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Diamine Intercalates of Titanium and Vanadium Oxychloride. Evidence for the Subsequent Substitution Reactions of TiOCl with Amines

I. Kargina and D. Richeson*

Department of Chemistry, 10 Marie Curie, University of Ottawa,
Ottawa, Ontario, Canada K1N 6N5

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The intercalation reactions of several new guest molecules [ethylenediamine (EN), *N,N′*-dimethylethylenediamine (DMEN), *N,N,N′*-trimethylethylenediamine (TMEN), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and diethylenetriamine (3N)] into the layered compounds VOCl and TiOCl are reported. At 75 °C, both TiOCl and VOCl reacted with EN to yield dark blue-gray solids. X-ray diffraction (XRD) of these materials indicated formation of new compounds with *b* axes of 11.45(4) and 11.39(5) Å, respectively. Microanalysis and thermogravimetry indicated formulas of $\mathrm{TiOCl(EN)_{0.4}}$ and $\mathrm{VOCl(EN)_{0.4}}$. Reaction with *N,N′*-dimethylethylenediamine (DMEN) resulted in the formation of the new intercalation products $\mathrm{TiOCl(C_4H_{12}N_2)_{0.4}}$ and $\mathrm{VOCl(DMEN)_{0.3}}$ with *b* axes of 11.38(9) Å (M = Ti) and 11.33(7) Å (M = V). Both TMEN and TMEDA were intercalated into VOCl (48 h at 100 °C). The products in this case were $\mathrm{VOCl(TMEDA)_{0.25}}$ and $\mathrm{VOCl(TMEN)_{0.3}}$ with $\Delta b = 5.63$ Å ($b = 13.54(5)$ Å) 4.33 Å, respectively. In contrast, even under forcing conditions (170 °C, 5 days), TiOCl does not intercalate TMEDA or TMEN. Reaction of MOCl with diethylenetriamine (3N) gave $\mathrm{TiOCl(3N)_{0.2}}$ ($b = 12.06(4)$ Å) or $\mathrm{VOCl(3N)_{0.15}}$ ($b = 12.07(4)$ Å). As expected for the product of an intercalation reaction, rapidly heating these intercalates under N_2 regenerated the XRD patterns of the starting materials. These guests appear to adopt preferentially a parallel orientation relative to the MO planes of the host. With extended reaction times, the intercalation products of TiOCl with EN and DMEN gave products of substitution reactions: $\mathrm{TiOCl_{0.5}(C_2H_7N_2)_{0.5}}$, $b = 14.46(9)$ Å, and $\mathrm{TiOCl_{\mathit{x}}(C_4H_{11}N_2)_{1-\mathit{x}}}$, $b = 14.57(2)$ Å. Concurrent appearance diammonium salt of EN, $\mathrm{(H_3NC_2H_4NH_3)Cl_2}$, or the diammonium salt of DMEN, $\mathrm{[H_2(Me)NC_2H_4N(Me)H_2]Cl_2}$, is confirming evidence that the amines are now directly bonded to the Ti−O double layers by substitution of Cl anions.

The intercalation of guest species into layered materials offers an elegant, low-temperature means of tailoring the physical and chemical properties of low-dimensional solids.[1,2] Among the layered solids represented by the formula MOX, several (M = Ti, V, Cr, In; X = Cl, Br) possess the FeOCl structure. This structure is characterized by a strongly interconnected double layer network of distorted edge-shared octahedral M−O atoms with more weakly bonded interlayer halides.[1,3] The intercalation of polar organic molecules into materials of this family has been recognized for some time, but investigations have largely been restricted to FeOCl with only a few examples of intercalation studies of VOCl and TiOCl.[1,4−10] These studies have encompassed a variety of guest species and have focused on investigations of the mechanism of the intercalation process and on the orientation of the guest molecules within the interlamellar space.

A fundamental question in all intercalation reactions is the nature of the interaction between the guest and the host materials. It is generally agreed that the mechanism for FeOCl intercalation involves charge transfer; however, the degree of charge transfer and the possibility that other processes, such as substitution, may assist in the intercalation reaction are active areas of investigation.[2,5]

The possibility that the interlamellar halides of these metal oxychlorides might be susceptible to substitution reactions presents an enticing prospect for preparing hybrid materials in which the organic or inorganic guest species is covalently bonded to the inorganic layers. The

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(7) (a) Vénien, J. P.; Palvadeau, P.; Schleich, D.; Rouxel, J. *Mater. Res. Bull.* **1979**, *14*, 891. (b) Clough, S.; Palvadeau, P.; Vénien, J. P. *J. Phys. C: Solid State Phys.* **1982**, *15*, 641.

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few examples of substitution reactions that have been reported for layered MOCl materials fall into two categories: substitution by ammonia and primary amines or exchange of chloride by alkoxide anions. The reactions of VOCl and FeOCl with NH_3 are reported to yield X-ray amorphous materials with IR bands, indicating the presence of NH functions. An important observation in these reactions, which provides strong evidence for substitution, is the formation of NH_4Cl.[10,11] A less well-characterized material which was X-ray amorphous has been suggested for the reaction of FeOCl with CH_3NH_2.[10]

In contrast, the two reported substitution products with alkoxide have been more thoroughly characterized. In the case of $FeOOCH_3$, which was prepared by the reactions shown by eqs 1 and 2, the product was

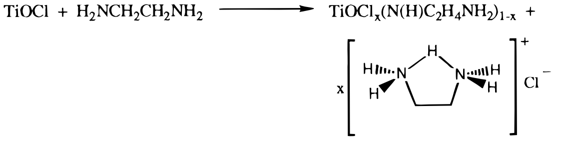
$$\mathrm{FeOCl} + \mathrm{NaOCH_3} \xrightarrow[\mathrm{CH_3OH}]{60\ ^\circ\mathrm{C}} \mathrm{FeOOCH_3} + \mathrm{NaCl} \quad (1)$$

$$\mathrm{FeOCl(4\text{-}aminopyridine)} + \mathrm{CH_3OH} \xrightarrow[6\ \mathrm{days}]{110\ ^\circ\mathrm{C}} \mathrm{FeOOCH_3} + \mathrm{4\text{-}aminopyridine{\cdot}HCl} \quad (2)$$

$$\mathrm{FeOCl(4\text{-}aminopyridine)} + {}^{1}/_{2}\mathrm{HOC_2H_4OH} \xrightarrow[6\ \mathrm{days}]{110\ ^\circ\mathrm{C}} \mathrm{FeO(OC_2H_4O)_{0.5}} + \mathrm{4\text{-}aminopyridine{\cdot}HCl} \quad (3)$$

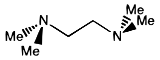
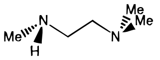
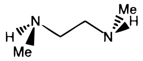
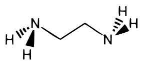
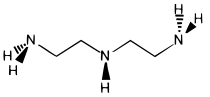
characterized by powder X-ray diffraction (2.05 Å expansion), IR, and thermogravimetic analysis (19% weight loss at 300 °C).[12] The vanadium analogue, $VOOCH_3$, cannot be prepared via this synthetic methodology.[12] The substitution of FeOCl with ethylene glycol to yield $FeO(O_2C_2H_4)_{0.5}$ is reported to proceed by the reaction shown in eq 3.[13] In this case, the basal spacing of 10.98 Å for the dry material was most consistent with an intralayer bridging model having the ethylene units oriented parallel to the FeO layers. The thermal behavior of this material was very similar to the methoxide-substituted product.

One aspect of our investigation into the intercalation and substitution reactions of TiOCl and VOCl has been focused on the use of diamines as guest species. In contrast to the considerable attention that has been given to the intercalation of aromatic amines[7,8] (e.g., py) into FeOCl and VOCl, only a few characterized examples for the intercalation of aliphatic amines into FeOCl and VOCl have been reported.[6,10] No amines have been reported as a guest species for TiOCl. We anticipated that by using a series of diamines with a range of ionization potentials some light may be shed on the mechanism of the intercalation reactions for MOX materials. It also seemed likely that diamines could serve the dual role of participating in the chloride substitution reaction and providing a base to assist in this reaction (e.g., eq 4). To this end, we wish to report results for the intercalation reactions of a series of diamines and diethylenetriamine into TiOCl and VOCl. All of these species represent new guest molecules for metal oxychlorides. Evidence for subsequent substitution reactions of some of these intercalates is also reported.



(4)

Table 1. Summary for the New Materials Prepared by the Intercalation of Amines into TiOCl and VOCl

intercalated species	abbreviation	conditions	Δb (Å)/formula
	TMEDA	2 d, 100°C	5.63 / $VOCl(TMEDA)_{0.29}$
	TMEN	2 d, 100°C	4.33 / $VOCl(TMEN)_{0.3}$
	DMEN	2 d, 80°C	3.38 / $TiOCl(DMEN)_{0.4}$ 3.42 / $VOCl(DMEN)_{0.3}$
	EN	9 hr, 75°C	3.43 / $TiOCl(EN)_{0.4}$ 3.48 / $VOCl(EN)_{0.4}$
	3N	5 d, 90°C	4.04 / $TiOCl(3N)_{0.2}$ 4.16 / $VOCl(3N)_{0.15}$

Results and Discussion

The synthesis of TiOCl proceeded according to the literature to yield a clean material with the reported X-ray diffraction pattern.[14] In our hands, the preparations found in the literature for VOCl did not result in isolation of pure materials.[15] Fortunately, by modification of the reaction stoichiometry and temperature, we have successfully developed a synthetic methodology which allows preparation of VOCl in high yield and high purity with the reported X-ray diffraction pattern. Although both of these materials are rather stable to air and moisture, all of the reactions in this report were performed with guest molecules that were thoroughly dried and distilled using Schlenk techniques in order to exclude any participation of water or oxygen in our investigations.

Intercalation Reactions. The conditions and results for the intercalation of a series of amines are summarized in Table 1.

Both TiOCl and VOCl underwent reaction with ethylenediamine (EN) at 75 °C over a period of 9 h with vigorous magnetic stirring as indicated by a slow color change of the solid to dark blue-gray. Powder X-ray diffraction (XRD) of these two solids showed the disappearance of starting material and formation of new compounds with *b* axes of 11.45(4) and 11.39(5) Å (Δ = 3.43 and 3.48 Å), respectively (Figure 1). The presence of amine is further confirmed by appearance of IR absorptions for NH and CN stretching and NH bending modes. Microanalysis and thermogravimetry (TGA) indicated formulas of $TiOCl(EN)_{0.4}$ and $VOCl(EN)_{0.4}$. Confirming evidence that these were indeed intercala-

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(11) Vorob'ev, N. I.; Pechkovskii, V. V.; Kobets, L. V. *Zh. Neorg. Khim.* **1974**, *19*, 3.

(12) (a) Son, S.; Kikkawa, S.; Kanamaru, F.; Koizumi, M. *Inorg. Chem.* **1980**, *19*, 262. (b) Kikkawa, S.; Kanamaru, F.; Koizumi, M. *Inorg. Chem.* **1976**, *15*, 2195.

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(14) Schäfer, H.; Wartenpfuhl, F.; Weise, E. *Z. Anorg. Allg. Chem.* **1958**, *295*, 268.

(15) Schäfer, H.; Wartenpfuhl, F. *J. Less-Common Met.* **1961**, *3*, 29.

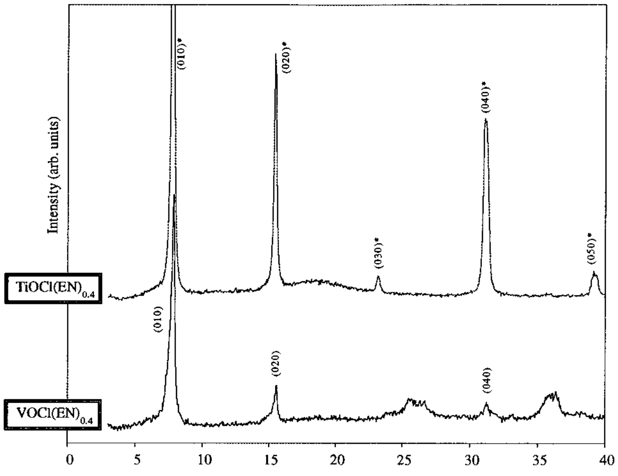

Figure 1. Powder X-ray diffraction patterns for the intercalation products of TiOCl with ethylenediamine (EN) and of VOCl with EN along with their respective formulas. Indexing is for the amine intercalated materials.

tion reactions was provided by the fact that rapid heating of these materials to 380 °C regenerated the XRD for the starting materials.

Comparing the VOCl(EN)$_{0.4}$ results to those from the intercalation NH_3 ($\Delta b = 3.02$ Å)[6b] and $EtNH_2$ ($\Delta b = 4.03$ Å)[6b] shows that there is very little difference in the interlayer expansion exhibited by these three species. These results indicate that the CH_2CH_2 axis of the EN molecule is probably lying parallel to the M−O double layers. This contrasts with the ethanol intercalate of FeOCl which exhibits a basal spacing of 17.48 Å corresponding to a Δb of 9.57 Å.[16]

A similar reaction of MOCl (M = Ti, V) and *N*,*N*′-dimethylethylenediamine (DMEN) at 80 °C for 2 days resulted in the formation of dark blue products. FTIR spectroscopy clearly confirmed the presence of amine and powder patterns indicated the formation of new intercalation products with *b* axes of 11.38(9) Å (Δ = 3.38 Å) for M = Ti and 11.33(7) Å (Δ = 3.42 Å) for M = V. These values are surprisingly close to those of the EN intercalates. Elemental and thermal analyses gave TiOCl($C_4H_{12}N_2$)$_{0.4}$ and VOCl(DMEN)$_{0.3}$ as the respective compositions for these new materials. As expected for the product of an intercalation reaction, the solid remaining after rapidly heating these intercalates under N_2 was TiOCl and VOCl as determined by XRD.

We note that in the case of DMEN intercalation, more forcing conditions were required for the reaction, relative to EN intercalation, and that some starting material remained when TiOCl was used as the host. Attempts to get complete intercalation of DMEN into TiOCl by either longer reaction time or higher temperature produced new materials derived from a substitution reaction (vide infra). It thus appears that the introduction of *N*-methyl groups on the diamines presents an additional barrier to the reactions with these hosts. This trend is further illustrated by the fact that both *N*,*N*,*N*′-trimethylethylenediamine (TMEN) and *N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) required even higher temperatures in order to produce intercalation products (Table 1).

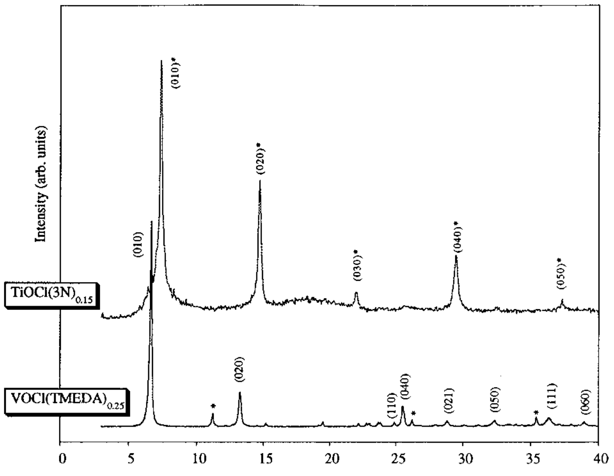

Figure 2. Powder X-ray diffraction patterns for the intercalation products of VOCl with *N*,*N*,*N*′,*N*′,-tetramethylethylenediamine (TMEDA) and of TiOCl with diethylenetriamine (3N) along with their respective formulas. Indexing is for the amine intercalated materials. The presence of deintercalated VOCl is indicated by *.

Both TMEN and TMEDA can be intercalated into VOCl after approximately 48 h at 100 °C. In the case of TMEDA, a new product with $\Delta b = 5.63$ Å ($b = 13.54$(5) Å) was evident by XRD (Figure 2). On the basis of FTIR, TGA, and elemental analysis, the formula VOCl(TMEDA)$_{0.25}$ is proposed. A similar material was obtained from the intercalation of TMEN into VOCl. This compound, VOCl(TMEN)$_{0.3}$, exhibited an XRD pattern indicating a Δb of 4.33 Å and IR absorptions for the amine. As with the previous intercalates, the reversibility criterion and a constant V:Cl ratio from X-ray fluorescence (XRF) spectroscopy were confirming evidence that this reaction is intercalation (i.e., the X-ray diffraction pattern for VOCl was regenerated after rapidly heating amine intercalate samples to 350 °C under N_2). In contrast, even under forcing conditions (170 °C, 5 days) TiOCl does not intercalate TMEDA or TMEN.

To explore the general ability of amines to behave as guest species for TiOCl and VOCl we attempted the intercalation with diethylenetriamine (3N) (Table 1). The optimal conditions for the reaction of MOCl (M = Ti, V) with 3N were 5 days at 90 °C during which time the solids changed from brown to gray. The XRD pattern of TiOCl(3N)$_{0.2}$ indicating a new *b* axis of 12.06(4) Å ($\Delta b = 4.04$ Å) is shown in Figure 2. The product of the VOCl reaction gave very similar analytical data: VOCl(3N)$_{0.15}$, Δb = 4.16 Å. The ability of 3N to intercalate into TiOCl is consistent with the idea that methyl substituents inhibit the ability of TiOCl to react with amines. In both the V and Ti cases, rapidly heating the solids regenerated the XRD of the starting materials.

As a result of the fact that all of the amines under investigation are able to intercalate into VOCl, we are not able to draw conclusions regarding the importance of ionization potential of the guest in these reactions. However, it should be noted that the ability of the guest species in this investigation to intercalate into TiOCl does not correlate with the guest ionization potential. It would seem that other factors, including perhaps steric considerations, play the dominant role in the

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(16) Weiss, A.; Choy, J. H. *Z. Naturforsch.* **1980**, *35b*, 157.

ability of these reactions to proceed.

The systematic but relatively small increase of the interlamellar expansion (Δb) with increasing methyl substitution of the diamines from EN to TMEDA and a corresponding decrease in the amount of intercalated amine with this increasing steric bulk is consistent with the proposal that the amines used in this study preferentially adopt a parallel orientation relative to the MO planes of the host. This feature is also exhibited for the intercalate of 3N which exhibits a Δb value intermediate to those of DMEN and TMEN and a stoichiometry for the intercalated molecules that has dropped by a factor of 2. However, from the diffraction data it is not possible to distinguish whether the amines are adopting a highly tilted all-trans configuration or an eclipsed configuration of the central ethylene unit.

The factors that cause the stoichiometry of the V compounds to be consistently lower than the corresponding Ti materials and their Δb to be systematically larger are unclear at this stage and are presently under investigation. Qualitatively, the fact that all of the materials have fairly sharp diffraction peaks as well as higher order reflections indicates a high degree of order for the diamine and triamine intercalates.

Substitution Reactions of Diamines with TiOCl. Realizing that, with the amine intercalates, reactions similar to eq 4 might be operative and having noticed that some interesting changes in the intercalated materials occurred when the reaction times were longer than those outlined in Table 1, we explored the thermal behavior of TiOCl(EN)$_{0.4}$ and TiOCl(DMEN)$_{0.4}$.

When the intercalation of TiOCl with EN was run under similar conditions but with a reaction time of 16 h, the formation of TiOCl(EN)$_{0.4}$ was accompanied by the appearance of a small peak in the XRD pattern with a *b* axis of approximately 14 Å. In an effort to identify this new material, we explored the effect of extended reaction times on the intercalation of EN. After 4 days of reaction at 75 °C the color of the solid remained the same but the solution took on a cloudy appearance and a white solid was observed on the walls of the Schlenk flask. Removal of the excess EN gave what appeared to be a mixture of blue-gray and white solids. The XRD pattern of this mixture (Figure 3b) indicated the presence of the new material, intercalated TiOCl(EN)$_{0.4}$, and several peaks which were confirmed to be the diammonium salt of EN [$(H_3NC_2H_4NH_3)Cl_2$ = EN salt] by comparison with an authentic sample.[17] In addition, a broad IR band centered at 2404 cm^{1} was assigned to the diammonium salt. The observation of the EN salt clearly indicates that chloride substitution is occurring and the concurrent appearance of the material with increased *b* axis indicates that this compound is likely the substitution product. Extending the reaction time to 7.5 days produced a material in which the XRD pattern showed a mixture of the new solid and EN salt and the absence of intercalated TiOCl. Removal of the EN salt was achieved through washing the mixture with neat EN. Figure 3c displays the XRD pattern for the final product of this transformation which indicates a new *b* axis of 14.46(9) Å (Δb = 6.44 Å). XRF spectroscopy and microanalysis yielded a formula for the new material of $TiOCl_{0.5}(C_2H_7N_2)_{0.5}$. All indications are that EN is now directly bonded to the Ti–O double layers by substitution of Cl anions.

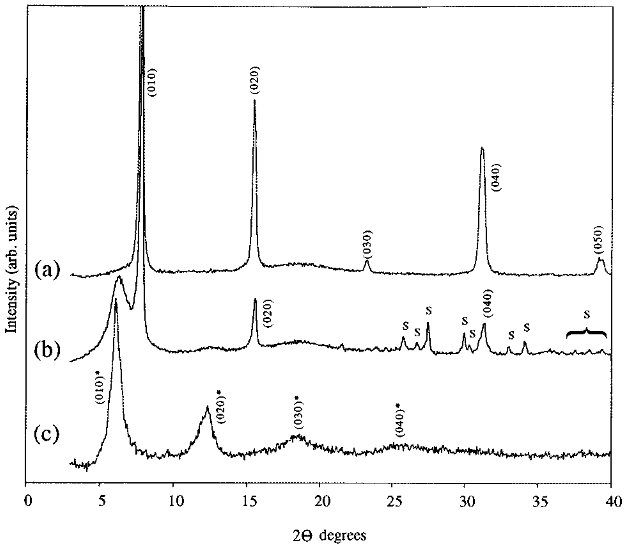

Figure 3. Stack plot showing the evolution of the powder X-ray diffraction pattern for the reaction of TiOCl with ethylenediamine (EN). Pattern (a) shows the intercalated material TiOCl(EN)$_{0.4}$ obtained after 9 h of reaction time. The appropriate (0*k*0) indexing is indicated. The center pattern (b) is for the material after 16 h of reaction time and shows the presence of TiOCl(EN)$_{0.4}$, $TiOCl_{0.5}(C_2H_7N_2)_{0.5}$, and $[H_3NC_2H_4NH_3]^{2+}Cl_2^{-}$ (EN salt, indexed by S). Pattern (c) is for $TiOCl_{0.5}(C_2H_7N_2)_{0.5}$ obtained after extended reaction time (7.5 days) and removal of the EN salt by washing with pure EN. The indexing for pattern (c) is indicated with (0*k*0)*.

The formation of a chloride substitution product was also observed, albeit less cleanly, in the TiOCl/DMEN system. As we noted above, the preparation of TiOCl(DMEN)$_{0.4}$ was continually hampered by the presence of some starting material or by the appearance, during extended reaction times, of a new material with an increased *b* axis. These two features can be seen in the XRD patterns shown in Figure 4a,b. Figure 4a gives the pattern for the intercalate (TiOCl(DMEN)$_{0.4}$) and indicates a very small amount of TiOCl. When the reaction time was extended (3 weeks at 80 °C) in an effort to achieve complete conversion of the starting material, a new material with an interlayer distance of 14.57(2) Å (Δb = 6.55 Å) was observed. The emergence of this new material was reminiscent of the features observed with EN intercalation and we suspected that chloride substitution was again taking place. The concurrent appearance of the diammonium salt of DMEN, $[H_2(Me)NC_2H_4N(Me)H_2]Cl_2$, is confirming evidence for this proposition.[17] The presence of TiOCl in this mixture presents a problem with stoichiometry calculation although a final Ti:Cl of approximately 2 (XRF spectroscopy) points to a similar reaction as in the case of EN. Clarification of the DMEN substitution reactions is an area that we have currently under investigation.

As with the reported substitution product of FeOCl with ethylene glycol ($FeO(O_2C_2H_4)_{0.5}$), several models can be considered for the orientation of the EN molecule in $TiOCl_{0.5}(C_2H_7N_2)_{0.5}$.[13] At this stage we favor a model with the EN moiety oriented perpendicular to the Ti–O

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(17) Authentic samples of $(H_3NC_2H_4NH_3)Cl_2$ (EN salt) and $(H_2(Me)NC_2H_4N(Me)H_2)Cl_2$ (DMEN salt) were prepared by the reaction of ethylenediamine and dimethylethylenediamine with HCl, respectively. Satisfactory elemental analysis (CHN) confirmed the formulation of these materials.

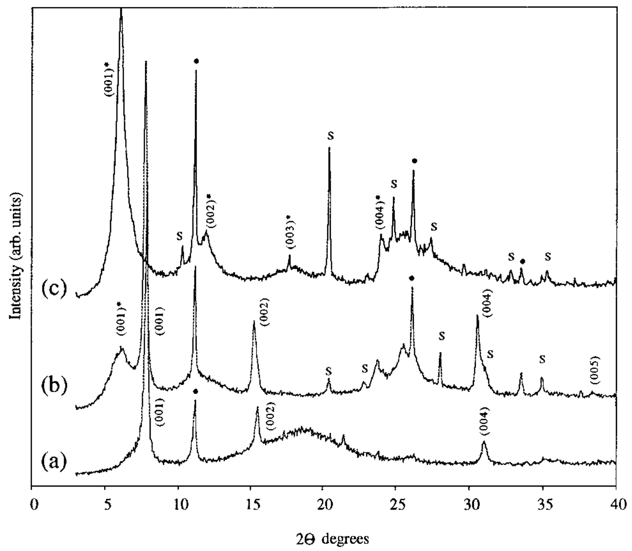

Figure 4. Stack plot showing the powder X-ray diffraction patterns for the reaction of TiOCl with *N*,*N*′-dimethylethylenediamine (DMEN). Pattern (a) is for the intercalated material $TiOCl(DMEN)_{0.4}$ obtained after 2 days of reaction time. The appropriate (0*k*0) indexing is indicated. Pattern (b) is for the material after 3 weeks of reaction time and shows the presence of $TiOCl_x(DMEN)_{1-x}$ [indexed with (0*k*0)*], and $[H_2(Me)NC_2H_4N(Me)H_2]^{2+}Cl_2^-$ (DMEN salt, indexed by S). The presence of deintercalated TiOCl is indicated by ●.

layers. The extended length of an EN molecule, based on the projections of the bonds in the perpendicular direction of 1.5 Å for the Ti−N, 1.25 Å for the C−N, 1.3 Å for the C−C and 1.5 Å for the radius of a terminal NH_2, is about 6.8 Å, a value which is in good agreement with what was found for the substitution product. In an intralayer bridging model, where the two ends of a single EN molecule bond to Ti centers within one layer and the ethylene units are oriented parallel to the Ti−O layers, we would expect an interlayer distance of about 11 Å.[13] Our preliminary results for the DMEN substitution reaction with an expansion value of 6.55 Å are in good agreement with what was found for the EN reaction.

The 3N intercalation product $TiOCl(3N)_{0.2}$ also has the potential to undergo further substitution reactions. Thermal treatment of this material did give indications of ammonium salt formation. However, due to the fact that 3N has the possibility of forming more than one substitution product it is not surprising that the XRD pattern for the product of this reaction exhibited several peaks in the low-angle region.

Conclusion

This report significantly extends the guest molecules that have been intercalated into metal oxychlorides in general, and TiOCl and VOCl in particular, by establishing the first example of intercalation of diamines and a triamine into these materials. In addition, the substitution reactions of EN and DMEN with TiOCl are the first examples of such reactions for this solid. In the case of EN substitution, the observation of the conversion of the intercalated material to the substituted compound is unique and adds substantially to the few well characterized examples of substitution reactions in the MOX family of materials.

Our current efforts are directed at understanding the variations in stoichiometry of the intercalates and in extending our results to include other amines in order to improve information about the orientational preferences for these materials. In addition, the physical and chemical properties of these new hybrid organic/inorganic composites is the subject of investigation. The information gained through this inquiry will provide direction for further modifications and may, by increasing the accessibility of the interlamellar space, facilitate future reactions of these solids.

Experimental Section

General Methods. $TiCl_3$, TiO_2, VCl_3, and V_2O_3 were purchased (Aldrich) and used without further purification. Ethylenediamine, *N*,*N*′-dimethylethylene diamine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and diethylenetriamine were purchased from Aldrich and dried and purified according to the literature.[18]

TiOCl was prepared according to the literature and characterized by powder X-ray diffraction, X-ray fluorescence, and TGA.[14] Analytical data: $a = 3.76$ Å, $b = 8.02$ Å, $c = 3.35$ Å; 44.6% weight loss with an onset of 700 °C; X-ray fluorescence spectroscopy gave Ti:Cl ratio of 1:1.

Synthesis. *VOCl*:[15] A mixture of VCl_3 and V_2O_3 in a 1.8:1 stoichiometry was sealed in an evacuated quartz tube and set along a temperature gradient of 620−580 °C for 60 h. The solid thus obtained was washed with DMF, ethanol, and diethyl ether in order to remove impurities (VCl_3, VCl_4, and $VOCl_3$). Confirmation of the structure was given by powder X-ray diffraction ($a = 3.75$ Å, $b = 7.91$ Å, $c = 3.28$ Å), X-ray fluorescence spectroscopy (V:Cl ratio of 1:1) and thermogravimetric analysis (23% weight loss with an onset of 640 °C, 15% weight loss with an onset of 800 °C).

Intercalation of amines: All intercalation reactions were carried out with the exclusion of air and moisture under a N_2 atmosphere using dried and distilled amines and standard Schlenk techniques. In a typical experiment, 0.5 g of MOCl (M = Ti, V) was mixed with 5 mL of the appropriate amine in a Schlenk flask. This heterogeneous mixture was heated with vigorous stirring for various times (see Table 1). The excess amine was removed under vacuum to yield a blue to blue-gray solid. In the case of diethylenetriamine (3N) the excess amine was removed by washing the blue solid with THF.

Analytical Data for the Amine Intercalates. *VOCl(TMEDA)*$_{0.25}$: Anal. Calcd for $VOCl(TMEDA)_{0.25}$: C, 15.20; H, 3.47; N, 5.91. Found: C, 15.20; H, 3.38; N, 5.59. Thermogravimetric analysis: 25% weight loss with an onset of 185°C [$VOCl(TMEDA)_{0.29}$]. FTIR (cm^{-1}) 1640 (w, br), 1260 (w), 1064 (s, br), 802 (m).

VOCl(TMEN)$_{0.3}$: Anal. Calcd for $VOCl(TMEN)_{0.3}$: C, 13.54; H, 3.42; N, 6.31. Found: C, 13.75; H, 3.68; N, 6.02. Thermogravimetric analysis: 26% weight loss with an onset of 183°C [$VOCl(TMEN)_{0.35}$]. FTIR (cm^{-1}) 3250 (m, br), 1645 (w), 1261 (s), 1140 (s, br).

VOCl(DMEN)$_{0.3}$: Anal. Calcd for $VOCl(DMEN)_{0.3}$: C, 11.19; H, 2.82; N, 6.52. Found: C, 11.37; H, 3.10; N, 6.13. Thermogravimetric analysis: 23% weight loss with an onset of 185 °C [$VOCl(DMEN)_{0.34}$]. FTIR (cm^{-1}) 3251 (m), 1110 (s, br).

TiOCl(DMEN)$_{0.4}$: Anal. Calcd for $TiOCl(DMEN)_{0.4}$: C, 14.28; H, 3.60; N, 8.32. Found: C, 13.90; H, 3.33; N, 7.96. Thermogravimetric analysis: 26% weight loss with an onset of 241 °C [$TiOCl(DMEN)_{0.4}$]. FTIR (cm^{-1}) 3200 (m, br), 1110 (s, br).

VOCl(EN)$_{0.4}$: Anal. Calcd for $VOCl(EN)_{0.4}$: C, 7.60; H, 2.56; N, 8.86. Found: C, 7.44; H, 2.34; N, 8.48. Thermogravimetric analysis: 19.9% weight loss with an onset of 193°C [$VOCl(EN)_{0.42}$]. FTIR(cm^{-1}): 3273 (s), 1589 (w), 1043 (m, br).

TiOCl(EN)$_{0.4}$: Anal. Calcd for $TiOCl(EN)_{0.4}$: C, 7.78; H, 2.68; N, 9.18. Found: C, 7.80; H, 2.81; N, 8.97. Thermogravimetric analysis: 22% weight loss with an onset of 200 °C [$TiOCl(EN)_{0.46}$]. FTIR (cm^{-1}) 3292 (s), 1585 (w), 1105 (m, br).

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(18) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

VOCl(3N)$_{0.15}$: Anal. Calcd for VOCl(3N)$_{0.15}$: C, 6.11; H, 1.67; N, 5.34. Found: C, 6.29; H, 1.38; N, 4.99. Thermogravimetric analysis: 14% weight loss with an onset of 220 °C [VOCl(3N)$_{0.16}$]. FTIR (cm^{-1}) 3220 (m), 1594 (w) 1105 (s, br).

TiOCl(3N)$_{0.15}$: Anal. Calcd for TiOCl(3N)$_{0.15}$: C, 6.27; H, 1.72; N,5.49. Found: C, 6.31; H, 2.10; N, 5.29. Thermogravimetric analysis: 14% weight loss with an onset of 220 °C [TiOCl(3N)$_{0.16}$]. FTIR (cm^{-1}) 3251(m), 1598 (w), 1090 (s, br).

Substitution Reactions. *Preparation of TiOCl$_{0.5}$(C$_2$H$_7$N$_2$)$_{0.5}$*: In a Schlenk flask, 0.5 g of TiOCl and approximately 5 mL of ethylenediamine were heated under N_2 with vigorous stirring. After 7.5 days, the excess amine was removed under vacuum to yield a blue-gray and white solid. The mixture was washed twice with approximately 10 mL of EN in order to remove the white solid. The resultant blue-gray material was dried under vacuum. Anal. Calcd for $TiOCl_{0.5}(C_2H_7N_2)_{0.5}$ C, 10.6; H, 3.5; N,12.4. Found: C, 10.24; H, 3.52; N, 11.9. FTIR (cm^{-1}) 1761 (m), 1261 (s), 1022 (s, br). XRF spectroscopy gave a Ti:Cl ratio of 2.

Analysis. Powder X-ray diffraction patterns were collected with a Philips PW 3710 based Xpert system using Cu Kα radiation and with the samples mounted on a no-background Si holder. The diffractometer was calibrated regularly with Si powder. Elemental analysis were obtained with a Perkin-Elmer 2400 Series 2 CHN Analyzer. Thermal gravimetric analysis were performed with a Polymer Laboratories STA1500HF. All measurements were carried out with an alumina sample pan. Infrared spectra were recorded with a Mattson 3000 FTIR system. A Philips PW2400 spectrometer was used for X-ray fluorescence measurements.

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