Intrazeolitic Reaction between Transition Metal Ions and Open or Closed Polyamine Ligands

Dirk E. De Vos, Dominic L. Vanoppen, Xiao-Yuan Li, Steven Libbrecht, Yvan Bruynseraede, Peter-Paul Knops-Gerrits, and Pierre A. Jacobs*

Abstract: Intrazeolitic transition metals, such as Ni^{2+} and Co^{2+}, were chelated by open or closed, tetra- or pentadentate polyamine ligands. Their coordination and redox chemistry was studied by IR-Raman, EPR, diffuse reflectance, and magnetic techniques. For pseudo-octahedral complexes with tetradentate ligands, the presence of the zeolite favors *cis* coordination over the *trans* form. This is explained by the very low tendency of the zeolite surface to bind as a monodentate ligand to a planar metal complex. However, if *trans* complexes are formed (as with Ni^{2+}), the axial positions on the complex are available for ligand exchange. Such intracrystalline complex syntheses result in the formation of new redox solids. For example, $[Co^{II}(cyclam)]^{2+}$-NaY (cyclam = 1,4,8,11-tetraazacyclotetradecane) is a reversible, high-affinity ($p_{1/2} < 1$ mbar) and high-capacity (> 90 $\mu mol\,g^{-1}$) dioxygen-sorbing material.

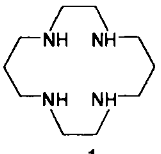
Keywords
chelate ligands · dioxygen activation · EPR spectroscopy · redox systems · SQUID · zeolites

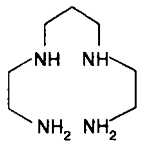
Introduction

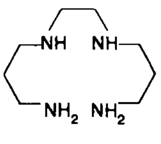
Encapsulation of metal complexes in the cavities of zeolites allows the surface of these inorganic molecular sieves to be functionalized in a versatile way.[1] Moreover, the dispersion of the complexes in the cages provides a unique vista of many coordination compounds; the mononuclear superoxo adduct of $[Co(NH_3)_5]^{2+}$, for example, was first observed in zeolite Y.[2] For steric reasons, most of these supported metal complexes must be assembled in situ by bringing together metal and ligand(s) inside the zeolite cages. Such a synthesis can differ from complex synthesis in solution, because of the chelating character of the surface itself and because of ligand physisorption. Careful design of tetra- and pentadentate Schiff base ligands is a convenient way of controlling the number, nature, and disposition of the donor atoms around zeolite-hosted transition metals.[3] However, for other ligand classes such as polyamines, the potential of varying the ligand structure inside a zeolite has hardly been explored.

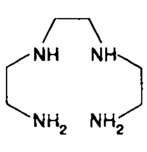
As is known from solution chemistry, changing the polyaza ligand is a way of tuning the electron density of the metal ion in a polyamine complex.[4] Moreover, one can use not only open ligands, but also cyclic molecules. The topological constraints within such macrocyclic ligands lead to a very high inertness towards ligand dissociation and can also yield unexpectedly high or low ligand field strengths in the metal accepting cavity.[5]

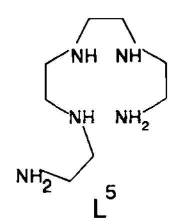
In this study we therefore concentrate on the intrazeolitic complexation of transition metal ions (TMIs) with open and closed polyamines. While till now only tetren (tetraethylenepentamine, L^5) has been used in a zeolitic environment,[6] we employ tetra- and pentadentate open and closed ligands, such as cyclam (1,4,8,11-tetraazacyclotetradecane, L^1), 2,3,2-amine (*N,N'*-bis(2-aminoethyl)propylenediamine, L^2), 3,2,3-amine (*N,N'*-bis(3-aminopropyl)ethylenediamine, L^3), trien (triethylenetetramine, L^4), and tetren. The fate of the ligand is monitored by IR spectroscopy and thermogravimetry. In order to understand the coordination chemistry of Ni^{2+} and Co^{2+}, EPR, UV-Vis-NIR diffuse reflectance, Raman, and magnetic


L^1


L^2


L^3


L^4


L^5

---

[*] Prof. Dr. P. A. Jacobs, Dr. D. E. De Vos, D. L. Vanoppen, P. P. Knops-Gerrits
Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit Leuven
Kardinaal Mercierlaan 92, 3001 Heverlee (Belgium)
Telefax: Int. code + (32)1632-1998
e-mail: pierre.jacobs@agr.kuleuven.ac.be.

Prof. Dr. X. Y. Li
Chemistry Department, Hong Kong University of Science and Technology

Prof. Dr. Y. Bruynseraede, Dr. S. Libbrecht
Afdeling Vaste Stof-Fysica en Magnetisme, Katholieke Universiteit Leuven

0570-0833/95/0202-0144 $ 20.00+.25/0

techniques are applied. Attention is primarily focused on the influence of coordination chemistry on the redox activity in polyamine complexes, such as the activation of dioxygen on Co^{2+} or the formation of low-spin Ni^{2+} complexes, which may catalyze olefin epoxidation. The spectra of the complexes entrapped in zeolites are compared in detail to those of their homogeneous counterparts, especially for samples containing cyclam; this allows the role of the zeolite in the complexation to be evaluated. Redox properties of the new materials are discussed.

Results and Discussion

Adsorption of polyamines on NaY zeolites exchanged with transition metal ions: A slight excess (10%) of ligand was adsorbed on zeolite Y by mixing the dry ligands and zeolites and heating for four hours. This procedure did not change the color of NaY, MnNaY (white), or CrNaY (greenish white), but for all ligands, the blue CoNaY turned brownish white, and NiNaY samples assumed hues between yellow and light purple.

Though there is little doubt that all *open* polyamines easily pass into the 7.3 Å pores of zeolite Y, it is not obvious whether the same applies to the *closed* cyclam ligand. Cyclam and tetren adsorptions were therefore repeated using the small-pore (4.1 Å) CoNaA and NiNaA zeolites. In the reflectance spectra of these A zeolites, we were unable to detect complexation of the TMIs by any of the polyamines; this was even true of acyclic ligands such as tetren. This proves not only that all polyamine ligands are size-excluded from NaA zeolites, but that complexation at the outer surface of dry zeolites does not cause noticeable alterations in the spectra. Hence, the color changes for Y zeolites must be ascribed to reactions *inside* the pore system, even for cyclam.

The IR spectra show how this bulky cyclam ligand manages to diffuse inside the zeolite pores (Table 1). Though on symmetry grounds only one N–H stretching band may be expected for cyclam, the free crystalline ligand exhibits two, at 3260 and 3170 cm^{-1}. This splitting is ascribed to the existence of intramolecular H-bonds, which confer a rigid, planar structure to the cyclam molecule.[7] After adsorption of cyclam on dry NaY, a single dominant band is observed at 3290 cm^{-1}. This suggests that adsorption results in the H-bonds being broken, and cyclam becomes flexible. The rate of diffusion of cyclam inside a zeolite must be comparable to that of large cycloalkanes, which diffuse easily into Y zeolites.[8]

Table 1. N–H stretching frequencies for cyclam(L)-loaded Y zeolites; spectra were recorded after evacuation at 373 K.

(L)–NaY	$[Cr^{III}(L)]^{3+}$–NaY	$[Mn^{II}(L)]^{2+}$–NaY	$[Co^{II}(L)]^{2+}$–NaY	$[Ni^{II}(L)]^{2+}$–NaY
3321 (sh)				
3290	3265	3255	3235	3190
3273 (sh)			3150 (sh)	3110 (sh)

Especially in the case of cyclam, the high-frequency IR vibrations are also informative for studying the metal environment. In cyclam-loaded TMI zeolites, the N–H stretching bands are shifted to lower frequencies. As the cyclam:TMI ratio was nearly 1, this strongly indicates that the reaction between the divalent TMI and the ligand is close to quantitative. The order of the main ν_{N-H} frequency ($NaY > Cr^{III}NaY > Mn^{II}NaY > Co^{II}NaY > Ni^{II}NaY$) matches, for the divalent cations, the Irving–Williams order for complex stability; increasing the M–N bond strength does indeed lower the ν_{N-H} frequency.[9] In spite of the high σ-donor strength of the cyclam ligand, Cr^{3+} is clearly not chelated. This is surely related to the high substitution stability of this cation; indeed, there are no reports of successful chelation of exchanged Cr^{3+} in zeolites.

Thermogravimetric analysis allows the ligand–metal interaction to be quantified. Some results are summarized in Table 2. The cyclam:zeolite weight ratios for nonextracted samples reflect the ligand:zeolite stoichiometry used in the synthesis (ca. 0.135 g of cyclam per gram of dry zeolite). While cyclam was already fully desorbed from NaY at 650 K, complete removal of cyclam from Ni^{2+} or Co^{2+} zeolites required heating up to 820 K. Even more marked differences were observed between NaY and Co^{2+} or Ni^{2+} zeolites after a 10 h dichloromethane extraction of the samples. While more than 80% of the ligand was washed out of NaY, the cyclam ligand was almost quantitatively retained on NiNaY and CoNaY. This confirms that the reaction between cyclam and Ni^{2+} or Co^{2+} is close to quantitative.

Table 2. Weight ratios cyclam:dry zeolite for $[Ni^{II}(cyclam)]^{2+}$–NaY, $[Co^{II}(cyclam)]^{2+}$–NaY, and cyclam-loaded NaY, determined by differential thermal analysis. Measurements were performed before and after extraction with CH_2Cl_2.

	before extraction	after extraction
NaY + cyclam	0.136	0.026
$[Ni^{II}(cyclam)]^{2+}$–NaY	0.140	0.138
$[Co^{II}(cyclam)]^{2+}$–NaY	0.152	0.144

Coordination of Ni^{2+} in polyamine-loaded Ni^{2+} zeolites: Upon dehydration of a Ni^{2+}-exchanged zeolite, the octahedral $[Ni(H_2O)_6]^{2+}$ complexes were converted into lattice-coordinated Ni^{2+} species with bands at 5700, 9600, 16200, and 21100 cm^{-1} (Fig. 1). These features disappeared upon adsorption of the polyamine ligands; this suggests a major change of the coordination environment of Ni^{2+}.

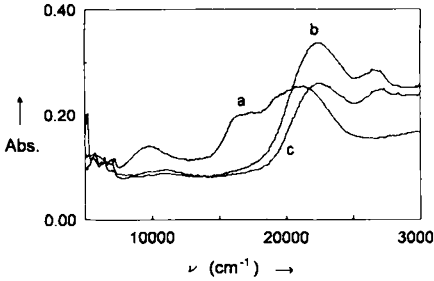


Fig. 1. Diffuse reflectance spectra of a) dehydrated NiNaY zeolite; b) $[Ni^{II}(cyclam)]^{2+}$–NaY, dry atmosphere; c) $[Ni^{II}(cyclam)]^{2+}$–NaY, rehydrated for 4 h in an atmosphere with a relative humidity of 79%.

The reflectance spectra of $[Ni^{II}(L)]^{2+}$–NaY (where $L = L^2$, L^3, L^4, L^5) exhibit intense absorptions around 11000, 18400, and 28000 cm^{-1} (Fig. 2). These bands are indicative of at least fivefold but probably sixfold coordination of Ni^{2+}.[10] For the tetra- or pentadentate ligands, coordination of Ni^{2+} by residual OH^- or H_2O or by the zeolite has to be invoked to reach a total coordination number of six. The relatively high energy of the transitions proves that the majority of the coordinating atoms are amine nitrogens.

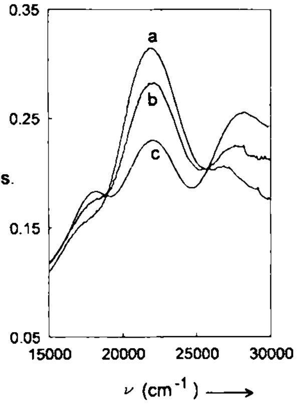


Fig. 2. Diffuse reflectance spectra of $[Ni(3,2,3\text{-amine})]^{2+}$-NaY at various water contents: a) dry sample; b) after 2 h of rehydration in a 79% relative humidity; c) after 4 h of rehydration. After renewed dehydration, the spectrum cannot be distinguished from trace a).

For all tetradentate ligands (L = L^1, L^2, L^3, L^4), a band of varying strength was observed between 22000 and 22800 cm^{-1}, dominating the spectrum in case of $[Ni^{II}(cyclam)]^{2+}$-NaY (Fig. 1). This band is readily identified as the single d–d transition of four-coordinate, square-planar Ni^{2+} complexes.[10] The energy of this band depends on the ligand structure; the observed order (trien > 2,3,2-amine, cyclam > 3,2,3-amine; 22800, 22400, and 22000 cm^{-1}, respectively) reflects that the in-plane field increases as the size of the coordination quadrangle decreases.[11] This shows that subtle variation of the ligand enables the fine-tuning of the ligand field experienced by TMIs located in zeolites.

The complexation of Ni^{2+} by four N atoms in a square-planar complex is coupled to a transition from a high-spin to a low-spin state. Therefore the extent of the reaction between Ni^{2+} and the ligand can be estimated by measuring the amount of high-spin Ni^{2+} in the samples with a highly sensitive SQUID (superconducting quantum interference device) magnetometer. Cooling is necessary in order to determine precisely the residual Ni^{2+} paramagnetism, which may be masked at room temperature by the diamagnetic effect of the zeolite matrix. For $[Ni^{II}(cyclam)]^{2+}$-NaY, the plot of the magnetization m vs. $1/T$ yields a straight line, which indicates Curie–Weiss behavior (Fig. 3). Based on the Ni^{2+} concentration in the zeolite sample, one finds that $\chi_M T = 0.11\ cm^3\,mol^{-1}\,K$ for $[Ni^{II}(cyclam)]^{2+}$-NaY, whereas $\chi_M T = 1.29\ cm^3\,mol^{-1}\,K$ for NiNaY. The over 90% reduction in the Ni^{2+} molar susceptibility by cyclam adsorption proves that the reaction between Ni^{2+} and cyclam is an almost stoichiometric one.

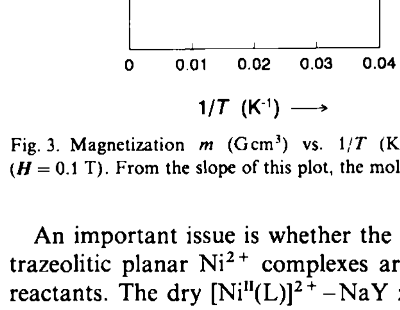


Fig. 3. Magnetization m (G cm³) vs. $1/T$ (K^{-1}) for $[Ni^{II}(cyclam)]^{2+}$-NaY (H = 0.1 T). From the slope of this plot, the molar value for $\chi_M T$ is calculated.

An important issue is whether the axial positions of the intrazeolitic planar Ni^{2+} complexes are accessible to incoming reactants. The dry $[Ni^{II}(L)]^{2+}$-NaY zeolites (L = L^1, L^2, L^3) were therefore exposed to water. In case of $[Ni^{II}(cyclam)]^{2+}$-NaY, the only effect of hydration was a weakening of the 22400 cm^{-1} band (Fig. 1). This band was restored in its original strength by a renewed dehydration at 373 K. For $[Ni^{II}(3,2,3\text{-amine})]^{2+}$-NaY, the effect was more complex (Fig. 2): the bands at 11000, 18200, and 28400 cm^{-1} grew stronger by hydration, while the 22000 cm^{-1} band was weakened. Visually, these changes were observed as a color change from yellow to light purple. The reverse effect was observed upon renewed dehydration. Essentially the same phenomena were observed for $[Ni^{II}(2,3,2\text{-amine})]^{2+}$-NaY.

The effect of water adsorption on Ni^{2+} zeolites containing tetradentate amines may be twofold: protonation of the amines and axial coordination by H_2O of the square-planar complexes. The first reaction should result in a diminished coordination of Ni^{2+} by the ligand and a shift of the d–d transitions to lower energies; this was not observed. The clean isosbestic points, observed for $[Ni^{II}(3,2,3\text{-amine})]^{2+}$-NaY and $[Ni^{II}(2,3,2\text{-amine})]^{2+}$-NaY, indicate that the only effect of hydration is axial water binding on the planar complexes and a shift of the blue–yellow equilibrium, just as is observed in aqueous solution [Eq. (a)].[12] For $[Ni^{II}(cyclam)]^{2+}$-NaY, the tetragonal form

$$\underset{\text{(yellow, low spin)}}{[Ni(L)]^{2+}} + 2\,H_2O \rightleftharpoons \underset{\text{(blue, high spin)}}{[Ni(L)(H_2O)_2]^{2+}} \qquad \text{(a)}$$

was not directly observed; however, this may be due to the large difference between the extinction coefficients of the planar and tetragonal forms of this particular complex ($\varepsilon \approx 60$–$70\ mol\,L^{-1}\,cm^{-1}$ at 22400 cm^{-1} for $[Ni^{II}(cyclam)]^{2+}$; $\varepsilon < 1\ mol\,L^{-1}\,cm^{-1}$ at the maxima of 15400 and 30000 cm^{-1} for $[Ni^{II}(cyclam)(H_2O)_2]^{2+}$).[13] Therefore, the weakening of the planar, yellow band of $[Ni^{II}(cyclam)]^{2+}$-NaY with adsorption of water is presumably due to a planar$\rightleftharpoons$tetragonal equilibrium. Though it is improbable that the equilibrium can be shifted completely to the left or to the right in any of the materials, the variation of the water content demonstrates that a considerable part of the axial positions on the planar complexes is accessible for reversible coordination. In this respect the chemistry of the zeolite-supported Ni^{2+} complexes differs from that of their clay supported counterparts; the intercalation of planar Ni^{2+} complexes between clay platelets prevents axial coordination.[14]

Coordination of Co^{2+} in $[Co^{II}(cyclam)]^{2+}$-NaY and $[Co^{II}(tetren)]^{2+}$-NaY; electronic spectra: In the reflectance spectrum of oxygen-free $[Co^{II}(cyclam)]^{2+}$-NaY, the typical triplet structure between 14000 and 18000 cm^{-1} of zeolite-coordinated Co^{2+} has disappeared, while a broad d–d transition shows up at 21500 cm^{-1} (Fig. 4). This proves that the oxygen atoms of the tetrahedral Co^{2+} coordination sphere have largely been replaced by nitrogen atoms. The frequency of the new d–d band matches that of the dominant absorption of square-planar, low-spin Co^{2+} complexes, such as $[Co(en)_2]^{2+}$.[15] However, five or six coordinate Co complexes with amine ligands all show absorptions in the same frequency range; hence, the spectrum could also be that of a square pyramidal or pseudo-octahedral Co^{2+} complex. Adsorption of tetren on CoNaY also gives rise to a new d–d band at 20500 cm^{-1}, albeit with a low intensity.

EPR spectra of oxygen-free Co zeolites: As $[Co^{II}(tetren)]^{2+}$ is a high-spin complex, $[Co^{II}(tetren)]^{2+}$-NaY samples are EPR silent under an inert atmosphere. In contrast, deoxygenated $[Co^{II}(cyclam)]^{2+}$-NaY displays an axially symmetric signal. Even at room temperature, relaxation times are sufficiently long for the signal to be observed. The line widths are field-dependent, especially for the perpendicular component of the spec-

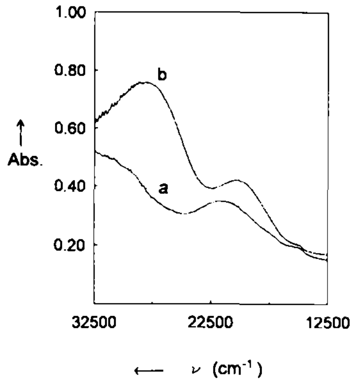


Fig. 4. Diffuse reflectance spectra of [Co^{II}(cyclam)]$^{2+}$–NaY during an oxygenation-evacuation cycle: a) original sample, under vacuum; b) after exposure to 40 mbar of pure O_2.

trum. This has been attributed to motional phenomena and was also observed, for example, for low-spin [Co(phthalocyanine)] complexes.[16] The EPR spectrum was simulated to second order in perturbation; the line width was modeled as a linear function of the spin quantum number m_I. The best fit of the experimental spectrum was obtained with $g_\perp$ = 2.70, $g_\parallel$ = 1.95, $|A_\perp|$ = 0.020 cm^{-1}, $|A_\parallel|$ = 0.015 cm^{-1} (Fig. 5).

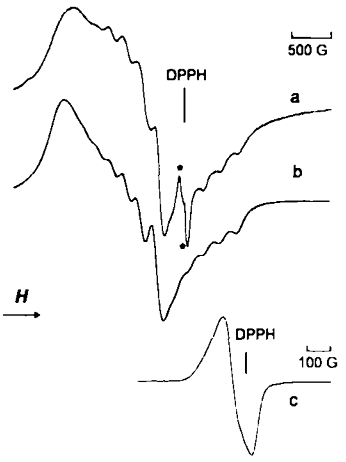


Fig. 5. EPR spectra of [Co^{II}(cyclam)]$^{2+}$–NaY recorded at 9.51 GHz and 293 K: a) sample under vacuum; b) simulation of a); c) trace a) after exposure to 40 mbar of pure O_2. The asterisks denote the signal of a superoxo impurity.

Both low-spin and high-spin forms of [Co^{II}(cyclam)]$^{2+}$ have been reported.[17, 18] The observation of a small amount of low-spin complexes implies that a fraction of the cyclam molecules assumes a planar, *trans* conformation around Co^{2+}.[19] The parameters of this low-spin [Co^{II}(cyclam)]$^{2+}$ complex are very close to those of planar, four-coordinate low-spin Co^{2+} complexes such as [Co^{II}(porphyrin)][20] or [Co^{II}(ethylenediamine)$_2$]$^{2+}$ intercalated in a hectorite clay [21] (Table 3). Based on the criteria for low-spin Co^{2+} proposed by Nishida and Kida,[22] the unpaired electron in the zeolitic low-spin [Co^{II}(cyclam)]$^{2+}$ can be located with certainty in a d_{z^2} orbital, since $g_1, g_2 > g_3$ and $|A_\parallel|$ is very large. The magnitude of $|A_\perp|$ can then be used to estimate the strength of the axial coordination to planar complexes. For low-spin [Co^{II}(cyclam)]$^{2+}$ complexes in solution, $|A_\perp|$ is small (typically < 0.003 cm^{-1}); these complexes must therefore be formulated as five-coordinate adducts of planar [Co^{II}(cyclam)]$^{2+}$ with a base such as water or pyridine.[17a] For the same complex in a zeolitic environment, $|A_\perp|$ is much larger; this indicates that the axial coordination position on the complex is vacant and excludes any direct coordination of the zeolite lattice or of residual water to the complex. A similar trend was observed for the Schiff base complex [Co^{II}(acacen)] synthesized in zeolite Y[3b] and for low-spin Co^{2+} or Ni^{2+} complexes in clay materials.[14, 21, 23] In other words, it seems to be a general trend that the ligand field exerted by inorganic surfaces on planar TMI complexes is negligible. While in the case of clays electronic arguments have been invoked to account for this observation,[23] the coordination of the complex by the inorganic (zeolite) surface may also be impeded for steric reasons; an analogous situation is encountered, for example, in the hindered interaction between [Co^{II}(porphyrin)] and 2,6-substituted pyridine.[24]

It is, however, all but certain that the low-spin EPR signal and the 21 500 cm^{-1} DRS (diffuse reflectance spectroscopy) band for [Co^{II}(cyclam)]$^{2+}$–NaY correspond to the same species. Evidence for the presence of two distinct species is presented in the next sections.

Table 3. EPR parameters of low-spin [Co^{II}(cyclam)]$^{2+}$ in NaY zeolite and of some related low-spin Co^{2+} complexes.

Complex	Solvent	$g_\perp$	$g_\parallel$	$\|A_\perp\|$ [a]	$\|A_\parallel\|$ [a]	Ref.
[Co^{II}((p-CH$_3$)TPP] [b]	toluene	2.709	1.994	200	135	[20]
[Co^{II}(en)$_2$]$^{2+}$ [c]	hectorite	2.579	1.964	174	149	[21]
[Co^{II}(cyclam)]$^{2+}$	NaY zeolite	2.67	1.95	160	150	this work
[Co^{II}(cyclam)]$^{2+}$	H_2O	2.28	2.021	10	123	[17a]

[a] *In units of* 10^{-4} cm^{-1}. [b] *TPP = tetraphenylporphyrin.* [c] *en = ethylenediamine.*

Reactivity of [Co^{II}(cyclam)]$^{2+}$–NaY and [Co^{II}(tetren)]$^{2+}$–NaY towards O_2: [Co^{II}(cyclam)]$^{2+}$–NaY turns pink upon exposure to 40 mbar of O_2. In the electronic spectrum two intense bands appear at 20 100 and 28 000 cm^{-1}, obscuring possible changes of the d–d bands (Fig. 4). In the EPR spectrum, a strong, anisotropic signal appears around the free-electron value (Fig. 5). The original low-spin [Co^{II}(cyclam)]$^{2+}$ signal is not affected by O_2 exposure. The chemisorbed dioxygen can be removed by a 300 s evacuation at 373 K; renewed O_2 exposure results in full restoration of the oxygen-induced EPR and DRS signals. This oxygenation-evacuation cycle can be repeated at least three times without observation of intensity loss.

Spectral characteristics, such as the bands assigned to charge transfer between Co^{3+} and O_2^-, allow us to distinguish between 1:1 superoxo, 2:1 μ-peroxo and 2:1 μ-superoxo adducts. For 1:1 superoxo species, the main LMCT (ligand-to-metal charge-transfer) band is expected between 27 000 and 29 000 cm^{-1}, while dimers absorb between 31 000 and 33 000 cm^{-1}. The less intense MLCT (metal-to-ligand charge-transfer) bands are even more distinctive (20 000–20 700 cm^{-1} for 1:1, 14 000 cm^{-1} for 2:1 complexes).[25] Comparison of these frequencies with those of [Co^{II}(cyclam)]$^{2+}$–NaY (20 100 and 28 000 cm^{-1}) leaves no doubt that the O_2 activation on [Co^{II}(cyclam)]$^{2+}$–NaY is of a mononuclear nature. Even after two cycles, there is no evidence for irreversible oxidation to Co^{3+}. The oxygen-dependent EPR signal of [Co^{II}(cyclam)]$^{2+}$–NaY is too broad to allow determination of the number of hyperfine lines, but the shape of the signal and its total width (about 300 G) are typical for [Co^{III}L·O_2^-]$^{2+}$ adducts; the signal is therefore easily distinguished from that of, for example, free superoxo species in zeolites.

These data prove that the reaction between [Co^{II}(cyclam)]$^{2+}$ and O_2 does not proceed beyond the monomeric cobalt superoxo adduct. The reversibility and stability of the [Co^{II}(cyclam)]$^{2+}$–NaY system enable the construction of a dioxygen sorption isotherm (Fig. 6). Such a graph illustrates the potential of [Co^{II}(cyclam)]$^{2+}$–NaY as a dioxygen sorbing material. Its high affinity ($p_{1/2}$ < 1 mbar) and capacity (about

0570-0833/95/0202-0147 $ 20.00+.25/0

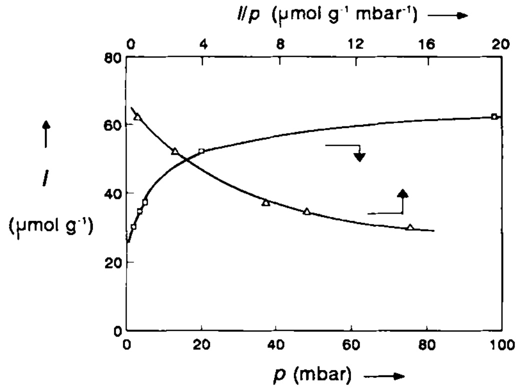


Fig. 6. Oxygen sorption behavior of $[Co^{II}(cyclam)]^{2+}$ – NaY: □: $[Co^{III}(cyclam) \cdot O_2^-]^{2+}$ concentration (I, µmol g^{-1}) vs. O_2 pressure (mbar); △: $[Co^{III}(cyclam) \cdot O_2^-]^{2+}$ concentration (I, µmol g^{-1}) vs. I/p_{O_2} (µmol g^{-1} mbar^{-1}). The slope of the latter plot equals the pressure $p_{1/2}$ at which half of the active sites are saturated.

95 µmol g^{-1}, or 15% of the Co content in our best synthesis) mean that the system ranks among the very best comparable dioxygen sorbing materials, such as $[Co^{II}(bipyridine)(terpyridine)]^{2+}$ – NaY or $[Co^{II}(CN)_5]^{3-}$ – NaY.[26] An advantage of our system is clearly that its synthesis involves the adsorption of only a single ligand.

Dioxygen sorption on $[Co^{II}(tetren)]^{2+}$ – NaY is much less reversible, as is illustrated by the appearance of an intense 33000 cm^{-1} band of μ-peroxo complexes already after one oxygenation–evacuation cycle. Though several procedures were attempted, $[Co^{III}L \cdot O_2^-]^{2+}$ concentrations in $[Co^{II}(tetren)]^{2+}$ – NaY never exceeded 3 µmol g^{-1}.[27] The extremely high electron density provided by the tetren ligand may be one of the reasons for the limited reversibility in this system.

***cis/trans* Complexation in cyclam-containing zeolites**: The O_2 sorption experiments allowed us to complete our view of Co^{2+} complexation in $[Co^{II}(cyclam)]^{2+}$ – NaY. The low-spin Co^{2+} complex in $[Co^{II}(cyclam)]^{2+}$ – NaY has an unpaired electron in the d_{z^2} orbital. Although this orbital is ideally oriented for spin-pairing with O_2, the axial coordination of Co^{2+} is far too weak to allow superoxo formation, as was shown by analysis of the EPR hyperfine parameters. The oxygen-binding capacity of the material therefore must be ascribed to a second $[Co^{II}(cyclam)]^{2+}$ complex, which is EPR silent; hence this complex must have a high-spin electronic configuration and a folded, *cis* cyclam conformation.[19] The active oxygen-binding complex is probably structurally similar to the oxygen binding $[Co^{II}(s\text{-}N,N'\text{-diethylethylenediamine})_2]^{2+}$, for which a *cis* conformation was proposed.[28] Quantification of the EPR data for oxygenated and deoxygenated $[Co(cyclam)]^{2+}$ – NaY shows that the *cis* complexes by far outnumber the *trans* complexes.

The predominance of *cis* complexes in $[Co^{II}(cyclam)]^{2+}$ – NaY is in contrast to the *trans* character of the complexation in $[Ni^{II}(cyclam)]^{2+}$ – NaY, which was inferred from, inter alia, magnetic measurements. This difference is confirmed by analysis of the FT-Raman spectra (Fig. 7). Previous Raman studies on comparable materials have highlighted the Co–O or O–O vibrations under resonance Raman conditions.[6,29] The present spectra were recorded with a NIR excitation FT-Raman spectrometer. Although the signals are weak, clear features can be seen below 500 cm^{-1}. For samples under inert atmosphere, the following bands were observed: for $[Co^{II}(cyclam)]^{2+}$ – NaY: 480, 452, 390, 373, 318, 300, and 245 cm^{-1}; for $[Ni^{II}(cyclam)]^{2+}$ – NaY: 444, 373, 350, 303, and 245 cm^{-1}; and for cyclam-containing NaY: 418, 361, 303, and 245 cm^{-1}. A detailed (normal mode) analysis of the spectra of cyclam complexes is at present still lacking, but the differences in the spectra are most probably related to the different conformations of the ligand around the transition metals. Indeed, while *trans* $[Ni^{II}(cyclam)]^{2+}$ has D_{4h} symmetry, *cis* $[Co^{II}(cyclam)]^{2+}$ can have at most C_{4v}. The lower symmetry is expected to lead to a higher number of Me–N vibrations, as observed upon going from $[Ni^{II}(cyclam)]^{2+}$ – NaY to $[Co^{II}(cyclam)]^{2+}$ – NaY.

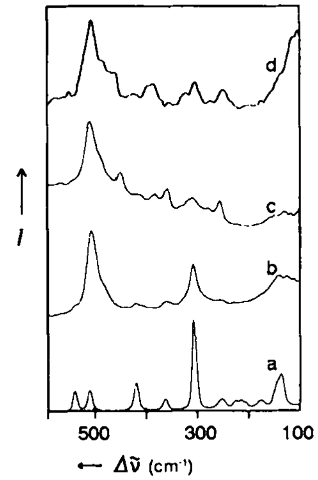


Fig. 7. Low-frequency FT-Raman spectra: a) cyclam; b) cyclam adsorbed on NaY; c) $[Ni^{II}(cyclam)]^{2+}$ – NaY; d) $[Co^{II}(cyclam)]^{2+}$ – NaY.

Conclusion

Interaction between a zeolite and a metal ion can often be described as the chelation of an ion by a bi- or tridentate, *cis*-complexing surface. A new aspect brought forward in this work is that the same zeolite surface cannot bind transition metal complexes in a *monodentate* fashion; the approach between the planar metal complex and the concave zeolite surface is most probably hindered. This implies that working in a dehydrated zeolite environment instead of in solution may shift the complexation equilibrium from *trans* to *cis*, especially when complexes have no obvious preference for either form, as in some Co^{2+} complexes. This explains why square-planar *trans* $[Co^{II}(Schiff\ base)]^{[3]}$ or $[Co^{II}(polyamine)]^{2+}$ complexes are formed in quite small amounts in zeolites, if they are observed at all. Clay minerals also lack the ability to bind in a monodentate fashion. However, they often favor *trans* over *cis* complexes by intercalating the complexes between the planar clay surfaces and thus blocking the axial binding sites.[14,21,23] Against this background, the specificity of complexation in a zeolite can now fully be appreciated: *cis* is favored over *trans*, but if *trans* is formed (as with Ni^{2+}), the axial sites (e.g., for H_2O) are still accessible.

In these zeolite-based systems, ligand variation can be as precise a tool for modification of the redox properties of a transition metal as in solution. For square-planar Ni^{2+}, for instance, the ligand field can be tuned by varying the size of the ligand. The new dioxygen binding system $[Co^{II}(cyclam)]^{2+}$ – NaY is a fine example of a new microporous redox solid; its properties were optimized by ligand variation. We are presently studying the catalytic potential of the parent Ni^{2+} systems.

Experimental Procedure

Sample preparation: The NaY zeolite was a sample from the PQ Corp., with a Si:Al ratio of 2.46. NaA (type 4 A) was a product from Union Carbide. Following products were purchased commercially: 1,4,8,11-tetraazacyclotetradecane (cyclam), triethylenetetramine (trien), tetraethylenepentamine (tetren) (from Aldrich), *N,N'*-bis(2-aminoethyl)propylenediamine (2,3,2-amine), *N,N'*-bis(3-aminopropyl)ethylenediamine (3,2,3-amine, from Akros Chimica). The zeolite samples were ion-exchanged by stirring the appropriate amount of NaY or NaA at room temperature over 4 h in a 2 mM solution of $Co(CH_3COO)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 6H_2O$, or $CrCl_3 \cdot 6H_2O$, resulting in loadings of about 3.6 wt% for Co^{2+} and Ni^{2+}, 3.4 wt% for Mn^{2+}, and 0.8 wt% for Cr^{3+}. The pH of the exchange suspension was kept between 5 and 6. The Co^{2+}, Mn^{2+}, and Ni^{2+} zeolites were dried by gradual heating (1 K min^{-1}) to 573 K under a nitrogen flow (50 mL min^{-1}); the Cr^{3+} zeolite was dried under vacuum with gradual heating to a final temperature of 473 K, in order to prevent hydrolysis of Cr^{3+} as much as possible. The dried zeolites were mixed in a dry atmosphere glove box with a 10% excess of the dry ligands. The mixture was heated at 473 K under an atmosphere of N_2 at 10^5 Pa. The resulting samples are denoted as $[Ni^{II}(tetren)]^{2+}$–NaY, $[Co^{II}(cyclam)]^{2+}$–NaY, etc. Where necessary, Soxhlet extractions were performed for 4 h with dichloromethane. To observe the spectral features of faujasite adsorbed cyclam, NaY was dried in the same way as the other zeolites, followed by an identical ligand adsorption. Rehydrations were performed at room temperature in a relative humidity of 79% over a saturated NH_4Cl solution.

Instrumentation: FT-IR spectra were recorded on a Nicolet 730 spectrometer. KBr pellets or self-supporting zeolite wafers were used. Measurements on these wafers were performed in transmission mode in a purpose-built evacuation chamber with temperature control. N–H stretching bands were observed after evacuation for 1 h at 373 K. FT-Raman spectra were recorded with a Bruker IFS100 spectrometer (1064 nm irradiation, 100 mW power, 3000 scans). For UV-Vis-NIR diffuse reflectance measurements, a Cary 5 photometer with integration sphere was employed. Spectra were recorded between 5000 and 50000 cm^{-1}. EPR spectra were recorded at X-band (9.50 GHz) in a TE_{104} cavity with a Bruker ESP 300E apparatus, equipped with a liquid nitrogen cooling accessory. In order to remove traces of dioxygen, which were evident in the EPR spectra, the samples were outgassed for 5 min at 373 K before the spectra of the oxygen-free samples were recorded. Spin densities were estimated by double integration using KBr-diluted $[Cu(acac)_2]$ for calibration. Magnetic experiments were performed with a MPMS Squid magnetometer from Quantum Design, at field strengths between 0.1 and 0.8 T and at temperatures between 30 and 400 K. Thermogravimetric experiments were performed with a Setaram-92 balance. Samples were heated under He–O_2 atmosphere at 1 K per 12 s.

Acknowledgements: We are indebted to the N. F. W. O. (National Fund for Scientific Research; DEDV and PPKG) and to the I. W. T. (Vlaams Instituut voor de bevordering van het Wetenschappelijk-Technologisch Onderzoek in de Industrie; DLV) for research-assistant fellowships. We thank R. A. Schoonheydt for fruitful discussions. This work was sponsored by the Belgian Government as part of the Interuniversitary Attraction Pole on Supramolecular Catalysis.

Received: October 31, 1994 [F12]

---

[1] a) G. A. Ozin, C. Gil, *Chem. Rev.* **1989**, *89*, 1749; b) D. R. Corbin, N. Herron, *J. Mol. Catal.* **1994**, *86*, 343; c) D. E. De Vos, F. Thibault-Starzyk, P. P. Knops-Gerrits, R. F. Parton, P. A. Jacobs, *Makromol. Chem. Macromol. Symp.* **1994**, *80*, 157.

[2] E. F. Vansant, J. H. Lunsford, *Adv. Chem. Ser.* **1973**, *100*, 441.

[3] a) N. Herron, *Inorg. Chem.* **1986**, *25*, 4714; b) D. E. De Vos, E. J. P. Feijen, R. A. Schoonheydt, P. A. Jacobs, *J. Am. Chem. Soc.* **1994**, *116*, 4746.

[4] E. C. Niederhoffer, J. H. Timmons, A. E. Martell, *Chem. Rev.* **1984**, *84*, 137.

[5] a) L. Y. Martin, L. J. DeHayes, L. J. Zompa, D. H. Busch, *J. Am. Chem. Soc.* **1974**, *96*, 4046; b) D. H. Busch, *Chem. Rev.* **1993**, *93*, 847.

[6] P. K. Dutta, C. Bowers, *Langmuir* **1991**, *7*, 937.

[7] H. Stetter, K. H. Mayer, *Chem. Ber.* **1961**, *94*, 1410.

[8] X. G. Lei, C. E. Doubleday, M. B. Zimmt, N. J. Turro, *Pure Appl. Chem.* **1986**, *58*, 1219.

[9] H. Irving, R. J. P. Williams, *Nature* **1948**, *162*, 746.

[10] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., in *Studies in Physical and Theoretical Chemistry*, Elsevier, Amsterdam, **1984**.

[11] L. Fabbrizzi, *Inorg. Chem.* **1977**, *16*, 2667.

[12] R. G. Wilkins, R. Yoon, D. W. Margerum, D. C. Weatherburn, *J. Am. Chem. Soc.* **1969**, *91*, 4326.

[13] a) A. Anichini, L. Fabbrizzi, P. Paoletti, R. M. Clay, *Inorg. Chim. Acta* **1977**, *24*, L21; b) N. Herron, P. Moore, *Inorg. Chim. Acta* **1979**, *36*, 89.

[14] a) R. A. Schoonheydt, F. Velghe, J. B. Uytterhoeven, *Inorg. Chem.* **1979**, *18*, 1842; b) R. A. Schoonheydt, F. Velghe, R. Baerts, J. B. Uytterhoeven, *Clays Clay Min.* **1979**, 27, 269.

[15] Y. Nishida, S. Kida, *Bull. Chem. Soc. Jpn* **1972**, *45*, 461.

[16] J. A. De Bolfo, T. D. Smith, J. F. Boas, J. R. Pilbrow, *J. Chem. Soc. Dalton Trans.* **1976**, 1495.

[17] a) J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, G. M. Simic, M. D. Glick, P. D. Rillema, *J. Am. Chem. Soc.* **1977**, *99*, 429; b) S. Matsuoka, K. Yamamoto, T. Ogata, M. Kusaba, N. Nakashima, E. Fujita, S. Yamagida, *ibid.* **1993**, *115*, 601; c) Y. Hung, L. Y. Martin, S. C. Jackels, M. A. Tait, D. H. Busch, *ibid.* **1977**, *99*, 4029.

[18] a) G. McLendon, M. Mason, *Inorg. Chem.* **1978**, *17*, 362; b) R. D. Jones, D. A. Summerville, F. Basolo, *Chem. Rev.* **1979**, *79*, 139.

[19] EPR spectra of low-spin $[Co^{II}(cyclam)]^{2+}$ are only detected after reduction of $[Co^{III}(cyclam)]^{3+}$, for example, by sodium amalgam or by photolysis [17]. The *trans* cyclam conformation of $[Co^{III}(cyclam)]^{3+}$ is probably preserved upon reduction, leading to *trans* low-spin $[Co^{II}(cyclam)]^{2+}$. On the other hand, stability constant data for the direct reaction between divalent Co^{2+} and cyclic polyamines in aqueous solution indicate that the direct complexation of Co^{2+} by cyclam leads to *cis* complexes, for which a high-spin state is observed: M. Kodama, E. Kimura, *J. Chem. Soc. Dalton Trans.* **1980**, 327.

[20] F. A. Walker, *J. Magn. Res.* **1974**, *15*, 202.

[21] R. A. Schoonheydt, J. Pelgrims, *J. Chem. Soc. Faraday Trans. II* **1983**, *79*, 1169.

[22] Y. Nishida, S. Kid a, *Coord. Chem. Rev.* **1979**, *27*, 275.

[23] L. Ukrainczyk, M. Chibwe, T. J. Pinnavaia, S. A. Boyd, *J. Phys. Chem.* **1994**, *98*, 2668.

[24] F. A. Walker, *J. Am. Chem. Soc.* **1970**, *92*, 4235.

[25] A. B. P. Lever, H. B. Gray, *Acc. Chem. Res.* **1978**, *11*, 348.

[26] a) S. Imamura, J. H. Lunsford, *Langmuir* **1985**, *1*, 326; b) R. J. Taylor, R. S. Drago, J. P. Hage, *Inorg. Chem.* **1992**, *31*, 253.

[27] Stabilization of $[Co^{III}(tetren)\cdot O_2^-]^{2+}$ in the supercages of NaA zeolite has been claimed [6]. Though we have adsorbed tetren on Co zeolites both in its pure form or from aqueous solution, we have not observed higher superoxo concentrations on CoNaA than on CoNaY (<4 µmol g^{-1}). Moreover, tetren seems to be size-excluded from 8-ring zeolites (see above); hence reaction of hydrated CoNaA with tetren probably leads to complexation on the outer zeolite surface.

[28] a) G. P. Khare, E. Lee-Ruff, A. B. P. Lever, *Can. J. Chem.* **1976**, *54*, 3424; b) S. R. Pickens, A. E. Martell, G. McLendon, A. B. P. Lever, H. B. Gray, *Inorg. Chem.* **1978**, *17*, 2190.

[29] P. K. Dutta, R. E. Zaykoski, *J. Phys. Chem.* **1989**, *93*, 2603.