Cation–Cation Association between *cis*-$[M(en)_2(CN)_2]^+$ (M = Co(III) and Cr(III), en = $NH_2CH_2CH_2NH_2$) and Hydrated Metal Ions and the Structure of Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$

USHIO SAKAGUCHI*, KANJI TOMIOKA and HAYAMI YONEDA**

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

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Abstract

The *cis*-$[M(en)_2(CN)_2]^+$ (M = Co(III) and Cr(III), en = ethylenediamine) ions have been shown to associate with various hydrated metal ions in aqueous solution. The association constants obtained between *cis*-$[M(en)_2(CN)_2]^+$ and several hydrated metal ions indicate that the nitrogen end of the CN group is rather soft and prefers soft metal cations. The Δ-*cis*-$[Cr(en)_2(CN)_2]^+$ ion is converted by Ag(I) or Hg(II) to the corresponding diisocyano complex coordinated with these metals, with retention of absolute configuration. The structure of an isomerization product Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$ was determined by X-ray techniques. The crystal is monoclinic, space group *C2* with a = 13.738(4) Å, b = 9.033(4) Å, c = 16.908(4) Å, β = 101.71(2)°, and Z = = 4.

Introduction

Cation–cation association in solution is an interesting phenomenon in view of the fact that strong interionic electrostatic repulsion is expected between the two cations. In an attempt to obtain *cis*-$[Co(en)_2(CN)_2]ClO_4$ (en = ethylenediamine) by metathesis of *cis*-$[Co(en)_2(CN)_2]Cl$ with silver perchlorate, we isolated a crystalline material which has a much lower solubility than that of both the perchlorate and chloride salts of *cis*-$[Co(en)_2(CN)_2]^+$. By chemical analysis the material was shown to possess a composition consistent with the formulation *cis*-$[Co(en)_2(CN)_2]Ag(ClO_4)_2$. The CN stretching frequency in the infrared (IR) spectrum (Nujol mull) of this compound has shifted to 2180 cm^{-1} from 2120 cm^{-1} of *cis*-$[Co(en)_2(CN)_2]ClO_4$. Further, we observed that the UV/VIS and circular dichroism (CD) spectra of the optically active *cis*-$[Co(en)_2(CN)_2]^+$ cation change upon addition of the silver(I) ion.

On the other hand, Heatherington *et al.* [1] recently reported a similar phenomenon for the corresponding chromium(III) complex. The isolated adduct, *cis*-$[Cr(en)_2(CN)_2]Ag(ClO_4)_2$, exhibited an absorption spectrum whose band maxima were close to those of $[Cr(en)_3]^{3+}$ rather than the parent *cis*-$[Cr(en)_2(CN)_2]^+$. Thus, they inferred that the adduct is, in fact, the diisocyano complex *cis*-$[Cr(en)_2(NC)_2]Ag(ClO_4)_2$ and not the dicyano complex.

The spectral changes observed for both cobalt(III) and chromium(III) complexes are evidence that these complex cations interact with Ag^+ in solution, as well as in solids, against the electrostatic repulsion. Thus we decided to examine in more detail these systems, as well as systems involving other metal cations such as Cu^{2+}, Hg^{2+} and Ba^{2+}. We have measured the association constants for these systems. The mode of interaction in solution was not fully clear and we have determined the crystal and molecular structure of one of the adducts, Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$, by single crystal X-ray diffraction.

Experimental

Materials

The perchlorate salts of Cu(II), Ag(I), Ba(II), Pb(II), Cd(II) and Mg(II) were commercially available and were used without further purification. The stock solution of the perchlorate salt of Hg(II) was prepared from HgO and perchloric acid in water. Since the ions Pb(II) and Hg(II) are reported to be partially hydrolyzed in water [2], all the solutions containing these ions were made slightly acidic with perchloric acid. Sodium perchlorate monohydrate was recrystallized three times from hot water to remove a trace amount of sodium chloride, which made the sample solution turbid in the presence of Ag(I).

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*Present address: Kumamoto University of Commerce, Ooe-2-5-1, Kumamoto 862, Japan.

**Author to whom correspondence should be addressed.

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Racemic *cis*-$[Co(en)_2(CN)_2]ClO_4$ was prepared from $[Co(en)_2(CO_3)]ClO_4$ by the method of Kuroda [3] and recrystallized twice from warm water. Optical resolution was effected by ammonium bromocamphorsulfonate [4]. The adduct, racemic *cis*-$[Co(en)_2(CN)_2]Ag(ClO_4)_2$, was obtained by addition of $AgClO_4$ to a concentrated aqueous solution of *cis*-$[Co(en)_2(CN)_2]ClO_4$, followed by addition of excess sodium perchlorate. Anal. Found: C, 13.45; H, 3.11; N, 15.89. Calcd for $[Co(en)_2(CN)_2]Ag(ClO_4)_2$: C, 13.40; H, 3.00; N, 1.562%.

The chromium(III) analogue, racemic *cis*-$[Cr(en)_2(CN)_2]Cl \cdot H_2O$, was prepared by a method similar to that of Kirk and Porter [5]. Thirteen grams (0.20 M) of potassium cyanide was dissolved in a mixture of 12 g (0.20 M) of ethylenediamine and 800 ml of methanol. To the resulting solution, 26.7 g (0.10 M) of chromium(III) chloride hexahydrate and about 5 g of zinc flowers were added and the mixture was heated under reflux for 2 h. The supernatant deep red solution of the cooled mixture was decanted off and the remaining yellow crystals were dissolved in a minimum amount of water. After filtration, the reddish yellow solution was concentrated on a rotary evaporator below 55 °C, yielding yellow crystals of *cis*-$[Cr(en)_2(CN)_2]Cl \cdot H_2O$. The yield was about 14 g (5%). Optical resolution of *cis*-$[Cr(en)_2(CN)_2]^+$ was effected in a way similar to that for the corresponding cobalt complex [6]. The perchlorate salt of the optically active *cis*-$[Cr(en)_2(CN)_2]^+$ was recrystallized twice from warm water.

Preparation of Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$

Silver perchlorate and the perchlorate salt of optically active *cis*-$[Cr(en)_2(CN)_2]^+$, which was obtained from the more soluble diastereomeric salt with bromocamphorsulfonate, were dissolved (in a molar ratio of 1:2) in a minimum amount of degassed water. If the water is saturated with an atmospheric carbon dioxide, acid hydrolysis of the complex cation is accelerated (see below). The yellow solution was kept in the dark at temperatures below 10 °C for 7 to 10 days. Substantial aquation of the complex cation occurred. The solution turned to red and deposited orange crystals, which were collected and washed with methanol. *Anal.* Found: C, 15.03; N, 17.64; H, 3.12. Calcd for Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$: C, 15.31; N, 17.86; H, 3.21%.

Measurements

The absorption spectra were run on a Shimadzu UV 200 double-beam spectrophotometer at ambient temperature. The CD spectra were obtained on a JASCO J-40CS recording spectropolarimeter and the sample cell (10 cm path length) was kept at 25 ± 0.2 °C by a Haake circulator Model FK. The difference CD (DCD) spectrum, defined as the CD spectrum with an additive minus the CD spectrum without the additive, was obtained by using the data processor compartment operating at 0.2 nm/step of processor resolution. The DCD data, collected as a function of the concentration of added metal ions, were least-squares fitted to the equation [7]:

$$c_M/\mathrm{DCD} = 1/(\Delta\epsilon_{MA} - \Delta\epsilon_M) + 1/K(c_A - x)(\Delta\epsilon_{MA} - \Delta\epsilon_M) \quad (1)$$

to obtain the association constant, K, and the CD of the ion pair, $\Delta\epsilon_{MA}$, where c_M and c_A are the initial concentrations of the complex perchlorate and the metal perchlorate respectively, and x refers to the concentration of the ion pair. The complex concentration, c_M, was kept constant at 2.5×10^{-3} mol dm^{-3} and c_A was changed from 0 to 5.0×10^{-2} mol dm^{-3}. The ionic strength was adjusted to $\mu = 0.1$ with sodium perchlorate which had been recrystallized (see above).

Collections of the X-ray Diffraction Data of Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$

An orange plate-like crystal of *cis*-$[Cr(N_2C_2H_8)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$ with the dimensions of 0.2 X 0.2 X 0.07 mm was used for the data collection. The cell constants were determined from Weissenberg photographs taken with Ni K_α radiation and were refined with reflection data collected at 20 °C on a Rigaku AFC5 automated four-circle diffractometer utilizing Mo K_α radiation made monochromatic with a graphite plate ($\lambda = 0.71069$ Å). The possible space groups deduced from the systematic absences for *hkl* ($h + k = 2n + l$) are *Cm* (No. 8), *C*2 (No. 5), and *C*2/*m* (No. 12). Of these three, only *C*2 is consistent with the crystal being optically active. The cell constants, determined by a least-squares method using 25 reflections with $20.63° < 2\theta < 27.33°$, were $a = 13.738(4)$ Å, $b = 9.033(4)$ Å, $c = 16.908(4)$ Å, $\beta = 101.71(2)°$, and $V = 2054.4(30)$ Å^3. The measured density of 2.06 g cm^{-3}, obtained by the flotation method using a $CHCl_3$–$CHBr_3$ mixed solution, agreed well with the calculated value of 2.019 g cm^{-3} for $Z = 4$. The intensity data were measured for $h = 0$ to 17, $k = 0$ to 11, and $l = -22$ to $+22$ up to $2\theta = 55°$ using the w-28 scan technique with a scan speed of 8°/min. (50 kV, 170 mA). Three reference reflections (hkl) = (401), (021), and (004) monitored after every cycle of 200 measurements showed significant variation in intensity during the data collection, resulting finally in a 16.5% decrease, and the intensity data were corrected according to the equation $|F_o| = |F_o| \times (1 + an + bn^2 + cn^3)$, where $a = -0.104 \times 10^{-3}$, $b = 0.274 \times 10^{-7}$, $c = -0.526 \times 10^{-11}$, and n is the data number assigned according to the order of measurements. Out of 2671 unique reflections measured, 935 reflections with $|F_o| > 3\sigma(|F_o|)$ and $\sin\theta/\lambda < 0.5$ were used for the structure determination. They were corrected for Lorentz-polarization factor but no absorption correction was applied since the linear absorption coefficient of μ(Mo K_α) = 25.5 cm-’ was low.

Structure Determination and Refinement

The positions of Ag and Cr atoms were located by using the results of MULTAN direct-method analysis (MULTAN 78 [8]). All other computations were carried out using the Universal Crystallographic Computation Program System, UNICS III [9]. Subsequent Fourier difference maps revealed the positions of the remaining non-hydrogen atoms. A series of refinements, using isotropic thermal parameters for all non-hydrogen and hydrogen atoms (situated at fixed positions) excepting the hydrogen atoms of water molecules, produced an R_1 value, $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of 0.1395. A series of refinements without hydrogen atoms of water molecules, using anisotropic thermal parameters for Ag, Cr and Cl atoms and isotropic thermal parameters for other non-hydrogen atoms as well as hydrogen atoms (situated at calculated positions), reduced the R_1 value to 0.0901. Similar refinements assuming an alternative model for the cation, *i.e., cis*-$[Cr(en)_2(CNAgCN)_2]^+$ not *cis*-$[Cr(en)_2(NCAgCN)_2]^+$, yielded R_1 = ***0.0903*** and anomalous thermal parameters for the relevant N and C atoms. Also, equivalent refinements of the enantiomeric model (A complex) converged R_1 to 0.0904. The anomalous dispersion coefficients of Cromer and Liberman [IO] were used for Ag, Cr and Cl. The final R_2 value, $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, was 0.1018. The positions of hydrogen atoms of water molecules were not determined. The weighting scheme used was as follows; for $|F_o| < 20$, w = 0.8: for $20 < |F_o| < 150$, w = 1.0: for $|F_o| > 150$, w $= |F_o|/150$. The largest residuals 1.8 e/Å^3 and 1 .3e/Å^3 in the final difference Fourier map are located near Ag and Cr atoms respectively. The other prominent residuals of 1.0 e/Å^3 are near ClO_4 and C5, C6, C7, C8, N2 and N3 atoms.

All the scattering factors were taken from Cromer and Waber [11] . The final atomic coordinates for non-hydrogen atoms are given in Table II according to the atom labels of Fig. 3. All the computations, including ORTEP drawings [12], were carried out by a HITAC M-200H computer at the Hiroshima University Information Processing-Center.*

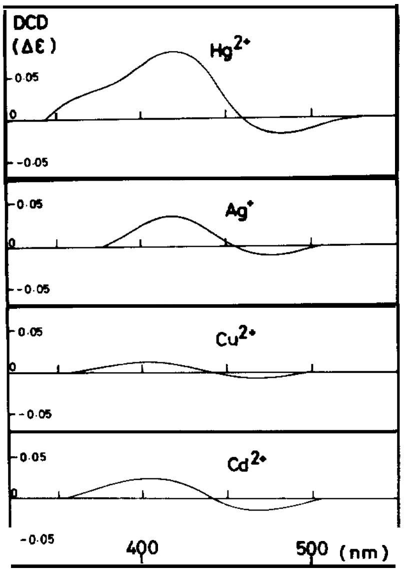

Fig. 1. DCD spectra of Λ-*cis*-$[Co(en)_2(CN)_2]^+$ due to Hg(II), Ag(I), Cu(II), and Cd(II).

Results and Discussion

The Cobalt(III) Complex

The UV/VIS and CD spectra of ***A-cis-*** $[Co(en)_2(CN)_2]^+$ have been found to change measurably upon addition of several hydrated metal ions. These spectral changes may be used to estimate the association constant. It should be noted here that the copper(II) ion, for example, absorbs strongly in the UV/VIS region and thus interferes with the spectrum of *cis*-$[Co(en)_2(CN)_2]^+$. However, the Cu(II) ion, because of its achirality, does not interfere with the CD spectrum of optically active *cis*-$[Co(en)_2(CN)_2]^+$, and the CD spectra have been used in this work to measure the association constants between ***A-cis-*** $[Co(en)_2(CN)_2]^+$ and several metal ions under the condition of μ = 0.1 ($NaClO_4$) and 25 °C. The metal ions examined here are Cu(II), Hg(II), Cd(II), Ba(II), Pb(II), Mg(II), Ag(I) and Na(I). Of these ions, Hg(II), Ag(I), Cu(II) and Cd(II) significantly affected the CD spectrum of Λ-*cis*-$[Co(en)_2(CN)_2]^+$ and no measurable CD change was observed for Ba(II), Mg(II), Pb(II), and Na(I). Figure 1 shows the DCD spectra due to the former group of ions, where the DCD is given as the difference in the CD spectra of fully ion-associated species and A-cis- $[Co(en)_2(CN)_2]^+$. The association constants obtained by analysing the CD variation are summarized in Table I, together with those for the corresponding chromium(III) complex.

Several possibilities may be conceived for the mode of interaction between Λ-*cis*-$[Co(en)_2(CN)_2]^+$ and M^{n+} ions in solution, and some of them are illustrated in Fig. 2 for M^{n+} = Ag(I). Figure 2

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*A listing of observed and calculated structure factor amplitudes is available upon request from the author (H.Y.).

TABLE I. Association Constant, ***K*** ($mol^{-1} dm^3$), of Λ-*cis*-$[M(en)_2(CN)_2]^+$ with M' ions at μ = 0.1 ($NaClO_4$) and 25 °C.[a]

M	M'	λ(nm)	*K*	η_A[d]
Co(III)	Hg(II)	400	225(11)	7.7
	Ag(I)	400	104(5)	6.9
	Cu(II)	400	32(6)	8.3
	Cd(II)	400	4(2)	10.3
Cr(III)	Hg(II)	470	large[b]	1.7
	Ag(I)		$>10^5$ [c]	6.9
	Cu(II)	480	362(36)	8.3
	Cd(II)	480	35(10)	10.3

[a] $K \simeq 0$ in the case of Ba(II) (η_A = 12.8), Mg(II) (η_A = 32.5), Pb(II) (η_A = 8.5), and Na(I) (η_A = 21.1) for both Co(III) and Cr(III) complexes. [b] See text. 'Ref. [1]. [d] Hardness parameter, defined in ref. [17].

includes the modes Co–CN···Ag (1: 1 association), Ag···NC–Co–CN···Ag (1:2 association), Co–NC···Ag (1: 1 association with linkage isomerization), silver(I) coordination to π-electrons of coordinated CN groups. These ion-associated species may or may not be solvent-separated. The Ag(I) ion might be considered to interact with the complex cation through coordination to the n-electrons of CN groups by analogy with olefin-silver(I) coordination [I 3]. Likewise, there is no ***apriori*** reason to rule out the 2: 1 association such as Co–CN···Ag·· *NC-Co, because the complex *cis*-$[Ru(bpy)_2(CN)_2]$ (bpy = 2,2'-bipyridine), for example, in acetonitrile has been reported [14] recently to interact with Ag(I) with this stoichiometry, as well as in 1: 1 and 1:2 modes. Examples where two cyano groups in a complex bind to one metal ion are also known [15].

Of these possibilities, 1:2 association and 2:1 association are eliminated by the observation that the plots of eqn. 1, namely c_M/DCD *vs.* $1/(c_A - x)$ plots, were linear for all the cobalt(III) systems, at least over the whole concentration range of metal ions investigated. This is usually taken as evidence for 1: 1 association [7]. Also, the λ_{max} value in the UV/VIS spectrum of *cis*-$[Co(en)_2(CN)_2]^+$ is unaffected by addition of metal ions, except copper(H). Thus, the modes of interaction involving the Co–NC(isocyano) group are unlikely, which is quite reasonable because the cobalt(III)–cyano linkage is the most stable thermally among ordinary cobalt-ligand bonds. Further, as seen from Fig. 1, all the DCD spectra are rather similar in shape, suggesting that Hg(II), Ag(I), Cu(II), and Cd(II) ions behave similarly. Since Cu(II), unlike Cu(I) [16], may not interact with the CN group ***via*** π-coordination, all the metal ions may be assumed to associate with the cobalt(III) complex at one nitrogen end of the coordinated CN groups. Thus, for the cobalt(III) complex, NC–Co–CN···M^{n+} (top left of Fig. 2) may be considered as the only possibility.

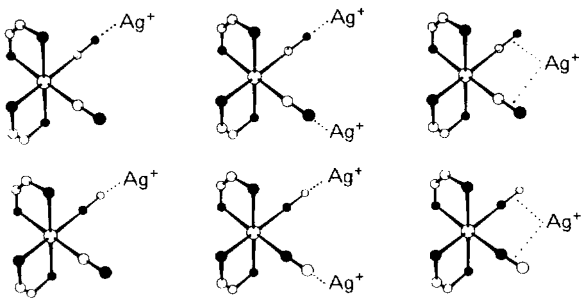

Fig. 2. Probable modes of association between Λ-*cis*-$[Co(en)_2(CN)_2]^+$ and Ag(I). Open and closed circles represent carbon (and cobalt) and nitrogen atoms, respectively. Hydrogen atoms are omitted for clarity.

The association constant of the cobalt(III) complex decreases in the order Hg(II) > Ag(I) > Cu(II) > Cd(II) > Ba(II), Mg(II), Pb(II), Na(I) ≃ 0 (see Table I). Clearly, this order is irrelevant to the electric charge (+1 or +2) of the ions, which may be an important factor in ordinary outer-sphere association of unlike-charged ions. In Table I, the hardness parameter, η_A, recently defined by Parr and Pearson [17], is also given for each metal ion; a low value of η_A means high softness. The ***K*** value appears to increase as the metal ions get softer, and in fact a good linear correlation exists between log ***(K)*** and η_A values, at least for Hg(II), Ag(I), Cu(II), Cd(II) and Ba(II). A linear regression analysis for these ions yields 0.953 as the correlation coefficient. Therefore, it may be concluded that the nitrogen end of coordinated CN groups of the cobalt(III) complex is rather soft and prefers soft metal ions. Implicit in this conclusion is the assumption of contact ion pairs.

The Chromium(III) Complex

In the case of the chromium(III) complex, difficulties were encountered in measuring the association constants. The Cr(III) complex was hydrolyzed rather rapidly in aqueous solution and this aquation reaction is known to be acid-catalyzed [I]. The Hg(II) ion itself catalyzes the aquation, as well as the cyano-isocyano linkage isomerization [18]. The Ag(I) ion is also known to catalyze the linkage isomerization [1]. For these reasons, only limited data were obtained for *cis*-$[Cr(en)_2(CN)_2]^+$. In Table I, the ***K*** value estimated for Ag(I) and Hg(II) are assumed to correspond to the association involving the isomerized complex cation, i.e., diisocyano complex (see below). Though we could not determine the ***K*** value for Hg(II), Birk and Espenson [IX] placed a lower limit of K > $10^5 mol^{-1} dm^3$ (μ = 0.1 and 25 °C) for the formation of an ion pair supposed to be $(H_2O)_5CrNC$···Hg.

A cursory examination of Table I seems to indicate (i) that the order of *K* values of the Cr(III) complex runs roughly parallel to that of the Co(III) complex, and (ii), that the *K* value of the Cr(III) complex is greater than that of the Co(III) complex by approximately a factor of ten. The difference in *K* values of the Cr(III) and Co(III) systems clearly indicates that the driving force for ion association of the present systems is different from that of an ordinary ion association between oppositely-charged ions. Usually, outer-sphere association constants are rather insensitive to the identity of the central metal ion of the complex. For example, the association constant between *cis*-$[M(en)_2Cl_2]^+$ and Cl^- in dimethylsulfoxide or dimethylformamide is reported to be almost independent of whether M = Co(III), Cr(III), or Rh(III) [19]. The correlation, between log (*K*) and η_A found here is evidence that soft-acid/soft-base interaction dominates over other factors that may contribute to outer-sphere association constants, e.g. interionic electrostatic force, solvation energies of the ions, hydrogen bonding, or crystallographic volume of the interacting ions. A discussion about the relative importance of these factors in outer-sphere association has been given elsewhere [20].

The finding that the nitrogen end of the coordinated CN group is soft was unexpected, but a brief survey of the literature revealed many scattered examples of complexes that involve bridging cyanide groups. The *cis*-$[Fe(phen)_2(CN)_2]$ (phen = 1,10-phenanthroline) and *trans*-$[Pt(H)(PEt_3)_2(CN)]$ (Et = C_2H_5) complexes form adducts with various Lewis acids [21]. Kinnaird and Whitten [14] isolated an adduct *cis*-$[Ru(bpy)_2(CN)_2]AgClO_4 \cdot H_2O$ and Siebert [22] reported several super complexes of $[Co(NH_3)_5CN]^{2+}$ with Hg(II) and Ag(I). The first point noted from these examples, as well as the present result, is that the soft nature of the nitrogen end of coordinated CN group may not be characteristic of the tripositive charge of Co and Cr ions, nor of the overall charge of the complexes. Though it is tempting to infer that the soft nature is a common feature of transition-metal coordinated cyanides, this point requires further investigation.

The second point noted from the above examples is that in all cases cited above, the CN stretching frequency is blue-shifted upon adduct formation, which has been taken to indicate the bridging cyanide. Thus, a blue-shift of about 60 cm^{-1} observed for *cis*-$[Co(en)_2(CN)_2]Ag(ClO_4)_2$ suggests the interaction mode Co–CN···Ag in the solid state, which is similar to that proposed in solution. In contrast, the crystal of a similar composition, *cis*-$[Cr(en)_2(CN)_2]Ag(ClO_4)_2$, is reported [1] to show the CN stretching band at 2128 cm^{-1}, very close to 2130 cm^{-1} of *cis*-$[Cr(en)_2(CN)_2]ClO_4$. This similarity may be indirect evidence that in the former crystal, the CN group is isomerized and the Ag(I) ion is interacting in the manner Cr–NC···Ag, as suggested for the Cr(III) complex in solution [1].

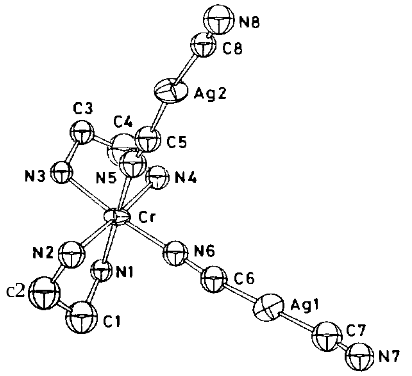

Fig. 3. ORTEP drawing of the cation Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]^+$ with atom labels. Thermal ellipsoids are drawn to include 50% of probability distribution.

Structure of Δ-cis-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$

Owing to the highly insoluble nature of Δ-*cis*-$[Cr(en)_2(CN)_2]Ag(ClO_4)_2$, we could not prepare X-ray quality crystals of this compound. The crystal Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]ClO_4 \cdot 2H_2O$ was grown by slow evaporation of an aqueous solution containing the optically-active *cis*- $[Cr(en)_2(CN)_2]^+$, which was obtained from the more-soluble diastereoisomer with bromocamphorsulfonate, and $AgClO_4$ in a 1:2 molar ratio. Substantial aquation of the complex cation was observed during evaporation and the terminal CN group that is ***trans*** to Cr(III) (see below) should be produced by the aquation reaction. Though the accuracy of the X-ray structure determination was rather low owing to a very high sensitivity of the complex salt to X-ray irradiation, several important conclusions can be drawn from the crystal structure.

The structure of the cation Δ-*cis*-$[Cr(en)_2(NCAgCN)_2]^+$ with atom labels is depicted in Fig. 3. The chromium(III) ion is surrounded in a distorted octahedron by six nitrogen atoms, four from ethylenediamine and two from isocyano groups. Alternatively, the chromium ion is coordinated by two ethylenediamine molecules and two $Ag(CN)_2$ molecules. Bond lengths and angles in the $Cr(en)_3$ moiety appear quite normal [23]. The Cr–N5–C5, C5–Ag2–C8, Cr-N6-C6, and C6–Ag1–C7 angles are all close to 180°, rendering the whole assembly of the Cr-NC-Ag-CN group approximately linear. The geometrical features of this part of the cation also appear normal. The atomic coordinates of non-hydrogen atoms are given in Table II.

The complex cation has the A absolute configuration. The parent complex, namely optically active *cis*-$[Cr(en)_2(CN)_2]^+$, was obtained from the more

TABLE II. Atomic Parameters ($\times 10^3$).

Atom	*x*	Y	z
Ag1	132.1(0.3)	0(0.5)	506.9(0.3)
Ag2	−133.6(0.3)	613.6(0.5)	503.9(0.2)
Cr	−54.3(0.4)	306.3(1.3)	263.5(0.4)
Cl	−169.0(1.0)	258.7(1.4)	−40.6(0.7)
OW1	150(3)	832(6)	110(2)
OW2	310(2)	553(3)	753(1)
O1	−162(2)	279(4)	−117(2)
O2	−122(3)	271(5)	25(2)
O3	−274(4)	265(8)	−41(3)
O4	−113(5)	131(9)	−26(3)
N1	−16(2)	171(4)	178(2)
N2	−174(3)	170(4)	255(2)
N3	−134(2)	451(4)	183(2)
N4	66(3)	452(4)	256(2)
N5	−95(3)	436(4)	352(2)
N6	24(3)	183(4)	351(2)
N7	225(2)	178(6)	669(2)
N8	−154(3)	787(6)	664(2)
C1	−74(4)	20(7)	181(3)
C2	−180(4)	73(6)	182(3)
C3	−74(3)	587(5)	181(2)
C4	34(4)	547(7)	193(3)
C5	−109(3)	495(6)	410(2)
C6	75(3)	99(5)	409(2)
C7	187(4)	108(6)	616(3)
C8	−144(3)	726(5)	608(3)

soluble diastereoisomer with bromocamphorsulfonate and exhibited negative CD bands in the visible region. Since it is unlikely that the cyano-isocyano linkage isomerization (Cr-CN to Cr-NC-Ag-CN) accompanies the inversion of the absolute configuration, the enantiomer showing positive CD bands in the visible region may be assigned the A configuratin, as for the corresponding Co(III) complex [24]. This assignment is also consistent with the assignment made based on the CD spectrum [6].

The cyano groups isomerized into the isocyano groups by coordination with AgCN. This result strongly supports the inference that the Cr(III)-bound CN group is isomerized by Ag(I) into the isocyano form in solution. The possibility that Cr-CN groups in $[(H_2O)_5Cr(CN)]^{2+}$ might be transformed into Cr-NC by Hg(II) [18, 25, 26] and Ag(I) [25, 26] has been pointed out previously, and the high stabilities of adducts such as Cr-NC-Hg and Cr-NC-Ag have been ascribed to the natural affinity of carbon end of the cyanide ligand for the very soft cations Hg(II) and Ag(I). It is probable that metal ions associate first at the nitrogen end of the CN group in both Co(III) and Cr(III) complexes, ans since the Cr(III)-CN bond is less stable compared with the Co(III)–CN bond, very soft cations can induce cyano-isocyano linkage isomerization and form rather stable adducts. Adduct formation of a similar nature has also been noted for M–NCS···Hg(II) and M–N=N=N···Hg(II) systems [27] and for Co(III)–S···M′ (M’ = Ag(I) or CH_3-Hg’) and Co(III)–S(O)···Pd(II) systems [28].

References

1 A. Heatherington, S. M. Oon, R. Vargas and N. A. P. Kane-Maguire, ***Znorg. Chim. Acta, 44, L279 (1980).***

2 F. A. Cotton and G. Wilkinson, ‘Advanced Inorganic Chemistry, 2nd Edn.‘, Interscience Publishers, New York, 1966, p. 483 and 616.

3 K. Kuroda, ***Nippon Kagaku Zasshi, 89, 720 (1968).***

4 S. C. Chan and M. L. Tobe, *J. Chem. Soc.,* 966 (1963).

5 A. D. Kirk and G. B. Porter, Znorg. ***Chem., 19. 445 (1980).***

6 S. Kaizaki, J. Hidaka and Y. Shimura, ***Bull. Chem. Soc. Jpn., 48. 902*** (1975).

7 (a) U. Sakaguchi, A. Tsuge and H. Yoneda, *Inorg.* Chem., 22, 3745 (1983);
(b) U. Sakaguchi, A. Tsuge and H. Yoneda, ***Znorg.*** Chem., 22, 1630 (1983).

8 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, ‘MULTAN’, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univ. of York, England, and Univ. de Louvain, Belgium, 1978.

9 T. Sakurai and K. Kabayashi, ***Rikagaku Kenkyusho Hokoku, 55, 69 (1979).***

10 D. T. Cromer and D. Liberman, ***J. Chem. Phys., 53,*** 1891 (1970).

11 D. T. Cromer and J. T. Waber, ‘International Tables for X-ray Crystallography, Vol. IV’, Kynoch Press, Birmingham, England, 1974, p.72, 79.

12 C. K. Johnson, ‘Report ORNL-5138’, Oak Ridge Nat. Lab., 1976.

13 (a) D. F. Evans, J. N. Tucker and G. C. de Villardi, ***J. Chem. Soc., Chem. Commun., 205*** (1975).
(b) T. J. Wenzel and R. E. Sievers, ***J. Am. Chem. Soc., 104, 382 (1982);***
(c) T. J. Wenzel and R. E. Sievers, ***Anal. Chem., 53, 393*** (1981) and refs. therein.

14 M. G. Kinnaird and D. G. Whitten, ***Chem. Phys. Lett., 88, 275 (1982).***

15 M. Rüegg, A. Ludi and K. Rieder, ***Znorg. Chem., 10,*** 1773 (1971).

16 J. S. Thompson, R. L. Harlow and J. F. Whitney, ***J. Am. Chem. Soc., 105,*** 3522 (1983).

17 R. G. Parr and R. G. Pearson. ***J. Am. Chem. Soc., 105.*** 7512 (1983).

18 J. P. Birk and J. H. Espenson, ***Znorg. Chem., 7, 991*** (1968).

19 D. A. Palmer and D. W. Watts, ***Znorg.*** Chem., IO, 281 (1971).

20 U. Sakaguchi, S. Tamaki, K. Tomioka and H. Yoneda, submitted for publication.

21 (a) J. J. Rupp and D. F. Shriver, ***Znorg. Chem., 6, 755 (1967);***
(b) D. F. Shriver and J. Posner, ***J. Am. Chem. Soc., 88, 1672*** (1966);
(c) L. E. Manzer and G. W. Parshall, ***J. Chem. Soc., Chem. Commun., 227 (1975).***

22 H. Z. Siebert, ***Anorg. Allg. Chem.,*** 327, 63 (1964).

23 (a) K. N. Raymond, P. W. R. Corfield and J. A. Ibers, *Znorg. Chem., 7, 1362* (1968);
(b) S. Jagner, E. Ljungström and N.-G. Vannerberg, *Acta Chem. Scand., Ser. A:. 28, 623* (1974).

24 K. Matsumoto, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Jpn., 44, 2721* (1971).

25 J. H. Espenson and W. R. Bushey, *Inorg. Chem., IO, 2451* (1971).

26 S. N. Frank and F. C. Anson, *Inorg. Chem., 11, 2938 (1972).*

27 (a) W. C. Waggener, J. A. Mattern and G. H. Cartledge, *J. Am. Chem. Soc., 81, 2958* (1959):
(b) D. A. Loeliger and H. Taube, *Inorg. Chem., 5, 1376* (1966);
(c) L. C. Falk and R. G. Linck, *Inorg. Chem., IO, 215* (1971).

28 (a) J. D. Lydon and E. Deutsch, *Inorg. Chem.,* 21, 3180 (1982);
(b) M. J. Heeg, R. C. Elder and E. Deutsch, *Inorg. Chem.. 18, 2036* (1979).