The results presented here also indicate that high-resolution techniques are not able to give information on the sites identified by CP/MAS NMR, as there is no, or very slow, exchange between these species and the more mobile species visible to the high-resolution NMR experiment even in samples loaded to maximum capacity with pyridine. One reason may be the very large shielding anisotropy of ^{15}N in pyridine,[10] so that any slow anisotropic motions of the adsorbed molecules lead to severe line broadening.

Registry No. ^{15}N, 14390-96-6; Al_2O_3, 1344-28-1; mordenite, 12173-98-7; pyridine, 110-86-1.

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(10) The shielding tensor for ^{15}N in solid pyridine has been reported to be $\sigma_{xx} = -313$, $\sigma_{yy} = -94$, and $\sigma_{zz} = 469$ ppm: D. Schweitzer, H. W. Spiess, *J. Magn. Reson.*, **15**, 529 (1974). Preliminary measurements indicate that the Brønsted acid pyridine-^{15}N site in the mordenite sample has an axially symmetric shielding tensor with $\Delta\sigma \sim 270$ ppm.

A New Class of σ-Bonded Aliphatic Aza-Macrocyclic Complexes of Transition Metals: Synthesis and X-ray Crystal Structures of Nitrogen-Bridged $[(TiN_4C_{12}H_{24})_2]$ and Oxo-Bridged $[(N_4C_{12}H_{25})TiOTi(N_4C_{12}H_{25})]$[†]

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Transition-metal complexes having aliphatic macrocyclic ligands with several nitrogen donor atoms have been intensively investigated over the past 20 years.[1] In the saturated macrocyclic ligands the ring nitrogens are usually secondary, and two types of metal–nitrogen bonding are possible. These are (a) each nitrogen behaves as a classical two-electron donor, exemplified by $M \leftarrow :N(H)<$, resulting in the formation of an amine complex or (b) each nitrogen σ-bonds to the metal, as shown by $M-\ddot{N}<$, giving an amide complex. Only complexes of type a have been reported in the literature. During the course of our attempts to induce unusual early-transition-metal geometries with these macrocycles, we have isolated the first examples of type b complexes. These are (i) the dimeric d^0 titanium(IV) derivative of 1,5,9,13-tetraazacyclohexadecane $[(TiN_4C_{12}H_{24})_2]$ (**1**), and (ii) the μ-oxo-bridged species formed via the reaction of **1** with water, $[O(TiN_4C_{12}H_{25})_2]$ (**2**).

Compounds **1** and **2** were synthesized in good yield by Scheme I.

The structures of **1**[2a] and **2**[2b] possess several unique features and are illustrated in Figures 1 and 2. For **1** the X-ray crystal structure is the first reported for a homoleptic titanium(IV) dialkylamide. The geometry at Ti is distorted trigonal bipyramidal and a rare example of five-coordinate Ti(IV).[3] The terminal nitrogens, N(2), N(3), and N(4), possess near-planar geometry, and the average Ti–N distance, 1.94 Å, is close to the value found in other Ti(IV) amides.[4] The Ti–N bonds involved in bridging have the longer values of 2.191 (2) Å for Ti–N(1) and 2.147 (2) Å for Ti–N(1)′. The Ti···Ti distance, 3.380 (1) Å, precludes significant metal–metal interactions. The dimeric structure is similar to that proposed by Richman for the strained cyclic 12- and 13-membered ring systems PN_4^+ on the basis of ^{31}P and ^{13}C NMR spectroscopy.[5,6] In the phosphorus system dimerization is seen only if the geometry is constrained by ring size. Monomeric species are obtained if the size of the ring is increased to a 16-membered ring for phosphorus. The dimerization seen in **1** probably reflects the relatively larger size of titanium.

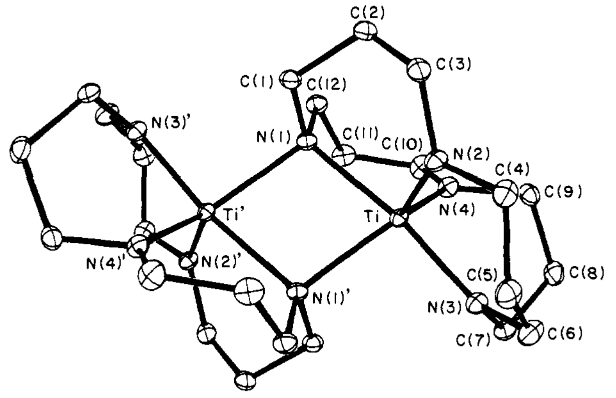


Figure 1. Computer-generated representative diagram of $[(TiN_4C_{12}H_{24})_2]$, **1**. Important bond distances (Å) and angles (deg) are Ti–N(1) = 2.191 (2), Ti–N(2) = 1.928 (2), Ti–N(3) = 1.947 (2), Ti–N(4) = 1.943 (3), Ti–N(1)′ = 2.147 (2); N(1)–Ti–N(3) = 167.1 (1), N(2)–Ti–N(4) = 115.3 (1), N(1)′–Ti–N(2) = 115.3 (1), N(1)′–Ti–N(4) = 128.6 (1), Ti′–N(1)–Ti = 102.4 (1), and N(1)–Ti–N(1)′ = 77.6 (1).

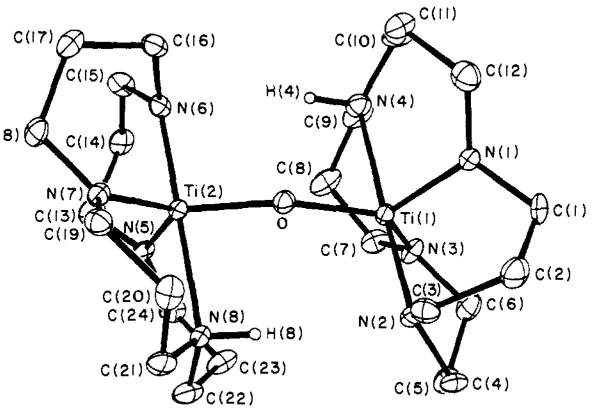
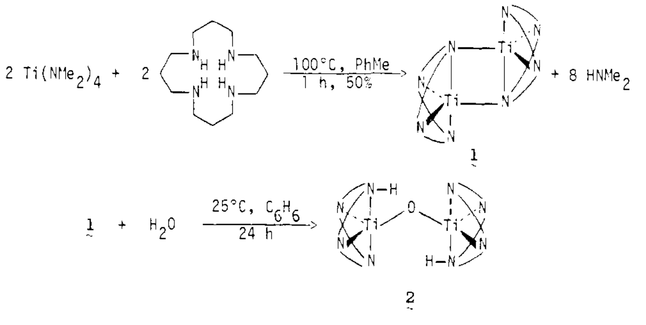


Figure 2. Computer-generated representative diagram of $[O(TiN_4C_{12}H_{25})_2]$, **2**. Important bond distances (Å) and angles (deg) are Ti(1)–N(1) = 1.942 (4), Ti(1)–N(2) = 1.962 (4), Ti(1)–N(3) = 1.941 (4), Ti(1)–N(4) = 2.283 (4), Ti(1)–O = 1.838 (3); Ti(1)–O–Ti(2) = 152.0 (2), N(1)–Ti(1)–N(3) = 117.4 (2), N(2)–Ti(1)–N(4) = 178.7 (1), N(1)–Ti(1)–O = 114.4 (1), and N(3)–Ti(1)–O = 126.7 (2). The angles and distances surrounding Ti(2) are similar to those above.

Scheme I



[†] No reprints available.

(1) Melson, G. A. "Coordination Chemistry of Macrocyclic Compounds"; Plenum Press: New York, 1979. Izatt, R. M.; Christensen, J. J. "Synthetic Multidentate Macrocyclic Compounds"; Academic Press: New York, 1978.

(2) (a) Crystal data for **1** at 140 K with Mo Kα radiation (λ 0.71069 Å): triclinic, $P\bar{1}$ (no. 2); $a = 8.500$ (2) Å, $b = 9.282$ (2) Å, $c = 9.312$ (3) Å; $\alpha = 98.45$ (2)°, $\beta = 115.69$ (2)°, $\gamma = 90.95$ (2)°; $Z = 1$; $\mu = 6.33$ cm^{-1}; 2552 unique observed data, 250 parameters; $R = 0.044$. (b) **2**: triclinic, $P\bar{1}$, (no. 2); $a = 9.435$ (2) Å, $b = 11.280$ (3) Å, $c = 14.036$ (3) Å; $\alpha = 84.88$ (2)°, $\beta = 84.22$ (2)°, $\gamma = 69.69$ (2)°; $Z = 2$; $\mu = 5.98$ cm^{-1}, 3826 unique observed data, 324 parameters; $R = 0.059$.

(3) Dwyer, P. D.; Puppe, L.; Bushler, J. W.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 1782–1786.

(4) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Horwood-Wiley: Chichester, 1978.

(5) Richman, J. E.; Gupta, O. D.; Flay, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1291–1292.

(6) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955–3956.

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The structure of **2** is also unique in several respects. The most outstanding feature is the μ-oxo structure in which an oxygen atom bridges two titanium(IV) atoms. Although a few similar complexes are known,[7] **2** has by far the lowest Ti–O–Ti angle, 152.0 (2)°. The low angle suggests reduced Ti–O π-bonding, and this view is supported by the greater Ti–O bond lengths (average 1.84 Å), which are about midway between the predicted Ti–O single-bond length, 1.9 Å, and the values (ca. 1.79 Å) in most of the linear Ti–O–Ti moieties.[7] The geometry at titanium is close to trigonal bipyramidal, and the titanium amido nitrogen distances average 1.94 Å as in **1**. The Ti(1)–N(4) and Ti(2)–N(8) distances are unique, having the fairly long values of 2.283 (4) and 2.300 (4) Å. The hydrogen atoms on N(4) and N(8) are illustrated in Figure 2. They both display a weak interaction with the central oxygen atom; O···H(4) = 2.37 (2) Å and O···H(8) = 2.33 (2) Å.

The ^{1}H NMR (90 MHz) spectra of both **1** and **2** in C_6H_6 (27 °C) are complex. For **1**, the spectrum consists of two multiplets at δ 3.3 ($N-CH_2$) and 2.0 ($C-CH_2-C$) in a 2:1 ratio; for **2** the multiplets are centered at δ 3.4, 3.1, ($N-CH_2$) and 1.95 ($C-CH_2-C$). In the IR spectrum (Nujol) of **2**, the band at 720 cm^{-1} has been assigned to the Ti–O stretch. The lower position[7] of the band is consistent with the weaker nature of the Ti–O bond.

Studies of related systems involving vanadium and molybdenum with macrocycles of various ring sizes and their reactions are in progress.

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Supplementary Material Available: List of atom coordinates, temperature factors, bond distances and angles, and experimental details (4 pages). Ordering information is given on any current masthead page.

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(7) (a) [$(TiCl_2Et)_2O$], Ti–O–Ti = 180°, Ti–O = 1.78 (3) Å: Corradini, P.; Alligra, G. *J. Am. Chem. Soc.* **1959**, *81*, 5511–5514. (b) [$\{TiCl(C_5H_7O_2)_2\}O$]·$CHCl_3$, Ti–O–Ti = 167.3 (5)°, Ti–O = 1.79 (2) Å; Watenpaugh, K.; Caughlin, C. N. *Inorg. Chem.* **1967**, *6*, 963–967. (c) $K_2[Ti_2O_5(C_7H_3O_4N)_2]$, Ti–O–Ti = 178.1 (8)°, Ti–O = 1.805 (2) Å: Schwartzenbach, D. *Ibid.* **1970**, *9*, 2391–2397. (d) Thewalt, U.; Schleussner, G. *Angew. Chem.* **1978**, *90*, 559–560 ([$\{Ti(\eta\text{-}C_5H_5)_2(H_2O)\}_2O$]·$S_2O_6$, Ti–O–Ti = 177.0°, Ti–O = 1.834 Å).

Absorption and Emission Characteristics of Merocyanine 540 in Microemulsions

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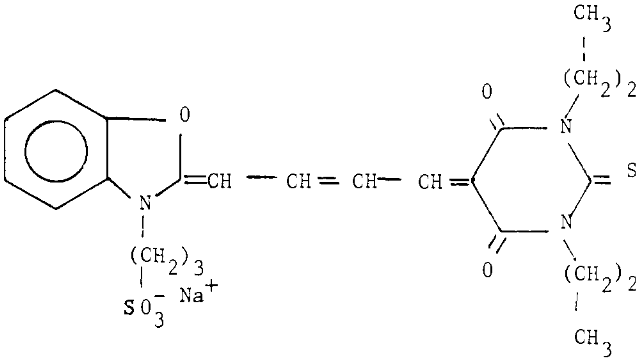
Cyanine dyes are heterocyclic chromophores that are extensively used in a number of areas. For example, they are used as photographic sensitizers, in photographic filter layers, for textiles, and in chemotherapy.[1] Recently they have also been examined as possible candidates for solar energy conversion in the form of monolayers and thin films on glass substrates.[2-4] The efficiency of the cyanine dyes as photosensitizers depends upon their emission properties and also on their photostability. Unfortunately, it is commonly observed that the cyanine dyes with a polymethine chain in the molecular framework degrade in light. In a recent communication, Humphrey-Baker et al.[5] have shown that both the fluorescence yield and photostability of a cyanine dye are significantly enhanced in anionic micellar solution, and they have attributed it to a microviscosity effect. We report here on the absorption and fluorescence properties of merocyanine 540 in anionic and cationic microemulsion. Measurements have also been performed in water, ethanol, 1-pentanol, and aqueous micellar solutions to serve as a basis of comparison.

Table I. Absorption Maxima and Solubility of Merocyanine 540 in Various Media at Room Temperature[a]

medium	λ_{max}, nm	10^{-5}, M^{-1} cm^{-1}	solubility, mM (±3%)
H_2O	533	0.47	0.08
ethanol	559	1.38	4.00
SDS (84 mM)	558	1.02	6.20
60% SCS microemulsion	560	1.21	>10.00
1-pentanol	562	1.28	0.20
50% 1-pentanol + 50% mineral oil	564	0.40	
80% mineral oil + 20% 1-pentanol	566	0.22	
benzene	567	0.32	

[a] All spectra were recorded at 1.76 μM dye concentration.



merocyanine 540

Merocyanine 540 (Eastman) was recrystallized twice from anhydrous ethanol. Aqueous (60% water) sodium cetyl sulfate (SCS) and cetyltrimethylammonium bromide (CTAB) microemulsions were prepared as previously described.[6] Sodium dodecyl sulfate (SDS, Sigma) was used as received. Absorption spectra were recorded on a Perkin-Elmer 320 spectrophotometer. Steady-state fluorescence and polarization measurements were carried out on a SLM instrument equipped with a corrected spectra unit. The details of the instrument are published elsewhere.[7]

The absorption maxima (λ_{max}) along with the molar extinction coefficients (ϵ) of the dye in various solvents are summarized in Table I. Two points are immediately evident from these results. First, λ_{max} is considerably red shifted (ca. 30 nm) in microemulsion, ethanol, and SDS micellar solution. Second, the band intensities are higher by a factor of 2 in these media compared to water. The large shift in λ_{max} to longer wavelength in organized media may be attributed to the decrease in the polarity experienced by the dye molecules, comparable to that of ethanol.

The spectrum in water changes with the dye's concentration. The absorption ratio (A_{533}/A_{501}) decreases as the dye concentration increases. This is common behavior of dyes undergoing aggregation.[8] The low- and high-energy bands are assignable respectively to electronic transitions of monomeric and dimeric dye. Thus, the lower value of the extinction coefficient at λ 533 nm in water is due to dye aggregation, which is extensive even at 1 μM. At this concentration, little if any aggregation is occurring in the other media. For example, the dye obeys Beer's law at

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(1) F. M. Hamer, "The Chemistry of Heterocyclic Compounds. The Cyanine Dyes and Related Compounds", Interscience, New York, 1963, p 816.

(2) W. Arden and P. Fromherz, *Ber. Bunsenges. Phys. Chem.*, **82**, 868 (1978).

(3) W. Arden and P. Fromherz, *J. Electrochem. Soc.*, **127**, 372 (1980).

(4) O. Inacker, H. Kuhn, D. Möbius, and G. Debuch, *Z. Phys. Chem.*, **101**, 337 (1976).

(5) R. Humphrey-Baker, M. Gratzel, and R. Steiger, *J. Am. Chem. Soc.*, **102**, 847 (1980).

(6) C. E. Jones, L. E. Weaner, and R. A. Mackay, *J. Phys. Chem.*, **84**, 1495 (1980).

(7) J. M. Vanderkooi, P. Glatz, J. Casadei, and G. V. Woodrow, III, *Eur. J. Biochem.* **110**, 189 (1980).

(8) A. H. Herz, *Adv. Colloid Interface Sci.*, **8**, 237 (1977).

0002-7863/83/1505-2928$01.50/0