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Preparation and dioxygen binding property of a new zeolite encapsulated cobalt tetramethylporphin complex

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Abstract

The cobalt tetramethylporphin (tmp) complex in zeolite Y has been prepared and the dioxygen affinity of this material has been measured as a function of the partial pressure of dioxygen and the temperature. Dioxygen binding curves at four temperatures have been constructed and the equilibrium constant (K_{eq}), $\Delta H°$ and $\Delta S°$ of the dioxygenation reaction have been deduced. The dioxygen complex formation reaction is exothermic with a strongly negative entropy change. The compound can undergo reversible oxygenation. Cyclic experiments have shown that the complex encaged in zeolite Y is more stable to irreversible oxidation than the equivalent complex without zeolite. The kinetic data obey a pseudo first-order reaction with a rate constant of 2.7×10^{-5} s^{-1} at 25 °C.

Key words: Cobalt complexes; Porphyrin complexes; Dioxygen complexes; Zeolite complexes

Introduction

Synthesizing transition metal complexes inside the cage of a zeolite has received increasing attention in recent years, since the compounds prepared in this way create favorable conditions for reversible addition of molecular oxygen and decrease considerably the rate of the irreversible oxidation of the central ion. These compounds may be used as catalysts combining the advantages of homogeneous and heterogeneous catalysis or as absorbents for the energy-efficient separation of oxygen from air [1]. The general area of zeolite encapsulated transition metal complexes has been reviewed in several reports [2–4]. Some zeolite encapsulated cobalt complexes which reversibly bind dioxygen have been reported [5–8]. Recently, Tatsumi and coworkers synthesized zeolite encapsulated iron and manganese tetramethylporphin complexes, and used them with hydrogen peroxide as the oxidizing system [9]. The interests of these researchers have been focused on the ability of transition metal complexes to interact with dioxygen and their utilization as models to mimic oxygen-carrying metalloenzymes and as oxidases that activate dioxygen in the oxidation of organic substrates. We have become interested in the use of zeolite encapsulated transition metal complexes to separate oxygen from air. Here we wish to report our studies on the preparation of the cobalt tmp complex inside the cage of a zeolite and of its dioxygen binding property. In addition, some preliminary thermodynamic and kinetic studies on the reaction of dioxygen with Co(tmp)–Y are reported.

Experimental

Preparation of cobalt-exchanged zeolite

A Linde LZY-52 Na–Y zeolite was used for cobalt ion exchange. It was pretreated with 0.1 M of NaCl aqueous solution to remove sodium deficiency in Na–Y. Chloride ions were completely removed by washing with deionized water until AgCl was not precipitated when $AgNO_3$ was added to the spent deionized water. The Co–Y sample was prepared by the published method [10]. A sample of zeolite (20 g) was suspended in distilled water (1000 cm^3). Cobalt(II) acetate tetrahydrate (1.5 g) was dissolved in distilled water (50 cm^3) and the solution was added to the Na–Y suspension. The mixture was stirred at 90 °C for 24 h. The slurry was filtered and washed with water. The resulting pink solid was dried at 200 °C under vacuum yielding a blue–purple solid. The cobalt loading of Co–Y was found to be 8.1 wt.%.

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Preparation of Co(tmp)–Y

Methanol was distilled from Mg turnings under nitrogen and degassed by repeated evacuation and filling with dry argon which was passed through a P_2O_5 column. Pyrrole and acetaldehyde were freshly distilled and degassed by mean of the repeated freezing–pumping method. Co–Y zeolite was dried at 200 °C under vacuum for 2 days and subsequently dried by the application of a Bunsen flame prior to use. The solid was cooled under vacuum and filled with dry argon. Pyrrole (46 cm^3) and acetaldehyde (76 cm^3) were added to a suspension of Co–Y zeolite (2 g) in methanol (500 cm^3). The mixture was refluxed for a few hours, and then it was filtered off, washed with methanol, and dried under vacuum. The crude material was Soxhlet-extracted with diethyl ether to remove surface species, and then stirred with NaCl to reexchange uncomplexed cobalt. The product was washed with water and dried *in vacuo.*

Solid-uptake of gases by Co(tmp)–Y

Two methods were used for the gas uptake measurement of the Co(tmp)–Y complex.

(a) *By weight.* The Co(tmp)–Y material was finely ground and approximately 2 g of the sample were placed in a pre-weighed argon filled Rotaflo tube fitted with a greaseless polytetrafluoroethylene seal and a 10 mm high vacuum tap. The sample was then degassed *in vacuo* at 70 °C, filled with argon, and re-weighed to determine the mass of the sample. The vacuum was again applied and removed with 1 atm of dry dioxygen. This was weighed immediately to give the starting mass of the uptake. Before each successive weighing, the sample was made up to 1 atm of dioxygen to compensate for the dioxygen absorbed by the complex. The sample was weighed at intervals until the mass of the sample had stopped changing. The total mass of dioxygen added was converted into moles and the ratio $Co:O_2$ calculated.

(b) *By volumetric technique.* The apparatus used to measure the quantitative absorption of dioxygen is illustrated in Fig. 1. The flask (F) containing the solid under study and the large gas reservoir (G) were maintained at the same temperature by means of a large constant bath. The remainder of the apparatus consisted of a standard gas burette fitted with three two-way taps, a mercury manometer and a mercury leveling bulb (R). A typical experiment is described below. The flask (F) was evacuated, weighed and then charged with *c.* 0.5 g of the solid complex to be studied. It was then connected to the gas burette and vacuum line. The flask was evacuated *in vacuo* at 70 °C, and then weighed. The weight of sample can be obtained from the difference between the two weights. The flask was then placed in the bath. Once thermal equilibrium was attained the uptake could be started. The gas reservoir (G) was evacuated via T_1, tap T_2 was kept closed throughout this procedure. The gas mixture of known partial pressure of dioxygen was introduced into reservoir (G) and left for 1 h to allow thorough mixing. The gas burette (A) was evacuated via taps T_2 and T_3 and filled with the gas mixture. With T_3 closed and T_4, T_5 opened, the system was evacuated and filled with the gas mixture. With tap T_2 closed and T_3 opened, the mercury levels in B and C were equalized by adjusting the height of the bulb (R) and a zero reading could then be taken from the burette (A). The volume of dioxygen absorbed was measured by levelling B and C and reading the volume from the burette (A). The temperature was monitored during each experiment and did not vary more than ±0.5 °C. On removal of the flask (F) from the bath (tap T_3 closed and T_2 opened) desorption could be examined. On heating the solid to 70 °C under vacuum the dioxygen desorbed from the solid.

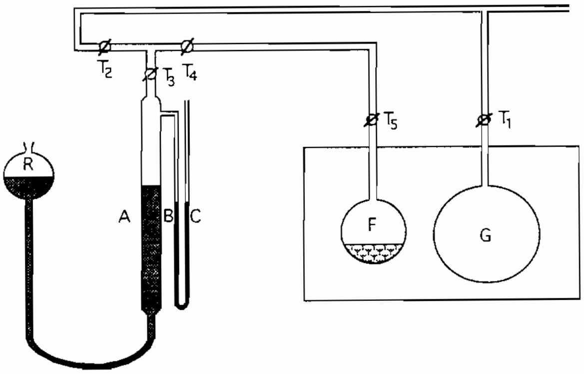

Fig. 1. Thermostatted apparatus for dioxygen uptake measurements on the solid complex using a gas burette.

$\Delta H°$ was calculated from the temperature coefficient of the dioxygenation constants using a van't Hoff plot. $\Delta S°$ was calculated from the standard relationships $-\Delta G° = RT \ln K$ and $T\Delta S° = \Delta H° - \Delta G°$.

Ion-exchanged zeolite was dissolved with hydrofluoric acid and the cobalt concentration was determined by atomic absorption analysis. X-ray powder diffraction patterns were recorded with a Siemens D500 X-ray diffractometer. All IR spectra were recorded as Nujol mulls using a Nicolet DXB FTIR spectrophotometer. The electronic spectra were obtained using a diffuse reflectance attachment to a Perkin-Elmer 559 spectrophotometer with a standard reference plate of barium sulfate or native zeolite. Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Results and discussion

It is well known that 5,10,15,20-tetraphenylporphin (tpp) is thermostable and easily accessible as the model compound of synthetic dioxygen carriers. However, the molecule is too large to be accommodated within the large pole zeolite Na–Y. We believe that the pore dimensions are sufficiently large to allow the 5,10,15,20-tetramethylporphin ligand approach to all cobalt sites within the supercage of zeolite by using the method of template synthesis of metalloporphyrins.

The IR and diffuse reflectance visible spectra of the Co(tmp)–Y material are almost identical with that of the same complex without zeolite. The absorption band at 416 nm can be assigned to the Soret band of the porphyrin ring and is a strong evidence of porphin ring formation in the zeolite. Elemental analyses are in good agreement with the calculated Co:C:N ratio for complete conversion of all cobalt atoms into Co(tmp). X-ray powder diffraction patterns for samples of Na–Y and Co(tmp)–Y are shown in Fig. 2, from which it can be seen that there was no appreciable loss in zeolite crystallinity for the Co(tmp)–Y sample compared to Na–Y. The relative peak intensities at 331, 311 and 220 follow the normal pattern reported in the literature [2]. As can be seen from Fig. 2, the cations are randomly distributed within the lattice for Na–Y, ($I_{331} > I_{220} > I_{311}$), but significant cation redistribution occurred following complex formation ($I_{331} > I_{311} > I_{220}$).

It was well established [7] that the absorption isotherms of Na–Y for O_2 and Ar are very close and argon absorption can be used as the blank when trying to determine any increase in dioxygen uptake resulting from the active dioxygen-binding complex. The absorption isotherms for dioxygen and argon on Co(tmp)–Y are reported in Fig. 3, from which it can be seen that more than eight times as much dioxygen is absorbed as argon. This increase in dioxygen uptake relative to argon gives credit to the presence of the active dioxygen binding complex. The difference between the dioxygen and argon absorption isotherms at the same gas pressure above Co(tmp)–Y is equal to the amount of CoO_2 formed at that pressure. From this a dioxygen absorption isotherm may be constructed. Isotherms constructed by this method for Co(tmp)–Y at different temperatures are shown in Fig. 4, from which it can be seen that the shape of the curves are hyperbolic and the position of the curves moves to the right with the increase of temperature. A plateau is reached at *c.* 1:1 absorption at all the temperatures studied and there is little tendency for a second dioxygen molecule to bind.

The equilibrium constants at different temperatures for binding of dioxygen by the Co(tmp)–Y complex, K_{eq}, eqn. (1), were calculated from the isotherms using the Hill equation (eqn. (2)) where Y is the fraction of the dioxygenated sites, K_{eq} is the equilibrium constant for the reaction, and $P_{1/2}(O_2)$ is the partial pressure at which 50% of the sites are dioxygenated.

$$\mathrm{Co(tmp){-}Y} + O_2 \xrightleftharpoons{K_{eq}} [\mathrm{Co(tmp)}(O_2)\mathrm{{-}Y}] \qquad (1)$$

$$\frac{Y}{1-Y} = \frac{[\mathrm{Co(tmp)}(O_2)\mathrm{{-}Y}]}{[\mathrm{Co(tmp){-}Y}]} = K_{eq}P(O_2)^n$$

$$= [P_{1/2}(O_2)]^{-1}P(O_2)^n \qquad (2)$$

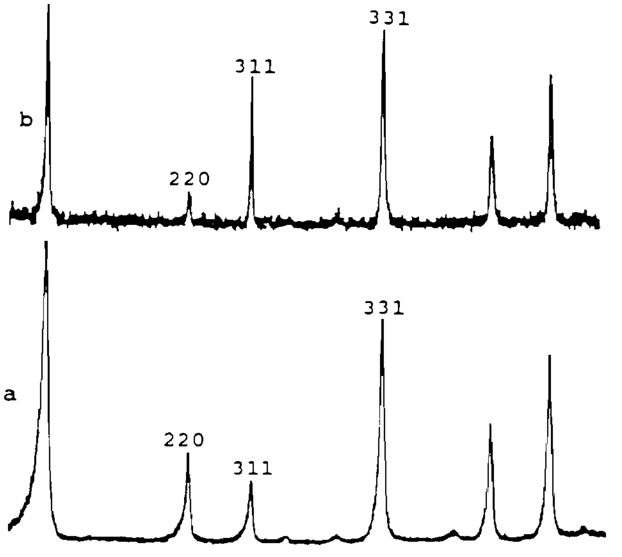

Fig. 2. X-ray powder diffraction patterns of (a) Na–Y and (b) Co(tmp)–Y.

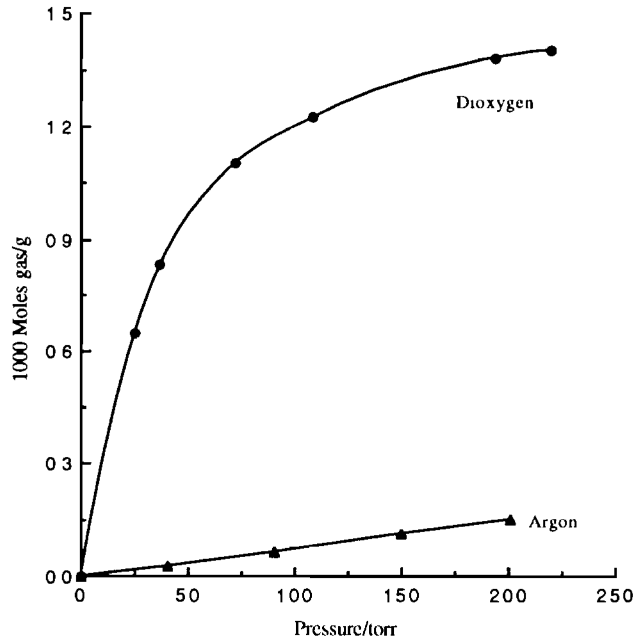

Fig. 3. Comparison of dioxygen and argon absorption isotherms for Co(tmp)–Y material at 25 °C.

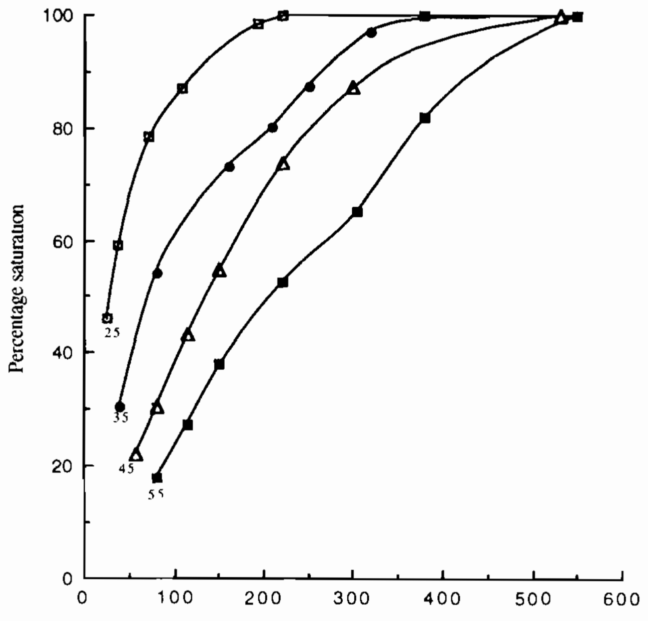

Fig. 4. Combined isotherms at T = 25, 35, 45 and 55 °C for the absorption of dioxygen by Co(tmp)–Y

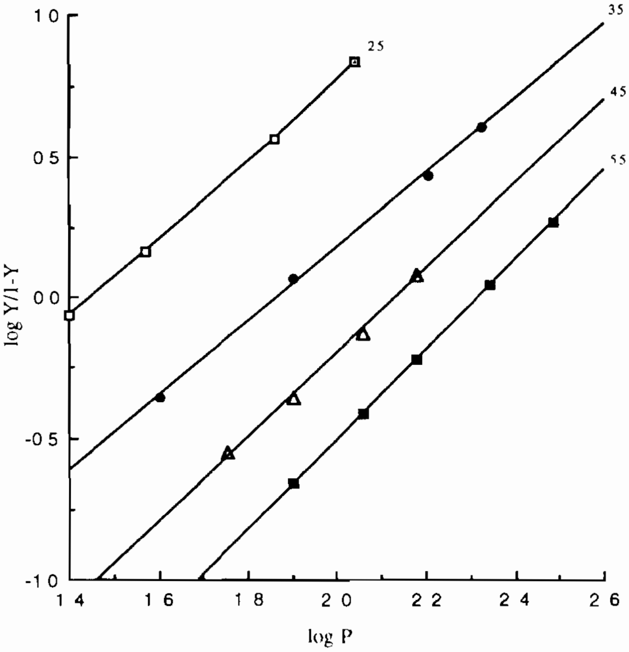

Fig 5. Hill plots for Co(tmp)–Y at T = 25, 35, 45 and 55 °C.

A plot of log $[Y/(1-Y)]$ versus log $P(O_2)$ yields a Hill plot, Fig. 5, with slope n, the Hill coefficient. The values of log K_{eq} are obtained from the intercept of the best straight line. The equilibrium data derived from the Hill plots are summarized in Table 1. From the K_{eq} values it is clear that the complex has the highest affinity (and the lowest $P_{1/2}(O_2)$ value) for dioxygen at 25 °C. The fact that n lies in the range 1.4–1.6 indicates some cooperativity in dioxygen binding, although the reason for this is unclear.

That the active Co(tmp)–Y material binds dioxygen in the solid state is further shown by the plot of dioxygen absorbed against complex concentration, Fig. 6. The slope of the plot is 1.1, indicative of a 1:1 complex, [Co(tmp)(O_2)–Y], in the solid state. Desorption of dioxygen is accomplished by either heating the solid to *c.* 70 °C, applying a slight vacuum or by joint temperature/pressure drop method.

The active species is much more stable to repeat absorbing/desorbing cycles either in the solid state or in water suspension compared to the equivalent complex without zeolite (Fig. 7) and the active Co(salen)–Y material [6]. The reaction was studied through 60 completely reversible cycles by accurate successive gas burette measurements over a two-week period without losing its dioxygen-binding capacity. Although long-term absorption/desorption cycles were not studied it appears to us that the system is a stable one and many more than 60 cycles may be possible without any decomposition of the system.

If the $P_{1/2}(O_2)$ value of Co(tmp)–Y is compared with those found in other Co(II) complexes inside zeolite, Table 2, it is found that the $P_{1/2}(O_2)$ value for the complex reported here is less than that reported for the Co(salen)py complex [6]. Since the porphin ligand has a stronger ligand field than salen, this results in raising the energy of the d_{z^2} orbital and lowering the

TABLE 1. Equilibrium and thermodynamics data for the reaction of dioxygen with solid state Co(tmp)–Y

Temp. (K)	log K_{eq} (torr^{-1})	$10^3 \times K_{eq}$ (torr^{-1})	$P_{1/2}(O_2)$ (torr)	n	Other constants
298	−2.02	9.55	1.05×10^2	1.4	$\Delta G°$ = 2.8 kcal(mol of O_2)$^{-1}$ $\Delta H°$ = −24.2 kcal(mol of O_2)$^{-1}$ $\Delta S°$ = −90.6 eu
308	−2.74	1.82	5.50×10^2	1.5	
318	−3.20	0.63	1.59×10^3	1.5	
328	−3.70	0.20	5.00×10^3	1.6	

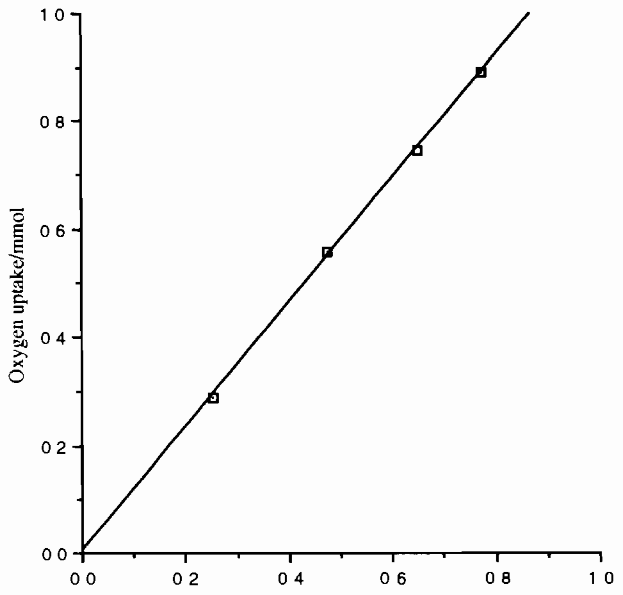

Fig. 6. Dioxygen uptake as a function of Co(tmp)–Y concentration.

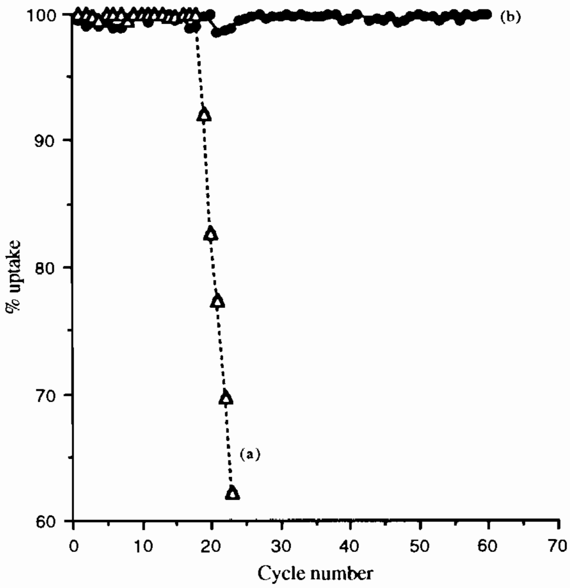

Fig. 7. Comparison of number of absorption/desorption cycles for (a) Co(tmp) and (b) Co(tmp)–Y.

TABLE 2. Comparison of $P_{1/2}(O_2)$ values for Co–O_2 adducts

Complex	$P_{1/2}(O_2)$ (torr)	Reference
Co(tmp)–Y	105	this work
Co(salen)py^{2+} in Na–Y	306	6
Co(CN)–Y	9	7
Co(3-Fsalen)$^{2+}$ solid	2	11
Co(terpy)(bpy)$^{2+}$ in Na–Y	0.59	5
Co(terpy(bpy)$^{2+}$ in Li–Y	0.34	11

$P_{1/2}(O_2)$ value. By comparing Co(tmp)–Y with other complexes it was found that our complex has a larger $P_{1/2}(O_2)$ value, indicating a weaker overall ligand field. The explanation of such an observation is that the axial position of the Co(tmp)–Y complex may be occupied by a lattice oxygen of the zeolite framework whereas in the case of other complexes except Co(CN)–Y the axial position is occupied by the stronger nitrogen donor ligand. The weaker axial coordination in our material results in a lower energy d_{z^2} orbital and a correspondingly larger $P_{1/2}(O_2)$ value. In the case of Co(CN)–Y, the cyanide ligands produce a stronger ligand field than porphin, resulting in a lower $P_{1/2}(O_2)$ value.

A plot of ln K_{eq} against $1/T$ gives the van't Hoff plot, Fig. 8, from which $\Delta H° = -24.2$ kcal(mol of $O_2)^{-1}$ and $\Delta S° = -90.6$ eu are deduced. The large negative values of $\Delta H°$ and $\Delta S°$ seem to follow the normal pattern observed for dioxygen complexes reported in the literature [12]. The main contribution to the negative $\Delta S°$ value is the loss of translational entropy of free dioxygen and the loss of translational and vibrational freedom of the coordinated ligand as its coordinate bonds to the metal are strengthened and tightened up as the result of oxygenation.

The reaction of dioxygen with Co(tmp)–Y with time has also been studied using the same apparatus. Again saturation is reached with the formation of a 1:1 adduct. The data obey pseudo first-order kinetics with rate constant of 2.7×10^{-5} s^{-1} at 25 °C.

In summary, this work has demonstrated that the zeolite encapsulated cobalt tetramethylporphin complex can be made and that such a material is much more stable toward irreversible oxidation than the equivalent complex without zeolite. This system appears to have potential as a practical means as an oxidation catalyst

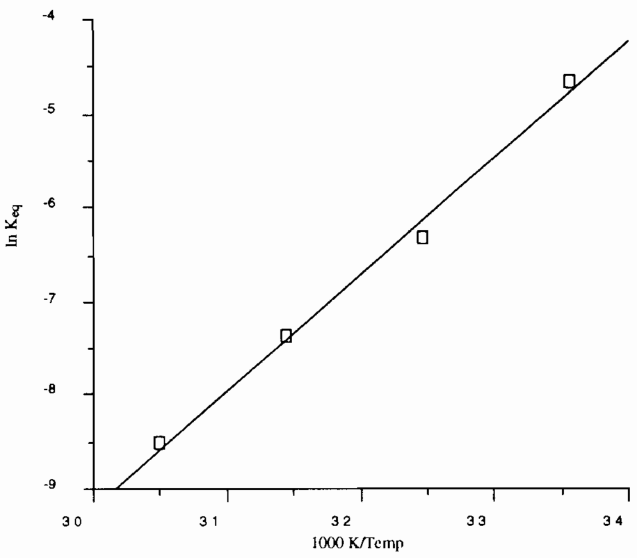

Fig. 8. The van't Hoff plot for Co(tmp)–Y.

and as an absorbent for removing oxygen from air because of its stability with respect to cycling at 25 °C. The formation and decomposition of the dioxygen adduct is also attractive. We have prepared a number of other zeolite-encapsulated dioxygen complexes with properties similar to those reported above, and these results will be reported in the near future.

Acknowledgements

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