ADSORPTION OF $Cr(NH_3)_6^{3+}$ AND $Cr(en)_3^{3+}$ ON CLAY MINERALS AND THE CHARACTERIZATION OF CHROMIUM BY X-RAY PHOTOELECTRON SPECTROSCOPY

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Abstract—The nature of $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$ (en = ethylenediamine) adsorbed on chlorite, illite, and kaolinite has been studied by X-ray photoelectron spectroscopy (XPS). The interaction of the chromium complexes with the clays began at pH 3. During the 7-day interaction time the pH of the complex-clay suspension increased to 8 for illite and chlorite. For kaolinite the pH increased to about 3.6 with $Cr(NH_3)_6^{3+}$ and to 6.4 with $Cr(en)_3^{3+}$. These pH changes appear to be associated with a clay-catalyzed hydrolysis of the chromium-amine complexes. XPS binding-energy data for adsorbed chromium indicate that the dominant species are chromium aqua complexes. Nitrogen/chromium atom ratios, calculated from the XPS photopeak intensities, are less than 6:1 for complexes adsorbed on the clays, suggesting that chromium complexes are initially adsorbed but subsequently hydrolyze to produce aqua-chromium surface species.

Key Words—Adsorption, Chlorite, Chromium, Complex ions, Illite, Kaolinite, X-ray photoelectron spectroscopy.

INTRODUCTION

In recent years sophisticated spectroscopic techniques have routinely been employed to investigate the adsorption reactions of transition metal complexes with clays, soils, zeolites, and inorganic substances, including infrared (IR), electron spin resonance (ESR), and electronic spectroscopic (ES) methods (see Table 1). Considerable information has been obtained on these reactions; for example, Knudson and McAtee (1973) and Swartzen-Allen and Matijevic (1975) found that the adsorption of cobalt chelates on montmorillonite exceeds the exchange capacity of the clay, although the latter authors suggested that the enhanced adsorption may be due to ion exchange. Koppelman and Dillard (1978) found that the adsorption of $Co(NH_3)_6^{3+}$ on chlorite proceeded with hydrolysis of the complex and reduction of Co(III) to Co(II). Chaussidon et al. (1962) and Fripiat and Helsen (1966) reported that adsorbed cobalt complexes may be destroyed by drying or outgassing procedures.

Burkheiser and Mortland (1977) showed that complexes of iron and copper are reduced upon adsorption on hectorite; however, $Cu(en)_3^{2+}$ interacts with montmorillonite to yield $Cu(en)_2^{2+}$ with the clay oxygens acting as ligands coordinated to the $Cu(en)_2^{2+}$ ion (Burba and McAtee, 1977). Farrah and Pickering (1967a, 1967b) demonstrated that anionic complexes of copper are not adsorbed to any appreciable extent on kaolinite, illite, or montmorillonite. Ligands in the complex ion apparently inhibit the precipitation of metal hydrox-

ides. Velghe et al. (1977) reported that $Cu(en)_3^{2+}$ adsorbs on montmorillonite as a square planar complex between the clay layers. Using electronic spectral methods, Hathaway and Lewis (1969a) showed that for some ligands, nickel may be adsorbed in hexacoordinate and pentacoordinate ligand environments. The formation of the six-coordinate complex is favored at high ligand:metal ratios, whereas low ligand:metal ratios favor the formation of the five-coordinate complex.

The interaction of chromium with clays has received little attention, although Bartlett and Kimble (1976a, 1976b) reported that chromium complexes, formed with organic matter in soil, appeared to stabilize and solubilize Cr at pHs where chromium hydroxide should precipitate. In addition, Coughlan et al. (1977) observed that $Cr(NH_3)_6^{3+}$ formed upon exposing outgassed mordenite containing chromium to gaseous NH_3, but that for L zeolite, the same treatment produced Cr(III) bound to NH_3 and lattice oxygen. Cary et al. (1977) observed no differences in the accumulation mechanism for aqua chromium and chromium-organic complexes in plants, and Cornet and Burwell (1968) showed from EPR and optical absorption spectroscopic data that adsorbed $Cr(NH_3)_6^{3+}$ on silica gel is in the same environment as that of an aqueous solution. The complex decomposes to chromia polymer on desiccation.

The present investigation was therefore initiated to examine the chemical nature of surface chromium species following reactions of chromium complexes with illite, kaolinite, and chlorite. Using binding energy data and photopeak intensities from X-ray photoelectron spectroscopy (XPS), attempts were made to determine the nature of the chromium species adsorbed

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Table 1. Characterization of transition metal complex ion/mineral systems.

Metal	Technique[1]	Reference
Cobalt	IR	Chaussidon et al. (1962)
	ES	Hathaway and Lewis (1969b)
	XRD	Knudson and McAtee (1973)
	EK	Swartzen-Allen and Matijevic (1975)
	IR, XRD	Fripiat and Helsen (1966)
	XPS	Koppelman and Dillard (1978)
Iron	XRD, ORP	Berkheiser and Mortland (1977)
Copper	ESR, XRD	Berkheiser and Mortland (1977)
	IR, ESR, XRD	Burba and McAtee (1977)
	IR	Farmer and Mortland (1965)
	ADS	Farrah and Pickering (1967a, 1967b)
	ADS	Thompson and Brindley (1969)
	ESR, ES, XRD	Peigneur et al. (1977)
	ESR, ES, XRD	Velghe et al. (1977)
Nickel	ES	Hathaway and Lewis (1969a)
	EK, IR	Catone and Matijevic (1976)
Chromium	ES	Coughlan et al. (1977)
	ADS	Bartlett and Kimble (1976a, 1976b)
	ADS	Bartlett and James (1979)
	ESR, ES	Cornet and Burwell (1968)

[1]ADS = Adsorption isotherms
EK = Electrokinetic
IR = Infrared spectroscopic
ESR = Electron spin resonance
ES = Electronic spectroscopic studies
ORP = Oxidation/reduction potential measurements
XPS = X-ray photoelectron spectroscopy
XRD = X-ray powder diffraction

on the surface of these clay minerals and to establish the significance of hydrolysis and oxidation-reduction in the adsorption reaction.

EXPERIMENTAL
Materials and methods

The identity and characteristics of the clays studied were described by Koppelman and Dillard (1977) and are briefly summarized here. Chlorite from Ishpeming, Michigan, was obtained from Ward's Natural Science Establishment and has a cation-exchange capacity (CEC) of 16 meq/100 g and a N_2-BET surface area of 14 m^2/g. Illite (API #35) from Fithian, Illinois, has a CEC of 20 meq/100 g and a N_2-BET surface area of 49 m^2/g. Kaolinite, Hydrite RT, from Georgia Kaolin Company has a N_2-BET surface area of 12 m^2/g and a CEC of 7 meq/100 g. $[Cr(NH_3)_6](NO_3)_3$ was prepared according to the method outlined by Oppegard and Bailar (1950). $[Co(en)_3](NO_3)_3$ was prepared from the sulfate by dissolving the crude product in a solution containing 17 ml of concentrated HNO_3 and 60 ml of water at 60–65°C (Rollinson and Bailar, 1946). The solution was rapidly filtered, and 90 ml of concentrated nitric acid dissolved in 85 ml of 100% ethanol was added to the filtrate. Bright orange, needle-like crystals appeared upon cooling. The crude product was recrystallized from water. The following carbon-hydrogen-nitrogen analyses were obtained:

$[Cr(NH_3)_6](NO_3)_3$(calculated): N = 37.06; H = 5.29.
(found): N = 37.00; H = 5.35.

$[Cr(H_2NCH_2CH_2NH_2)_3](NO_3)_3$(calculated):
C = 17.21; N = 30.10; H = 5.72.
(found): C = 16.99; N = 29.88; H = 5.64.

Samples of the complexes were stored in the dark to prevent photodecomposition. Solutions of the complexes (approximately 100 ppm total Cr) were prepared using argon- or nitrogen-saturated, double-distilled deionized water. The pH of the solution was adjusted to 3 upon addition of the chromium complexes to the clay suspension. The clay suspensions were prepared by mixing 2.5 g of the clay with 800 ml of argon- or nitrogen-saturated double-distilled deionized water. Adsorption experiments were conducted at 25 ± 0.5°C. The methods of metal ion, pH, and silicon analysis were outlined in earlier publications (Koppelman and Dillard, 1977, 1978).

XPS measurements

X-ray photoelectron spectra were measured using a DuPont model 650 instrument and an AEI ES 100 spec-

Table 2. Analytical data for chromium-complex solutions before and after reaction with clays.[1]

| | $Cr(NH_3)_6^{3+}$ solution | | | | | | | | $Cr(en)_3^{3+}$ solution | | | | | | | |
| | Chlorite | | Illite | | Kaolinite | | Control | | Chlorite | | Illite | | Kaolinite | | Control | |
	i	f	i	f	i	f	i	f	i	f	i	f	i	f	i	f
pH	3.00	8.60	3.00	8.50	3.00	3.64	3.02	3.63	3.00	7.50	3.02	7.05	3.00	6.40	3.00	6.40
Cr	90	79	100	83	90	85	90	89	85	72	85	65	85	76	85	85
Si	0	2	0	2	0	0	—	—	0	2	0	2	0	0	—	—
Mg	0	9	0	7	0	0	—	—	0	10	0	8	0	0	—	—
K	0	23	0	11	0	1	—	—	0	24	0	11	0	1	—	—
Time to attain equilibrium pH, (days)	2		5		>7		>7		5		5		5		5	

[1] i = initial solution (ppm); time = 0 days. f = final solution (ppm); time = 7 days. Analyses by atomic absorption spectroscopy.

trometer. A magnesium anode was used on the DuPont instrument while an aluminum target was employed with the AEI spectrometer. Calibrations were carried out using vapor-deposited gold, carbon background from the spectrometer, or silicon in the clays (Koppelman and Dillard, 1977, 1978). Calculation of the atom ratios was accomplished in a manner similar to that presented by Alvarez et al. (1976). Photoionization cross sections were taken from Scofield (1976). No alterations in the XPS photopeak relative intensities were noted as a function of time or X-ray power level. Samples were exposed to the X-rays for no longer than 3 hr for each measurement. The measured binding energies and atom ratios represent the average of no less than four separate determinations for each sample. Pressure in the sample region during X-ray bombardment was less than 1×10^{-7} torr. Sample temperature during the measurements was approximately 30°C.

RESULTS AND DISCUSSION

Table 2 lists the pH and elemental content of metal-complex solutions before and after seven days of reaction with the clays, as well as the time necessary to attain a pH value that remained constant to ±0.2 pH units over a 6–8-day period. The pH value measured after the time listed in Table 2 is hereafter referred to as the "equilibrium" pH. The "control" sample contained no clay, but was prepared in a manner identical to those that contained clay. All analyses of supernatant solutions were made by AA after the solutions had been separated from the clay.

XPS Al 2p, Cr 2p, and N 1s binding energies for the clay samples, the pure complexes, and selected chromium-containing compounds are presented in Table 3 along with N/Cr atom ratios as calculated from XPS photopeak intensities for the clay-chromium samples and the pure chromium complexes.

The quantity of chromium adsorbed on chlorite and illite is greater by about 3 ppm for the $Cr(en)_3^{3+}$ complex

than for the $Cr(NH_3)_6^{3+}$ complex. For kaolinite the chromium adsorbed is almost doubled, from 5 ppm for the $Cr(NH_3)_6^{3+}$ complex to 9 ppm for the $Cr(en)_3^{3+}$ complex. These results are similar to those previously reported (Koppelman and Dillard, 1977) for the adsorption of other transition metal ions on chlorite, illite, and kaolinite. The quantity of metal ion adsorbed varies in the manner illite ≅ chlorite > kaolinite. This result parallels the measured cation-exchange capacity noted previously (Koppelman and Dillard, 1977).

The increase in the pH of the test solutions upon interaction of $Cr(NH_3)_6^{3+}$ with illite and chlorite and the increase noted for $Cr(en)_3^{3+}$ with all three clays indicates reactions other than simple adsorption. For chlorite and illite, the "equilibrium" pH for both complexes was greater than that for the control sample. On the other hand, the pHs of the chromium complex-kaolinite solutions were equivalent to those of the control solutions. To explore the chemical nature of adsorbed chromium, XPS spectra were measured for the chromium-clay samples and for the pure chromium complexes.

The binding energy for chromium in aqua and amine complexes is influenced by the donor properties of the ligands. The relative donor strength of the ligands is known from the spectrochemical series to be en > NH_3 > H_2O (Cotton and Wilkinson, 1972). Because strong donor ligands place a greater electron density on the metal ion, it would be predicted that the metal binding energy would be lower for strong donor ligands. The observed Cr $2p_{3/2}$ binding energies vary in the manner, $Cr(H_2O)_6^{3+}$ > $Cr(NH_3)_6^{3+}$ > $Cr(en)_3^{3+}$, in accord with the predicted variation. Similar results have been noted for the variation in metal binding energy for cobalt complexes with nitrogen and oxygen donor atoms (Burness et al., 1973). It is reasonable to anticipate that the chromium binding energies for adsorbed complexes might show a similar variation with ligand donor properties.

The measured binding energy (BE) for the Cr $2p_{3/2}$ level of each chromium complex-clay sample is 577.3 ±

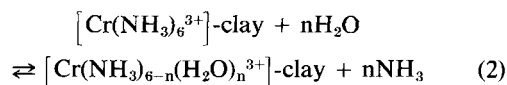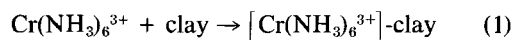Table 3. XPS binding energy (eV) for chromium-containing materials.

Compounds	Al	Cr $2p_{3/2}$	N (Amine N)	$1s_{1/2}$ (Nitrate N)	N/Cr (Amine N)
$Cr(NO_3)_3 \cdot 9H_2O$	—	577.9	—	—	—
$[Cr(NH_3)_6](NO_3)_3$	—	577.6	399.8	406.8	5.8
$[Cr(en)_3](NO_3)_3$	—	577.3	400.7	406.3	5.9
$Cr(OH)_3$	—	576.7	—	—	—
Cr_2O_3	—	576.4	—	—	—
$Cr(NH_3)_6^{3+}$-clay					
Chlorite	74.1	577.2	400.3		3.2
Illite	74.2	577.2	400.5		2.8
Kaolinite	74.4	577.3	400.4		3.8
$Cr(en)_3^{3+}$-clay					
Chlorite	74.1	577.4	400.2		2.1
Illite	74.3	577.4	400.2		4.2
Kaolinite	74.3	577.4	400.0		4.1

0.1 eV, which is greater than the values measured for $Cr(OH)_3$ (576.7 eV), and Cr_2O_3 (576.4 eV). These data indicate that the chromium species adsorbed in the clay-chromium complex reaction is not the oxide or the hydroxide. In another investigation, Koppelman *et al.* (1980) presented results indicating that at pH > 5 chromium was present as chromium hydroxide on clays. This conclusion was supported by the fact that BE [Cr $2p_{3/2}$ ($Cr(OH)_3$)] = BE [Cr $2p_{3/2}$ (adsorbed $Cr(H_2O)_6^{3+}$)-clay] for chromium-clay samples prepared at pH > 5.

The chromium $2p_{3/2}$ binding energies (Table 3) for chromium complexes adsorbed on the three clays are equal, within experimental error, to the Cr 2p binding energies for adsorbed chromium aqua ions (Koppelman *et al.,* 1980). In addition, the N/Cr atom ratio is less than that expected if the complexes were adsorbed as $Cr(NH_3)_6^{3+}$ or $Cr(en)_3^{3+}$. It should be noted that the measured N/Cr atom ratio for the pure complexes is equal to that required by the stoichiometry of $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$. These results suggest that upon adsorption the chromium complexes must be converted into an aqua complex. It is of interest that the N/Cr ratio for $Cr(NH_3)_6^{3+}$ adsorbed on chlorite and illite is approximately 3:1. If the amine is coordinated to the metal, the complex may be adsorbed as the $Cr(H_2O)_3(NH_3)_3^{3+}$ ion. Alternatively, the uncoordinated amine or the ammonium cation may adsorb on the clay along with an aqua chromium species. From these XPS data it is not possible to distinguish between these two possibilities. For $Cr(NH_3)_6^{3+}$ adsorbed on kaolinite, the N/Cr ratio 4:1 suggests that dissociation of the complex may be less extensive. That the pH of the kaolinite solution did not increase significantly during the adsorption experiments is in agreement with the N/Cr ratio.

For the $Cr(en)_3^{3+}$ samples, the N/Cr ratio is 2:1 for chlorite and approximately 4:1 for illite and kaolinite. These results indicate that loss of two en ligands occurs upon interaction of $Cr(en)_3^{3+}$ with chlorite while only one en ligand dissociates from $Cr(en)_3^{3+}$ in the reaction with illite and kaolinite. From the XPS results it is not possible to decide whether $Cr(en)(H_2O)_4^{3+}$ is adsorbed on chlorite or whether $Cr(en)_2(H_2O)_2^{3+}$ is adsorbed on illite and kaolinite. The N/Cr atom-ratio data and the binding energy results for chromium and nitrogen do not exclude the possibility that en or enH^+ may be adsorbed on the clays along with aqua-chromium complexes. The nitrogen binding energies are not sufficiently different from those of nitrogen in the pure complexes to identify readily the chemical nature of the nitrogen.

In studies of the adsorption of $Co(NH_3)_6^{3+}$ on chlorite Koppelman and Dillard (1978) reported that adsorption of the complex proceeded via hydrolysis of the complex and subsequent reduction of Co(III) to Co(II). Because the mechanisms for hydrolysis of chromium and cobalt complexes are alike in many aspects, it is likely that a similar process may occur with chromium (Basolo and Pearson, 1967). The XPS results suggest that hydrolysis occurs *after* adsorption. If hydrolysis occurred before adsorption, the pH of the solution would be sufficiently high to initiate the formation of chromium hydroxide. From the measured binding energies it is evident that the chromium species after hydrolysis is not chromium hydroxide. It is not likely that Cr(III) is reduced to Cr(II). The equivalence of the binding energies for adsorbed $Cr(H_2O)_6^{3+}$ (Koppelman *et al.*, 1980) and the hydrolysis products of $Cr(en)_3^{3+}$ and $Cr(NH_3)_6^{3+}$ suggests that the hydrolysis products are Cr(III) species. Of particular significance is the fact that for $Cr(NH_3)_6^{3+}$ adsorption, the change in pH is greatest and fastest for chlorite and illite and slowest for kaolinite. A suggested mechanism for the adsorption/hydrolysis process (illustrated for $Cr(NH_3)_6^{3+}$) is:

$$Cr(NH_3)_6^{3+} + clay \rightarrow \left[Cr(NH_3)_6^{3+}\right]\text{-clay} \quad (1)$$

$$\left[Cr(NH_3)_6^{3+}\right]\text{-clay} + nH_2O$$
$$\rightleftarrows \left[Cr(NH_3)_{6-n}(H_2O)_n^{3+}\right]\text{-clay} + nNH_3 \quad (2)$$

$$nNH_3 + nH_2O \rightleftarrows nNH_4^+ + nOH^- \quad (3)$$

In reactions (2) and (3), 2 < n < 4 if the N/Cr ratios are indicative of partially hydrolyzed chromium amine complexes. Unfortunately, the present XPS data can not be used unequivocally to determine the chemical nature of the adsorbed chromium or nitrogen species, although it is clear that neither $Cr(OH)_3$ nor Cr_2O_3 is present.
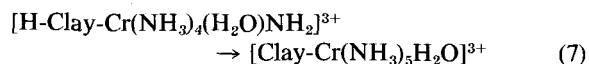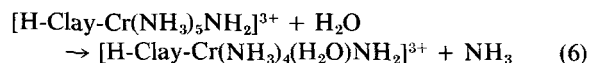
Fripiat and Helsen (1966) suggested that decomposition of a cobalt complex on montmorillonite at tem-

peratures $\geq 100°C$ is promoted by proton transfer from residual water on the clay surface. In such a process, proton transfer labilizes the corrdinated ammonia ligand and thus facilitates loss of NH_3 from the complex. The decomposition process initiated by heating or dehydration in vacuo for $Co(NH_3)_6Cl_3$ adsorbed on montmorillonite (Fripiat and Helsen, 1966) was represented by reaction (4) below:

$$6\ (Co(NH_3)_6{}^{3+})_{ads} + 12\ H_2O$$
$$\rightarrow 6\ (Co(OH)_2)_{ads} + 18\ (NH_4{}^+)_{ads}$$
$$+ 16\ NH_3 + N_2 \qquad (4)$$
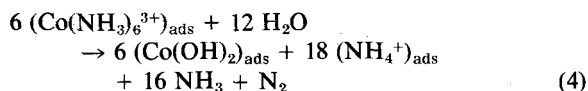
Infrared evidence was presented to support the presence of adsorbed $NH_4{}^+$ following complete decomposition of the complex. The experiments reported here for chromium complexes and previously for cobalt complexes (Koppelman and Dillard, 1978) differ from those presented by Fripiat and Helsen (1966). For the present study hydrolysis (decomposition) of the complexes is noted in the complex-clay aqueous suspension.

A mechanism for enhanced hydrolysis of the complexes could involve either acid- or base-catalyzed hydrolysis since the acidity of the surface has not been determined or controlled under the experimental conditions of this study. If acid hydrolysis occurs, a process similar to that suggested by Fripiat and Helsen (1966) could proceed in the clay-solution system. Alternatively, base-catalyzed hydrolysis could occur in which the clay surface acts as a proton acceptor for a coordinated amine ligand hydrogen. Deprotonation of a coordinated amine ligand would yield a clay-$(Cr(NH_3)_5NH_2{}^{2+})$ species, in which the chromium ligand bond is labilized. Hydrolysis of the labilized complex would lead to chromium-aqua species on the clay surface. The reactions for a proposed base-catalyzed hydrolysis are summarized below for $Cr(NH_3)_6{}^{3+}$.

$$Clay + Cr(NH_3)_6{}^{3+} \rightarrow [H\text{-}Clay\text{-}Cr(NH_3)_5NH_2]^{3+} \qquad (5)$$

$$[H\text{-}Clay\text{-}Cr(NH_3)_5NH_2]^{3+} + H_2O$$
$$\rightarrow [H\text{-}Clay\text{-}Cr(NH_3)_4(H_2O)NH_2]^{3+} + NH_3 \qquad (6)$$

$$[H\text{-}Clay\text{-}Cr(NH_3)_4(H_2O)NH_2]^{3+}$$
$$\rightarrow [Clay\text{-}Cr(NH_3)_5H_2O]^{3+} \qquad (7)$$

Similar reactions could lead to further hydrolysis of the adsorbed complexes. The product of complete hydrolysis of the adsorbed complex would ultimately lead to adsorbed aqua-chromium(III). The formation of chromium hydroxide or chromium oxide as the final chromium-containing product is not consistent with the binding energy results. Because no effort was made to control the pH during adsorption, it is not possible to distinguish whether acid or base catalysis is the dominant process from the present experiments. Additional studies of the metal-complex adsorption processes using other complexes may aid in providing details re-

garding the hydrolysis mechanism. The role of pH in the proposed reactions is under investigation.

ACKNOWLEDGMENT

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Резюме—С помощью рентгеновской фотоэлектронной спектроскопии (РФС) изучалась природа $Cr(NH_3)_6^{3+}$ и $Cr(эн)_3^{3+}$(эн = этилендиамин), адсорбированных хлоритом, иллитом, и каолинитом. Взаимодействие соединений хрома с глинами началось при pH = 3. За период взаимодействия в течение 7 дней pH суспензии глины (иллита или хлорита) и рассматриваемых соединений увеличилось до 8. При использовании каолинита pH увеличилось примерно до 3,6 с $Cr(NH_3)_6^{3+}$ и до 6,4 с $Cr(эн)_3^{3+}$. Эти изменения pH, по-видимому, связаны с гидролизом хром-аминовых соединений, причем глина выступала как катализатор. Данные РЭС о связующей энергии для адсорбированного хрома указывают на то, что преобладающими видами являются водные соединения хрома. Отношения атомов азота к атомам хрома, вычисленных по данным интенсивностей фотопиков РФС, оказались меньше, чем 6:1 для соединений, адсорбированных глинами. Это позволяет предположить, что соединения хрома сначала адсорбируются, но потом гидролизуются, образовывая водно-хромовые поверхностные виды. [N. R.]

Resümee—Die Natur von $Cr(NH_3)_6^{3+}$ und $Cr(en)_3^{3+}$ (En = Äthylendiamin), die am Chlorit, Illit sowie Kaolinit adsorbiert waren, wurden mittels Röntgenphotoelektronen-Spektroskopie (XPS) untersucht. Die Einwirkung der Chromkomplexe auf die Tone wurde bei pH 3 begonnen. Während der 7-tägigen Einwirkungszeit wuchs der pH der Komplex-Tonsuspension bei Illit und Chlorit auf 8. Bei Kaolinit wuchs der pH mit $Cr(NH_3)_6^{3+}$ auf etwa 3,6 und mit $Cr(en)_3^{3+}$ auf 6,4. Die pH-Veränderungen scheinen mit einer durch den Ton katalysierten Hydrolyse des Chrom-Aminkomplexes zusammenzuhängen. XPS-Bindungsenergiedaten für adsorbiertes Chrom zeigen, daß die vorherrschenden Arten Chrom-Wasserkomplexe sind. N/Cr-Atomverhältnisse, die aus den XPS-Peakintensitäten berechnet wurden, sind kleiner als 6:1 bei Komplexen, die an den Tonen adsorbiert sind. Dieses Ergebnis deutet darauf hin, daß die Chromkomplexe in ihrem ursprünglichen Zustand adsorbiert werden, aber anschließend hydrolysieren und Wasser-Chrom-Oberflächenarten bilden. [U.W.]

Résumé—La nature de $Cr(NH_3)_6^{3+}$ et de $Cr(en)_3^{3+}$ (en = éthylenediamine) adsorbée sur la chlorite, l'illite, et la kaolinite a été étudiée par spectroscopie photoélectronique aux rayons-X (XPS). L'interaction des complexes de chromium avec les argiles a commencé au pH 3. Pendant le temps d'interaction de 7 jours, le pH de la suspension de complex d'argile a augmenté à 8 pour l'illite et la chlorite. Pour la kaolinite, le pH a augmenté à à peu près 3,6 avec $Cr(NH_3)_6^{3+}$ et à 6,4 avec $Cr(en)_3^{3+}$. Ces changements de pH semblent être associés avec une hydrolyse des complexes chromium amine catalysée par l'argile. Les données de l'énergie de liaison de XPS pour le chromium adsorbé indique que les espèces dominantes sont des complexes aqua achromium. Les proportions nitrogène/chromium, calculées d'après les intensités des sommets XPS, sont sous 6:1 pour les complexes adsorbés sur les argiles, suggérant que les complexes chromium sont initialement adsorbés, mais ensuite hydrolisent pour produire des espèces de surface aqua chromium. [D.J.]