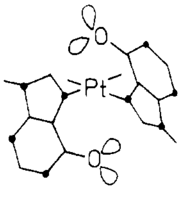
much as in the corresponding d(pGpG) adduct,[4] are displaced reasonably rapidly by excess CN^- at pH 8 according to

$$cis\text{-}[(NH_3)_2Pt(9\text{-}EtGH\text{-}N^7)_2]^{2+} + 4CN^- \rightarrow 2NH_3 + [Pt(CN)_4]^{2-} + 2(9\text{-}EtGH)$$

A recent discussion[1g] on the phenomenon of incomplete removal of *cis*-DDP from single-stranded DNA prompted us to extend our earlier studies. We postulated that Pt displacement by CN^- might also be slow if two nucleobases having *a single* exocyclic oxygen each (O6 of 9-methylguanine and O2 of 1-methylcytosine) were trapped in a head–tail arrangement without the possibility of rotating about the Pt–N(nucleobase) bond. It is well established[5–8] that bulky substituents at the amine ligands in A_2PtBX entities can successfully prevent nucleobase (B) rotation. We thus reasoned that compounds with a fixed head–tail orientation of two bases having a single exocyclic oxygen (e.g. two guanines, structure I) might represent adequate species to test this hypothesis. Cramer and Dahlstrom[5a] had suggested that the Pt complex with the bulky *N,N,N′,N′*-tetramethylethylenediamine (tmeda) ligand, on reaction with guanosine, gave two diastereomers with head–tail orientation of the two bases only. No head–head isomer was observed. Orbell et al.[9] demonstrated that 9-MeGH and 9-EtGH also form head–tail complexes when reacted with $[(tmeda)Pt(H_2O)_2]^{2+}$.



I

We have prepared $[(tmeda)Pt(D_2O)_2](NO_3)_2$ (**1**)[10] and $[(tmeda)Pt(9\text{-}MeGH\text{-}N^7)_2](ClO_4)_2\cdot 3H_2O$ (**2**)[11] according to published methods. $[(tmeda)Pt(1\text{-}MeC\text{-}N^3)_2](ClO_4)_2\cdot H_2O$ (**3**)[12] and $[(tmeda)Pt(py)_2)](ClO_4)_2\cdot 2H_2O$ (**4**)[13] were prepared in an analogous manner. The compounds were treated with a 20-fold excess of CN^- in D_2O at pD ~ 8 and 30 °C, as previously described,[2] and the reaction was followed by ^1H NMR spectroscopy.[14] The previously studied reaction of $cis\text{-}[(NH_3)_2Pt(9\text{-}EtGH\text{-}N^7)_2]^{2+}$ with CN^- was repeated as a control.

The following observations were made: (1) CN^- quickly displaces all ligands in **1** and **4**, half-lives being less than 15 min each. (2) In the case of **2**, it takes between 150 and 200 h to displace 50% of the guanine ligands. This time is to be compared with ca. 12–15 h for $cis\text{-}[(NH_3)_2Pt(9\text{-}EtGH\text{-}N^7)_2]^{2+}$. Although 9-MeGH precipitates in part from solution, the intensities of the signals of the intact complex confirm our previous observations that CN^- displaces *all* ligands, including tmeda, from **2**. (3) The bis(1-methylcytosine) complex **3** proves to be the one that resists CN^- treatment most effectively. After 120 h, less than 10% of 1-MeC was substituted.

Although we have not characterized **3** by X-ray crystallography as yet, we propose a head–tail orientation of the two nucleobases as in the case of $cis\text{-}[(NH_3)_2Pt(1\text{-}MeC)_2]^{2+}$.[7a,15] The observation that **3** exhibits the greatest inertness toward CN^- among the compounds described here could be due either to the additional shielding effect of the NH_2 group at the 4-position[16] or—more likely—to the greater barrier of rotation about the Pt–N bond as compared to purine-N^7 compounds.[7a]

Our findings unambiguously demonstrate that a single exocyclic oxygen on either side of the Pt coordination plane in bis(nucleobase) complexes makes an associative substitution mechanism by CN^- very difficult and causes a remarkable kinetic stability. The steric bulk of the amine substituents is, at least in the compounds studied (cf. behavior of **1** and **4**), not primarily responsible for this effect. With respect to the nature of DNA-bound *cis*-DDP that resists CN^- treatment, the previously suggested possibilities[2] need to be extended: Apart from thymine-N^3-containing adducts which, in every possible combination with a second nucleobase give inert complexes, any of the following combinations is expected to behave similarly, *provided the DNA structure fixes the respective nucleobase orientation*: (C-N^3),(C-N^3) (*head–tail*), (C-N^3),(GH-N^7) (*head–head*), (C-N^3),(G-N^1) (*head–head*), (G-N^1),(G-N^1) (*head–tail*), (GH-N^7),(GH-N^7) (*head–tail*). It thus appears likely that involvement of donor sites that normally are in the interior of the duplex (T-N^3, C-N^3, G-N^1) can lead to an inert cross-link. As far as guanine-N^7 binding is concerned, a binding pattern generally believed to be kinetically favored, a *head–tail* geometry as proposed for the interstrand (GH-N^7),(GH-N^7) adduct of *cis* DDP,[17] probably makes this cross-link CN^- resistant. In contrast, the major adduct of *cis*-DDP in double-stranded DNA, the intrastrand guanine,guanine (*head–head*) complex, reacts relatively fast with CN^-.

Note Added in Proof. The X-ray structure of **3** has now been performed. It confirms the head–tail orientation of the two 1-MeC rings. Details will be published elsewhere.[18]

Acknowledgment. We acknowledge, with thanks, financial support from the Fonds der Chemischen Industrie, experimental assistance from Oliver Renn (NMR spectra) and Markus Höpp, and useful discussions with Prof. L. G. Marzilli.

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(10) A solution of $[(tmeda)Pt(D_2O)_2](NO_3)_2$ (**1**) was prepared as follows: 0.018 mmol of $(tmeda)PtI_2$ (prepared according to: Dhara, S. G. *Indian J. Chem.* **1970**, *8*, 193) and 0.035 mmol of $AgNO_3$ were stirred for 5 h at 50 °C; then AgI was filtered off.

(11) Anal. Calcd (found) for $C_{18}H_{36}N_{12}O_{13}Cl_2Pt$ (**2**): C, 24.17 (24.5); H, 4.06 (3.7); N, 18.79 (18.5). ^1H NMR [δ (ppm); pD 8]: 9-MeGH, 8.17 (H8, s), 3.65 (CH_3, s); tmeda, 2.65–3.20 (m).

(12) Anal. Calcd (found) for $C_{16}H_{32}N_8O_{11}Cl_2Pt$ (**3**): C, 24.69 (24.8); H, 4.18 (4.0); N, 14.39 (14.0). ^1H NMR [δ (ppm); pD 8]: 1-MeC, 7.61 (H6, d), 6.03 (H5, d), 3.42 (CH_3, s); tmeda, 2.76–3.03 (m).

(13) Anal. Calcd (found) for $C_{16}H_{30}N_4Cl_2O_{10}Pt$ (**4**): C, 27.28 (26.9); H, 4.29 (3.9); N, 7.98 (7.8). ^1H NMR [δ (ppm); pD 8.1]; py 8.96 (H2, H6, d), 8.00 (H4, t), 7.60 (H3, H5, t); tmeda, 3.11 (CH_2, s), 2.79 (CH_3, s).

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Layered Titanate Pillared with Alumina

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Introduction

The pillaring of synthetic clays with large polymeric aluminum-bearing cations has led to the preparation of a whole new family of microporous materials with well-defined pores of di-

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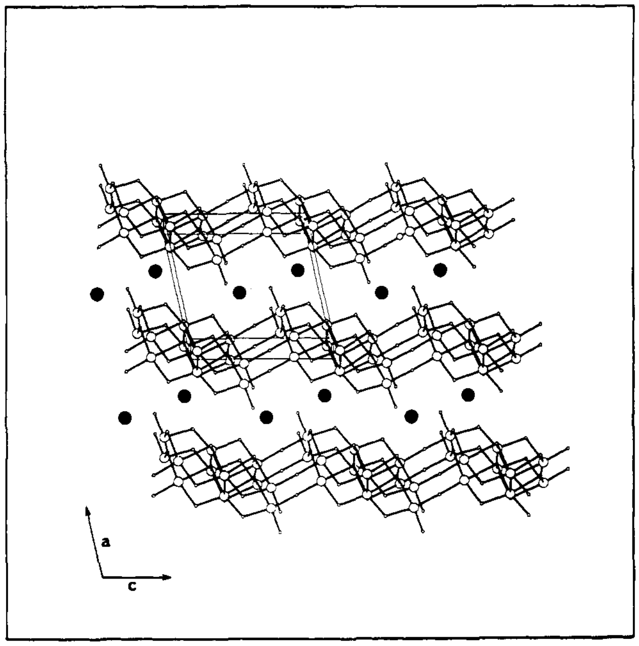

Figure 1. The structure of sodium trititanate. Large open circles denote titanium atoms; smaller open circles denote oxygen. Filled circles represent the interlamellar sodium cations.

mensions considerably larger than those found in zeolites.[1-4] This has provided scope for molecular sieving and shape-selective catalysis for relatively high molecular weight species. There has been much work aimed at extending further the range of molecular sieves with large pore dimensions. VPI-5, the recently synthesized porous aluminophosphate, is the first material to contain 18-membered rings 12 Å in diameter.[5] There are also reports of the successful pillaring of fluoromicas,[6] layered zirconium and titanium phosphates,[7] and potassium tetratitanate, $K_2Ti_4O_9$.[8] Such materials are of considerable interest as molecular sieves and shape-selective catalysts with properties controlled by the structure and composition of the inorganic layers. We report that layered sodium trititanate, $Na_2Ti_3O_7$, can be pillared by using $[Al_{13}O_4(OH)_{24+x}(H_2O)_{12x}]^{(7-x)+}$ Keggin ions. One significant difference between our work and that on titanium phosphates and titanium tetratitanite is that we were able to pillar the structure using the Keggin ion without first prizing the layers apart by intercalating alkylammonium cations. We demonstrate that (i) under the right conditions the aluminum-bearing cations exchange directly for Na^+ and (ii) the products have a high surface area and are resistant to high-temperature calcination.

Experimental Section

$Na_2Ti_3O_7$ was prepared as described by Andersson and Wadsley.[9] Sodium carbonate and TiO_2 (anatase) in the 1:2 mole ratio were heated in a platinum crucible to 1000 °C for 3 h and then to 1300 °C for 3 h and finally cooled slowly to room temperature. The trititanate crystallizes as colorless needles. The structure (Figure 1) has the space group $P2_1/m$, with unit cell dimensions, $a = 8.57$ Å, $b = 3.80$ Å, $c = 9.14$ Å, and $\beta = 101.6°$, and is built of layers of the composition $(Ti_3O_7)^{2-}$. Three TiO_6 octahedra are linked in the a direction by sharing edges and are connected to two other groups of three octahedra by sharing corners. The layers are held together by the Na^+ ions, which occur in two different kinds of crystallographically nonequivalent sites.

The pillaring agent was aluminum chlorohydrate from Reheis Chemical, Ireland. The chlorohydrate was hydrolyzed in water at 80 °C for 2 h. This gave a solution containing the polymeric $[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{(7-x)+}$ cation with the Keggin ion structure.[10] The solution was cooled to room temperature and mixed with ground $Na_2Ti_3O_7$. The resultant mixture was heated with stirring to 80 °C for 1 h. The quantities of the pillaring agent, water, and $Na_2Ti_3O_7$ used for the various preparations are given in Figure 2. In the successful preparations the expanded pillared titanate formed a colloidal dispersion which did not sediment rapidly from the solution. This material was separated from that which sedimented rapidly from solution at 120 °C and dried. Pillared materials were subsequently calcined at 500 °C in air.

X-ray diffractograms were collected on a Philips automatic powder diffractometer with a vertical goniometer. ^{27}Al magic-angle-spinning (MAS) NMR spectra were recorded on a Bruker MSL-400 spectrometer. Samples were spun at 5 kHz and 0.6-μs radio frequency pulses were used with a repetition time of 200 ms. The use of such short pulses is essential for the spectra to be quantitatively reliable.[11,12] Nitrogen adsorption isotherms of samples activated at 400 °C were measured with a volumetric apparatus.

Results and Discussion

The X-ray diffraction pattern of $Na_2Ti_3O_7$ is consistent with that reported previously.[9] The charge-balancing Na^+ cations are located between $(Ti_3O_7)^{2-}$ sheets in rather unusual 9-fold and 7-fold coordination. It is known that the titanate layers can be expanded by ion-exchanging Na^+ for alkylammonium cations.[13] Use of organic molecules up to C_{24} can increase the spacing of layers to as much as 45 Å. However, such expanded materials are not thermally stable and the organic component decomposes under typical conditions of catalyst activation.

Figure 3 shows the X-ray diffraction pattern after incorporation of the Keggin cations. The sharp lines indicate the presence of a degree of ordering between adjacent $Ti_3O_7^{2-}$ sheets with $b = 3.68$ Å and $c = 8.67$ Å. The broad reflections correspond to the (100) direction. Their considerable width indicates that the separation of the layers is not uniform. This is very often the case with pillared layered materials. The very broad unresolved peak at low 2θ (3–5°) probably corresponds to the (100) reflection. Other broad reflections occur at spacings of 6.33, 3.19, 2.37, and 1.86 Å and correspond to the (300), (600), (800), and (10,0,0) reflections, respectively, giving a basal plane spacing of 19.0 Å. The Keggin ion pillars are approximately 8.6 Å in diameter[10] and the $(Ti_3O_7)^{2-}$ layers are approximately 9.5 Å in width in the a direction. The width of the layers is slightly greater than the d_{100} spacing of the unpillared material (8.57 Å) because of the zigzag arrangement of the individual blocks of six titanium atoms.[9] The thickness of the layers was measured between the nearest O_3 oxygens belonging to the same layer, taking into account the fact that the pillars span a complete unit cell in the b direction. From the size of the pillars and the layer width a basal plane spacing for the pillared material is therefore 19.0 Å, as expected. This interlayer spacing did not change upon calcination of the samples. After calcination at 500 °C, the (100) and (300) reflections remain but the higher reflections diminish considerably in intensity. Figure 2 lists those preparations which resulted in a pillared material based on X-ray diffraction data. The most critical parameter for successful pillaring is the ratio of $Na_2Ti_3O_7$ to aluminum chlorohydrate. Successful pillaring occurs for the composition of 1 mol of chlorohydrate:3.0 ± 0.4 mol of $Na_2Ti_3O_4$:7000 ± 1000 mol of H_2O. Figure 4 shows the nitrogen adsorption isotherm and BET plot of both $Na_2Ti_3O_7$ and the pillared titanate after calcination at 500 °C in air followed by dehydration under vacuum at 400 °C. The surface area of the unpillared material is negligible compared with the value of 105 m^2/g measured from the BET plot for the pillared material. This indicates the stability of the pillared materials to activation at high temperatures, which is essential if they are to be useful as het-

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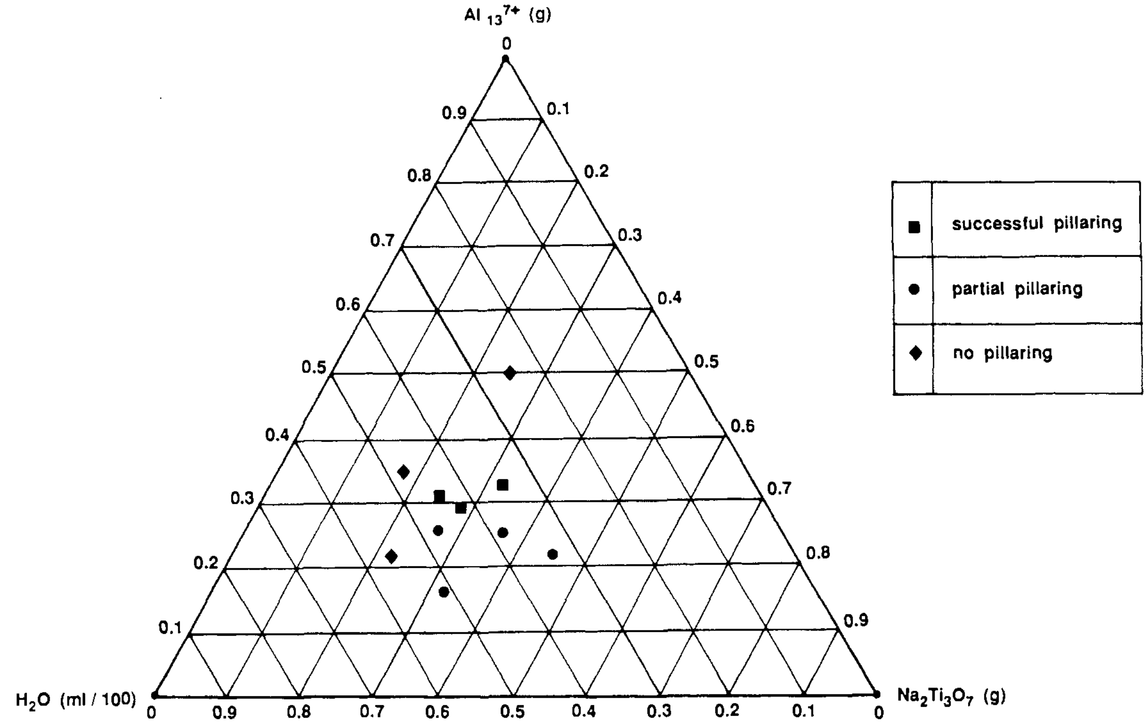

Figure 2. Composition diagram indicating relative concentrations of sodium trititanate, pillaring agent, and water.

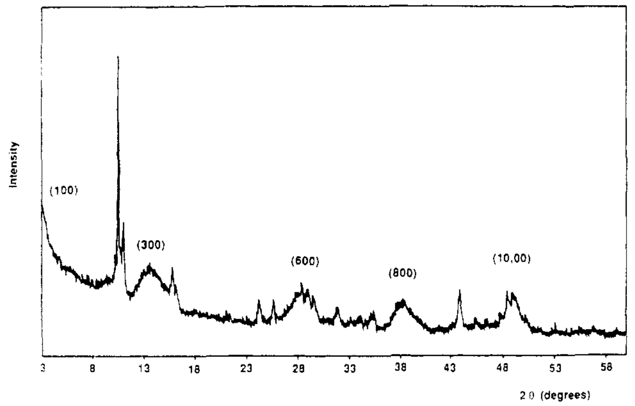

Figure 3. X-ray diffractogram of a successfully pillared material, as prepared.

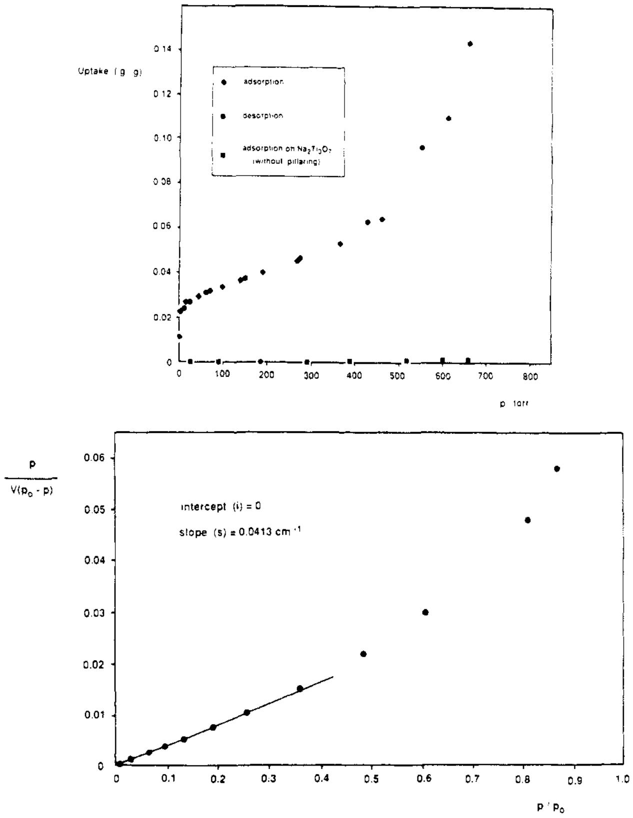

Figure 4. (a) Nitrogen adsorption isotherm and (b) BET plot for pillared sodium trititanate recorded at 196 °C.

erogeneous catalysts. The onset of hysteresis in the adsorption isotherm at $p/p_0 \sim 0.6$ indicates the presence of pores of diameter larger than 17 Å, which is in good agreement with X-ray diffraction data. Such surface areas are typical of pillared titanium phosphates.[5]

Figure 5 shows the ^{27}Al MAS NMR spectrum of a pillared material before and after calcination. Before calcination, 6-coordinated (octahedral) aluminum dominates and there is only a very small amount of 4-coordinated (tetrahedral) Al. The octahedral-to-tetrahedral ratio is 11.7:1, very close to that expected for the cation composed of 12 octahedral and 1 tetrahedral Al atoms. It is interesting that the signal from the octahedral aluminum atoms is readily observed in the solid state although it is absent from the spectra of the Keggin ion in solution.[14-16] The reason for this is that the large quadrupolar interaction of the ^{27}Al nucleus leads to very rapid nuclear relaxation, which in turn broadens NMR signals via the lifetime-broadening mechanism. For instrumental reasons, broad signals from solutions cannot be observed in the presence of much narrower resonances.

It is interesting to note that the tetrahedral signal in the spectrum in Figure 5b has no spinning sidebands, which indicates that, as a result of its inherent symmetry, the central tetrahedral aluminum atom in the calcined pillared titanate is subject to small quadrupole interactions. By contrast, the signal from octahedral aluminum displays considerable spinning sidebands, reflecting the lower symmetry of the site. After calcination at 500 °C, the octahedral-to-tetrahedral ratio is 1.44:1 and the octahedral signal

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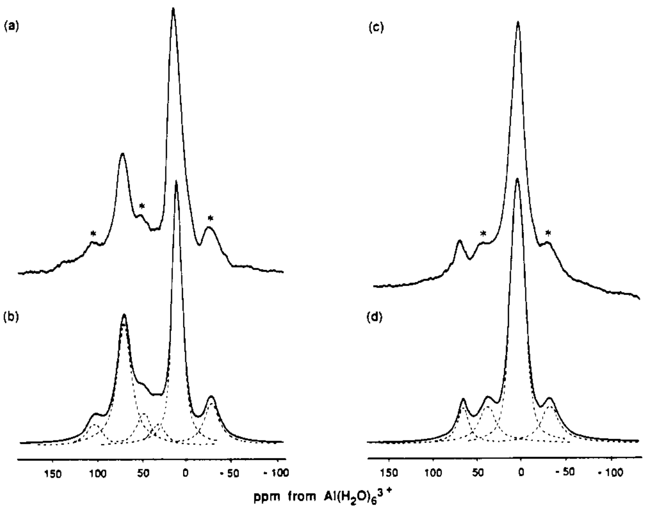

Figure 5. ^{27}Al MAS NMR spectra of pillared sodium trititanate: (a) As-prepared sample; (b) sample calcined at 500 °C. Asterisks denote spinning sidebands. The actual spectra are given above with their deconvolution given below.

has associated spinning sidebands, indicating the lowering of site symmetry. The spectrum is now identical with that of γ-alumina in every respect: chemical shift of the two species; octahedral-to-tetrahedral intensity ratio for aluminum; line-shape and sideband patterns.[17-19] We conclude that the Keggin ion pillars have become completely dehydrated to give alumina pillars according to the reaction[4]

$$n[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{(7-x)+} \rightarrow 6.5nAl_2O_3 + (7-x)H^+$$

Brønsted acidity is thus generated in the same way as is found in pillared smectite clays. The ^{27}Al MAS NMR spectra after calcination are very similar to those of pillared laponite.[20] The layered titanate structure expands to produce a microporous, thermally stable molecular sieve. The material offers potential as a shape-selective catalyst for selective NO_x processing and other important reactions. The structures of a number of layered oxides are similar to that of sodium tritanate, and they may therefore be amenable to permanent expansion.

Acknowledgment. We are grateful to Shell Research, Amsterdam, for support.

Registry No. $Na_2Ti_3O_7$, 12034-36-5; aluminum chlorohydrate, 1327-41-9; nitrogen, 7727-37-9.

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Chromatographic Separation and Characterization of Linkage Isomers of the 3-(Pyridin-2-yl)-1*H*-1,2,4-triazole Complex of Ruthenium(II) Bis(2,2′-bipyridyl)

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We are at present engaged in the investigation of the effect of the asymmetry of the ligands on the physical properties of ruthenium complexes containing ligands derived from 3-(pyridin-2-yl)-1*H*-1,2,4-triazole (HL1) (see Figure 1a).[2] Of particular interest are dinuclear compounds containing as the bridging ligand the anion of 3,5-bis(pyridin-2-yl)-1,2,4-triazole (HL2) (Figure 1b) because, contrary to most of the previously used polypyridyl bridges, this ligand carries a negative charge and combines low π-acceptor ability with strong σ-donor properties.[3] In the dinuclear complexes the coordination of the $M(bpy)_2$ units is taking place at two different coordination sites. In addition to the pyridine ring the central triazole ring binds one metal center through N^2 and the other one through N^4. At present nothing is known about the coordinative differences between these two coordination sites. From Figure 1a it can be seen that two linkage isomers are possible for the compound $[Ru(bpy)_2(HL1)]^{2+}$, involving either coordination of the N^2 or the N^4 atom of the triazole ring. These isomers are, therefore, good model compounds for the investigation of the two coordination sites in HL2. In this contribution the separation of these isomers by semipreparative high-performance liquid chromatography (HPLC) is reported. They have been characterized by using NMR techniques, and their physical properties are reported. The relevance of the results obtained for the properties of the above-mentioned type of dinuclear compounds is discussed.

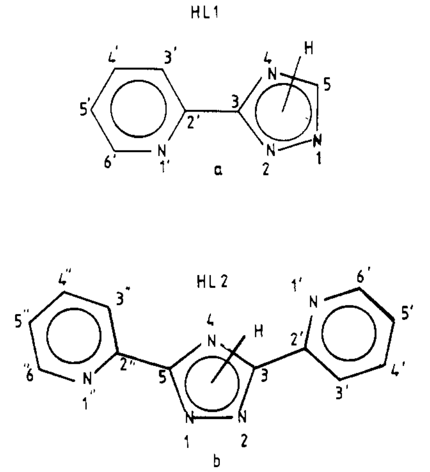

Figure 1. Structural formulas: (a) 3-(pyridin-2-yl)-1,2,4-triazole (HL1); (b) 3,5-bis(pyridin-2-yl)-1,2,4-triazole (HL2).

Experimental Section

An isomer mixture of $[Ru(bpy)_2(HL1)](PF_6)_2$ was prepared as reported in the literature.[2a] All solvents were of HPLC grade and used as received.

UV-visible spectra were recorded on a Shimadzu UV-240 spectrophotometer using matched 1-cm cells. Molar extinction coefficients are accurate up to 5%. Emission spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrometer, equipped with a red-sensitive Hamamatsu R928 detector, using an emission slit width of 10 nm at room temperature and of 2.5 nm at 77 K and are not corrected for photomultiplier response. Electrochemical measurements were carried out by using an EG&G Par Model 174A polarographic analyzer with an EG&G Par 175 universal programmer. A saturated potassium calomel electrode (SCE) was used as a reference electrode. Cyclic voltammetry was carried out in Analar grade acetonitrile dried over molecular sieves, with 0.1 mol/L NEt_4ClO_4 as a supporting electrolyte, a glassy-carbon working electrode, and a scan rate of 100 mV/s. Preparative HPLC was carried out with a HPLC Technology RR 066 pump, adapted for semipreparative chromatography, together with an adapted ACS UV/VIS detector, a 1-cm³ injector loop, and a Whatman Magnum 9 SCX 10-μm column. The mobile phase used was 80:20 acetonitrile/water containing 0.08 mol/L $LiClO_4$, with a flow rate of 5 mL/min and a detection

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