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Amorphous Aluminosilicates Containing Trivalent Chromium in a Non-Octahedral Coordination Environment

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Amorphous aluminosilicates containing up to 5.8 wt.% chromium have been prepared by cation exchange on an amorphous sodium aluminosilicate using Cr(III) salts. Electronic spectroscopy has shown that the ligand arrangement around the Cr(III) sites does not correspond to the octahedral geometry. No isomorphous substitution of Al^{3+} by Cr^{3+} in the aluminosilicate occurs, and it is not possible to exchange back chromium by Na^+ ions. The amorphous chromium-substituted aluminosilicates (abbr. ACSAS) are slightly acidic and when heated in air at 800 °C no oxidation of Cr(III) takes place. The chromium species in the ACSAS undergoes ligand replacement reactions.

[Keywords: Alluminosilicates; Chromium(III) complexes; Coordination geometry distortion; Electronic spectra]

Amorphe Alumosilicate mit dreiwertigem Chrom in nicht-oktaedrischer Koordinationsumgebung

Bis zu 5,8 Gew.% Chrom enthaltende amorphe Alumosilicate wurden durch Kationenaustausch am amorphen Natriumalumosilicat unter Anwendung von Cr(III)-Salzen hergestellt. Elektronenspektroskopische Untersuchungen zeigten, daß die Ligandanordnung um die Cr(III)-Lagen nicht der oktaedrischen Geometrie entspricht. Im Alumosilicat erfolgt keine isomorphe Substitution von Al^{3+} durch Cr^{3+} und es ist nicht möglich, Chrom durch Na^+ zurückzuersetzen. Die amorphen durch Chrom ersetzten Alumosilicate (abgekürzt ACSAS) sind schwach sauer und wenn sie in der Luft auf 800 °C aufgeheizt werden, erfolgt keine Oxydation von Cr(III). Das in den ACSAS vorliegende Chrom unterliegt Ligandaustauschreaktionen.

Introduction

Solid state systems containing chromium supported in various aluminosilicates have been of considerable interest in recent years due to their catalytic activity[1—4], e.g. in the polymerization of ethylene. The research work in this area has been primarily centered on systems where trivalent chromium is supported in a crystalline aluminosilicate (e.g. zeolite). Preparation of such chromium-containing materials generally involves the introduction of the Cr(III) species into a crystalline aluminosilicate by ion exchange, using aqueous solutions of the $[Cr(H_2O)_6]^{3+}$ ion[1,5].

The aim of this work has been to synthesize solid materials that would contain trivalent chromium supported in amorphous aluminosilicates[6—9]. The method chosen for their preparation was analogous to that used for Cr(III)-zeolites[1,5], the differences being that the cation exchange has been carried out on an amorphous sodium aluminosilicate.

Experimental

Reagents

The sodium aluminate solution and the sodium silicate solution were of technical grade. All other reagents were of p.a. purity.

Electronic Spectroscopy

The UV-VIS spectra were recorded using a Varian Superscan-3 spectrophotometer, while for the near-IR spectra a Beckman DK-1A spectrophotometer was employed. The solid state absorption spectra were taken on samples in the form of nujol mulls or fluorolube mulls that were spread as films on transparent quartz plates[10,11]. For solution samples the standard 1 cm-path quartz cuvettes were used.

Preparation of the Amorphous Sodium Aluminosilicate

This material was prepared by a literature procedure[8] using 220 g of the sodium aluminate solution containing 22.8 wt.% Na_2O and 9.62 wt.% Al_2O_3, and 182 g of the sodium silicate solution containing 4.45 wt.% Na_2O and 13.1 wt.% SiO_2. After mixing the two solutions the resulting suspension was stirred at room temperature for 30 min, and filtered. The filter-cake was washed with water until the filtrate had *pH* 10, and dried in air at room temperature to a constant mass (for about 5 days). The yield was 64 g of a white powdered product. Analysis: Al 13.78, Na 11.15, Si 15.72, H_2O 25.26%. This corresponds to the following oxide formula: $0.95\,Na_2O \cdot 1.0\,Al_2O_3 \cdot 2.2\,SiO_2 \cdot 5.5\,H_2O$; thus the yield is 78% based on Al_2O_3. An X-ray powder diffraction analysis showed that the product is an amorphous material. Its electronic spectrum (nujol mull) exhibits no absorption maxima in the 350–700 nm region.

Preparation of the Chromium(III) Perchlorate Solution

This solution was obtained by mixing the stoichiometric amounts of concentrated solutions of $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$ and $AgClO_4 \cdot H_2O$, and allowing the resulting solution to stand in darkness for about a month. The suspension obtained was filtered and the filtrate diluted to a $[Cr(H_2O)_6](ClO_4)_3$ concentration of 0.1 mol dm^{-3}. The electronic spectrum of the solution exhibits two absorption maxima in the 350–700 nm region: at 410 nm and 577 nm ($A_{410}/A_{577} = 1.20$), as expected[12] for the $[Cr(H_2O)_6]^{3+}$ ion.

Preparation of the ACSAS

a) *Using Chromium(III) Perchlorate.* About 8 g of the amorphous sodium aluminosilicate were suspended in 1 dm^3 of the 0.1 *M* $[Cr(H_2O)_6](ClO_4)_3$ solution, and the suspension was kept for 24 h at room temperature with occasional stirring. It was then filtered, the precipitate thoroughly washed with H_2O and finally air-dried at room temperature giving a light-green solid. Analysis: Al 9.81, Cr 5.79, Na-not found, Si 16.45, H_2O 37.16%. This corresponds to the following oxide formula: $0.31 Cr_2O_3 \cdot 1.0 Al_2O_3 \cdot 3.23 SiO_2 \cdot 11.36 H_2O$ (**I**). An X-ray powder diffraction analysis showed that the product has amorphous structure. Its electronic spectrum (nujol mull) exhibits in the 350–700 nm region absorption maxima at 587 nm and 376 nm (Fig. 1 *a*). In the 800–1 500 nm range, the product (fluorolube mull) shows only very weak absorptions at 1 150–1 200 nm.

b) *Using Chromium(III) Chloride.* The procedure was the same as under (a) except that the suspending had been carried out in a 0.1 *M* $[CrCl_2(H_2O)_4]Cl \cdot 2 H_2O$ solution. The product was a light-green solid. Analysis: Al 10.81, Cl—not found, Cr 5.42, Na—not found, Si 16.45, H_2O 37.18%. This corresponds to the following oxide formula: $0.26 Cr_2O_3 \cdot 1.0 Al_2O_3 \cdot 2.93 SiO_2 \cdot 10.31 H_2O$ (**II**). An X-ray powder diffraction analysis showed that the material is of amorphous nature. It has the same spectral features as the solid **I**, the only difference being that the second absorption maximum is at a slightly higher wavelength (387 nm, Fig. 1 *b*).

Test for Hexavalent Chromium in the ACSAS

0.24 g of the material **I** or **II** were dissolved in 25 cm^3 4 *M* HNO_3 at room temperature. The precipitated SiO_2 was removed by filtration and thoroughly washed with water. The entire (green-colored) filtrate was neutralized with aq. NH_3, resulting in the precipitation of $Al(OH)_3$ and $Cr_2O_3 \cdot xH_2O$. The precipitate was removed by filtration and thoroughly washed with water. The entire filtrate was evaporated to 20 cm^3 and made alkaline by 30% NaOH. The electronic spectrum of the final (colorless) solution exhibited no absorption maxima in the 350–700 nm region, the absorbancy values throughout the region being about 0.005. Therefore, if hexavalent chromium is at all present in the starting sample, its amount cannot exceed $5 \cdot 10^{-4}$ wt.% (0.01% of the total chromium content) [for CrO_4^{2-}, ε (370 nm) = 4 800 $dm^3 mol^{-1} cm^{-1}$][13].

Treatment of the ACSAS with aq. NaCl

0.25 g of the material **I** or **II** were suspended in 250 cm^3 2 *M* NaCl, and the suspension was stirred at room temperature for 24 h. The suspension was then filtered, the colorless filtrate rendered alkaline and treated with Br_2 to convert any Cr(III) to Cr(VI). After that, the excess bromine was removed by boiling. The electronic spectrum of the final alkaline solution showed no presence of the CrO_4^{2-} species: the absorbancy at 370 nm was less than 0.005.

Thermal Treatment of the ACSAS

A sample of the material **I** or **II** was heated in air at 800 °C for 1 h. After this treatment the color of the solid was not perceptibly changed. The electronic spectrum of the solid (nujol mull) exhibited in the 350–700 nm region three maxima: at 600 nm, 470 nm and 375 nm (Fig. 1 *c*). 0.3 g of the heated sample were destroyed by standing in 50 cm^3 of 2 *M* HNO_3 at room temperature for 24 h. The resulting suspension was filtered and the filtrate made alkaline by the addition of

NaOH. The electronic spectrum of the alkaline solution showed no presence of CrO_4^{2-} ions [A(370 nm) < 0.005].

Treatment of the ACSAS with aq. Ethylenediamine

A sample of the material **II** was suspended in a 10% aqueous ethylenediamine at room temperature. After 10 days the suspension was filtered, the solid washed with H_2O and air-dried at room temperature, yielding a light-violet powdered product. The electronic spectrum of the solid (nujol mull) exhibited in the 350–700 nm range two maxima: at 548 nm and 371 nm (Fig. 1 *d*).

Table 1. *Electronic absorption maxima and B′ values*[a] *for the ACSAS and for some typical octahedral* Cr(III) *complexes with oxygen and/or nitrogen ligands*

Sample	λ_1 (nm)	λ_2 (nm)	B' (cm^{-1})		Ref.
Product **I** (nujol mull)	587	376	1 171		
Product **II** (nujol mull)	587	387	1 001		
ACSAS-*en*[b] (nujol mull)	548	371	940		
Cr^{3+} (free ion)			918	(= B)	18
$Cr_2O_3 \cdot xH_2O$ (nujol mull)	590	410	771		
$[Cr(H_2O)_6]^{3+}$ (aq)	578	411	707		12
$[Cr(NH_3)_6]^{3+}$ (aq)	465	351	662		12
Alkaline Cr(III) solution[c]	590	426	645		
$[Cr(C_2O_4)_3]^{3+}$ (aq)	571	418	624		
cis-$[Cr(H_2O)_2(en)_2]^{3+}$ (aq)	484	367	622		19
$[Cr(en)_3]^{3+}$ (aq)	456	351	612		12
α-Cr_2O_3 (nujol mull)	602	465	455		
trans-$[Cr(H_2O)_2\,(en)_2]^{3+}$ (aq)	508	442	256		19

[a] The B' values were obtained by the following equation[17]:

$$B' = 10^7(2\lambda_1^{-2} + \lambda_2^{-2} - 3/\lambda_1\lambda_2)/(15/\lambda_2 - 27/\lambda_1).$$

[b] The ACSAS that had been treated with 10% aq. ethylenediamine.

[c] The solution was $1.6 \cdot 10^{-2}$ molar in Cr(III) and 4.9 molar in NaOH, and it was freshly prepared by dissolving $CrCl_3 \cdot 6H_2O$ in aq. NaOH[20].

Results and Discussion

If the amorphous sodium aluminosilicate of the composition $0.95\,Na_2O \cdot 1.0\,Al_2O_3 \cdot 2.2\,SiO_2 \cdot 5.5\,H_2O$ is treated with a 0.1 *M* aqueous chromium(III) salt for 24 h at room temperature, a light-green product is obtained in which trivalent chromium has completely replaced Na^+ ions. When chromium(III) perchlorate is used in the reaction the product contains 5.79 wt.% chromium and has the composition $0.31\,Cr_2O_3 \cdot 1.0\,Al_2O_3 \cdot 3.23\,SiO_2 \cdot 11.35\,H_2O$ (**I**), whereas with chromium(III) chloride the composition obtained is

$0.26\,Cr_2O_3 \cdot 1.0\,Al_2O_3 \cdot 2.93\,SiO_2 \cdot 10.31\,H_2O$ (**II**), the product containing 5.42 wt.% chromium. The water content and the SiO_2/Al_2O_3 molar ratio in the products increase relative to the values in the starting material. The higher SiO_2/Al_2O_3 molar ratio indicates that the cation exchange of Na^+ by Cr^{3+} is accompanied by a partial dealumination of the aluminosilicate framework. Such dealumination of the lattice is known to occur especially if the cation exchange had taken place to a high degree[5,14]. However, the dealumination is not caused by an isomorphous substitution of Al^{3+} by Cr^{3+} in the aluminosilicate framework (vide infra). It is the result of a partial lattice decomposition due to the acidic character of the Cr(III) solutions used in the ion exchange[15,16]. The partial decomposition also explains the fact that for both products the molar $Na^+ : Cr^{3+}$ exchange ratio is apparently greater than 3 : 1.

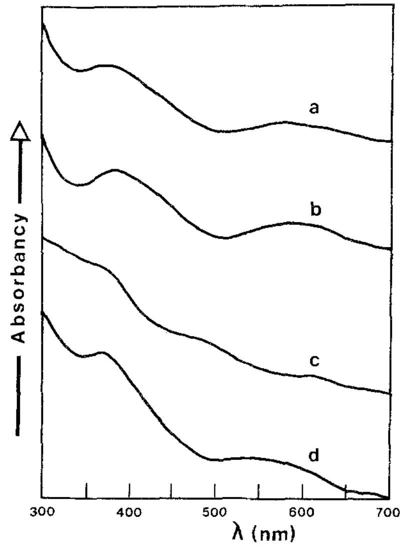

Fig. 1. Solid state electronic spectra (nujol mulls) of the ACSAS: *a* product **I**; *b* product **II**; *c* ACSAS after having been heated in air at 800 °C for 1 h; *d* ACSAS after having been treated with aq. ethylenediamine

The electronic spectra of the ACSAS (Fig. 1 *a* and 1 *b*, and Table 1), taken on solid samples in the form of nujol mulls exhibit in the 350–700 nm region two absorption maxima. The maxima are centered at 587 nm and 376 nm for the product **I**, and at 587 nm and 387 nm for the product **II**.

In both cases, the energy separation between the two maxima gives rise to a question regarding the exact nature of the chromium species in the product. The relative positions of the two absorptions are not in accord with those expected for an octahedral d^3-complex. That can be concluded from the following argument. If the value of the reduced *Racah* parameter (B') is calculated[17] from the experimentally obtained maxima by assuming that they are due to the expected ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions at an octahedrally coordinated chromium(III) site[21,22], the following results are obtained: for the product **I**, $B' = 1\,171\ \mathrm{cm}^{-1}$; for the product **II**, $B' = 1\,001\ \mathrm{cm}^{-1}$ (Table 1). In both cases the calculated B' values are considerably larger than the B' values for known octahedral Cr(III) complexes, and are even larger than the *Racah* parameter for the free Cr^{3+} ion ($B = 918\ \mathrm{cm}^{-1}$)[18].

The 376 nm peak for the product **I** and the 387 nm peak for the product **II** are essentially situated in the spectral region where hexavalent chromium exhibits a very strong charge transfer transition[13,23]. Therefore it might be argued that the 376 nm (387 nm) absorption is not a Cr(III) feature but instead that it is due to the presence of a Cr(VI) impurity. Since the Cr(VI) absorption at around 370 nm is typically 50–300 times more intense than the d–d transitions of octahedral Cr(III) species[12,13,19,24,25], it seems plausible that such a Cr(VI) band, if present, could effectively mask the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ band of the Cr(III) [the latter being found around 410–420 nm for octahedral Cr(III) complexes with oxygen ligands, cf. Table 1]. This would then easily account for the apparently unusual separation between the two maxima in Fig. 1*a* and 1*b*. However, such an interpretation of the spectra is not acceptable due to the fact that no hexavalent chromium is found in the materials **I** and **II**. More precisely, the chemical analysis shows that Cr(VI) cannot constitute more than 0.01% of the total chromium content [that being the Cr(VI) detection limit under the prevailing experimental conditions], which is far below the amount required for a masking effect. If the Cr(VI) maximum at about 370 nm and the hypothetical Cr(III) maximum at 410–420 nm were to be of about the same intensity, the content of hexavalent chromium in the materials would have to be at least 0.3% of the total chromium, and considerably larger than 0.3% if the Cr(VI) absorption were to completely mask the Cr(III) maximum. Therefore, it can be concluded that the two absorption maxima in the spectra of the ACSAS are entirely due to the trivalent chromium, and consequently that the Cr(III) is situated in a non-octahedral environment (the amorphous sodium aluminosilicate exhibits no significant absorption in the 350–700 nm region).

It is also not possible to describe the Cr(III) coordination geometry in the ACSAS as the tetrahedral one. [Tetrahedral Cr(III) coordination would imply either that an isomorphous substitution of Al^{3+} by Cr^{3+} in the aluminosilicate skeleton had taken place[5], or that the Cr(III) cation is located in the aluminosilicate cavities of relatively small size[1,26]]. The electronic spectra of the ACSAS show an absence of absorption maxima in the 800–1 500 nm region (except for some very weak bands at 1 150–1 200 nm that are overtone bands of fundamentals in the mid-IR region[27]). However, the few known tetrahedral Cr(III) complexes all exhibit a near IR absorption maximum that corresponds to the expected $^4T_1$ (F) → $^4T_2$ (F) transition[21,22]. For example, the $Cr(O\mathit{But})_4^-$ ion shows this maximum at 990 nm[28], the $CrW_{12}O_{40}^{5-}$ ion at 1 205 nm ($\varepsilon = 20\,dm^3\,mol^{-1}\,cm^{-1}$)[29], and the $Cr(CH_2Si\mathit{Me}_3)_4^-$ ion at 1 282 nm[30]. For the hypothetical $[Cr(H_2O)_4]^{3+}$ ion the corresponding maximum would be expected at about 1 250–1 300 nm, since the $^4A_{2g}$ (F) → $^4T_{2g}$ (F) transition for the octahedral $[Cr(H_2O)_6]^{3+}$ ion occurs at 578 nm[12].

Particularly noteworthy among the above results is the non-octahedral coordination environment of the Cr(III) species. As octahedral geometry is characteristic of a large majority of Cr(III) complexes[31], the absence of such geometry in the ACSAS is probably due to steric requirements imposed on the Cr(III) ion by the aluminosilicate network. More specifically, this means that the Cr(III) ion is coordinated to at least two oxygen atoms of the network. If only one O-atom of the network were coordinated to chromium, this could cause no significant deviation from the octahedral geometry around Cr(III) since the only conceivable steric hindrance would be the one due to weak *Van der Waals* interactions of the network atoms with the remaining ligands around Cr(III). In contrast, if the Cr(III) were bound to two network oxygen atoms of the relatively rigid[32] aluminosilicate network, chances that attainable $O_{(network)}$—Cr—$O_{(network)}$ angles would closely correspond to the octahedral angle (90°) are quite limited. In that case the chromium coordination sphere could indeed be expected to deviate from octahedral geometry. This is in accord with the fact that transition metal ions coordinated inside aluminosilicate cavities can sometimes attain site symmetries not otherwise encountered in their strain-free complexes[33,34]. However, the available data do not make possible any closer specification of the actual coordination geometry of the Cr(III) ion in the ACSAS.

Although the ACSAS are prepared by cation exchange on an sodium aluminosilicate, they are not subject to back-exchange of chromium by Na^+ ions. The reason for this probably lies in the above-proposed chelate-type coordination of the aluminosilicate O-atoms to the Cr(III) center, which increases the stability of the Cr(III)-aluminosilicate complex through the chelate effect[35].

The ACSAS have a slightly acidic character as their suspension in water has $pH \approx 4$. When the ACSAS are heated in air at 800 °C for 60 min, there is no conversion of trivalent into hexavalent chromium. This is consistent with the fact that Cr(III) shows reducing properties only in alkaline media[36]. However, the electronic spectrum of the heated product does exhibit some new characteristics relative to the spectrum of the starting material. The high-wavelength absorption maximum shifts slightly, so that it is now centered at ≈ 600 nm (Fig. 1 *c*), and a third maximum appears at 470 nm. The new spectral features can be assigned to the α-Cr_2O_3 (Table 1) which is obviously formed following the structural destruction of the ACSAS that occurs at the high temperature[37]. The fact that the absorption maximum below 400 nm has not entirely disappeared indicates that under the experimental conditions the structural decomposition is incomplete.

The chromium(III) species in the ACSAS can undergo ligand replacement reactions. When an aqueous suspension of material **II** is treated by aqueous ethylenediamine, the color of the solid component changes from green into violet. The electronic spectrum of the solid exhibits a shift of its higher wavelength band by about 40 nm relative to the starting material (Fig. 1 *d*). This shift is toward lower wavelength, as expected when Cr(III) exchanges some of its oxygen ligands for nitrogen ligands (Table 1). Notwithstanding the shift, the energy separation between the two maxima in Fig. 1 *d* is still unusually large: the maxima give for the octahedral B' a value of 940 cm^{-1}, indicating that the actual Cr(III) coordination geometry still deviates from the octahedral one. This is not surprising as it can be expected that the active Cr(III) coordination sites in the ligand replacement reaction would be those that have not been connected to the aluminosilicate network. Therefore, the chelate-type function of the aluminosilicate O-atoms (as proposed above) remains essentially unchanged following the coordination of the ethylenediamine to Cr(III).

A closer study of this and other ligand replacement reactions of the ACSAS is currently in progress.

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References

[1] *Pearce J. R., Sherwood D. E., Hall M. B., Lunsford J. H.*, J. Phys. Chem. **84**, 3215 (1980).
[2] *Naccache C., Taarit Y.*, J. Chem. Soc., Faraday Trans. I **69**, 1475 (1973).
[3] *Rubinstejn A. M., Slinkin A. A., Loktev M. I., Fedorovskaya E. A., Bremer H., Vogt F.*, Z. anorg. allg. Chem. **423**, 164 (1976).
[4] *Kugler E. L., Kadet A. B., Gryder J. W.*, J. Catal. **41**, 72 (1976).
[5] *Garwood W. E., Lucki S. J., Chen N. Y., Bailar J. C.*, Inorg. Chem. **17**, 610 (1978).
[6] *Reinwald E., Schwuger M. J., Smolka H.*, US-Pat. 4126574 (1977).

[7] *Schwuger M. J., Smolka H. G.,* Colloid Polym. Sci. **254**, 1062 (1976).
[8] a) *Smolka H., Schwuger M. J.,* D.O.S. 2412838 (1974). b) *Murata M., Sai F., Fujino T.,* D.O.S. 2754835 (1976).
[9] *Breck D. W.,* Zeolite Molecular Sieves, Ch. 1. New York: J. Wiley. 1974.
[10] *Stojakovic D.,* Diss. Abstr. Int. B **38**, 5930 (1978).
[11] *Surles T., Erickson J. O., Priesner D.,* International Laboratory, May/June 1975, p. 29.
[12] *Childers R. F., Vander Zyl K. G., House D. A., Hughes R. G., Garner C. S.,* Inorg. Chem. **7**, 749 (1968).
[13] *Gordon A. J., Ford R. A.,* The Chemist's Companion, p. 213. New York: J. Wiley. 1972.
[14] *Kerr G. T.,* J. Phys. Chem. **72**, 2594 (1968).
[15] Ref.[9], Ch. 6.
[16] *Riley P. E., Seff K.,* J. Phys. Chem. **79**, 1594 (1975).
[17] *König E.,* Inorg. Chem. **10**, 2632 (1971).
[18] *Huheey J.,* Inorganic Chemistry, 2nd ed., p. 418. New York: Harper and Row. 1978.
[19] *Gmelins* Handbuch der Anorganischen Chemie, 8 Aufl., Chrom, Teil C, System-Nummer 52. Weinheim: Verlag Chemie. 1962.
[20] *Vasović D., Stojaković Dj., Radosavljević S.,* Bull. Soc. Chim. Beograd **47**, 605 (1982).
[21] *Ballhausen C. J.,* Ligand Field Theory, Ch. 10. New York: McGraw-Hill. 1962.
[22] *Schläfer H. L., Glieman G.,* Ligand Field Theory, Part B, Ch. 3. New York: Wiley-Interscience. 1969.
[23] *Englis D. T., Wollerman L. A.,* Anal. Chem. **24**, 1983 (1952).
[24] *Laswick J. A., Plane R. A.,* J. Amer. Chem. Soc. **81**, 3564 (1959).
[25] *Yager T. D., Eaton G. R.,* J. Chem. Educ. **56**, 635 (1979).
[26] *Andrews L. J., Lempicki A., McCollum B. C.,* J. Chem. Phys. **74**, 5526 (1981).
[27] *Nakamoto K.,* Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Ch. III-5. New York: J. Wiley. 1978.
[28] *Alyea E. C., Basi J. S., Bradley D. C., Chisholm M. H.,* Chem. Commun. **1968**, 495.
[29] *Brown D. H.,* J. Chem. Soc. **1962**, 3322.
[30] *Mowat W., Shortland A., Yagupsky G., Hill N. J., Yagupsky M., Wilkinson G.,* J. Chem. Soc. D **1972**, 533.
[31] *Cotton F. A., Wilkinson G.,* Advanced Inorganic Chemistry, 4th ed., p. 727. New York: J. Wiley. 1980.
[32] Ref.[9], Ch. 2.
[33] *Yanagida R. Y., Vance T. B., Seff K.,* Inorg. Chem. **13**, 723 (1974).
[34] *Seff K.,* Acc. Chem. Res. **9**, 121 (1976).
[35] Ref.[31], p. 71.
[36] Ref.[31], p. 734.
[37] Ref.[9], p. 493.