contained in a two-necked, 250-mL round-bottomed flask. Immediate exothermic reaction produced a thick, crusty slurry that had to be mechanically broken at intervals during 2 h of stirring. After a period of reflux for 2 h, the reaction mixture was cooled and excess hydride destroyed by addition of 20 mL of 2-propanol followed by 25 mL of water. The voluminous solid was separated by vacuum filtration and the filtrate concentrated to 50 mL under vacuum. The solid was stirred with 250 mL of water and the 50 mL of filtrate in an open beaker by using a magnetic stirring bar. After 12 h of stirring, the solid was separated from the mixture by vacuum filtration and discarded. The filtrate was reduced under vacuum to 50 mL in a film evaporator and treated with 2.5 g (7 mmol) of triphenylmethylphosphonium bromide. The resulting precipitate of $Ph_3PCH_3^+$ salt was dried under vacuum and metathesized to the cesium salt by stirring in 25 mL of methanol containing 1.5 g (10 mmol) of CsF. The resulting solid was collected by filtration and dried to give 1.3 g (95%) of $Cs_2B_{12}H_{10}(CH_2OH)_2$.

$B_{12}H_{10}(CH_2I)_2^{2-}$. $Cs_2B_{12}H_{10}(CH_2OH)_2$ was stirred in 57% aqueous HI (in proportion of 10 mL/g of cesium salt) under nitrogen in a closed vessel in the dark for 8 h. The mixture was evaporated to dryness on a vacuum line. The residue was stirred with a small portion of aqueous CsF solution, filtered out, washed with small portion of water, and dried under high vacuum. The product showed no trace of the intense OH absorption in the infrared spectrum. A small sample was converted back to the original hydroxymethyl derivative by stirring with 10% aqueous sodium hydroxide for 1 h at 80 °C.

$B_{12}H_{10}(CH_2SCN)_2^{2-}$. $Cs_2B_{12}H_{10}(CH_2I)_2$, 98 mg (0.14 mmol), and 0.80 g (8.2 mmol) of potassium thiocyanate were heated into solution at 80 °C for 2 h. Crystals collected on cooling to room temperature and the crops collected by addition of 0.5 g of CsF and cooling to −22 °C were combined and recrystallized from hot water; 33 mg, 30% yield.

$B_{12}H_{10}(CH_2N_3)_2^{2-}$ was prepared in a similar way using sodium azide, and the product was identified by the strong infrared absorption characteristic of azide at 2103 cm^{-1}. Deviation of nitrogen analysis appears to be a problem of analysis (vide infra) rather than one of identification of product.

$B_{12}H_{10}(CH_2N(Me_2H)_2/B_{12}H_{10}(CH_2Nuc)_2$. $Cs_2B_{12}H_{10}(CH_2I)_2$, 0.55 g (0.80 mmol), and Me_2NH (20 mmol) were allowed to mix with continuous stirring (magnetic bar) in a sealed ampule at room temperature for 2 h. Evaporation of volatiles under vacuum left a residue, which was washed in water and recrystallized from hot acetonitrile; 0.13 g, 63% yield. In similar ways or with acetonitrile or methanol solvents, other nucleophilic displacements were carried out with PPh_3, PMe_3, and NH_3. These products analyzed low for carbon and hydrogen because of analytical difficulties investigated in some detail for the dimethylamine derivative:

		anal., %		
		C	H	N
calcd for $B_{12}H_{10}(CH_2NMe_2H)_2$		27.9	10.9	10.8
found	lab A	19.7	8.0	6.3
	lab A with V_2O_5	35.7	8.5	7.8
	lab A with V_2O_5/WO_3	21.3	8.4	6.0
	lab B	24.5	10.2	11.3
	lab C	27.8	11.2	10.6

$B_{12}H_{10}(CH_2NMe_2Y)_2$. $B_{12}H_{10}(CH_2NMe_2H)_2$, 68 mg (0.26 mmol), was stirred with 10 mL of THF at −78 °C while 5.6 mmol of *n*-butyllithium in hexane was added. The amount of insoluble material markedly decreased, and the mixture took on a yellow coloration. No attempt was made to isolate the presumed intermediate $B_{12}H_{10}(CH_2NMe_2)_2^{2-}$ salt. Addition of 0.3 mL of ethyl chloroformate and warming to 45 °C dissipated the color and produced a white solid. Collection of the solid by filtration, washing with ether and then water, and recrystallization from hot acetonitrile gave 85 mg (89%) of $B_{12}H_{10}(CH_2NMe_2CO_2Et)_2$. Treatment of the lithium salt with ethyl chloroacetate gave 32% $B_{12}H_{10}(CH_2NMe_2CH_2CO_2Et)_2$, and treatment with ethyl 2-bromopropionate gave 61% $B_{12}H_{10}[CH_2NMe_2C(CH_3)HCO_2Et]_2$. When the lithium salt was treated with methyl iodide, the product was identical by infrared analysis with that obtained from the iodomethyl derivative and trimethylamine, supporting assignment as $B_{12}H_{10}(CH_2NMe_3)_2$.

For only two compounds was the limited solubility in common solvents sufficient for proton magnetic resonance. A doublet PCH_3 peak at 1.69 ppm (J = 15 Hz) was observed for $B_{12}H_{10}[CH_2P(CH_3)_3]_2$ in dimethyl-d_6 sulfoxide. The four resonances observed for $B_{12}H_{10}[CH_2NMe_2C(CH_3)HCO_2Et]_2$ were assigned: 0.99 ppm triplet (J = 7 Hz) and 3.96 ppm quartet (J = 7 Hz) for ethyl; 1.22 ppm doublet (J = 7 Hz) for CCH_3; 2.82 ppm doublet (J = 6 Hz) for $N(CH_3)_2$.

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Registry No. 1,12-$B_{12}H_{10}(CO)_2$, 12541-42-3; $Cs_2B_{12}H_{10}(CH_2OH)_2$, 104375-56-6; $Cs_2B_{12}H_{10}(CH_2I)_2$, 104393-04-6; $Cs_2B_{12}H_{10}(CH_2SCN)_2$, 104375-57-7; $Cs_2B_{12}H_{10}(CH_2N_3)_2$, 104375-58-8; $B_{12}H_{10}[CH_2N(CH_3)_2H]_2$, 104375-59-9; $B_{12}H_{10}[CH_2N(CH_3)_2CO_2C_2H_5]_2$, 104375-60-2; $B_{12}H_{10}[CH_2N(CH_3)_2CO_2C_2H_5]_2$, 104375-61-3; $B_{12}H_{10}[CH_2N(CH_3)_2C(CH_3)HCO_2C_2H_5]_2$, 104375-62-4; $B_{12}H_{10}[CH_2N(CH_3)_3]_2$, 104375-63-5; $B_{12}H_{10}[CH_2P(CH_3)_3]_2$, 104375-64-6.

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Use of Infrared Spectroscopy To Study Incorporation of Trivalent Elements into Molecular Sieve Gels

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Numerous factors are critical for crystallization of the zeolite molecular sieve materials but an additional factor results from the differing behavior of the aluminum-replacing or silicon-replacing elements under conditions necessary for crystallization of non-aluminosilicate molecular sieves.[1,2] We have applied infrared spectroscopy to the examination of the gels used in crystallizing these non-zeolite materials. Gels containing iron and gallium in place of aluminum were investigated in order to determine the conditions necessary for successful incorporation of these elements into the gel before further attempting to crystallize a specific molecular sieve structure. The region between 500 and 900 cm^{-1}, associated with the symmetric stretching vibrations of the Si–O–Si and Si–O–T groups, was monitored in these studies. T denotes the trivalent elements, aluminum, gallium, or iron. These stretching vibrations are sensitive to metal incorporation.[3]

Shown in Figure 1 are the infrared spectra of metallosilicate gels where successful incorporation of the elements gallium and iron was obtained. The Si–O–T symmetric stretching vibration (B in Figure 1) occurs at a position consistent with the difference in mass of these two elements. The Si–O–Fe symmetric stretching vibration (Figure 1b) appears at 656 cm^{-1} and the Si–O–Ga vibration (Figure 1c) appears at 611 cm^{-1} in these gels. In comparison, for the aluminosilicate gel (Figure 1a), a broad band appears around 730 cm^{-1}. The Si–O–Si and Si–O–Al vibrations in the aluminosilicate gel are thought to mix due to the similar mass of silicon and aluminum.[3] The vibration due to the Si–O–Si oscillator for the ferri- and gallosilicate gels occurs near 770 cm^{-1}, separate from the Si–O–T vibration since the T atom for these two gels are significantly different in mass relative to silicon.

The success of this technique in identifying the correct conditions of metal incorporation for non-zeolite molecular sieve crystallization is confirmed through the successful crystallization of these gels. A new molecular sieve ferrisilicate with the sodalite structure was prepared from the gel whose infrared spectrum in shown in Figure 1b. This is described elsewhere.[4] The infrared symmetric stretching vibrations of this crystalline material are identical with that of the gel shown in the figure. The presence of the Si–O–Si vibration is observed in both the gel and the final crystalline phase as a silica-rich ferrisilicate analogue of sodalite was prepared. The SiO_2/Fe_2O_3 ratios for the gel and crystalline phase are 13 and 11, respectively, indicating that all of the iron is incorporated into the structure.

We have also used infrared spectroscopy to observe changes that occur upon aging a metallosilicate gel. Figure 2 shows the

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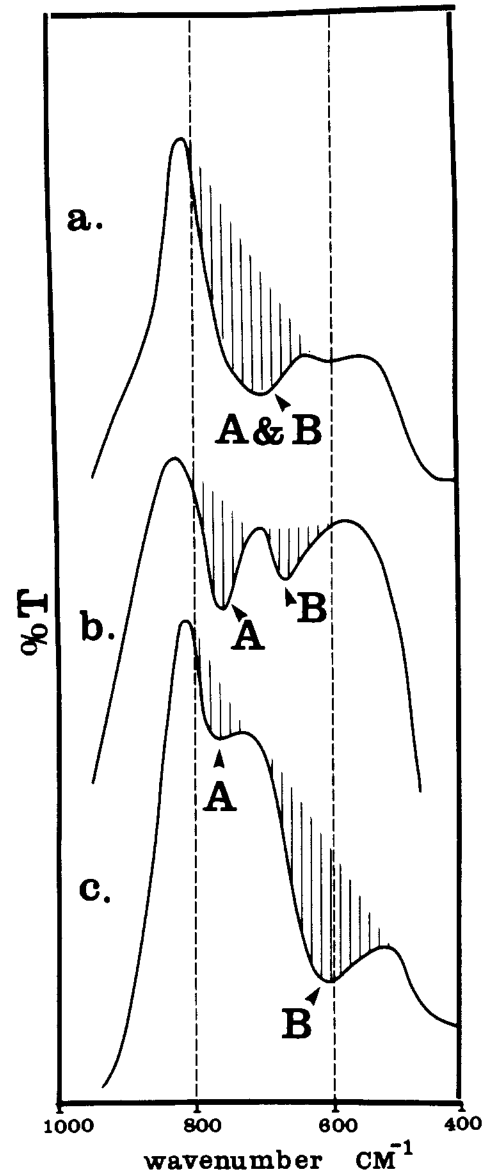

Figure 1. Comparison of the symmetric stretching vibration region of the infrared spectra of three metallosilicate gels showing successful incorporation of the metal into the silicate function: (a) aluminosilicate, (b) ferrisilicate, (c) gallosilicate. A refers to the Si–O–Si symmetric stretching vibration; B refers to the Si–O–T symmetric stretching vibration. The shift in B between parts b and c is consistent with the difference in the reduced mass of the two trivalent elements. Si–O–Si and Si–O–Al are indistinguishable for the aluminosilicate gel in part a.

formation of the Si–O–Ga linkage as a function of time when the colloidal silica Ludox (Du Pont Corp.) is used as a source of silica in this preparation. It is understandable that incorporation of the trivalent element would be slow due to the presence of small 150-Å beads of polymeric silica composing the colloidal material. A disruption of the Si–O–Si linkages must occur before incorporation of the trivalent element into the silica polymer. Initially, when Ludox is used as the source of silica only the Si–O–Si linkage is observed at 800 cm^{-1} in the symmetric stretching vibration region. This is shown in Figure 2a. No band associated with the formation of Si–O–Ga linkages appears. With time, 1–5 h, as the gallium begins to incorporate into the silica polymer, it is observed in the infrared spectrum as a formation and growth in intensity of the Si–O–Ga band at 611 cm^{-1}. This is shown in Figure 2b. A small shift in the Si–O–Si vibration to lower wavenumber is seen as the Si–O–Ga vibration appears.

It is anticipated that infrared spectroscopy may prove to be a powerful tool to assist in determining the range of metals that may complex with silica and ultimately form crystalline molecular sieve structures. In addition, the use of these elements as labels may provide insight into the understanding of the gel phase of molecular sieve synthesis.

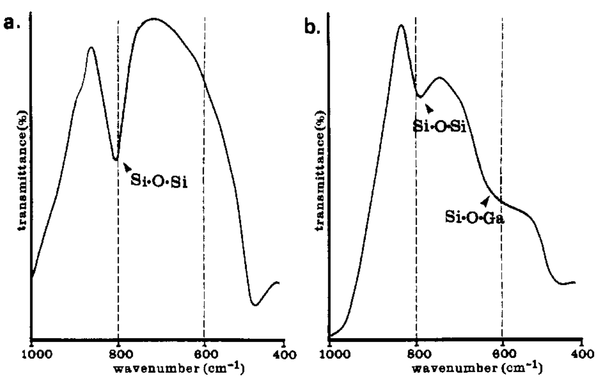

Figure 2. Incorporation of the trivalent gallium ion into the silicate fragment as a function of time followed by using the symmetric stretching vibration region of the infrared spectrum. (a) Initially, when Ludox is used as a source of silica no Si–O–Ga vibration is observed. (b) With time, 1–5 h, the band associated with the Si–O–Ga vibration appears.

Experimental Procedure

Gels were prepared by addition of the acidified (6.1 g of H_2SO_4) Al^{3+}, Fe^{3+}, and Ga^{3+} ions prepared from the corresponding nitrate (ca. 3 g $M(NO_3)_3 \cdot xH_2O$ (M = Al, Fe, Ga) in 25 g of H_2O) to a water solution of sodium metasilicate (24 g of $Na_2SiO_3 \cdot H_2O$ in 25 g of H_2O). The solid gel was separated from the liquid by filtration, washed with water, and dried at 50 °C. Preparation of samples for IR studies is described in ref 3.

Registry No. $Al(NO_3)_3$, 13473-90-0; $Fe(NO_3)_3$, 10421-48-4; $Ga(NO_3)_3$, 13494-90-1; silica, 7631-86-9; sodium metasilicate, 6834-92-0; sodium aluminosilicate, 1344-00-9; sodium ferrisilicate, 51142-60-0; sodium gallosilicate, 104619-11-6.

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First Synthesis of a Nitro Complex of Ruthenium(III), as a Key Intermediate in the Oxidation of Nitro Ligand To Give both Nitrosyl and Nitrato Ligands

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Recent investigations of the nitrosyl ligand coordinated to a transition metal have revealed a variety of interesting reactions.[1] For example, the oxidation of *cis*-$[RuCl(NO)(bpy)_2]^{2+}$ gives the corresponding nitrato complex via a reactive nitro complex of Ru(III).[2] We recently reported that the oxidation of *trans*-$[RuCl(NO)(py)_4]^{2+}$, under basic conditions, gave an oxo complex of Ru(IV), *trans*-$[RuCl(O)(py)_4]^{+}$, the first example of this type of complex.[3] If the same oxidation procedure is applied to *cis*-$[RuCl(NO)(bpy)_2]^{2+}$, the nitro complex of Ru(III), $[RuCl(NO_2)(bpy)_2]^{+}$, which can be regarded as a key intermediate for the preparation of the nitrato complex of Ru(III), was obtained as a black crystalline material. Isolation of the nitro complex of

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