

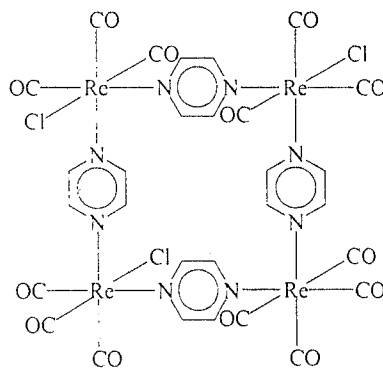
PRELIMINARY ELECTROCHEMICAL STUDIES OF THE PERMEATION OF
MESOPOROUS FILMS OF THE "MOLECULAR SQUARE" COMPOUND,
[Re(CO)₃(Cl)(μ-pyrazine)]₄, BY REDOX-SILENT CATIONS: REDOX-ACTIVE
COUNTER ANIONS AS REPORTERS ON THE CATION SIZE DEPENDENCE OF
THE PERMEATION PROCESS

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The permeation-controlled transport (or lack of transport) of cations of various size through thin films of the "molecular square" compound, [Re(CO)₃(Cl)(μ-pyrazine)]₄, was studied using cyclic voltammetry. Cations smaller than the available cavity in the square molecules were found to permeate the film, while cations larger than the cavity showed no appreciable permeation. The permeation by the redox-silent cations was indirectly observed by monitoring the oxidation of iodide or chloride counter ions. These results indicate that the available cavity size in the title compound is between 4.1 and 6.1 Å, which, as expected, is smaller than the ca. 7.2 Å Re...Re distance observed by X-ray crystallography.

INTRODUCTION

Neutral molecular squares based on Re(I) can be prepared with a variety of bridging imine ligands (1,2,3). X-ray diffraction studies on tetragonal single crystals of [Re(CO)₃(Cl)(μ-pyrazine)]₄ (**1**), as well as the closely related analogue with bridging 4,4'-bipyridine ligand, have shown that infinite unidirectional channels are present in the crystal, along the crystallographic *c* axis (1,4). Although a channel-like structure is also observed in related cationic squares (3,5,6,7), compound **1** is neutral, and no channel-blocking counter ions are present. We have recently shown that thin films of these materials



1

can act as molecular sieves, and that only species smaller than the available channel diameter show appreciable permeation through the films (4,8). (Other film or membrane based

materials exhibiting molecular sieving include electrochemically prepared organic polymers (9,10,11,12), electrochemically prepared metallopolymer (13,14,15,16,17), metal-plated polycarbonate membranes (18) and lipid-supported polypeptides tubules (19,20,21)).

We attributed the size selectivity, together with the dependence of permeation on film thickness, to membrane permeation behavior (22), in which the permeant molecule primarily diffuses in the film through nanometer-scale channels, rather than through much larger defects (pinholes, cracks). These earlier studies were conducted on squares with Re...Re distances ranging from ca. 7 to 20 Å. We found (4) that: 1) the size-cutoff for permeation coincides with the dimension of the molecular square cavity, and 2) the molecular squares are more permeable than the corner analogues which do not possess a cavity at the molecular level, and which do not self-assemble as porous structures in thin film materials (23). Furthermore, we have observed that, in the case of the larger molecular square, the permeation cutoff can be varied by changing the size and shape of the square cavity, upon binding of a guest molecule to the interior of the square cavity (8). These results imply that permeation is controlled by transport through intramolecular cavities, rather than intermolecular interstices.

We now wish to report on the permeability of films of the smallest molecular square prepared in our laboratory, $[\text{Re}(\text{CO})_3(\text{Cl})(\mu\text{-pyrazine})]_4$. In this tetranuclear pyrazine-bridged complex, the Re...Re distance (determined by X-ray diffraction) is 7.2 Å (1). Although the three dimensional structure and the crystallinity of the film material are not known precisely, comparison with the crystal structure allows for the prediction of the size cutoff for permeation. A space-filled representation of the tetranuclear assembly, obtained from the X-ray data in ref. 1, is shown in Figure 1. The accessible cavity size is in fact smaller than the Re...Re distance, since the pyrazine rings are tilted with respect to the square "walls", reducing the dimensions of the cavity available for transport, and because of finite van der Waals volumes for the component atoms. A space-filled representation of the channel array in single crystals of this material is shown in Figure 2, as well as a view of the molecular packing perpendicular to the channel array. The square cavities in 1 are aligned along the *c* crystallographic axis, but the molecules are offset from one layer to another, such that the position directly below one molecular square is occupied by solvent molecules.

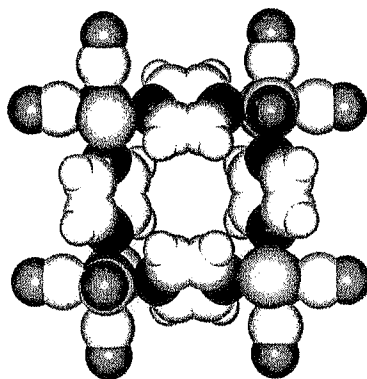


Figure 1. Space-filled model of the crystal structure of 1, determined by X-ray crystallography, and described in ref. 1. The Re...Re distance in the molecule is ca. 7.2 Å. Note the tilting of the bridging pyrazine ligand with respect to the square's edges.

In order to determine the available channel diameter in thin films of 1 more precisely, permeation (or *lack* of permeation) by a range of cations was studied. Permeation was

investigated using cyclic voltammetry, where a thin film of **1** is evaporatively deposited from solution onto an electrode. The resulting film is totally insoluble in water, and permeation of electroactive species is studied in aqueous solution. Since variable-size electroactive species with diameters smaller than ca. 7 Å are not readily available, we chose to study the permeation of alkali metal and ammonium cations. Although the cations studied are redox-silent, and therefore not directly observable by faradaic electrochemical techniques, it was possible to monitor the signal of an electroactive halide "probe" species, and to use the species to report indirectly on the transport of the cations. The experiment, schematically illustrated in Figure 3, is based on the fact that the film thickness is much greater than the coulombic separation distance typically achievable for anion/cation pairs. Thus, the electroactive halide anions are able to reach the electrode only if they can associate with a cation small enough to enter the permeation "channels" contained within the film.

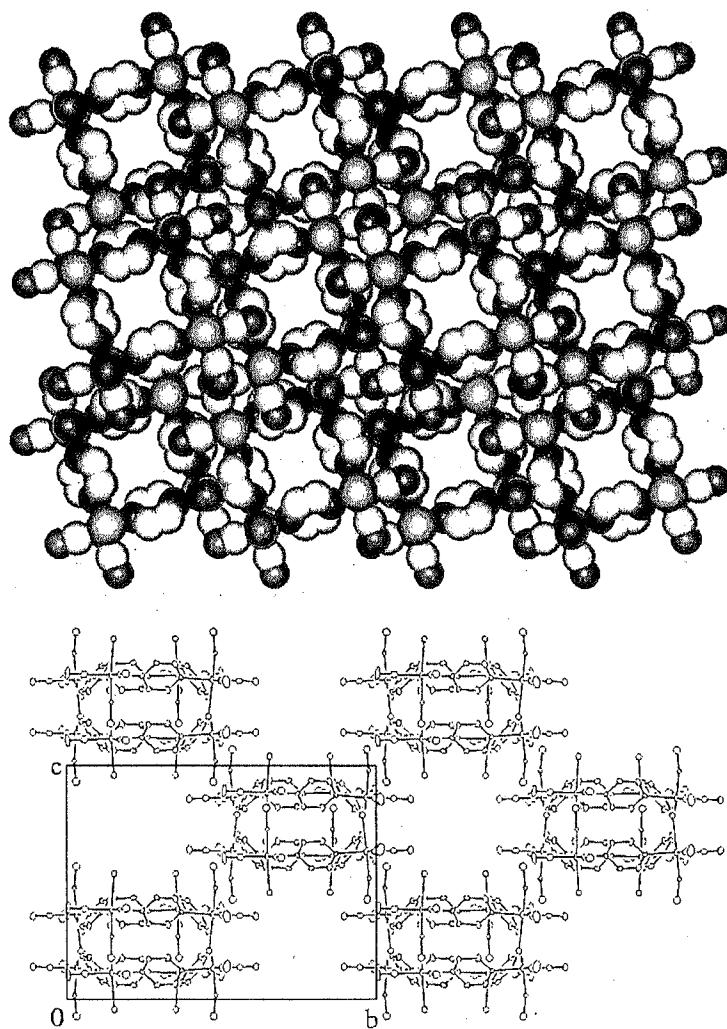


Figure 2. Top: Space filled representation along the *c* crystallographic axis of **1**, showing the presence of unidirectional open-ended channels. Bottom: ORTEP drawing in the *bc* plane, showing the offset between the molecular squares on adjacent layers. The solvent molecules (omitted for clarity) are located in the pockets between the tetranuclear assemblies. (Thermal ellipsoids represented at the 20% probability level; X-ray data from ref. 1.)

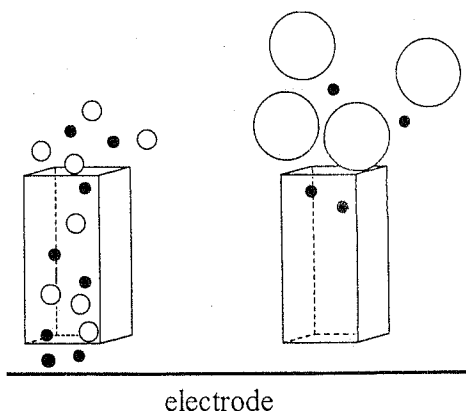


Figure 3. Schematic representation of the measurement of the permeation of variable size redox-silent cations (hollow spheres) using small electroactive anions (filled spheres) to report indirectly on permeation. Because of the need to maintain charge neutrality, the anion will only reach the electrode if the cation is small enough to fit through the permeation "channels", whose dimensions are determined by the Re...Re distance in the molecular square.

EXPERIMENTAL

Permeation studies were done using an EG&G PAR 264 or a PAR 273 potentiostat and a 3 mm glassy carbon or gold electrode (Cypress or Bioanalytical Systems). Rotating disk electrode experiments were done using a Pine Instruments Analytical Rotator (model MSR). Distilled and purified (Millipore) water was used to prepare the permeant solutions, which were typically 5 mM in electroactive species and 0.5 M in background salt. Solutions of NaI in NaNO_3 and $(\text{NR}_4)\text{I}$ in $(\text{NR}_4)\text{NO}_3$ ($\text{R} = \text{H}, \text{Me}, \text{Et}$) were prepared, in which the corresponding nitrate salt was used as the background salt for the electrochemical experiment. $(\text{NBu}_4)\text{NO}_3$, available from Aldrich, contains up to 3% chloride impurity, and the residual chloride signal was used instead of iodide, for the permeation studies. The study on the NBu_4^+ cation was effected at low concentrations ($[\text{NO}_3^-] = 0.3 \text{ M}$), because of the lower solubility of this salt in water. Solutions were deoxygenated with N_2 prior to the electrochemical measurements, and a three electrode setup was used (platinum wire counter electrode, saturated sodium chloride calomel reference electrode (SSCE)). The films were prepared as described previously, from acetonitrile and chloroform (4). All chemicals were from Mallinkrodt or Aldrich.

RESULTS AND DISCUSSION

Permeation of halides in solutions containing cations of various sizes was investigated. The permeants chosen were Na^+ (diameter (d) = 2.3 Å) and ammonium cations (NH_4^+ , NMe_4^+ , NEt_4^+ and NBu_4^+ ; $d = 3.2, 4.2, 7.2$ and 10.5 Å , respectively). For each of the cations, cyclic voltammetry was used to measure the halide oxidation current at a bare electrode, which was then compared to the current at an electrode covered with a thin film of 1. The film-covered electrode showed, as expected, a decrease in current intensity, indicating that

the flux of the electroactive species is lower in the film than in solution. Since the magnitude of the permeation is dependent on film thickness, the same film was used for all the solutions described above.

Ideally, for a perfect film, the current at a film-covered electrode for the large NEt_4^+ and NBu_4^+ cations should be zero, since these cations have diameters which are greater than that of the square cavity. In a typical experiment, the iodide current decreased to ca. 20-35% of the bare electrode signal intensity for the Na^+ , NH_4^+ and NMe_4^+ solutions, while solutions of the larger NEt_4^+ and NBu_4^+ cations showed currents which were reduced to 3-5% of the bare electrode intensity. A normalized plot of the film-covered vs bare electrode current ratio ($i_{\text{film}}/i_{\text{bare}}$), as a function of the diameter of the cation is shown in Figure 4. The dramatic decrease in current intensity between NMe_4^+ and the larger NEt_4^+ ammonium cation clearly indicates that permeation by the latter is strongly inhibited. The residual current observed for NEt_4^+ and NBu_4^+ is presumably due to small amounts of imperfections, such as cracks and/or pinholes in the films. The pinhole defects hypothesis is supported by the fact that large molecules such as $\text{Ru}(\text{NH})_5(\text{pyridine})^{2+}$ or $\text{Co}(1,10\text{-phenanthroline})_3^{2+}$ also show residual signals with these films.

The sharp current decrease between NMe_4^+ and NEt_4^+ implies that the effective pyrazine square "permeation channels" have dimensions between 4.2 and 7.2 Å, the respective diameters of these two cations.

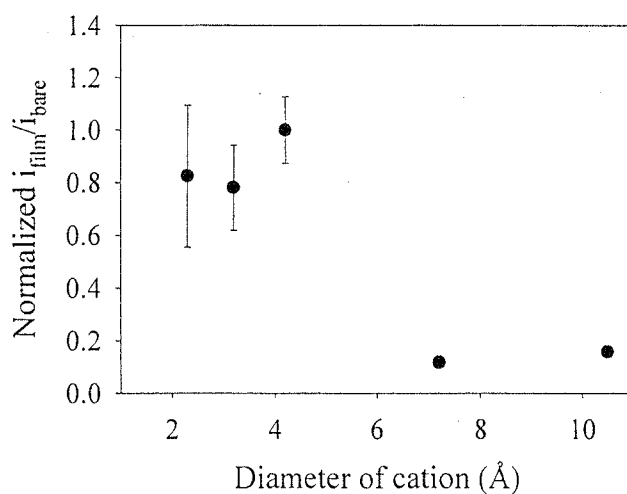


Figure 4. Normalized plot showing the $i_{\text{film}}/i_{\text{bare}}$ ratio measured at a glassy carbon electrode with and without a thin film of 1, as a function of the size of the cation. For the point at 7.2 Å, error bars fall within the dimensions of the symbol. The error bars for the point at 10.5 Å are necessarily zero, because this point has been used as the reference point for ratio normalization.

The nature of the solvent used in film casting appears to be important in the formation of low defect-density films. Films grown from acetonitrile/chloroform showed the best molecular sieving behavior, while films prepared from other solvents generally showed poor size-selectivity. Increased concentrations of the square in the "casting solution" improve the quality of the films, while the presence of chloroform appears to be important in slowing the evaporation process — slow growth being essential to the formation of clear, strongly adherent films. Because of the dependence of film morphology on the casting conditions, film quality varies widely between different experiments; the results described here were only observed for a fraction of the films prepared. The rest of the films apparently suffered from an excess of defects, which then dominated the transport and led to loss of selectivity. Work is currently underway to evaluate the influence of solvent composition on film morphology, and to correlate film morphology with sieving behavior.

CONCLUSION

In summary, this work has shown that the electrochemical signal of a small halide anion can be used to report on the transport or blockage of redox-silent cations, by thin films of molecular squares. For high-quality films, transport is achieved only with cations of diameter less than the minimum square cavity dimension. Pinhole-annealing is currently under investigation, which should lead to lower defect density films, on which permeation can be studied on a more quantitative basis. Apart from their potential applications as artificial ion channels, materials based on mesoporous $[\text{Re}(\text{CO})_3(\text{Cl})(\mu\text{-pyrazine})]_4$ (and on larger molecular squares) might be used to demonstrate separations of technological or commercial interest, such as hydrogen vs methanol or isomers in alkane mixtures.

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