

Intercalation Complex of Vanadium (III) oxychloride with *n*-alkylamine

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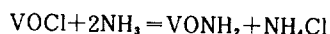
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Received August 16, 1985

Among the transition metal oxychlorides, the intercalation reaction of many kinds of guest molecules with FeOCl only has been widely studied.¹⁻⁷ But not much information is available for vanadium oxychloride and its intercalation complexes, except that the structure is isotype to the iron oxychloride.^{8,9} Though the intercalation reaction is expected by this structural similarity, the reported intercalation complexes of VOCl are only with ammonia,¹⁰ lithium,⁹ and pyridine derivatives.^{10,11} The preparation and characterization of VOCl-*n*-alkylmonoamine have been systematically studied in this work along with a model suggestion of interlayer structure of alkylchain.

Dark-brownish, leaflike vanadium oxychloride crystal was prepared by chemical vapor transport via heating the mixture of vanadium (III) oxide and vanadium (III) trichloride (mole ratio of 1:1.3) in sealed quartz tube under the temperature gradient of 600°C ~ 700°C for 7 days.¹² Unit cell parameters $a = 378$, $b = 330$, $c = 791$ pm, $Z = 2$, and the space group Pmmn were reported from previous work,^{8,9} and were also confirmed by our X-ray study.

Intercalation of ammonia was performed in dilute aqueous suspension and in concentrated aqueous ammonia. Both treatments gave identical results, but differed in reaction rate. On intercalation, the basal spacing increased by 302 pm from 791 pm to 1093 pm, which is quite similar to the values of TiOCl (306 pm), TiS₂ (315 pm), NbS₂ (302 pm) and kaolinite (300 pm) analogues.¹³⁻¹⁵ It is, therefore, deduced that the space demand for monolayer ammonia is almost similar to the various host lattices. Detailed information for the orientation of ammonia molecules could not be obtained from X-ray intensities due to the limited reproducibility. The ammonia-intercalate is stable in aqueous ammonia for a few days. A reaction of VOCl and NH₃ from the vapor phase has already been studied by Vorob'ev.¹⁰ The vapor phase intercalation is much slower than aqueous solution. At elevated temperature (110°C), ammonolysis reaction



becomes predominant.

Vanadium oxychloride crystal was submerged in excess alkylmonoamine with the carbon number (*Nc*) of 2, 6, 8, 10, and 12 respectively. The reaction was then performed at room temperature for $2 \leq Nc \leq 10$ and by heating at 70°C for $Nc = 12$ considering the melting point of corresponding *n*-dodecylamine. After the reaction was completed, excess amine was removed with water-free methanol.

The basal spacings of *n*-ethylamine intercalate are only slightly higher than that of ammonia-derivative (Table 1), indicating the axes C-C-N not to stand perpendicular to the VOCl-sheets, but to lie parallel. The absolute increases of 349 and 403 pm, are in the order of van der Waals diameter of

alkylchains perpendicular to the chain axes and corresponds to flatly lying amine molecules.

The basal spacings increase steeply in the amine complexes possessing six or more carbon atoms per unbranched chain. The exact values depend upon the temperature and the pretreatment. When the basal spacings at 25°C are plotted against the number of carbon atoms (*Nc*) in alkylchain, the data can be approximated by a straight line for $6 \leq Nc \leq 12$

$d(25^\circ\text{C}) = 245.0Nc + 1198.0$ (pm) with correlation coefficient of 0.997 for alkylmonoamine intercalate.

The average increase of 245 pm per carbon atom in alkylmonoamine-intercalates is slightly lower than the highest theoretical value (253 pm) for bilayers of alkylchains with extended chains in all anti-conformation and perpendicular arrangement to the layers. In this case extrapolation to $Nc = 0$ leads to 1198 pm, which is only 100 pm higher than the experimental value for the ammonia-intercalate.

Since the observed *d*-value is less than the calculated spacing for such a regular arrangement, the increase of bond angles C-C-C can be excluded. Such higher increase per carbon atom may be explained by decrease in the number of structural defects in the alkylchain monolayers with increasing chain length or by successive increase in the tilting angle of inclined chains. Also it may be explained by chains in a gauche-block structure, with the gauche bonds migrating toward the chain ends with increasing number carbon atoms. If we assume the alkyl-chain has all anti conformation, the in-

Table 1. Basal Spacings and Interlayer Orientation of *n*-alkylmonoamine in Intercalation Compounds

<i>Nc</i>	exp.	value	theor.	value	tilt. angle
	<i>d</i>	Δd	<i>d</i> (bi)	<i>d</i> (mono)	
2	1194	403	1938	1365	—
6	2183	1392	2950	1871	40.24
8	3136	2345	3456	2124	61.79
10	3692	2901	3962	2382	66.34
12	4116	3325	4468	2630	64.86

Nc: number of carbons in guest molecule, *d*: basal spacing after intercalation (pm), Δd : basal increment by intercalation (pm), *d*(bi): calculated value from perpendicular bilayer model $d(\text{bi}) = 791 + 2(126.5(Nc - 1) + 150 + 127 + 170)$ (pm), *d*(mono): calculated value from perpendicular monolayer model. $d(\text{mono}) = 791 + 126.5(Nc - 1) + 150 + 127 + 170$ (pm), 150pm = van der Waals radius of amino group, 127pm = projection of C-N distance along the chain axis, 170pm = van der Waals radius of end-standing CH₃-group, tilt.angle: cacuated from the basal increment assuming that the alkylchain has the all anti-conformation (deg).

Table 2. Calculation of alkylmonoamine contents from the volume increase by intercalation and the molecular volume of amine

with intercalates	VOCl · α · n-C _{12+n} H _{2n+1} NH ₂ -intercalate ×				
	2	6	8	10	12
Mw of amine	45.09	101.19	129.25	157.30	185.30
density	0.6829	0.7660	0.7826	0.7936	0.8015
V _m	109.63	219.33	274.21	329.09	383.97
ΔV	50.27	173.64	292.54	361.87	414.76
Z	0.459	0.792	1.067	1.099	1.080
α	0.229	0.396	0.533	0.550	0.540

MW; molecular weight of guests, density; density of guests (g/cm³), V_m; molecular volume of guests × 10⁻⁶ (pm³), ΔV ; unit cell volume increment by intercalation. × 10⁻⁶ (pm³), Z; number of amine molecules in unit cell, α ; amine content in VOCl formula (molecules/VOCl).

dividual basal increment means that the alkylchain has the tilted orientation with 40.0–66.0 deg. to the ab-plane of VOCl.

But it is also expected that the high temperature phase can be produced by some kinds of conformational changes in the alkylchains. Pechhold¹⁶ had suggested that these defects have the conformations ...aggagagaaa... as a special term "kink", and the most characteristic feature of the chain defects are the shortening of over-all length of the chains by multiples of 127 pm. Therefore, our experimental results can be explained by the formation of conformational defects in alkylchain with the 2g2kink (...aagaaagaa...) or 3g2kink (...aagagagaa...). The rotational isomerization into such conformations is thermodynamically probable, because the activation energy of formation of pairs g and \bar{g} with one chain does not exceed 30.1 kJ/mole and the internal energy does not differ by more than 5.0 kJ/mole.^{17,18}

The infrared spectra are obtained at the region from 4000 to 200 cm⁻¹. The major differences between VOCl and its amine-intercalates exist around the 2900, 1400, and 450 ~ 250 cm⁻¹ region. These frequencies are assigned to be methylene group stretching, amino group wagging, and V-Cl stretching vibration, respectively.¹⁰ The most characteristic features of IR spectra for all amine-intercalates are the intensity decrease of amino group and methylene group vibration modes, and the shift in the V-Cl stretching vibration might be resulted from the weak bonding between VOCl host and amine guest due to the charge transfer. Such charge transfer mechanism is reported on FeOCl-n-propylamine complexes by observing a blue shift of n→σ* absorption on propylamine.¹⁹

The bilayers of alkylamine formed between the layers of VOCl containing number of molecules equal to that of active

sites allowed in the interlayer space, and the composition of the intercalates, loaded to a maximum with amine, approaches the formula of VOCl · 0.55C_{12+n}H_{2n+1}NH₂. The long chained amine derivatives have approximately 1.08 ± 0.03 molecules per unit cell formula of VOCl (Table 2). The space requirement of an alkylchain standing perpendicular to the layers are not commensurate with the size of host lattice of the a · b plane (378 × 330 pm² = 12.47 × 10⁴ pm²). With the amine content (α) in VOCl (mole ratio of 0.55), the area per alkylchain becomes 22.68 × 10⁴ pm², which is slightly lower than that in mica or the other layer silicate complexes (23~25 × 10⁴ pm²/chain). This behavior is in good agreement with that expected from the values of the free area of vanadium (III) oxychloride.

Acknowledgement. Financial support by the Ministry of Education through the Research Institute for Basic Sciences, Seoul National University in 1985 was greatly appreciated. Also Prof. A. Weiss at the Universität München was appreciated for his kind discussion throughout this research.

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