the MCD for $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ displays a high-energy shoulder at about 460 nm, assigned to the $A_1 \rightarrow A_2$ transition, and a maximum at 487 nm, assigned to the $A_1 \rightarrow E$ transition, no splitting associated with the low-energy band is observed in the circular dichroism.[31]

The structural and spectroscopic implications of coordination of highly strained azetidine and 1,4-diazacycloheptane rings in $CoN_6$ complexes have been discussed and correlations between the average Co-N bond length and the position of the low-energy $^1T_{1g}$ band proposed.[7,19] Similarly, it is possible to attribute the shift in $\lambda_{max}$ of the low-energy $^1T_{1g}$ band for $[Co(amta)(en)]^{3+}$ and $[Co(atac)(en)]^{3+}$, compared to that observed for $[(en)Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$, in part to the presence of the strained chelate rings and to the subsequent effects on the Co-N and Co-S bond lengths in the former complexes. The spectral shifts are, however, not as marked as for the $CoN_6$ complexes, and a full examination of the effects of the incorporation of the thioether donor on the shifts in $\lambda_{max}$ for the lowest energy $^1T_{1g}$ band must await the preparation of further examples of these types of complexes.

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**Registry No.** $[Co(amta)(en)]I_2Cl$, 108418-39-9; $[Co(atac)(en)]NO_3(ClO_4)_2$, 108418-41-3; Δ-(−)-$[Co(amta)(en)]I_2Cl$, 108507-66-0; Λ-(+)-$[Co(amta)(en)]I_2Cl$, 108418-42-4; 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol, 108418-43-5; 2-methyl-2-(bromomethyl)-1,3-propanediol, 2210-03-9; 2-methyl-2-(mercaptomethyl)-1,3-propanediol, 41988-08-3; *N*-(2-bromoethyl)phthalimide, 574-98-1; 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol bis(benzenesulfonate), 108451-68-9.

**Supplementary Material Available:** Listings of thermal parameters and calculated hydrogen positions, close intermolecular contacts, and details of least-squares planes calculations (7 pages); listings of calculated and observed structure factors for both complexes (24 pages). Ordering information is given on any current masthead page.

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# Layered Chlorotin Arsenate and Chlorotin Phosphate[†]

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The chlorotin arsenate and chlorotin phosphate $H[SnCl(OH)XO_4]\cdot 2H_2O$ (X = As, P) are layered compounds with intriguing intercalation properties. Directly intercalated are some derivatives of short-chain fatty acids (*N*-methylformamide, *N*-ethylformamide, *N*-ethylacetamide) and many primary, secondary, and tertiary amines. A tilted arrangement of the molecules with the alkyl chains radiating away from the surface is preferred. With short-chain alkylamines complete delamination of the crystals can occur. Long-chain alkylamines can be directly intercalated or adsorbed from diluted solutions. Alkylammonium derivatives can also be obtained by exchanging the protons by alkylammonium ions. The long-chain alkylamines or alkylammonium ions assume upright positions in the interlayer space. Preferentially, monolayers of perpendicular alkyl chains and bilayers of tilted alkyl chains (tilting angle ~56°) are formed. Intercalation proceeds rapidly, and complete conversion into the guest-host structure is attained. The dehydrated forms of chlorotin arsenate and chlorotin phosphate maintain the capability of intercalating guest molecules up to dehydration temperatures of 300 °C.

## Introduction

Phosphate and arsenate anions show a pronounced tendency to connect metal ions to layered host materials. Several types of layered compounds have been synthesized, and recent studies open new opportunities for utilizing them as molecular sieves and catalysts.[1,2] Particular attraction is directed toward group IVA and group IVB (groups 4 and 14) compounds of the form $H_2[M^{IV}(XO_4)_2]\cdot xH_2O$ ($M^{IV}$ = Zr, Ti, Hf, Ge, Sn; X = P, As).[3] A second, structurally different group comprises phosphates and arsenates $M^VOXO_4\cdot xH_2O$, such as $VOPO_4\cdot xH_2O$ ($x$ = 1, 2), $VOAsO_4\cdot xH_2O$ ($x$ = 2, 3),[4-10] $NbOPO_4\cdot xH_2O$ ($x$ = 1, 3),[10-12] and $VO(HPO_4)\cdot 0.5H_2O$ (=$(VO)_2H_4P_2O_9$).[13,14] The alkaline-earth salts of monoalkyl phosphoric esters, for instance $CaPO_4CH_3\cdot H_2O$, form a third group of layered phosphates.[15]

The structure of $VOPO_4\cdot H_2O$ and $NbOPO_4\cdot H_2O$ is composed of neutral $M^VO(H_2O)PO_4$ layers. The puckered $NbO(H_2O)PO_4$ layers consist of distorted $NbO_5(OH_2)$ octahedra connected in the equatorial planes by $PO_4$ tetrahedra.[10] The additional water molecules of the higher hydrated forms are enclosed between the layers. $NbOPO_4\cdot 3H_2O$ = $[NbO(H_2O)PO_4]\cdot 2H_2O$ contains a monolayer of water molecules between the layers. Related are chlorotin phosphate $[SnCl(H_2O)PO_4]\cdot 2H_2O$ and chlorotin arsenate $[SnCl(H_2O)AsO_4]\cdot 2H_2O$. One proton in these compounds can be exchanged by metal ions, which may be expressed by the formulas $H[SnCl(OH)PO_4]\cdot 2H_2O$ and $H[SnCl(OH)AsO_4]\cdot 2H_2O$.

Preparation and properties of the chlorotin arsenate have been reported by Dêmaret,[16] who also described the intercalation of

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[†] Dedicated to Armin Weiss on the occasion of his 60th birthday.

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alkylamines. Tests with other possible guest compounds revealed the particular intercrystalline reactivity of both compounds.

## Experimental Section

**Preparation of Chlorotin Arsenate and Chlorotin Phosphate.** Chloritin arsenate and chlorotin phosphate form in solutions containing Sn and As(P) in a molar ratio of about 2/1. Démaret described formation of the tin arsenate from solutions of 0.25 mol of $As_2O_5$ and 1 mol of $SnCl_4$ in 55.6 mol of water at 110 °C. Thus, 28.7 g of $As_2O_5$ (0.125 mol) was dissolved in 500 mL of water, and 130.3 g of $SnCl_4$ (0.5 mol) was added. The mixture was transferred into a Teflon bottle and stored at 110 °C for 6 days. The white precipitate was washed with water and air-dried. Hydrated $SnCl_4{\cdot}5H_2O$ can be used instead of $SnCl_4$ and is easier to handle.

The corresponding phosphate was prepared in the same way from a solution of 8.6 g of $H_3PO_4$ (85%, 0.075 mol) and 52.6 g of $SnCl_4{\cdot}5H_2O$ (0.150 mol) in 125 mL of water that was allowed to stand at 110 °C for 5 days.

**Intercalation.** Liquid guest compounds were allowed to react directly with the tin arsenate or tin phosphate for several days at room temperature. When the X-ray diffractograms were not indicative of intercalation, the dispersion was allowed to react at 65 °C. The degree of reaction was checked after different time periods, up to several weeks. Water-soluble solids (urea and urea derivatives) were applied as concentrated aqueous solutions.

Long-chain alkylamines $C_nH_{2n+1}NH_2$ ($n$ = 6–18) were directly intercalated, amines with $n$ = 6–10 at room temperature and those with $n > 10$ at 65 °C. The reproducibility of the high spacings during intercalation of long-chain alkylamines ($n > 10$) required a standardized procedure. The best method was found to mix the sample thoroughly with the solid amine. The mixture was stored at 65 °C for 48 h and then cooled to room temperature and allowed to stand for at least 24 h before X-ray investigations were started. A large excess of amine has to be avoided because free amine reduces the quality of the X-ray diagrams. Alkylamines were also intercalated from ethanolic solutions of different concentrations.

The tin arsenate was also treated with aqueous solutions of alkylammonium chlorides ($C_nH_{2n+1}NH_3^+Cl^-$). Samples of 100 mg were dispersed in 2 mL of a 2 M solution for $n < 10$ (5 mL of 0.1 M solution for $n$ = 10–15 and 5 mL of 0.05 M solution for $n > 15$). After some days at 65 °C, the supernatant was poured off. The residues were washed twice with 5 mL of an ethanol/water mixture (1/1) and again reacted with the alkylammonium chloride solutions. The samples were X-rayed while in contact with the equilibrium solution, after washing with a water/ethanol solution (1/1) (five times with 5 mL) and after air-drying. To test the capability of swelling, the air-dried alkylammonium derivatives were dispersed in alkanols $C_nH_{2n+1}OH$ ($n$ = 2–18). After at least 24 h at room temperature ($n$ = 2–8) or at 65 °C ($n > 10$), the samples were X-rayed in the presence of some excess of alkanol.

All the X-ray investigations were made in Debye–Scherrer cameras with a diameter of 36.0 cm/$\pi$ = 11.46 cm and with CuK$\alpha$ radiation and a Ni filter. The basal spacings of the intercalated products were measured in the presence of an excess of guest compounds.

**Further Methods.** The Sn and As contents were determined by atomic absorption and plasma emission spectrometry (Spectrospan IV Beckman, dc plasma); the Cl content was determined by combustion with $V_2O_5$, adsorption of $Cl_2$ in $H_2O_2$, and titration with $Hg^{2+}$. The carbon content of the alkylammonium derivatives was obtained by combustion.

Isothermal dehydration and rehydration were studied by equilibrating 100-mg samples over standard solutions for humidity control at 25 °C.[17] The final basal spacings and weight changes were recorded after several months.

## Results and Discussion

**Properties of the Chlorotin Arsenate and Chlorotin Phosphate.** The arsenate was obtained in thin rectangular plates of 1 μm and smaller. The phosphate forms spherical aggregates of such plates (Figure 1, supplementary material). Anal. Calcd for $H[SnCl(OH)AsO_4]{\cdot}2H_2O$: Cl, 10.21; As, 21.59; Sn, 34.20. Found for air-dried arsenate: Cl, 10.2; As, 21.4; Sn, 34.5. Anal. Calcd for $H[SnCl(OH)PO_4]{\cdot}2H_2O$: Cl, 11.7; P, 10.2; Sn, 39.2. Found for air-dried chlorotin phosphate: Cl, 11.9; P, 10.6; Sn, 41.0.

The powder diagram of the chlorotin arsenate agrees with that reported by Démaret (Table I) (Figure 2, supplementary material), who derived the lattice constants $a_0$ = 6.64 Å, $b_0$ = 6.68 Å, and $c_0$ = 15.87 Å, and $\beta$ = 95.2°. The layer distance (basal spacing) is $d_L = (c_0/2) \sin \beta$ = 7.90 Å. The platelike shape of the particles promotes texture, which influences the intensity of the reflections of diffractometer patterns. Thus, striking differences in intensities might be observed between the patterns obtained by the Debye–Scherrer and diffractometer technique (Table I).

**Table I.** Powder Diffraction Data for $H[SnCl(OH)AsO_4]{\cdot}2H_2O$ (Air-Dried Samples) ($d$ in Å)

| no. | $d_{obsd}$[a] | $d_{obsd}$[b] | $d_{obsd}$[c] | $I$[b] | $I$[d] | $I$[e] | $hkl$[a] |
|---|---|---|---|---|---|---|---|
| 1 | 7.91 | 7.90 | | 100 | 100 | 560 | 002 |
| 2 | 5.32 | 5.32 | 5.33 | 20 | 3 | 14 | $10\bar{2}$ |
| 3 | 5.10 | 5.10 | 5.13 | 40 | 7 | 37 | 012 |
| 4 | 4.86 | 4.86 | 4.88 | 20 | 4 | 20 | 102 |
| 5 | 4.70 | 4.70 | 4.72 | 40 | 5 | 29 | 110 |
| 6 | 4.16 | 4.16 | 4.14 | 10 | 1 | 5 | 112 |
| 7 | 3.95 | 3.96 | 3.97 | 45 | 12 | 70 | 004 |
| 8 | 3.54 | 3.54 | 3.54 | 15 | 4 | 20 | $10\bar{4}$ |
| 9 | 3.40 | 3.41 | 3.41 | 20 | 10 | 55 | 014 |
| 10 | 3.34 | 3.32 | 3.35 | 100 | 20 | 110 | 020 |
| 11 | 3.31 | | 3.32 | | 18 | 98 | 200 |
| 12 | 3.27 | 3.26 | 3.28 | 5 | 1 | 7 | 104 |
| 13 | 3.15 | 3.15 | 3.16 | 60 | 10 | 55 | $20\bar{2}$ |
| 14 | 3.13 | | 3.12 | <5 | | | $11\bar{4}$ |
| 15 | 3.08 | 3.08 | 3.08 | 80 | 14 | 80 | 022 |
| 16 | 2.96 | 2.96 | 2.96 | 50 | 5 | 30 | 202 |
| 17 | 2.93 | | 2.94 | | 4 | 25 | 124 |
| 18 | 2.66 | 2.64 | 2.66 | 10 | | 5 | $20\bar{4}$ |
| 19 | 2.63 | | 2.64 | | 2 | 10 | 006 |
| 20 | 2.53 | 2.53 | 2.53 | 20 | 5 | 28 | $10\bar{6}$ |
| 21 | 2.47 | 2.46 | 2.46 | 40 | 8 | 45 | $21\bar{4}$ |
| 22 | 2.45 | 2.44 | | 40 | | | 016 |
| 23 | 2.37 | 2.38 | 2.38 | 20 | 5 | 28 | 106 |
| 24 | 2.35 | 2.35 | 2.35 | 60 | 8 | 45 | 220 |

[a] Reference 16. [b] Debye–Scherrer camera; diameter 11.46 cm; CuK$\alpha$; Ni filter. [c] Siemens powder diffractometer D 500; CuK$\alpha$, Ni filter. [d] Intensities from Figure 2a. [e] Intensities from Figure 2a, adjusted to $I_{022}$ = 80.

**Table II.** Powder Diffraction Data for $H[SnCl(OH)PO_4]{\cdot}2H_2O$ (Air-Dried Samples) ($d$ in Å)

| no. | $d$[a] | $I$[a] | $I$[b] | no. | $d$[a] | $I$[a] | $I$[b] |
|---|---|---|---|---|---|---|---|
| 1 | 7.60 | 100 | 100 | 12 | 2.28 | 25 | 12 |
| 2 | 5.16 | 10 | 8 | 13 | 2.26 | | 12 |
| 3 | 4.55 | 30 | 23 | 14 | ~2.19 | <5 | 1 |
| 4 | 4.16 | 5 | 5 | 15 | 2.12 | 5 | 2 |
| 5 | 3.91 | 10 | 5 | 16 | 2.04 | 30 | 12 |
| 6 | 3.77 | 10 | 7 | | 2.03 | | |
| 7 | 3.42 | 15 | 7 | 17 | 1.956 | 10 | 4 |
| 8 | 3.21 | 85 | 83 | 18 | 1.867 | <5 | 3 |
| 9 | 3.08 | 35 | 28 | 19 | 1.774 | 5 | 4 |
| 10 | 2.85 | 10 | 5 | 20 | 1.727 | <5 | 3 |
| 11 | 2.44 | 25 | 10 | 21 | 1.606 | 30 | 12 |

[a] Debye–Scherrer camera; diameter 11.56 cm; CuK$\alpha$; Ni filter; intensities by visual means and by densitometry. [b] Intensities from the diffractogram of Figure 2b.

**Table III.** States of Hydration of $H[SnCl(OH)AsO_4]{\cdot}xH_2O$

| rel. humidity, % | $x$ | basal spacing, Å | rel. humidity, % | $x$ | basal spacing, Å |
|---|---|---|---|---|---|
| 0 | 0 | 6.26 | 42.0 | 2.04 | 7.90 |
| 10.0 | 1.58 | 7.76 | 51.0 | 2.08 | 7.89 |
| 15.0 | 1.66 | 7.76 | 72.6 | (2.76) | 7.90 |
| 32.3 | 2.00 | 7.90 | 87.0 | (2.80) | 7.89 |

The dihydrate is stable between 30 and about 60% relative humidity at 25 °C (Table III). A stable dihydrate is expected by analogy to $NbOPO_4{\cdot}3H_2O$ = $[NbO(H_2O)PO_4]{\cdot}2H_2O$.[10] It contains a monolayer of water molecules between the $H[SnCl(OH)AsO_4]$ layers. For this reason, a monohydrate is not expected to be stable over a distinct range of humidity and, in fact, is not indicated by dehydration curves.

The area of the basal plane per formula unit is $a_0b_0/2$ = 22 Å$^2$, and a water molecule in the dihydrate occupies an area of

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11 Å$^2$. The monolayer is thus not close-packed. In close-packed monolayers a water molecule covers about 7 Å$^2$. The water molecules dip between the surface atoms of the layers, which impedes close-packing. The decrease of the basal spacing from 7.90 to 6.30 Å by dehydration is therefore smaller than the diameter of a water molecule (~2.8 Å).

The constancy of the basal spacing at humidities above 60% indicates that adsorption of interlamellar water remains restricted to a monolayer. The increased water content is caused by water adsorption on the external surfaces and in pores, which reduces the reproducibility of the weight changes at high humidities.

An aqueous dispersion of the chlorotin arsenate gives pH values of 2.5–3. Titration curves[16] clearly indicate the existence of half-exchanged forms $HM[SnCl(OH)AsO_4]_2$ and fully exchanged forms with a total exchange capacity of one proton by one $M^+$ cation per formula unit ($M^+ = Li^+, Na^+, K^+, NH_4^+$). The exchanges $H \rightleftharpoons Li^+$ and $H^+ \rightleftharpoons Na^+$ are reversible.[16]

**Intercalation of Small Molecules.** Possible guest molecules are selected by experience with other types of layered host compounds such as kaolinite,[18] crystalline silicic acids,[19] and group IV phosphates and arsenates.[20–24] Suitable guest compounds are as follows: aliphatic and aromatic amines; long chain alkylamines; hydrazine and derivatives; urea and its methyl and ethyl derivatives; short-chain fatty acid amides (formamide, acetamide) and their methyl and ethyl derivatives; dimethyl sulfoxide, trimethylamine *N*-oxide, trimethylphosphine oxide, pyridine *N*-oxides.

The behavior of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ toward the different groups of guest compounds is very intriguing. Highly reactive are aliphatic and aromatic amines and alkylamines. Among the other groups, only particular compounds are intercalated. No reaction was observed with hydrazine and nearly all urea derivatives. A concentrated aqueous solution of urea reacts slowly. The reactivity of acid amides is restricted to some *N*-methyl and *N*-ethyl derivatives: *N*-methylformamide, basal spacing $d_L = 13.8$ Å; *N*-ethylformamide, $d_L = 15.2$ Å; *N*-ethylacetamide, $d_L = 12.3$ Å.

Dimethyl sulfoxide, which reacts with most of the layered host compounds, is not intercalated. Trimethylamine *N*-oxide expands the spacing to 12.3 Å.

In general, if reaction occurs, the intercalation proceeds rapidly and complete conversion into the guest–host structure is attained.

**Intercalation of Amines.** Various primary, secondary, and tertiary amines are easily intercalated by chlorotin arsenate and chlorotin phosphate (Table IV). An amine/phosphate (or arsenate) ratio of about 1 is attained in most cases. After intercalation, the basal spacings of the arsenate and the phosphate are almost identical. Intercalation of alkylamines with displacement of the interlayer water should expand the lattice to about 11 Å when the alkyl chains (diameter 4.5 Å) are almost parallel to the layers (6.3 + 4.5 = 10.8 Å). Alkylamine bilayers require basal spacings of about 15 Å. Still higher spacings are often observed and indicate chains radiating away from the surface (monolayers of tilted chains). This arrangement is very likely because it allows close contacts between the terminal groups of the amine and the surface atoms of the layer. An example is the diaminoalkanes, which are intercalated in monolayers. The tilt angle (between the chain axis and the surface, calculated from the mean increase of the spacings with the chain length) is 60°. Aminoalkanes are adsorbed preferentially in bilayers. The spacings after intercalation of the different butylamines are thus markedly larger than for diaminobutane. Analogously, hexylamine increases the spacing to 23 Å; diaminohexane, to 14.2 Å. Methylation of the amine group destroys the bilayer arrangement; aminododecane gives a spacing of 39.8 Å; (dimethylamino)dodecane gives 25.6 Å. The bulky dimethyl end group renders close-packing of the chains difficult, which reduces the stabilizing van der Waals energy between the chains and makes the bilayer unstable.

**Table IV.** Intercalation of Amines into $H[SnCl(OH)AsO_4]\cdot 2H_2O$

| amines | basal spacing, Å |
|---|---|
| Primary Amines | |
| 1-aminobutane | 19.0 |
| 2-aminobutane | 16.3 |
| isobutylamine | 16.7 |
| 3-methylbutylamine | 19.0 |
| 4-aminobutanol-2 | 17.8 |
| 3-methoxypropylamine | 19.7 |
| 3-butoxypropylamine | 25.2 |
| diaminobutane | 12.2 |
| diaminohexane | 14.2 |
| diaminooctane | 16.9 |
| diaminododecane | 21.0 |
| cyclohexylamine | 17.0 |
| cyclododecylamine | 21.4 |
| benzylamine | 19.5 |
| ephedrine | 16.6 |
| Secondary Amines | |
| *N*-methylethylamine | 12.1 |
| *N*-methylpropylamine | 13.4 |
| *N*-methylbutylamine | 14.8, 18.9 |
| *N*-methylisobutylamine | 13.9 |
| *N*-ethylpropylamine | 13.4 |
| *N*-ethyldibutylamine | 17.8 |
| *N*-ethyldioctylamine | 25.6 |
| *N*-ethylcyclohexylamine | 15.1 |
| *N*-butylcyclohexylamine | 15.8 |
| dicyclohexylamine | 17.0 |
| piperazine | 10.0 |
| dimethylpiperazine | 11.0 |
| Tertiary Amines | |
| *N,N*-dimethylethylamine | 12.6 |
| *N,N*-dimethylbutylamine | 16.2 |
| (dimethylamino)dodecane | 25.6 |
| 1,12-bis(dimethylamino)dodecane | 20.6 |
| triethylenediamine (Dabco) | 16.8 |
| tris(hydroxymethyl)aminomethane (Tris) | 13.9 |
| Aromatic Amines | |
| aniline | 17.9 |
| *m*-toluidine | 20.0 |
| *p*-toluidine | 19.7 |
| *o*-toluidine | 7.9 |

The spacings of dialkylamine and alkylamine are comparable: dioctylamine, 25.6 Å; octylamine, 27 Å. The dialkylamine molecule adopts a V-conformation in which the amine group points toward the layer and the chains radiate away from the surface.[19,25]

Substitution of methylene groups does not affect the principal conformation of the chain and its main orientation: 3-methoxypropylamine, 19.7 Å; pentylamine, 20 Å; 3-butoxypropylamine, 25.2 Å; octylamine, 27.2 Å.

If one unit $H[SnCl(OH)AsO_4]$ binds one amine molecule, an area of $a_0b_0/2 = 22$ Å$^2$ (=equivalent area) is available on the surface for each guest molecule. This geometrical constraint promotes tilted or perpendicular orientations. Generally, a chain in a mono- or bilayer between solid surfaces requires about 22–24 Å$^2$ if it stands perpendicularly on the surface. The area is slightly increased when the chains are tilted.[26,27] The packing density

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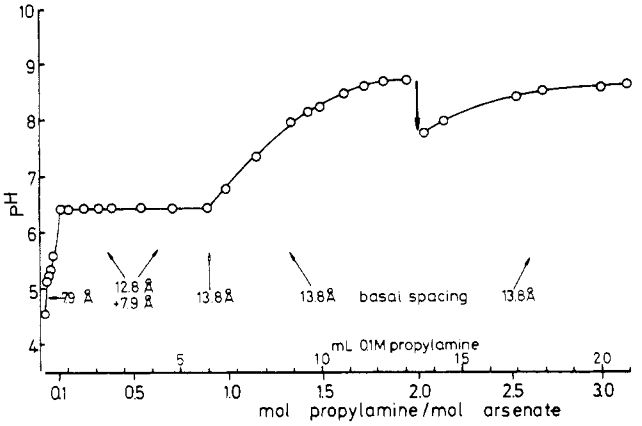

**Figure 3.** Titration of chlorotin arsenate with 0.1 M propylamine. Conditions: 251 mg of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ dispersed in 100 mL of $H_2O$; intervals between successive additions of propylamine of 1 h (<10 mL) or 2 h (>10 mL). The arrow indicates a pH change within 24 h.

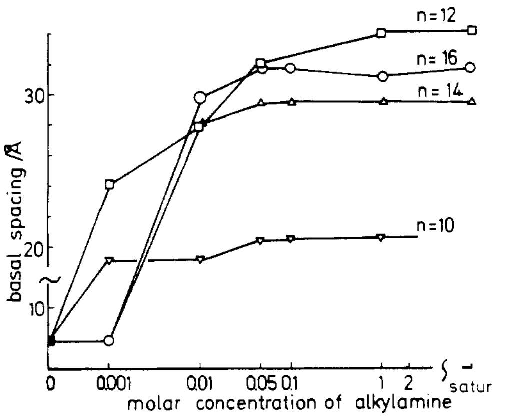

**Figure 4.** Basal spacings of chlorotin arsenate in equilibrium with ethanolic solutions of alkylamines $C_nH_{2n+1}NH_2$.

is somewhat lower than in crystalline paraffins and long-chain compounds (area about 19 Å²/chain) because of a less regular orientation of the C–C–C planes. A chain of $n$ carbon atoms lying flat on the surface requires $1.27 \times 4.5n + 14$ (Å²). A butylamine molecule, for instance, covers an area of 37 Å². The predominance of tilted or perpendicular chains is thus understandable. It also enables optimal contacts between the terminal groups and the surface.

Intercalation of amines is promoted by an acid–base reaction (proton transfer to the amine group). This reaction initiates intercalation of amines even from dilute solutions, in contrast to other guest molecules. (For instance: *N*-methylformamide is not intercalated if the molar ratio $H_2O$/NMFA exceeds 1/2). Titration of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ with 0.1 M propylamine produces a pronounced plateau at pH 6.4 between 0.1 and 1.0 mol of $C_3H_7NH_2$/mol of arsenate (Figure 3). The plateau corresponds to a two-phase region (7.9- and 12.8-Å phases). At the end of the plateau, when 1 mol of $H^+$ is neutralized by propylamine, the spacing increases to 13.8 Å. At higher additions of propylamine, colloidal dispersions form and the basal reflections disappear. Probably, the crystals are delaminated as in "pellicular" zirconium phosphate.[28] The dispersion then contains single layers and aggregates of two or more layers. Slowly decreasing pH of the dispersion after propylamine addition reveals that delamination of the crystals proceeds slowly. (The arrow in Figure 3 indicates the change of pH within 24 h; usually, propylamine was added in intervals of 1 h (up to 10 mL) or 2 h). Delamination consumes propylamine because the equivalent area on external surfaces is 2 × 22 = 44 Å², and additional propylamine can be adsorbed.

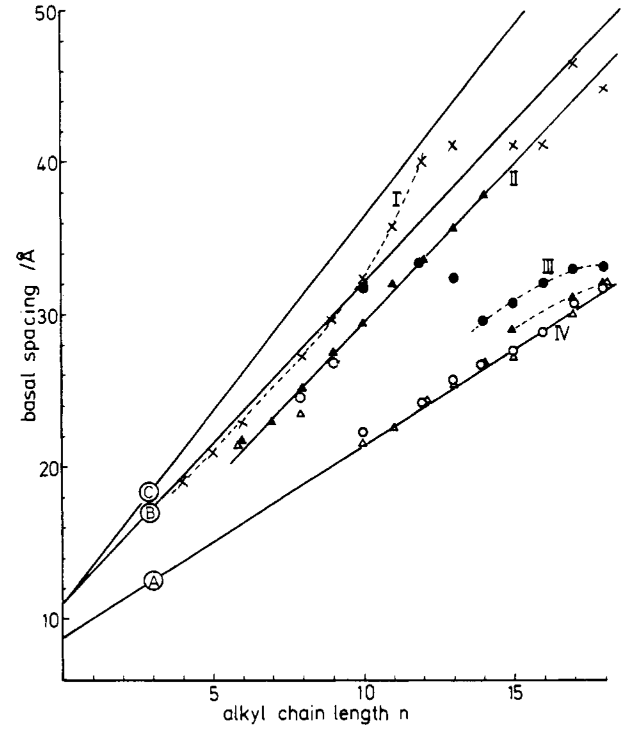

**Figure 5.** Basal spacings of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ after intercalation of long-chain alkylamines $C_nH_{2n+1}NH_2$ or alkylammonium ions $C_nH_{2n+1}NH_3^+$ (lines A–C calculated from eq 1–3, respectively): ×, samples in contact with pure alkylamines; ●, samples in contact with saturated ethanolic solutions; ○ samples washed with ethanol (four times) and air-dried; ▲, samples in contact wtih aqueous alkylammonium chloride solutions; △, samples washed and air-dried.

**Table V.** Thermal Dehydration of $H[SnCl(OH)AsO_4]\cdot xH_2O$

| temp,[a] °C | weight loss, % | basal spacing, Å<br>after dehydration | after rehydration |
|---|---|---|---|
| 25 | 0 | 7.89 | ... |
| 55 | | 7.89 | 7.90 |
| 80 | 5.85 | 7.66 | 7.89 |
| 110 | 10.21 | 7.63 | 7.89 |
| 200 | 10.56 | 7.63, +6.26 | 7.92 |
| 270 | 10.81 | 7.63, +6.26 | 7.80 |
| 300 | 13.29 | 7.73, +6.26 | 7.92 |
| 320 | 19.42 | 7.66[b] | 7.86[b] |
| 350 | 20.29 | amorphous | |
| 380 | 20.83 | amorphous | |
| 400 | 20.48 | amorphous | |
| 500 | 22.13 | amorphous | |
| 600 | 23.12 | formation of $SnO_2$ | |

[a] Below 350 °C the samples were heated for at least 3 days at the temperature indicated and 1 day at temperatures above 350 °C. [b] (001) very weak.

**Long-Chain Alkylamines and Alkylammonium Ions.** In Figure 5 are collected basal spacings of long-chain alkylamines $C_nH_{2n+1}NH_2$ ($n$ = 6–18) as a function of chain length $n$. When the amines are directly intercalated, the spacings up to $n$ = 12 follow curve I. The intercalation of longer chain alkylamines ($n$ > 12) is kinetically impeded by the large layer separation required. The spacings are scattered between 40 and 46 Å.

Alkylamines are also intercalated from ethanolic solutions, even at very low equilibrium concentrations of amine (<0.01 mol/L). The maximal spacing is reached at 0.05 mol/L for $n$ = 14 and 16 and 1 mol/L for $n$ = 12 (Figure 4). With shorter chain amines ($n$ < 12) the spacings approximate those after intercalation of pure amines (curve I, Figure 5); with longer chain amines lower spacings are observed (curve III, Figure 5). Washing with ethanol removes alkylamine from the interlayer space. When samples

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(28) Alberti, G.; Casciola, M.; Costantino, U. *J. Colloid Interface Sci.* **1985**, *107*, 256.

**Table VI.** Basal Spacings (Å) of Chlorotin Arsenate and Chlorotin Phosphate (Air-Dried and Heated Samples) after Intercalation of Various Guest Molecules

| | $H[SnCl(OH)AsO_4]$ | | $H[SnCl(OH)PO_4]$ | |
|---|---|---|---|---|
| guest compd | air-dried | heated | air-dried | heated[b] |
| | 7.90 | 6.24 | 7.60 | 6.07 |
| *N*-methylformamide | 13.8 | 13.3,[a] 13.7,[b] 13.3[c] | 13.8 | 6.07 |
| *N*-ethylformamide | 15.2 | 15.2[b] | 15.2 | 15.2[b] |
| trimethylamine *N*-oxide | 12.3 | 12.2[c] | 12.3 | 11.8 |
| Tris[d] | 13.9 | 15.0,[a] 14.0[c] | 13.9 | 13.8 |
| decylamine | 32.2 | 32.5[c] | 32.7 | 33.2 |
| aniline | 17.9 | 17.7,[a] 17.5[c] | 17.8 | 17.4 |
| ephedrine | 16.6 | 16.6,[a] 16.6[c] | 16.8 | 16.8 |
| dimethylpiperazine | 11.0 | 10.5,[a] 11.1[a] | 7.60 | 6.07 |

[a] Heated at 200 °C for 12 h. [b] Heated at 280 °C for 4 days. [c] Heated at 280 °C for 60 days. [d] Tris(hydroxymethyl)aminomethane, $(HOCH_2)_3CNH_2$.

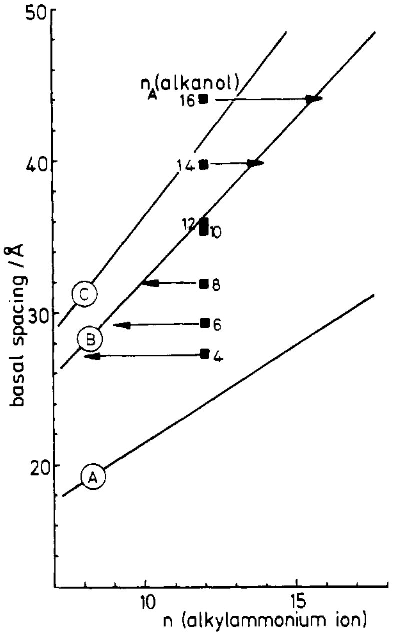

**Figure 6.** Basal spacings of dodecylammonium chlorotin arsenate in contact with alkanols $C_{n_A}H_{2n_A+1}OH$ ($n_A$ = 4–16) (lines A–C as in Figure 5).

(obtained by adsorption from saturated solutions) are washed with ethanol and air-dried, the spacings follow line IV in Figure 5.

Alkylammonium ions $C_nH_{2n+1}NH_3^+$ can also be exchanged for the protons in aqueous solutions at about pH 6. The spacings in equilibrium with the aqueous alkylammonium chloride solutions ($n < 15$) lie on a straight line (line II, Figure 5); the slope is 2.10 Å/Δ*n*. Washing and drying reduce the spacings (line IV, slope 1.27 Å/Δ*n*). Again, the reaction with very long alkylammonium ions ($n > 15$) is somewhat impeded; the spacings do not follow line II but are found slightly above line IV.

All experimental spacings are enclosed by lines A and C calculated for mono- and bilayers of perpendicular chains. The terminal $NH_2$ or $NH_3^+$ groups occupy approximately the position of the interlayer water molecules (Figure 7). The spacings for alkyl chain monolayers are obtained from the relation

$$d_L\ (\text{Å}) = 7.90/2 + 1.27n + 4.55 = 8.5 + 1.27n \qquad (1)$$

considering that the diameter of the terminal $CH_3$ group is 1.2 Å larger than that of a water molecule (2.8 Å): 3.95 + 0.6 = 4.55 Å. For bilayers (line C, Figure 5) the corresponding expression is

$$\begin{aligned} d_L\ (\text{Å}) &= 3.95 + 1.27n + 3 + 1.27n + 3.95 \qquad (2) \\ &= 10.9 + 2.54n \end{aligned}$$

An average distance of 3 Å is assumed between the terminal methyl groups. Line B gives the spacings for bilayers of tilted chains ($\alpha = 56°$):

$$d_L\ (\text{Å}) = 10.9 + 2.54n \sin \alpha = 10.9 + 2.11n \qquad (3)$$

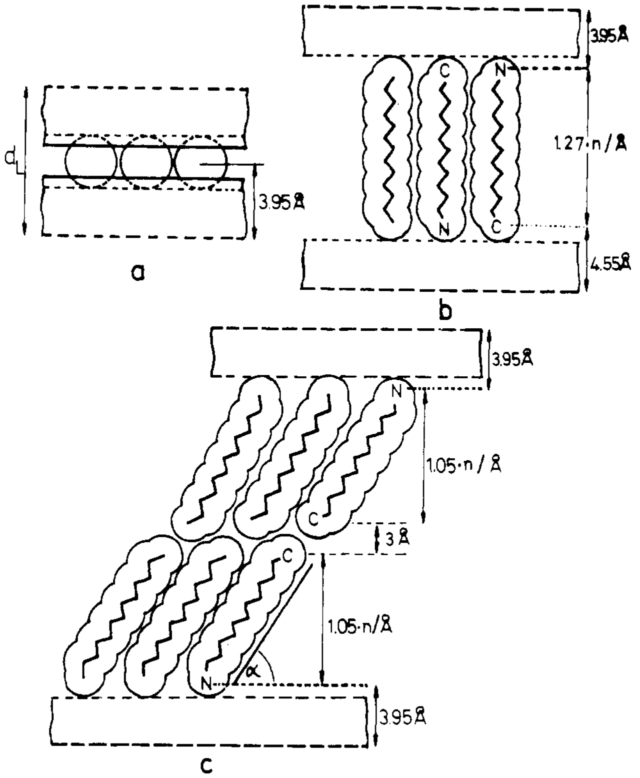

**Figure 7.** Interlayer structure of chlorotin arsenate and chlorotin phosphate and the alkylamine and alkylammonium derivatives: (a) structure of the dihydrate (interlayer water molecules in monolayers); (b) interlayer space with a monolayer of alkylamine molecules or alkylammonium ions; (c) interlayer space with a bilayer of alkylamine molecules or alkylammonium ions, tilt angle $\alpha = 56°$.

Bimolecular arrangements of perpendicular chains ($\alpha = 90°$, line C) are rarely formed. The highest spacings are observed when alkylamines are intercalated directly (curve I, Figure 5). For $n \leq 10$, the chains are tilted in angles of about 56° (section of curve I parallel to line B). Longer chains move in more perpendicular orientations, as is often observed for long-chain molecules in interlayer spaces.[27] An interlayer structure with tilted chains is also characteristic of the alkylammonium derivatives (line II). That line II is 1.3 Å below line B indicates formation of one kink per chain pair in the bilayer.[29]

All bilayer structures (curves I–III) collapse into a monolayer arrangement with perpendicular chains (line IV) when the samples

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(29) Lagaly, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 575. Lagaly, G. *Naturwissenschaften* **1981**, *68*, 82.

are washed with an ethanol/water solution. Determination of carbon content of these samples gives a ratio of 0.9–1.0 mol of $RNH_2$/mol of $SnCl(OH)AsO_4$. Each proton in $H[SnCl(OH)AsO_4]$ is replaced by an $RNH_3^+$ ion or is transferred to an intercalated $RNH_2$ molecule. A ratio slightly below 1.0 is understandable because the chains of the monolayer require an area of 22–24 Å$^2$/chain, which is slightly larger than the equivalent area of 22 Å$^2$. Bimolecular arrangements have to be stabilized by an additional uptake of alkylamine molecules or alkylammonium ions together with gegenions.

The bilayer can also be completed by interlamellar sorption of alkanols instead of $RNH_2$ or $RNH_3X$. The spacings then increase with the alkanol chain length, as shown in Figure 6 for the dodecylammonium derivative and alkanols $C_{n_A}H_{2n_A+1}OH$, $n_A$ = 4–16. When $n_A = n$, the spacings lie very near or on curve B for tilted bilayers. As the alkanol molecules become longer than the alkylammonium ions, the interlayer structure is determined by bilayers of the tilted alkanol molecules. The spacings with tetra- and hexadecanol thus correspond to those on line B for $n$ = 14 and 16 (Figure 6). In case of $n_A < n$ the spacing is determined by pairs $n_A + n$.[29,30] For instance, the spacing for $n$ = 12 and $n_A$ = 8 agrees with the spacing of the decylammonium derivative under decanol because $n_A + n = 20 = 2 \times 10$.

It is concluded from Figure 5, in which the basal spacings of different systems are collected, that the interlayer arrangement of long-chain alkyl compounds is restricted to a few types of structures: monolayers with perpendicular chains and bilayers with chains tilted at about 56° toward the layer. The all-trans conformation of the chains seems to be preferential. A tilt angle around 56° allows an optimal formation of hydrogen bonds between the terminal $NH_2$ and $NH_3^+$ groups and surface oxygen atoms.[26,27]

**Thermal Stability.** When chlorotin arsenate is heated to above 60 °C, the basal spacing is slightly reduced from 7.90 to 7.63 Å, but the water monolayer is not desorbed below 200 °C. The monolayer form persists up to 320 °C along with the dehydrated form with a spacing of 6.26 Å. At 350 °C the sample becomes amorphous, and at 600 °C, formation of $SnO_2$ starts. The dehydrated form and the 7.63-Å form rehydrate in contact with water to give spacings of 7.86–7.92 Å (Table V).

The dehydrated forms of chlorotin arsenate and chlorotin phosphate maintain the capability of intercalating guest molecules up to dehydration temperatures of 300 °C. Even if samples are heated at 280 °C for 60 days, the intracrystalline reactivity is not lost (Table VI). After intercalation, the basal spacings of the heated and the air-dried samples are identical or very similar. Only a few compounds (e.g. NMFA in Table VI) do not expand heated samples of chlorotin phosphate.

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**Supplementary Material Available:** Figure 1, showing scanning electron microphotographs of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ (a) and $H[SnCl(OH)PO_4]\cdot 2H_2O$ (b), and Figure 2, showing powder diffractograms of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ (a) and $H[SnCl(OH)PO_4]\cdot 2H_2O$ (2 pages). Ordering information is given on any current masthead page.

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[30] Lagaly, G.; Fitz, St.; Weiss, A. *Clays Clay Miner.* **1975**, *23*, 45.

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# Syntheses, X-ray Crystal Structures, and Ligand Substitution Kinetics of the Carbon-Bonded Chromium(III) Complexes *trans*-$[CrR(acac)_2(L)]$ (R = $CH_2Cl$, $CHCl_2$; L = $H_2O$, $CH_3OH$, Pyridine)

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The alkylchromium(III) complexes *trans*-$[CrR(acac)_2(H_2O)]$ (**a**) (R = $CHCl_2$, $CH_2Cl$; Hacac = 2,4-pentanedione) were prepared by the reaction of $[CrR(H_2O)_5]^{2+}$ with Hacac and triethylamine. Synthetic methods reported previously for $[CrR(H_2O)_5]^{2+}$ (R = $CHCl_2$, $CH_2Cl$) were improved to give approximately quantitative yields. The complexes *trans*-$[CrR(acac)_2L]$ (L = $CH_3OH$, pyridine) were derived by replacing a coordinated water molecule in **a** with L. The X-ray crystal structure analyses of *trans*-$[CrR(acac)_2(py)]$ (R = $CHCl_2$, $CH_2Cl$) have been performed. The carbon-bonded ligands $CHCl_2$ and $CH_2Cl$ lengthen specifically the Cr–N bond trans to the Cr–C bond in *trans*-$[Cr(CHCl_2)(acac)_2(py)]$ (**b**; Cr–N = 2.154 (7) Å) as well as in *trans*-$[Cr(CH_2Cl)(acac)_2(py)]$ (**c**; Cr–N = 2.201 (4) Å). The elongation of the Cr–N bonds in **b** and **c** is reflected in substantial labilization of the ligand substitution reactions at the position trans to R: *trans*-$[CrR(acac)_2(CH_3OH)] + L \rightleftharpoons$ *trans*-$[CrR(acac)_2L]$ + $CH_3OH$. The rate constants ($M^{-1}\ s^{-1}$) at 25 °C in methanol for the formation of *trans*-$[CrR(acac)_2L]$ are 85 ± 2 (R = $CHCl_2$, L = py), 98 ± 1 (R = $CHCl_2$, L = 4-methylpyridine), 57 ± 1 (R = $CHCl_2$, L = isonicotinamide), and (1.2 ± 0.5) × $10^3$ (R = $CH_2Cl$, L = py), and the rate constants ($s^{-1}$) for the backward reaction at 25 °C are 15 ± 1 (R = $CHCl_2$, L = py), 11 ± 1 (R = $CHCl_2$, L = 4-methylpyridine), 33 ± 1 (R = $CHCl_2$, L = isonicotinamide), and (5 ± 2) × $10^2$ (R = $CH_2Cl$, L = py). The rate constants and the activation enthalpies and entropies are consistent with the dissociative ligand substitutions. The results may arise from the weakening of the bond trans to the alkyl group. This study has shown that the alkyl group has a strong electronic effect on the bond trans to the Cr–C bond and has presented evidence for the trans labilization that has been proposed for the rapid ligand substitution reactions of $[CrR(H_2O)_5]^{2+}$ (R = alkyl, benzyl).

## Introduction

Organopentaaquachromium(III) complexes have covalent metal–carbon bonds and contain five water molecules. Therefore, they reveal properties of organometallic compounds as well as Werner type complexes. They have been actively studied especially from the kinetic and mechanistic viewpoints.[1] One of the characteristic properties of the organopentaaquachromium(III) complexes is that one of the five coordinated water molecules in them undergoes remarkably rapid substitutions.[2-7] Rapid in-

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