2-bromo-2-nitrosopropane (I) with some of the more reactive neutral bimetallic metal carbonyl derivatives such as $Fe_2(CO)_9$, $Co_2(CO)_8$, and $[C_5H_5NiCO]_2$ were uniformly unsuccessful apparently owing to complete destruction of the transition metal–organometallic system by the strongly oxidizing nitroso group.

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Registry No. IIIa, 50986-50-0; V (M=Cr), 28394-70-9; V (M=W), 50726-12-0; VI, 50986-63-5; VII, 50986-64-6; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Fe_3(CO)_{12}$, 15321-51-4; 2-bromo-2-nitrosopropane, 7119-91-7.

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Photochemistry of Mixed-Ligand Chromium(III) Complexes. III. *trans*-Chloroisothiocyanatobis(ethylenediamine)chromium(III)

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The photochemical behavior of *trans*-$Cr(en)_2(NCS)Cl^+$ in aqueous solutions (pH ~3) has been investigated. Regardless of the excitation wavelength (254, 313, 365, 404, 464, 506, 549 nm), the irradiation of the complex causes the release of SCN^- and Cl^- ions and the consumption of H^+ ions. The last photoreaction is due to the detachment of one ethylenediamine end from the coordination sphere, followed by the protonation of the free amine group. Spectrophotometric and chromatographic analyses have shown that SCN^- and Cl^- are released in distinct photoreactions which lead to *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(NCS)H_2O^{2+}$, respectively. The quantum yields of SCN^- ($\Phi = 0.18$) and Cl^- ($\Phi = 0.05$) release are wavelength independent, whereas the quantum yield of (one end) ethylenediamine detachment increases passing from the charge transfer ($\Phi = 0.02$) to the high-energy metal-centered bands ($\Phi = 0.05$), but it drops when the irradiation is performed in the lowest metal-centered band ($\Phi = 0.006$). The results suggest that the photoreactions leading to the release of SCN^- and Cl^- originate from the lowest quartet excited state, ^4E, whereas the photoreaction involving ethylenediamine mainly originates from the $^4B_2$ excited state. These conclusions are shown to be in agreement with the expectations based on a MO approach. The photochemical behavior of *trans*-$Cr(en)_2(NCS)Cl^+$ is compared to that of the previously investigated cis isomer.

Introduction

Recent investigations have shown that the study of the photochemical behavior of mixed-ligand Cr(III) complexes can give important information concerning the stereochemistry of the photoreaction[1] and the role played by the various excited states.[2,3] Specifically, the results of such investigations indicate that, in D_{4h}-symmetry complexes, the predominant reaction mode reflects the σ-antibonding orbital population of the lowest quartet excited state[1,2] and the photosubstitution reaction takes place with a change in the geometric configuration.[1] There is now the need to examine other mixed-ligand complexes in order to confirm the abovementioned results and elucidate more specific features of the photochemical behavior. The main problems which are still waiting a solution are the following ones: (i) the question as to what is the predominant reaction mode when the labilized axis contains two different ligands, (ii) whether the observed photoreactions originate from the same or different excited states, (iii) whether or not the CT excited states play a photochemical role, and (iv) whether π bonding is important in determining the photochemical behavior.[4,5] The reply to the above questions can only come from investigations carried out on suitably chosen systems. We wish to report here the results obtained from a systematic study on the photochemical behavior of *trans*-$Cr(en)_2(NCS)Cl^+$. A preliminary communication concerning some of the results obtained with this complex has already appeared.[6]

Experimental Section

Materials. *trans*-Chloroisothiocyanatobis(ethylenediamine)chromium(III) perchlorate, *trans*-$[Cr(en)_2(NCS)Cl]ClO_4$, was prepared following the procedure indicated in the literature.[7] The complex was recrystallized three times from cold acidic water by adding an excess of $NaClO_4$. *Anal.*[8] Calcd for $[Cr(en)_2(NCS)Cl]ClO_4$: C, 16.44; H, 4.42; Cl, 19.42; Cr, 14.24; N, 19.18; S, 8.78. Found: C, 16.33; H, 4.08; Cl, 19.47; Cr, 14.55; N, 19.05; S, 8.61. All of the other chemicals used were of reagent grade.

Apparatus. Radiations of 254, 313, 365, and 404 nm and narrow spectral bands centered at 464, 506, and 549 nm were obtained as described in ref 9. The intensity of the incident light, which was measured by means of the ferric oxalate[10] or Reineckate[11] actinometers, was of the order of 10^{-7}*Nhν*/min at each irradiation wavelength. Polychromatic radiations having wavelengths higher than 520 nm were obtained from an incandescent lamp[9] filtered with a 3-68 Corning glass filter. The photolysis cell was placed in a constant-temperature bath (±0.2°) equipped with a double quartz window to avoid moisture condensation. The absorbance measurements and the recording of the spectra were performed with an Optica CF4 NI spectrophotometer. A Knick KpH 34 pH meter was used for pH

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measurements. Differential potentiometric titrations of Cl^- and SCN^- were also made by using the Knick pH meter as a potentiometer. Chromatographic separations were performed on a H^+ Dowex 50W-X8 (200–400 mesh) column (56 × 1 cm), using a LKB peristaltic pump and a LKB Ultrorac fraction collector, which was equipped with a drop counting system.

Procedure. The procedure was essentially the same as that used for studying the cis isomer.[9] A weighed amount of the complex was dissolved in 10^{-3} *F* $HClO_4$ in red light. The concentration of the complex was 2×10^{-2} *F*. The reaction cell (optical path 2 cm, capacity 13 ml) was filled with a freshly prepared solution and then was placed in the thermostated cell holder of the irradiation equipment. A sample of the same solution was maintained in the dark at the same temperature in order to provide a control for the thermal reactions. Practically all of the incident light was absorbed by the solution under the experimental conditions used. When measuring quantum yields, no more than 10% of the reactant was decomposed, in order to avoid secondary photochemical reactions. For the chromatographic experiments, about 20% of the reactant was decomposed. The photochemical experiments were carried out at 1 or 15°. pH measurements were made directly in the reaction cell during irradiation by means of a glass–reference combined microelectrode. Spectrophotometric measurements were performed after suitable irradiation periods by interrupting the light beam and bringing a portion of the solution to the spectrophotometer. At the end of the irradiation, the solution was added to 6.5 g of H^+ Dowex 50W-X8 resin (100–200 mesh) for adsorption of the unreacted complex and its aquation products. The solution was then filtered and analyzed for Cl^- and SCN^-. In each case, a sample of the corresponding dark solution was treated in the same way as the irradiated solution in order to provide a control for the thermal reactions. In other experiments, a 6-ml sample of a solution irradiated with polichromatic light ($\lambda > 520$ nm) was poured into the column of the chromatographic apparatus for the separation of the various cationic species. This operation was carried out in a dark, cooled (0°) room, so as to minimize the thermal reactions. The elution was carried out with 700 ml of HCl whose concentration was continuously increased from 1 to 4.5 *N*. The effluent fractions (6 ml each) were collected automatically and then analyzed for ethylenediamine as described below. The chromatographic behavior of *trans*-$Cr(en)_2(NCS)Cl^+$ and *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ [12] was also examined under the same experimental conditions.

Analytical Methods. The detachment of amine groups from the complex was followed by pH measurements. For each experiment, the pH changes resulting from irradiation were converted to changes in H^+ concentration by means of a ΔpH *vs.* $\Delta[H^+]$ calibration plot, obtained by adding known amounts of base to a portion of the same solution maintained in the dark. Cl^- and SCN^- were determined by means of differential potentiometric titrations with 0.010 *F* $AgNO_3$. SCN^- was also determined spectrophotometrically at 450 nm as iron thiocyanate.[11] The two methods gave concordant results, but the spectrophotometric method was about 5 times more sensitive than the potentiometric titration. Ethylenediamine was determined spectrophotometrically by means of the ninhydrin method,[13] after decomposition of the Cr(III) complexes.

Results

Thermal Behavior. The thermal behavior of *trans*-$Cr(en)_2(NCS)Cl^+$ was unknown. Therefore, before studying the photochemical behavior, we briefly examined the thermal reactions of the complex with the aim of establishing whether they could interfere in the photochemical investigations. For slightly acidic solutions at 15°, we found that (i) no SCN^- was released ($k < 10^{-8}$ sec^{-1}), (ii) Cl^- was released with a rate constant of the order of 10^{-6} sec^{-1}, (iii) the pH of the solutions increased slightly, presumably because of a slow ethylenediamine aquation ($k \leqslant 1 \times 10^{-6}$ sec^{-1}), and (iv) an unidentified anionic species was formed, which could be titrated by Ag^+. Potentiometric titrations showed that this anionic species was not identifiable as CN^-, S^{2-}, or $SO_4{}^{2-}$, which are the most likely products of SCN^- decomposition. Assuming that the ionic charge of the unknown species was 1−, the solubility product for AgX was of the order of 10^{-13} and the formation rate constant of X^- was $\sim 1 \times 10^{-6}$ sec^{-1}.

The occurrence of these thermal reactions was always taken into consideration for the calculation of the quantum yields, even if the required corrections were very small for the experiments carried out at 1°.

Photochemical Behavior. Irradiation of *trans*-$Cr(en)_2(NCS)Cl^+$ caused the consumption of H^+ and the production of free Cl^- and SCN^- ions, regardless of the excitation wavelength. During the irradiation, the concentrations of H^+, Cl^-, and SCN^- changed linearly with the number of absorbed einsteins. No postphotochemical effects were observed. The quantum yields of H^+ consumption and SCN^- and Cl^- release, for the experiments carried out at 1°, are summarized in Table I. When irradiation was performed at 15°, the quantum yield values were found to be the same as those reported in Table I, within the experimental error. The erroneous observation that Φ_{Cl^-} increased with the temperature, reported in a preliminary communication,[6] was due to the fact that the interference by the unidentified thermal anionic product on the Cl^- determination had not been considered.

A differential spectrophotometric analysis of the irradiated (at $\lambda > 520$ nm) *vs.* dark solutions was performed, in order to elucidate the nature of the complexes obtained as a consequence of SCN^- and Cl^- release. The curve obtained (see Figure 2 of ref 6) was compared with the patterns expected for the formation of the following couples of photoproducts, taken in molecular ratios (given within brackets) so as to agree with the experimental quantum yields of SCN^- and Cl^- release (see Table I): *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(NCS)(H_2O)^{2+}$ [4.5:1]; *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *trans*-$Cr(en)_2(NCS)(H_2O)^{2+}$ [4.5:1]; *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(NCS)(H_2O)^{2+}$ [4.5:1]; *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ and *trans*-$Cr(en)_2(NCS)(H_2O)^{2+}$ [4.5:1]; *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ [3.5:1]; *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *trans*-$Cr(en)_2(H_2O)_2{}^{3+}$ [3.5:1]; *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ [3.5:1]; *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ and *trans*-$Cr(en)_2(H_2O)_2{}^{3+}$ [3.5:1]. The experimental spectrum was found to match that expected for the formation of *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(NCS)(H_2O)^{2+}$ (see Figure 2 of ref 6),[14] whereas it did not agree with the spectrum that would have been obtained if any other couple of possible aquation products was formed. The sole other couple whose spectrum was not too different from the experimental one was *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$. The formation of *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$, however, was excluded by means of chromatographic experiments, which showed that, within the experimental error, the upper limiting value for the concentration of this complex in the irradiated solution had to be at least 10 times lower than the Cl^- concentration which was produced photochemically.

Discussion

Nature of the Photochemical Reactions. The results obtained show that the irradiation of *trans*-$Cr(en)_2(NCS)Cl^+$ causes the detachment of SCN^- and Cl^- ions from the coordination sphere of the complex and the consumption of small amounts of H^+ ions.

Under our experimental conditions, the observed H^+ consumption can only be due to the photochemical rupture of a Cr–en bond, followed by the protonation of the free amine group. For a number of chromium(III)-ethylenediamine

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Table I. Quantum Yields for H^+ Consumption and SCN^- and Cl^- Release at 1°[a]

Irradiation wavelength, nm	Type of excitation[b]	Φ_{H^+}[c]	Φ_{SCN^-}[d]	Φ_{Cl^-}[d]
254	CT	0.02	0.18	0.04
313	CT	0.02	0.17	0.05
365	$^4T_{1g}$ (^4E, $^4A_2$)	0.03	0.17	0.05
404	$^4T_{1g}$ ($^4A_2$, ^4E)	0.05	0.19	0.05
464	$^4T_{2g}$ ($^4B_2$)	0.05	0.19	0.04
506	$^4T_{2g}$ (^4E, $^4B_2$)	0.02		
549	$^4T_{2g}$ (^4E)	0.006	0.18	0.04

[a] Some quantum yields are slightly different from those reported in a preliminary communication.[6] [b] CT = charge transfer; for the metal-centered excited states, the parent state in the octahedral symmetry is also indicated. [c] Precision ±15%. [d] Precision ±10%.

complexes, it has been established[2,9,15-17] that the primary photochemical step is the detachment of one end of an ethylenediamine molecule. By analogy, the photochemical reaction of *trans*-$Cr(en)_2(NCS)Cl^+$ responsible for H^+ consumption is assumed to be

$$trans\text{-}Cr(en)_2(NCS)Cl^+ \xrightarrow[H_3O^+]{h\nu} Cr(en)(enH)(H_2O)(NCS)Cl^{2+} \qquad (1)$$

For most of the chromium(III)-ethylenediamine complexes, the primary detachment of one ethylenediamine end is followed by a slow thermal reaction which causes the complete detachment of an ethylenediamine molecule and thus, a postphotochemical H^+ consumption.[15-17] For *cis*-$Cr(en)_2(NCS)Cl^+$, where the consumption of H^+ ions is the principal photoreaction, the lack of postphotochemical proton uptake and also chromatographic analyses of the irradiated solutions showed that the secondary thermal reaction leading to the complete detachment of an ethylenediamine molecule was practically negligible in the time scale of the photochemical experiments.[9] For *trans*-$Cr(en)_2(NCS)Cl^+$, the consumption of H^+ ions is a minor photoreaction, so that it was impossible to establish whether the secondary thermal reaction is fast or slow with respect to the time scale of the photochemical experiments. By analogy with the behavior of the other chromium(III)-ethylenediamine complexes, we assume that the secondary thermal reaction was so slow that the measured quantum yield of H^+ consumption can be taken as the quantum yield of photoreaction 1. It should be noted that such an assumption does not affect the discussion which will be reported later concerning the wavelength dependence of the photochemical behavior.

The photoreactions which cause the release of Cl^- and SCN^- have been identified by means of a differential spectrophotometric analysis and by chromatographic analysis and are respectively

$$trans\text{-}Cr(en)_2(NCS)Cl^+ \xrightarrow[H_2O]{h\nu} cis\text{-}Cr(en)_2(NCS)(H_2O)^{2+} + Cl^- \qquad (2)$$

$$trans\text{-}Cr(en)_2(NCS)Cl^+ \xrightarrow[H_2O]{h\nu} cis\text{-}Cr(en)_2(H_2O)Cl^{2+} + SCN^- \qquad (3)$$

As was emphasized in the preliminary communication,[6] an important result is that both photoaquations 2 and 3 occur with a change in the geometrical configuration. Other recent investigations have shown that stereomobility may indeed be the rule in Cr(III) photosubstitutions.[1b,18]

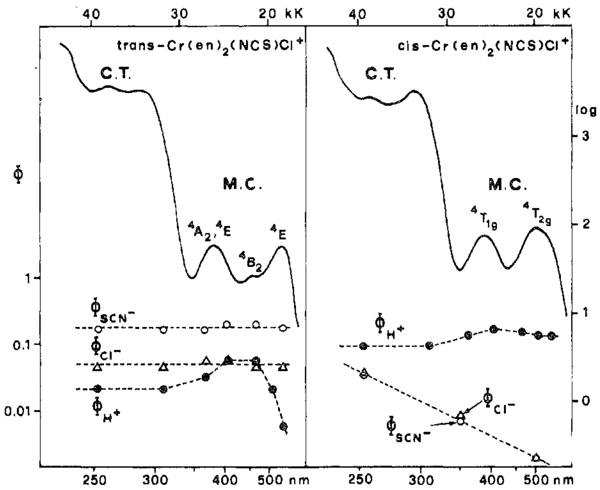

Figure 1. Electronic absorption spectra of *trans*- and *cis*-$Cr(en)_2(NCS)Cl^+$ and quantum yields of the observed photoreactions. The data concerning the cis isomer have been taken from ref 9. For the cis isomer, O_h symmetry labels were used because the MC (metal-centered) bands are not split and the relative energy position of the C_{2v} sublevels is not known.

Wavelength Dependence of the Photochemical Behavior. The electronic absorption spectrum of *trans*-$Cr(en)_2(NCS)Cl^+$ (Figure 1) shows high-intensity bands in the ultraviolet region, which can be attributed to ligand-to-metal charge-transfer transitions.[19,20] The low-intensity bands which appear in the visible part of the spectrum are due to metal-centered (d-d) spin-allowed transitions. In the actual symmetry of the complex, C_{4v}, the "octahedral" $^4T_{1g}$ and $^4T_{2g}$ excited states are split into ^4E and $^4A_2$ and into $^4B_2$ and ^4E, respectively. However, as generally happens for the trans-disubstituted complexes,[21] only the lowest "octahedral" quartet band is actually split. The excited states preferentially populated with the various excitation wavelengths are shown in Table I.

The quantum yields of Cl^- and SCN^- release are constant through the entire spectral region examined. This indicates that reactions 2 and 3 originate from the same excited state and that such a state must be either the lowest quartet excited state, ^4E, or the spin-forbidden doublet excited state, ^2E, which lies at a lower energy. It seems, however, that the latter hypothesis can be discarded on the basis of recent experimental[3,22-25] and theoretical[26] evidence.

The quantum yield of reaction 1 increases in going from 254 nm (CT excitation) to 464 nm (excitation to the $^4B_2$ metal-centered excited state) and then drastically drops when irradiation mainly leads to the lowest energy metal-centered quartet state, ^4E (see Figure 1). This trend suggests that (i) ethylenediamine aquation is unrelated to the two

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other photoreaction modes, (ii) the metal-centered excited state which is mainly responsible for ethylenediamine aquation is $^4B_2$, and (iii) there is scarce communication between the charge-transfer excited states and the metal-centered excited state responsible for the ethylenediamine aquation.

The increase in the quantum yield of ethylenediamine aquation passing from charge-transfer to metal-centered excitation does not seem to have any simple explanation, expecially if one considers that the quantum yields for Cl^- and SCN^- release are practically constant in the charge-transfer and metal-centered bands (see also later).

In summary, the results obtained seem to indicate that the state responsible for Cl^- and SCN^- aquation (reactions 2 and 3) is the lowest quartet, ^4E, whereas the state responsible for ethylenediamine aquation (reaction 1) is $^4B_2$. It is interesting to note that these conclusions are in agreement with the expectations based on a MO approach.[27-29] In this approach, the formation of the $^4B_2$ excited state involves the population of a σ-antibonding MO having predominant $d_{x^2-y^2}$ character, so that such an excited state is expected to be strongly distorted in the xy plane, with consequent ethylenediamine labilization. On the other hand, the formation of the lowest ^4E state corresponds to the population of a σ-antibonding MO having predominant d_{z^2} character. Therefore, this last state is expected to be predominantly distorted along the z axis, with consequent SCN^- and Cl^- labilization. The fact that SCN^- is preferentially labilized with respect to Cl^- can tentatively be explained on the basis of the π-bond changes which occur in going from the ground state to the lowest ^4E excited state.[4,5,30] The depopulation of the d_{xz}, d_{yz} orbitals caused by such an excitation is expected to reinforce the ligand→metal π bond, so that the stronger π-donor ligand, Cl^-,[28] is expected to be bound more strongly than the weaker π-donor ligand, SCN^-. The preferential aquation of SCN^- with respect to Cl^- is also expected on the basis of Adamson's second rule.[31] In this regard, it should be noted that our results are actually the first unequivocal verification of such a rule, in spite of its claimed "empirical" nature.

The results obtained in this work qualitatively agree with some theoretical models proposed in recent papers.[4,5,32,33] It should be noted, however, that the quantitative approach to the quantum yields given in those papers cannot be accepted. For example, the lower quantum yield of ethylenediamine aquation with respect to $\Phi_{SCN^-} + \Phi_{Cl^-}$ does not necessarily mean that the state responsible for ethylenediamine aquation ($^4B_2$) is less "distorted" or less "reactive" than the state responsible for SCN^- and Cl^- aquation (^4E). The quantum yield, in fact, is a composite quantity whose value depends not only on the rate constant with which the excited state undergoes the observed reaction but also on the excited-state lifetime. This last quantity is most probably very different for different excited states of the same complex and also for corresponding excited states of different (even if similar) complexes. It follows that, when information on excited-state lifetimes is lacking, the quantum yield values cannot be taken as a relative measure of the rate constants (*i.e.*, of the "reactivities") of different excited states or of different complexes. Such a limitation, unfortunately, seems to be overlooked in those theoretical models.

Comparison with *cis*-$Cr(en)_2(NCS)Cl^+$. In order to facilitate a comparison between the photochemical behavior of *trans*- and *cis*-$Cr(en)_2(NCS)Cl^+$, the quantum yield values and the electronic absorption spectra of both complexes have been plotted in Figure 1. The data relative to the cis isomer have been taken from ref 9.

Both complexes undergo all the three possible ligand photoaquation reactions, but the relative importance of the three reaction modes is very different. The main reaction, SCN^- aquation for the trans isomer and ethylenediamine aquation for the cis isomer, seems to originate in both cases from the lowest quartet excited state. It is worth noting that for neither the trans nor the cis isomer does the main photoreaction correspond to the nature of the major thermal reaction.

For both complexes, the photoreactions responsible for the release of SCN^- and Cl^- apparently originate from the same excited state, but such a state is most probably ligand-to-metal charge transfer for the cis isomer[9] and metal centered for the trans isomer.

The ethylenediamine photoaquation originates from a metal-centered excited state for both complexes. In both cases, its quantum yield shows an unusual wavelength dependence (Figure 1). This result cannot be attributed to a competition with the other photoreaction modes, whose quantum yields are constant for the trans isomer and monotonically decrease for the cis isomer (Figure 1). The trend of the quantum yields for the trans isomer seems to indicate that, although the conversion of the charge-transfer excited states to the lowest metal-centered excited state (^4E) occurs with almost unitary efficiency, part of this relaxation process can bypass some intermediate metal-centered excited states (particularly the $^4B_2$ one). On the other hand, the upper metal-centered excited states (particularly the ^4E ($^4T_{1g}$) one) seem to deactivate to $^4B_2$ with almost unitary efficiency. Finally, the $^4B_2$ excited state either gives ethylenediamine aquation (~5%) or decays to the lowest excited quartet, ^4E (~95%).

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Registry No. *trans*-$[Cr(en)_2(NCS)Cl]ClO_4$, 30177-83-4.

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