the crystal was fixed during the measurement so that the c axis of the crystal was parallel to the polarization direction of the light emerging from the linear polarizer.[15,16] Even though linear dichroism contributes,[26] the design of the phase modulation spectrophotometer makes this correction negligible.

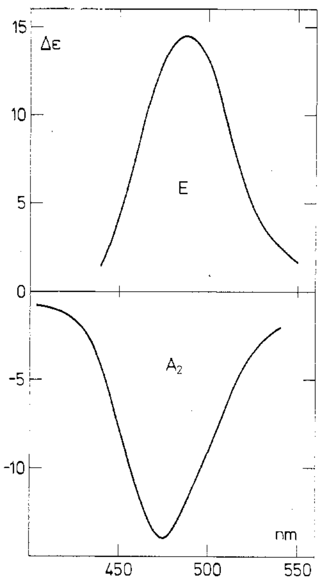

Figure 3. Analysis of the 21 000-cm^{-1} region of the experimental single-crystal spectra (Figure 2) to give the E and A$_2$ components. The experimental spectra have been corrected by the factor $^2/_3$ according to eq 6–8 to bring the single-crystal data to a random orientation scale (cf. ref 5 and 27).

The separation of the maxima of the two CD signals in the 21 000-cm^{-1} region is ca. 785 cm^{-1}. However, this is not a direct measure of the trigonal splitting since the positive curve corresponds to 3 times the average rotatory strength of the two E components (eq 6) and the negative curve to 3 times the average of one of the E components and the A$_2$ component (eq 7 and 8). An analysis of the spectra places the E transition below the A$_2$ transition in energy by ca. 500 cm^{-1} (Figure 3). Accepting the idea of residual wing absorptions arising from cancelation of rotatory strengths, the spectra of Figure 2 should be correlated with a rotatory strength of 4.3 × 10^{-40} cgsu for the chromophore in random orientation.[6,27] In solution the total rotatory strength is defined by $R = R(\text{E}) + R(\text{A}_2)$ with R ideally equal to zero for purely cubic parentage.[5]

If we place a Cartesian coordinate system in the molecular framework with the z axis along the molecular C_3 axis and the y axis along a C_2 axis, then the expressions for the rotatory strengths observed for a single crystal, R(cr), are as follows: for light propagating along the molecular C_3 axis (i.e., with the two electric vectors defining the circularly polarized light spanning the x, y plane)

$$R_{xy}(\text{cr}) = {}^1\!/_2\,[R_x(\text{cr}) + R_y(\text{cr})] \tag{1}$$

for light propagating along the y axis (i.e., with the two electric vectors defining the circularly polarized light spanning the z, x plane)

$$R_{zx}(\text{cr}) = {}^1\!/_2\,[R_z(\text{cr}) + R_x(\text{cr})] \tag{2}$$

and for light propagating along the x axis

$$R_{yz}(\text{cr}) = {}^1\!/_2\,[R_y(\text{cr}) + R_z(\text{cr})] \tag{3}$$

If the molecules are in random orientation, a rotatory strength, R_{rand}, will be observed where

$$\begin{aligned} R_{\text{rand}} &= {}^1\!/_3 R_{xy}(\text{cr}) + {}^1\!/_3 R_{zx}(\text{cr}) + {}^1\!/_3 R_{yz}(\text{cr}) \\ &= {}^1\!/_3 R_x(\text{cr}) + {}^1\!/_3 R_y(\text{cr}) + {}^1\!/_3 R_z(\text{cr}) \end{aligned} \tag{4}$$

the factor $^1/_3$ taking into account the fact that in a solution or a crystal powder on average only one-third of the molecules contribute in a given direction whereas in the single crystal all of the molecules are oriented in parallel directions. As rotatory strengths, absorptivities, etc. are usually referred to the situation where the molecules are randomly oriented, the rotatory strengths are redefined as

$$R(E_x) = {}^1/_3R_x(\mathrm{cr});\quad R(E_y) = {}^1/_3R_y(\mathrm{cr});\quad R(A_2) = {}^1/_3R_z(\mathrm{cr}) \qquad (5)$$

where $R(E_x) = R(E_y) = {}^1/_2R(E)$. Equations 1–4 now become

$$R_{xy}(\mathrm{cr}) = {}^3/_2[R(E_x) + R(E_y)] = {}^3/_2R(E) \qquad (6)$$

$$R_{zx}(\mathrm{cr}) = {}^3/_2[R(A_2) + R(E_x)] = {}^3/_2[R(A_2) + {}^1/_2R(E)] \qquad (7)$$

$$R_{yz}(\mathrm{cr}) = {}^3/_2[R(E_y) + R(A_2)] = {}^3/_2[{}^1/_2R(E) + R(A_2)] \qquad (8)$$

$$R_{\mathrm{rand}} = R(E_x) + R(E_y) + R(A_2) = R(E) + R(A_2) \qquad (9)$$

The rotatory strengths of the two $A_{1g} \rightarrow T_{1g}(O_h)$ split components in Figure 2 are found experimentally to be $R_{xy}(\mathrm{cr}) = 64 \times 10^{-40}$ and $R_{zx}(\mathrm{cr}) = 30 \times 10^{-40}$ cgsu. The value for R_{xy} should be compared with experimental values of 79, 94.4, and 76.4 ($\times10^{-40}$ cgsu) found by McCaffery and Mason,[4] by Kuroda and Saito,[6] and by Judkins and Royer,[28] respectively, with the values 68[4] and 89.9[6] ($\times10^{-40}$ cgsu) reported for $\Lambda(+)_D$-[Co(en)$_3$]Br$_3$·H$_2$O, with 62.3[28] and 57.2[6] ($\times10^{-40}$ cgsu) reported for $\Lambda(+)_D$-[Co{(*S*)(+)pn}$_3$]Br$_3$, and with the theoretical values 75.5 and 95.9 ($\times10^{-40}$ cgsu) obtained for the Λ-[Co(en)$_3$]$^{3+}$ chromophore by Evans et al.[29] and by Mason and Seal,[27] respectively. The theoretical values have been corrected according to eq 6. Inserting our experimental values into eq 6, 7, and 9, we find $R(E) = 43$, $R(A_2) = -41$, and $R_{\mathrm{rand}} = 1$ ($\times10^{-40}$ cgsu). We therefore conclude that the present measurements positively and independently demonstrate that both the microcrystalline and solution CD of the $A_{1g} \rightarrow T_{1g}(O_h)$ transition indeed stem from cancelation of E and A_2 bands. The value for R_{rand} is, of course, very uncertain as it is determined as the difference between two relatively large numbers.

Another interesting feature of the spectra shown in Figure 2 is the considerable intensity of the peak at ~335 nm in the parallel spectrum. McCaffery and Mason[4] and Kuroda and Saito[6] found this to be of very low intensity. The discrepancy may be attributable to the different experimental techniques used, one or both of which may give rise to artifacts in the ultraviolet region. However, Barron[30] has discussed mechanisms whereby electric quadrupole moments may contribute to the rotatory strength of the high-frequency E transition of the [Co(en)$_3$]$^{3+}$ chromophore when the latter is situated in an oriented crystal. The reason for the fact that we find a band with 10 times the rotatory strength found previously may very well be sought in our rather special host medium, in which the iridium centers give rise to large quadrupole transition moments, since such moments increase roughly as n^4/Z_{eff}^2. As indicated by Barron the $A_1 \rightarrow E(D_3)$ ($A_{1g} \rightarrow T_{2g}(O_h)$) transition may "borrow" quadrupole transition moment from other E transitions, especially those of the crystal charge-transfer type which may extend over large molecular distances.

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Registry No. 2[Ir(en)$_3$]Cl$_3$·NaCl, 62126-09-4; 2[Co(en)$_3$]Cl$_3$·NaCl, 14881-39-1; 2Λ(+)$_D$-[Co(en)$_3$]Cl$_3$·NaCl, 62210-58-6; [Co(en)$_3$]Cl$_3$, 13408-73-6.

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