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The Encapsulation of Rh(III) Phthalocyanines in Zeolites X and Y

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Abstract. The template syntheses of rhodium(III) phthalocyanine complexes within the supercage structures of zeolites X and Y are reported. These ship-in-a-bottle compounds are characterized by elemental analysis, UV-Vis, IR, XRD and X-ray photoelectron spectroscopy. The effect of temperature on the encapsulation process is also discussed.

Key words. Zeolites, phthalocyanines, rhodium.

1. Introduction

The reactivity of metal chelate complexes encapsulated in the supercage structures of synthetic faujasite type zeolites X and Y has resulted in these materials being termed *inorganic proteins* [1]. Metal complexes simply entrapped in the zeolite are expected to retain much of their solution chemistry. Coupling the physical properties of the zeolite, especially shape selectivity, with reactivity of the metal complex has resulted in enzyme mimetic chemistry. The metal complex must be small enough to be prepared in the supercage (12 Å) but large enough to prevent escape through the 7.4 Å apertures. There have been basically two approaches to the preparation of these *ship-in-a-bottle* chelate complexes, namely a flexible ligand or a template synthesis. A flexible ligand must be able to diffuse freely through the zeolite pores but upon complexation with a metal ion the complex becomes too large to escape the cage. We have recently reported the encapsulation of a Rh(III) Schiff base complex utilizing this approach [2]. The template synthesis is exemplified by the preparation of intrazeolite metallophthalocyanines [3–11]. Four dicyanobenzenes must diffuse into the zeolite where they can condense around a metal ion to form the tetradentate macrocycle which is much too large to exit (Scheme 1). Herein we report the synthesis and characterization of rhodium phthalocyanine complexes encapsulated in X and Y type zeolites.

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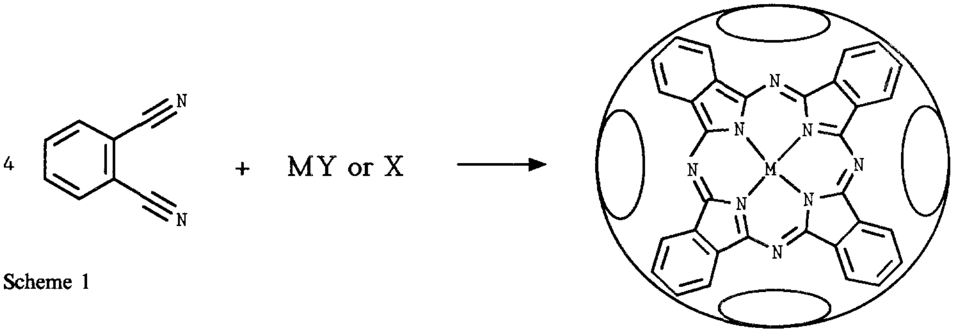

Scheme 1

2. Experimental

The zeolites were obtained from Union Carbide as the sodium forms of X and Y type faujasites (LZY-52 and 13X). Rhodium trichloride was obtained upon loan from Johnson-Matthey. All other reagents were used as received unless otherwise noted. IR samples were prepared as KBr pellets and the spectra recorded on a Nicolet 5DX FT spectrophotometer. Electronic spectra were obtained using a Varian Cary 219 spectrophotometer. The samples were prepared as Nujol mulls, pasted onto filter paper, and then taped into the beam path. Elemental analyses were performed in part by Galbraith Laboratories, Knoxville, TN. Other elemental determinations were made using a Perkin-Elmer 5000 AA spectrophotometer. X-ray powder diffraction patterns were obtained with a Scintag XDS 2000 using $\mathrm{Cu}K_{\alpha}$ radiation. Samples were analyzed from 5 to 40 degrees at $1\ \mathrm{deg\ min}^{-1}$ with a 0.01 chopper increment.

X-ray photoelectron spectroscopy was performed on a Vacuum Generator ESCALAB MKII spectrometer using $\mathrm{Al}K_{\alpha}$ radiation as the excitation source. The method of data collection, quantification, and fitting have previously been described [2]. Binding energies were normalized to a corrected value for Al of 74.0 eV with a standard deviation of ±0.2 eV.

The rhodium exchanged X and Y zeolites were prepared by slurrying the zeolites in aqueous solutions (pH of order of ~6.5) of rhodium trichloride at 80°C for 24 h. These solutions were then filtered, washed until no chloride ion was detected, and finally dried in a vacuum oven at 80°C for ~18 h. A complete description of this preparation and characterization of the rhodium exchanged zeolites has already been published [2].

The intrazeolite rhodium phthalocyanine complexes were prepared as follows. Rhodium exchanged zeolite and dicyanobenzene (w/w) were intimately mixed and placed in a 40 mL glass bomb with a small stir bar. The mixture was evacuated overnight (10^{-6} torr) at room temperature and then submerged in an oil bath at the desired temperature (150, 180 or 210°C), well above the melting point of dycyanobenzene, for 24 h. The resulting solid was Soxhlet extracted with acetone until the blue-green extractions became colorless. Then the zeolite was extracted with pyridine to remove surface species until the extractions were also colorless. XRD indicates there is no evidence of bulk Pc complexes associated with these samples. The complex-containing zeolite was dried then stirred in an aqueous NaCl solution, filtered, washed with copious amounts of deionized water, and dried in a vacuum oven at 80°C for ~ 18 h. The three different temperatures produced zeolites with a range of colors from yellow-green at 150° to blue at 210°C. The zeolites were analyzed for C, H, N, Na, Cl, Rh, and Al. The encapsulated complexes were characterized by XPS, XRD, UV-Vis and IR spectroscopy. These results for X and Y type zeolites are discussed below.

3. Results and Discussion

The condensation of dicyanobenzene to produce the aromatic phthalocyanine macrocycle is generally catalyzed by Lewis acids. However, there is no reaction between NaY and dicyanobenzene. There is also no evidence of included dicyanobenzene or Pc fragments. The rhodium exchanged NaY or X zeolites quickly produce the characteristic blue-green color of phthalocyanine complexes even at the surprisingly low temperature of 150°C. Generally, the phthalocyanine synthesis requires temperatures in the range of 200–400°C which is also typical of the synthesis conditions reported for other intrazeolite phthalocyanines. Initially, we had a well-founded concern that the exchanged rhodium would be reduced at higher temperatures so we attempted the synthesis at 150, 180 and 210°C. The melting point of dicyanobenzene is 140°C so that under the synthesis conditions at 150°C the molten DCB may diffuse into the zeolite and react with the rhodium. The two higher temperatures were explored in order to evaluate the effect of this variable on the encapsulation process.

The elemental analyses for the metal complex-containing zeolites are listed in Table I where the sample numbers, −1, −2, or −3 designate the preparation temperatures from 150 to 210°C. In general there appears to be an initial increase in the percentage of rhodium for the complexed samples compared with the exchanged zeolites followed by a decrease with increasing preparation temperature. We expect a loss in rhodium since metallophthalocyanines are formed at the surface and later extracted. Additionally a small amount of uncomplexed rhodium is reexchanged with sodium. An apparent increase in %Rh may reflect a loss in aluminum. Formation of the phthalocyanine ligand requires two reducing equivalents. If water is the source of the electrons then the acid produced might partially dealuminate the zeolite. Aluminum was detected in the extractions using AA

Table I. Elemental analysis (%wt)

Sample	Rh	Al	Na	C	N
RhNaY	2.10	8.18	6.12	–	–
RhNc·NaY-1	2.43	8.29	6.29	9.77	2.60
RhPc·NaY-2	2.31	8.13	5.81	11.27	2.83
RhPc·NaY-3	1.55	7.99	5.77	8.36	2.91
RhNaX	3.18	12.55	9.24	–	–
RhPc·NaX-1	3.31	12.31	10.61	8.34	2.36
RhPc·NaX-2	2.30	11.31	8.51	12.28	3.89
RhPc·NaX-3	1.76	12.72	9.84	9.34	3.21

Table II. Ratios of atomic percent based on Table I

Sample	Rh/C	Rh/N	N/C	Rh/Al
RhPcCl	0.268	0.918	0.292	–
RhNaY	–	–	–	0.257
RhPc·NaY-1	0.249	1.042	0.266	0.293
RhPc·NaY-2	0.205	0.722	0.251	0.284
RhPc·NaY-3	0.185	0.953	0.348	0.194
RhNaX	–	–	–	0.253
RhPc·NaX-1	0.397	1.476	0.283	0.269
RhPc·NaX-2	0.187	0.921	0.317	0.203
RhPc·NaX-3	0.188	1.362	0.344	0.138

spectroscopy. Infrared spectroscopy and X-ray powder diffraction also indicate a loss in crystallinity (vide infra). Both carbon and nitrogen content increase with an increase in preparation temperature which suggests the formation of intrazeolite phthalocyanines also increases with temperature.

Various ratios of these atomic percents are shown in Table II. The Rh/C, Rh/N and N/C ratios for the low temperature preparations are the closest in agreement with those calculated for RhPcCl. However, there is more than one rhodium atom per unit cell in these samples so that the zeolite crystals also contain uncomplexed rhodium, especially at the surface. Therefore, we can only qualitatively assess the degree of complexation. As the temperature increases the Rh/C, Rh/N and Rh/Al ratios decrease reflecting the loss in rhodium presumably as surface complexes. Samples RhPc·NaY-2 and RhPc·NaX-1 indicate a greater Rh/Al ratio than their respective starting materials because of some dealumination. Only for sample RhPc·NaY-2 is the Rh/N ratio less than expected, which for the most part would be in agreement with no included dicyanobenzene or uncomplexed ligand. This means at the higher temperatures more of the intrazeolite rhodium is complexed.

Although the higher temperatures appear to be more efficient, in terms of the preparation of rhodium phthalocyanine complexes, there was concern regarding metal reduction. There is a small amount of reduced rhodium in the starting zeolites RhNaY and RhNaX as evidenced by the X-ray photoelectron spectra. Table III provides the Rh $3d_{5/2}$ binding energies and atomic percents for the exchanged and complexed samples. The reduced rhodium in the exchanged zeolites may arise from the heating at 80°C under reduced pressure after preparation. It has been proposed that these reduced species are limited to the surface and therefore comprise a small fraction of the bulk rhodium [2]. There is also a large disparity between the bulk Rh/Al ratio and the surface Rh/Al ratio for the exchanged samples presumably because of rhodium migration to the surface during the mild dehydration.

Within experimental error, we cannot differentiate between uncomplexed and complexed rhodium in these samples using XPS. However, the Rh/Al ratios for the surface and bulk are much closer in agreement for the phthalocyanine containing zeolites, especially as one increases the reaction temperature. Assuming the reduction of uncomplexed rhodium is limited to the surface then the percentage of reduced species determined by XPS may become more representative of the complexes in the bulk as the Rh/Al ratios determined by elemental analysis and

Table III. X-ray photoelectron spectroscopy results

Sample	$Rh3d_{5/2}$ B.E. (eV)	Rh/Al Atomic %	Rh/Al Surface	Bulk
RhNaY	309.3	2.30	1.810	0.257
	308.0	1.30		
RhPc·NaY-1	309.2	1.06	1.056	0.293
	307.2	0.30		
RhPc·NaY-2	309.3	1.90	0.962	0.205
	307.7	0.60		
RhPc·NaY-3	309.9	0.30	0.105	0.194
	308.1	0.10		
RhNaX	309.7	2.29	0.536	0.253
	308.0	0.50		
RhPc·NaX-1	309.7	1.91	0.474	0.269
	308.3	0.32		
RhPc·NaX-2	309.9	0.87	0.296	0.203
	308.7	0.58		
RhPc·NaX-3	309.6	1.08	0.253	0.138
	308.1	0.26		

XPS become closer in agreement. Unfortunately the lower the surface concentration of rhodium the poorer the spectra and the less reliable the analyses. However, the XPS results are reinforced by the other spectroscopic techniques used in this study.

The primary rhodium species present are clearly in the +3 oxidation state with an average binding energy of 309.6 eV for the encapsulated complexes. The nature of the reduced species is less straightforward since the Rh XPS literature is ambiguous on the assignment of binding energies to the +1 and +2 oxidation states. We plan ESR experiments in order to characterize any paramagnetic Rh(II) species. If the zeolites contain rhodium(I)phthalocyanines then these would be rare examples of encapsulated anionic complexes.

Phthalocyanine complexes have a unique electronic spectrum that clearly indicates their formation within the zeolite. The main features of the UV-Vis spectrum include two intense ($\epsilon \sim 10^5$) π to π^* transitions, formally known as the Soret and *Q* bands, as well as several weaker L → M and M → L charge transfer bands. The high energy Soret band is masked by the zeolite charge transfer band but the lower energy *Q* band can easily be characterized. Figure 1 depicts the electronic spectra for the Y series of zeolite encapsulated phthalocyanines and Figure 2 the X series. The spectra for RhPc·NaY-1 and RhPc·NaX-1 show the diagnostic *Q* band centered at 656 nm accompanied by the weaker vibrational overtones (596 for the Y sample; 590 and 626 for the X sample). A comparison with the *Q* band reported for RhPcCl in CH_2Cl_2 at 646 nm reveals a bathochromic shift for the zeolite included complexes [12]. This may be a result of distortion of the phthalocynanine ring from planarity. This difference also provides evidence for the intrazeolite location of these complexes. The axial ligand on the Rh(III)Pc complexes is most likely Cl^- or a lattice oxygen (O_L). Both the Cl^- and O_L would provide similar ligand field strengths and similar electronic spectra.

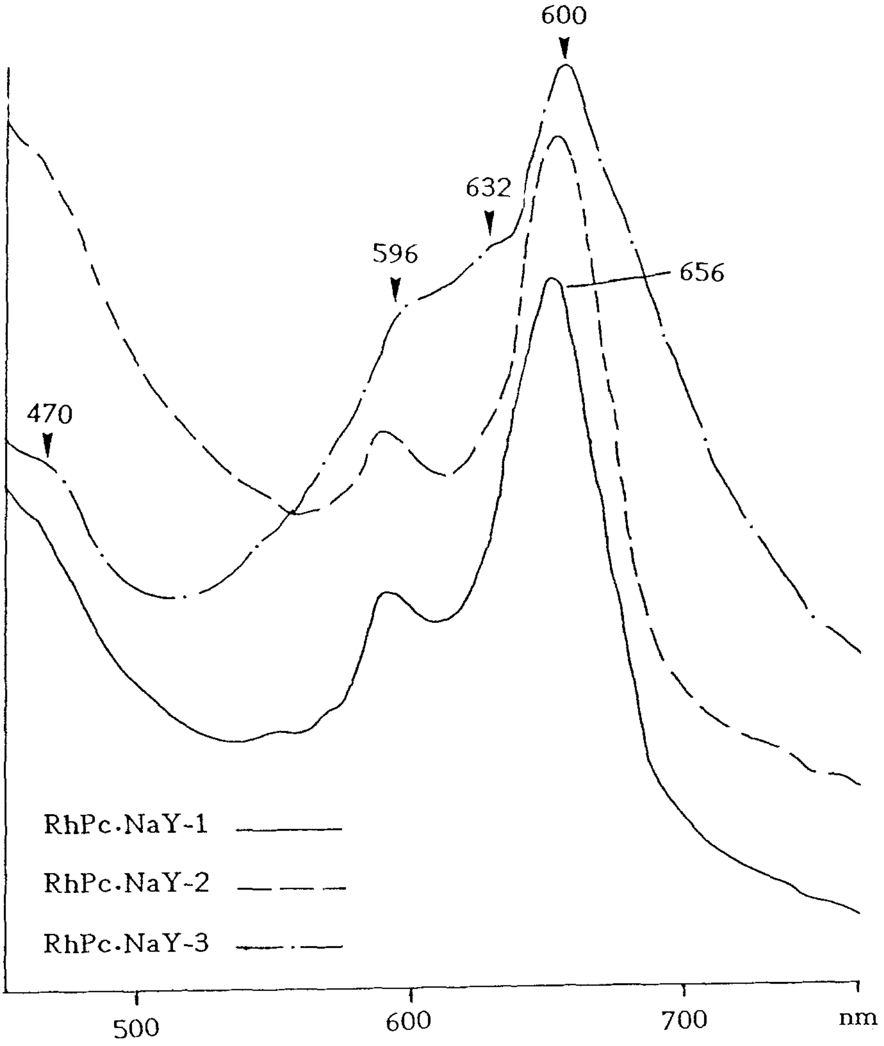

Fig. 1. The electronic spectra of samples RhPc·NaY-1, RhPc·NaY-2 and RhPc·NaY-3 recorded as Nujol mulls.

As the preparation temperature is increased the *Q* band appears to broaden and shift to higher energy. This is consistent with reduction of the rhodium complex. The electronic spectrum of the rhodium(I)phthalocyanine anion in pyridine has a *Q* band maximum at 623 nm and an accompanying vibrational overtone at 567 nm [13]. The Rh(II)Pc metal—metal bonded dimer has a broad *Q* band maxima at 656 nm and an overtone at 594 nm [13]. The spectrum for RhPc·NaY-3 has a peak at 632 and for RhPc·NaX-3 the maximum is at 636 nm. These peaks may coincide with an intrazeolite anionic Rh(I)Pc complex, which would be unusual. Additionally, the Rh(III)phthalocyanine halides are blue-green in color while the Rh(I) and Rh(II) complexes are dark blue. This parallels the trend in the zeolite colors that range

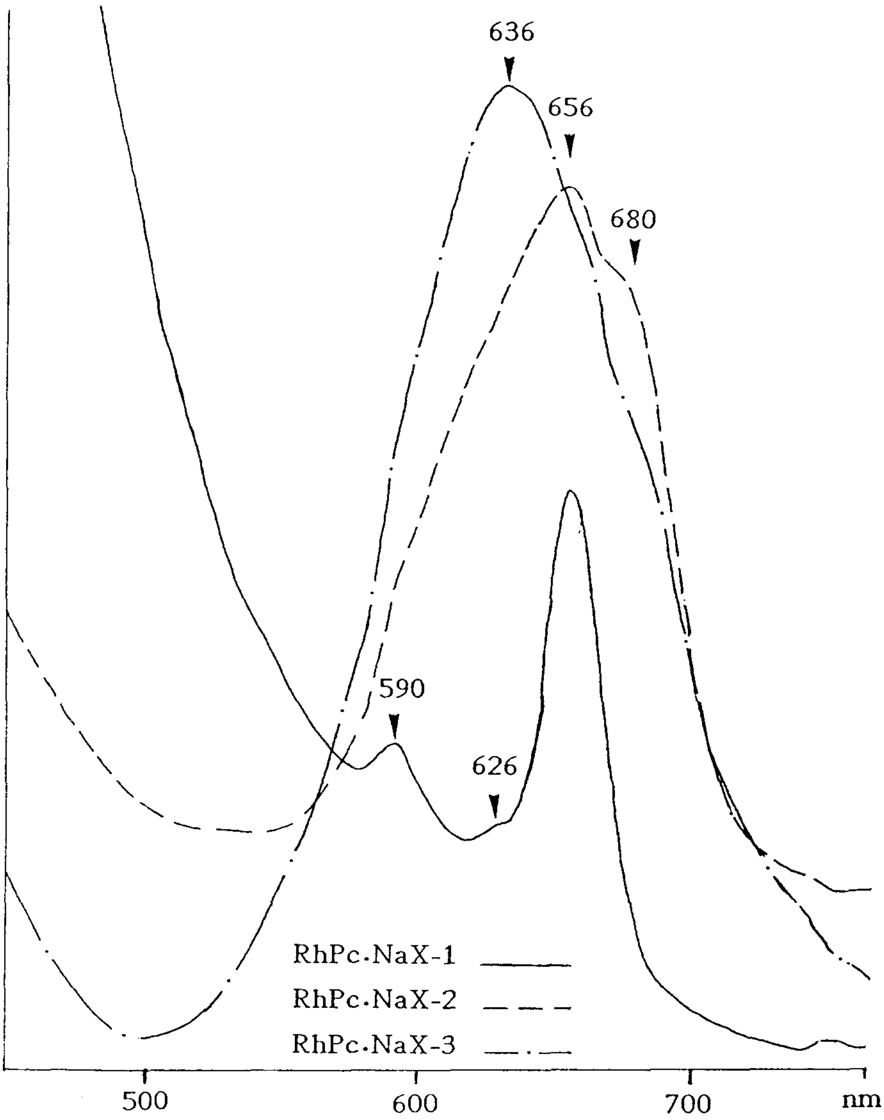

Fig. 2. The electronic spectra of samples RhPc·NaX-1, RhPc·NaX-2 and RhPc·NaX-3 recorded as Nujol mulls.

from a yellow-green for the lowest temperature preparation to blue for the highest temperature preparations. The broadening in the higher temperature spectra including the shoulder at 680 nm in the RhPc·NaX-2 sample may reflect the contribution from a Rh(II) species. The Rh(II)Pc dimer can be generated by heating solid RhPcI at reduced pressure [13] so that it may be possible to prepare the monomeric Rh(II)Pc complex inside the zeolite under the conditions employed in this study. The reduction of the intrazeolite rhodium complexes appears to be greater for the

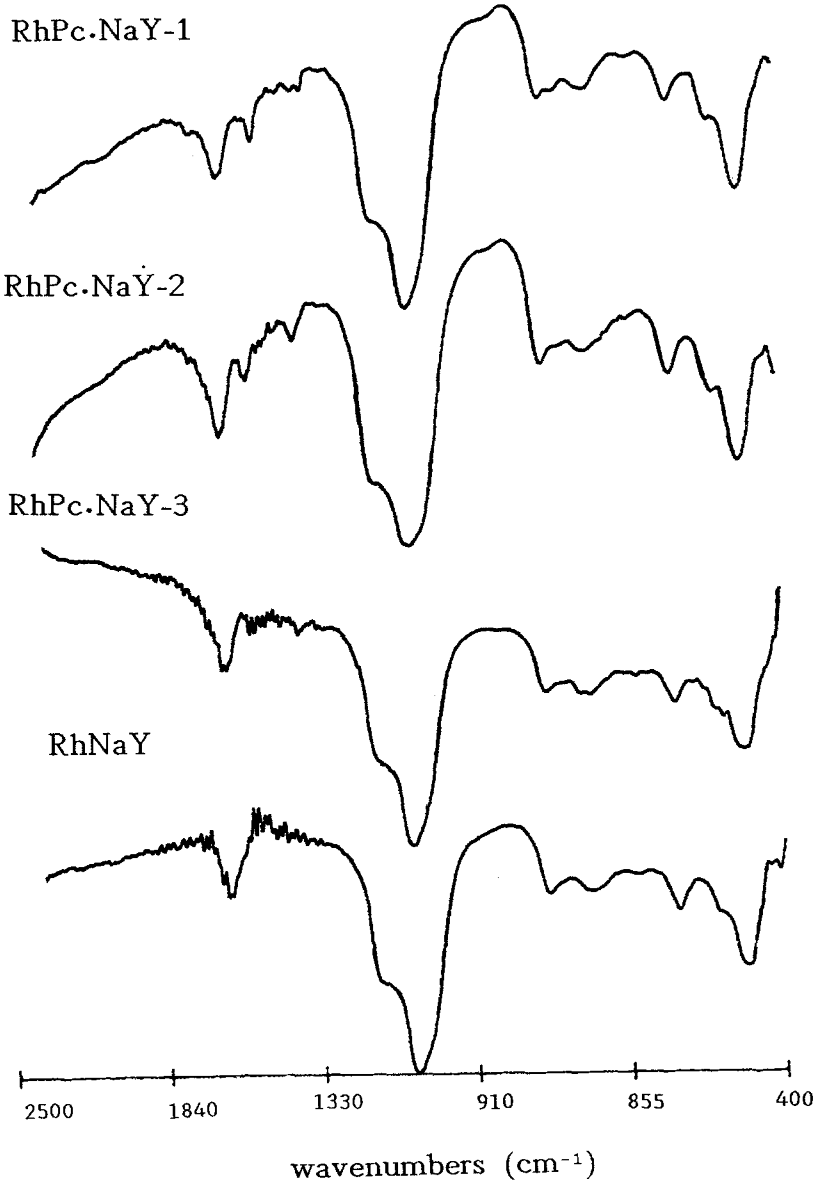

Fig. 3. The infrared spectra of RhPc·NaY-1, RhPc·NaY-2, RhPc·NaY-3 and RhNaY recorded as KBr pellets.

X series. The mechanism of and the effect of Si/Al ratio on the reduction process needs to be studied further.

The mid-infrared spectra for the Y and X series are shown in Figures 3 and 4, respectively. The spectra are clearly dominated by the zeolite fundamentals. Inclusion of the phthalocyanine complexes does not shift these bands significantly. The exception is the strong asymmetric stretch associated with internal tetrahedra which

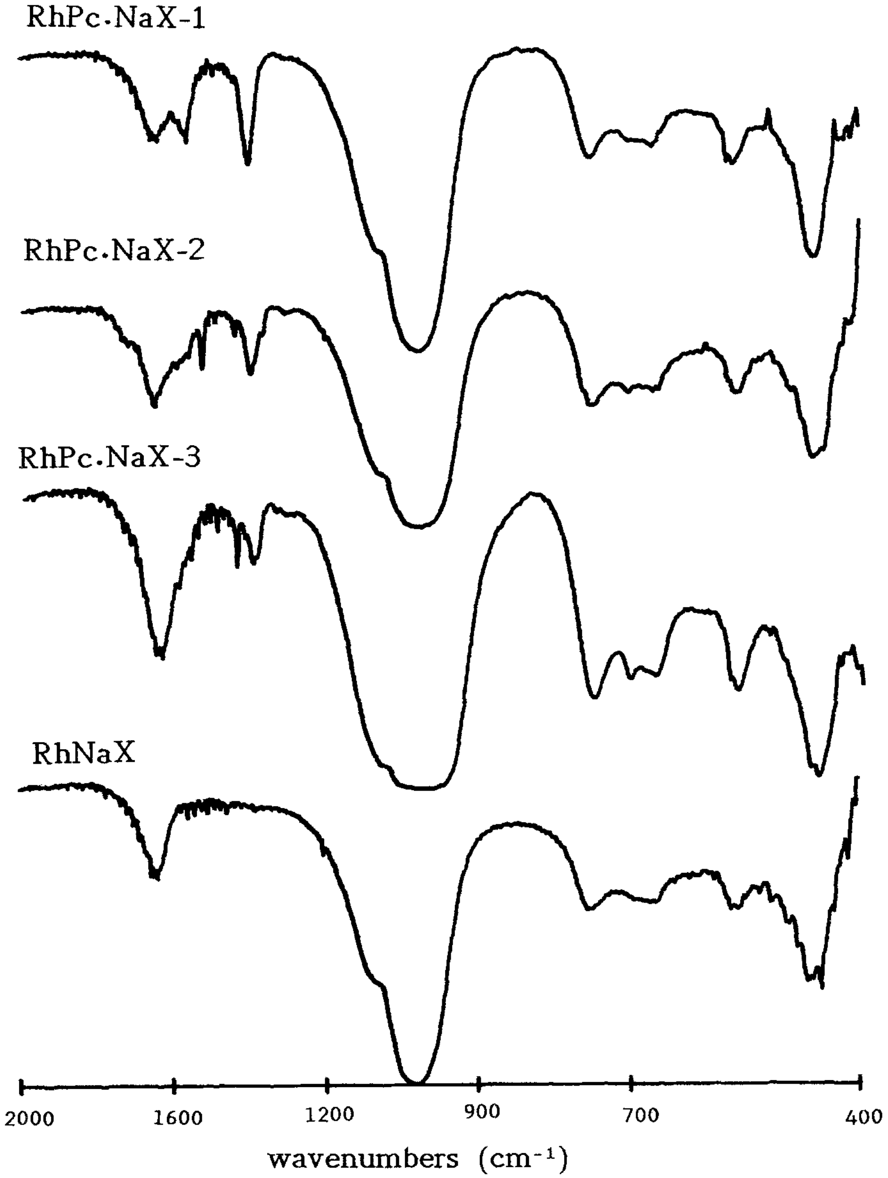

Fig. 4. The infrared spectra of RhPc·NaX-1, RhPc·NaX-2, RhPc·NaX-3 and RhNaX recorded as KBr pellets.

shifts to higher wavenumbers as the preparation temperature increases (RhPc·NaY-1, $\nu_{as} \sim 1002\,\text{cm}^{-1}$ and RhPc·NaY-3, $\nu_{as} \sim 1020\,\text{cm}^{-1}$; RhPc·NaX-1, $\nu_{as} \sim 968\,\text{cm}^{-1}$ and RhPc·NaX-3, $\nu_{as} \sim 980\,\text{cm}^{-1}$). Generally, the higher the shift for this band the higher the Si/Al ratio. There is also a noticeable broadening in the zeolite bands as the preparation temperature increases. This is most obvious for the X series in Figure 4. This broadening is associated with a loss in crystallinity, consistent with the dealumination of these samples discussed earlier. This is confirmed by the X-ray powder patterns for these samples which reveal a loss in crystallinity of 9.8% for RhPc·NaY-1, 31% for RhPc·NaY-2, 32.7% for RhPc·NaY-3, 18.7% for RhPc·NaX-1, 25.7% for RhPc·NaX-2, and 34.5% for RhPc·NaX-3 relative to RhNaY and RhNaX, respectively.

A few new IR bands emerge after reaction of the exchanged zeolites with dicyanobenzene. A comparison with the published IR spectra for RhPcCl reveal some similarities [12, 14]. However, a distortion of the phthalocyanine ring inside the zeolite in addition to contributions from complexes with rhodium in the lower oxidation states make the assignment of bands quite difficult. There are differences between the samples prepared at different temperatures. For example the low temperature samples exhibit a band at 1560 cm^{-1} which gradually disappears as the reaction temperature increases. Meanwhile bands at 1490 and 1440 cm^{-1} appear in the high temperature samples. A band at 1400 cm^{-1} seems fairly constant between the samples and may be a C=C stretch. Upon close inspection there are other bands below 700 cm^{-1} that appear inspite of the fact that the zeolite and water mask most of this region.

4. Conclusions

We have demonstrated the encapsulation of rhodium phthalocyanine complexes in zeolites X and Y using a template synthesis. The preparation temperature and type of zeolite has a profound effect on the degree of inclusion and the nature of the entrapped species. There is evidence for reduction of rhodium(III)phthalocyanines at the higher temperatures studied. Work in progress is directed towards clarifying the oxidation states of the high temperature intrazeolite complexes. Additionally, we are exploring the synthesis variables, including metal loading, in greater detail in order to better understand the encapsulation process. We anticipate these *ship-in-a-bottle* complexes will provide a wealth of new solid-state chemistry.

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References

1. N. Herron: *Chemtech*, 542 (1989).
2. K. J. Balkus, Jr., A. A. Welch, and B. E. Gnade: *Zeolites*, in press.
3. A. D. Gabrielov, A. N. Zakharov, B. V. Romanovsky, O. P. Tkachenko, E. S. Shpiro, and Kh. M. Minachev: *Koord. Khim.* **14,** 821 (1988).
4. A. N. Zakharov, B. V. Romanovsky, D. Luca, and V. I. Sokolov: *Metalloorg. Khim.* **1,** 119 (1988).
5. T. Kimura, A Fukuoka, and Ichikawa: *Shokubai* **30,** 444 (1988).
6. A. N. Zakharov and B. V. Romanovsky: *J. Incl. Phenom.* **3,** 389 (1985).
7. B. V. Romanovsky: *Acta Phys. Chem.* **31,** 215 (1985).

8. G. Meyer, D. Worhle, M. Mohl, and G. Schulz-Ekloff: *Zeolites* **4,** 30 (1984).
9. H. Diegruber, P. J. Plath, and G. Schultz-Ekloff: *J. Mol. Catal.* **24,** 115 (1984).
10. N. Herron: *J. Coord. Chem.* **19,** 25 (1988).
11. A. N. Zakharov, A. G. Gabrielov, B. V. Romanovsky and V. I. Sokolov: *Vestn. Mosk. Univ., Ser. 2: Khim.* **30,** 234 (1989).
12. T. H. Berg: *Dissertation* University of Iowa (1982).
13. K. J. Balkus, Jr. and B. B. Wayland: manuscript in preparation.
14. I. M. Keen and B. W. Malerbi: *J. Inorg. Nucl. Chem.* **27,** 1311 (1965).