Influences of Ligand and of Zeolite Topology on the Structure of Co^{II} Schiff Base Chelates in Faujasite Type Zeolites

D. E. De Vos, E. J. P. Feijen, R. A. Schoonheydt, and P. A. Jacobs*

Contribution from the Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, 3001 Heverlee, Belgium

Received July 12, 1993. Revised Manuscript Received January 19, 1994®

Abstract: The reaction in dehydrated faujasite zeolites of two different topologies between charge-compensating Co^{II} cations and five different Schiff base ligands was studied by EPR and vis–near-IR spectroscopy. Tetradentate as well as pentadentate ligands were used for this comparison, while the behavior of a faujasite with cubic symmetry (zeolite Y) was compared to that of EMT, a faujasite with hexagonal symmetry. After reaction of the Schiff bases salen (bis(salicylaldehyde) ethylenediimine) (**1**) and acacen (bis(acetylacetone) ethylenediimine) (**2**) with CoNaY zeolite, low-spin square-planar Co^{II} was observed in low concentrations in [Co^{II}(acacen)]NaY. In [Co^{II}(salen)]NaY, formation of planar complexes is doubtful. Use of these tetradentate ligands for oxygen activation in zeolite Y results in low concentrations of active, oxygen-binding Co^{II}. Incorporation of a nitrogen base into these Schiff bases results in the pentadentate ligands smdpt (bis(salicylaldehyde) methylnitrilodipropylenediimine) (**3**) and amdpt (bis(acetylacetone) methylnitrilodipropylenediimine) (**4**). Use of these ligands greatly raises the fraction of the Co^{II} participating in the oxygen activation. When the Co^{II} form of the hexagonal faujasite NaEMT is loaded with smdpt (**3**), up to 25% of the total Co^{II} reversibly binds dioxygen. Intrazeolitic Co^{II} was also reacted with pyren (bis(2-pyridinecarboxaldehyde) ethylenediimine) (**5**), a ligand which occupies a position structurally intermediate between Schiff bases and bipyridine. Different EPR parameters were observed for [Co^{III}(smdpt)·O_2^-] occluded in cubic faujasite (NaY) and hexagonal faujasite (NaEMT), reflecting the influence of the zeolite topology on complex formation. The dioxygen sorption of these new materials was studied quantitatively.

Introduction

Dioxygen-binding Co^{II} complexes have been formed in zeolites using ligands like amines, cyanide, and bi- or terpyridine.[1] In these materials the monodispersion of the active chelates over the zeolite cages retards formation of binuclear complexes and enhances the reversibility of O_2 binding. Optimization of such systems has led to some perspectives in air separation.[2,3] A major disadvantage of most of these systems is that the number of mono- or bidentate ligands surrounding the Co^{II} cation is not easily controlled.[1c,3] The use of polydentate ligands may solve such problems as the formed complexes are expected to be more stable and the number and nature of the coordinating atoms may be controlled more accurately by assembling them in a single ligand molecule.

This approach has been proposed by Herron[4] for [Co^{II}(salen)(pyridine)] in zeolite Y (salen (**1**) = bis(salicylaldehyde) ethylenediimine) and was also followed for [Co^{II}(tetren)]$^{2+}$ in NaA zeolite (tetren = tetraethylenepentamine).[5] As these complexes are too large to pass through the pore openings of the zeolite cages, they have to be assembled *in situ* in the cages. The characteristics of the zeolite Y entrapped [Co^{II}(salen)] seem though to be different from those of [Co^{II}(salen)] in solution or [Co^{II}(salen)] doped in diamagnetic crystals. Indeed, planar [Co^{II}(salen)] or its axial base adducts are generally EPR detectable low-spin complexes,[6] but [Co^{II}(salen)]NaY is EPR silent, even after treatment with pyridine.[4] Anomalies are found as well in the electrochemical behavior of [Co^{II}(salen)]NaY; cyclic voltammetry reveals a Co^{3+}/Co^{2+} redox transition which is absent in solution.[7] Schiff bases other than salen until now have not been used for complexation within zeolites.

The present paper therefore deals with the interaction of a number of tetra- and pentadentate Schiff bases with Co^{II} exchanged in faujasites. It not only describes the oxygen activation in a number of new supramolecular systems but attempts to compare and rationalize intrazeolitic complexation by different Schiff bases. Therefore, in the first step, the behavior of salen (**1**) in CoNaY zeolite is compared to that of the closely related tetradentate acacen (bis(acetylacetone) ethylenediimine) (**2**). However, oxygen binding on the planar Co^{II} complexes of these ligands requires axial coordination of a Lewis base, which provides a higher electron density at the metal center.[8] In previous work on zeolites, this base has been added separately,[4] but in the present case, it has also been incorporated in the ligand. Thus, in the second step, zeolitic Co^{II} was complexed with ligands in which a tertiary nitrogen group was inserted into tetradentate ligands, such as smdpt (bis(salicylaldehyde) methylnitrilodipropyldiimine) (**3**) and amdpt (bis(acetylacetone) methylnitrilodipropyldiimine) (**4**). Finally the Schiff base pyren (bis(2-pyridinecarboxaldehyde) ethylenediimine) (**5**) was used for Co^{II} complexation. This ligand occupies a position structurally intermediate between salen and bipyridine and provides a link with previous work of the Lunsford group on zeolite-hosted bipyridine complexes.[1c,2] The structures of the employed ligands have been assembled in Chart 1.

Some of the envisaged complexes (e.g., [Co^{II}(smdpt)]) are considerably larger than [Co^{II}(salen)], used in Herron's classic paper.[4] Therefore, not only cubic faujasite (zeolite NaY, with FAU topology) was used but also its hexagonal polytype (denoted as NaEMT, with EMT topology). The zeolite with this EMT topology contains smaller hypocages and larger hypercages. The hypercages in a hexagonal faujasite are delimited by five 12-

---

® Abstract published in *Advance ACS Abstracts*, May 1, 1994.

(1) (a) Howe, R. F.; Lunsford, J. H. *J. Phys. Chem.* **1975**, *79*, 1836. (b) Taylor, R. J.; Drago, R. S.; George, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 6610. (c) Mizuno, K.; Imamura, S.; Lunsford, J. H. *Inorg. Chem.* **1984**, *23*, 3510.

(2) Imamura, S.; Lunsford, J. H. *Langmuir* **1985**, *1*, 326.

(3) Taylor, R. J.; Drago, R. S.; Hage, J. P. *Inorg. Chem.* **1992**, *31*, 253.

(4) Herron, N. *Inorg. Chem.* **1986**, *25*, 4714.

(5) Dutta, P. K.; Bowers, C. *Langmuir* **1991**, *7*, 937.

(6) (a) Earnshaw, A.; Hewlett, P. C.; King, E. A.; Larkworthy, L. F. *J. Chem. Soc. A* **1968**, 241. (b) Von Zelewsky, A.; Fierz, H. *Helv. Chim. Acta* **1973**, *56*, 977. (c) Ochiai, E. *J. Chem. Soc., Chem. Commun.* **1972**, 489. (d) Busetto, C.; Cariati, F.; Fantucci, P.; Galizzioli, D.; Morazzoni, F. *J. Chem. Soc., Dalton Trans.* **1973**, 1712.

(7) Bedioui, F.; De Boysson, E.; Devynck, J.; Balkus, K. J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3831.

(8) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

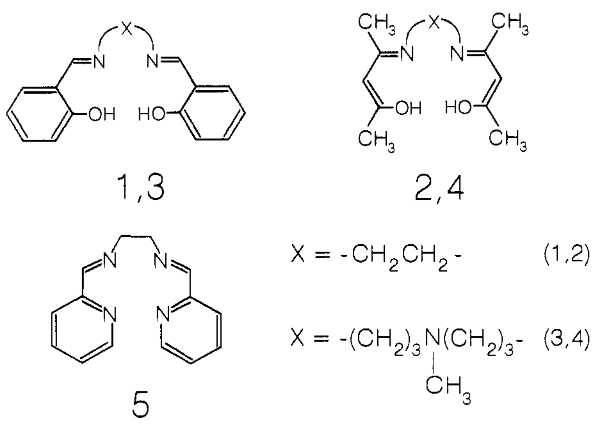
0002-7863/94/1516-4746$04.50/0

Table 1. Survey of EPR Observable Species in Schiff Bases Containing CoNa Faujasites

sample	extraction	EPR parameters[a]	assignment	concentration (μmol·g^{-1})[b]
[Co^{II}(salen)]NaY	none	$g = 1.80$[c]	Co^{II}, low spin[d]	*e*
	CH_2Cl_2 or pyridine	$g_\perp = 2.20$, $g_\parallel = 1.94$	Co^{II}, low spin	5
[Co^{II}(acacen)]NaY	none	$g_1 = 2.85$, $g_2 = 2.097$, $g_3 = 1.969$	Co^{II}, low spin, four-coordinate square planar	5
[Co^{II}(pyren)]NaY	*f*	$g_1 = 2.26$, $g_2 = 2.152$, $g_3 = 2.04$	Co^{II}, low spin[g]	26[g]
[Co^{II}(salen)]NaY	CH_2Cl_2 or pyridine	*h*	CoL·O_2[i]	2
[Co^{II}(acacen)]NaY	CH_2Cl_2 or pyridine	*h*	CoL·O_2[i]	2
[Co^{II}(smdpt)]NaY	*f*	$g_z = 2.099$, $A_z = 27$ G	CoL·O_2	12
[Co^{II}(smdpt)]NaEMT	none	*h*	CoL·O_2[i]	16
	CH_2Cl_2	$g_z = 2.090$, $A_z = 20$ G	CoL·O_2	38
[Co^{II}(amdpt)]NaY	*f*	$g_z = 2.080$, $A_z = 24$ G	CoL·O_2	6
[Co^{II}(pyren)]NaY	*f*	$g_z = 2.058$, $A_z = 14$ G	CoL·O_2	9[j]

[a] Only the most diagnostic values have been retained. For complete parameters sets, see text. Except where noted (notes *c* and *g*), the spectra had normal temperature dependence. [b] The total Co^{2+} content of the samples was 154 ± 10 μmol·g^{-1}. Spin concentrations were measured at 130 K under 1000 mbar N_2 or under 1000 mbar O_2 for CoL·O_2. The concentrations given are maximum values obtained through at least three independent syntheses of each material. [c] Sample is silent at room temperature, broad peak ($g = 1.80$) at 130 K. [d] Tentative assignment (see text). [e] Insufficient resolution for quantification. [f] The spectral characteristics were the same before and after CH_2Cl_2 extraction. [g] Low-spin Co^{II} in equilibrium with high-spin Co^{II}; low-spin Co^{II} concentration determined at 110 K. [h] Nearly axially symmetric signal; $g_\parallel$ (between 2.06 and 2.10) > $g_\perp$ (between 1.99 and 2.02). Insufficient resolution for precise parameter determination. [i] Superoxo assignment based on reversible O_2 dependence of the signals and on approximate parameters (see note *h*). [j] Superoxo concentration determined at 293 K because of interfering signals at 130 K.

Chart 1



membered rings of oxygen atoms and are therefore considerably more spacious than the supercages of the cubic faujasite NaY, which have only four 12-membered ring openings.[9,10] The variation of the zeolite topology may allow us to look at the effect of the cage size on the formation of the intrazeolitic Co^{II} complexes.

Results and Discussion

Characterization of [Co^{II}(salen)]NaY and [Co^{II}(acacen)]NaY before Soxhlet Extraction. Before extraction of the excess ligand and under an inert atmosphere, [Co^{II}(salen)]NaY has an EPR spectrum with an anomalous temperature dependence. At room temperature no signals can be attributed to Co^{II}, but cooling reveals some Co^{II}-linked features. At 130 K, a broad peak is seen around $g = 1.80$ and some structure (with spacings of 30 G) is observed between $g = 2.00$ and $g = 1.85$. In the absence of a well-resolved hyperfine structure, it is difficult to parametrize this spectrum or to quantify the amount of Co^{II} involved. In Table 1 the most important EPR observations of this study are assembled.

[Co^{II}(acacen)]NaY on the contrary presents an orthorhombic spectrum which is essentially temperature independent (see Figure 1). The Co^{II} hyperfine structure is well resolved on two of the three spectral components. From spectral simulation, the following parameters were obtained: $g_1 = 2.85 \pm 0.01$, $g_2 = 2.097 \pm 0.005$, $g_3 = 1.969 \pm 0.005$, $A_1 = 0.0029 \pm 0.0003$ cm^{-1}, $A_2 = 0.0043 \pm 0.0001$ cm^{-1}, $A_3 = 0.0030 \pm 0.0001$ cm^{-1}. This species is easily identified as a four-coordinate low-spin Co^{II} complex (see below). By double integration, the spin concentration is estimated to be on the order of 2.5×10^{18} spins per *g*, corresponding to 3% of the total Co^{II} content.

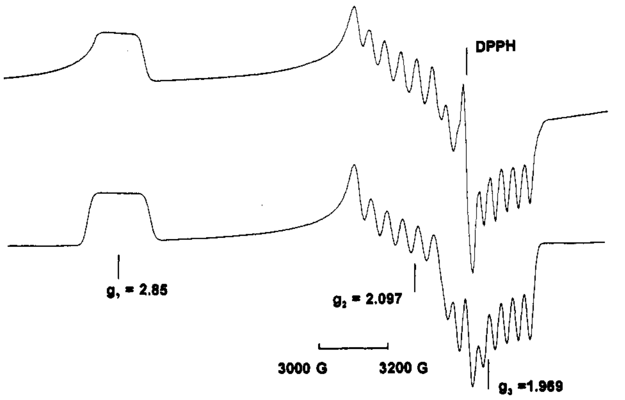


Figure 1. (top) X-band EPR spectrum (130 K, N_2 atmosphere, nonextracted sample) of [Co^{II}(acacen)]NaY. (bottom) Computer simulation of top.

While the EPR spectrum of [Co^{II}(salen)]NaY is not sensitive to replacement of the nitrogen atmosphere by oxygen, formation of a superoxo complex was observed on [Co^{II}(acacen)]NaY, merely as a superposition on the spectrum of the low-spin Co^{II} species. The low-spin [Co^{II}(acacen)] species itself does not seem to be reactive toward O_2.

In spite of their different EPR spectra, [Co^{II}(salen)]NaY and [Co^{II}(acacen)]NaY have very similar vis–near-IR reflectance spectra (Figure 2). On the starting dehydrated CoNaY zeolite, Co^{II} is in a mainly tetrahedral coordination and is characterized by a triplet of bands in the visible domain and a less resolved triplet in the near-IR.[11] The Schiff base loaded zeolites [Co^{II}(salen)]NaY and [Co^{II}(acacen)]NaY are characterized by (i) considerable weakening of the bands of tetrahedral Co^{II} as only a band at 14 700 cm^{-1} clearly subsists, (ii) a weak band around 8500 cm^{-1}, and (iii) intense charge transfer and ligand transitions beyond 18 000 cm^{-1}; the strong shoulder at 19 000 cm^{-1} in [Co^{II}(salen)]NaY may very well be of charge-transfer origin.

The changes in the reflectance spectra suggest that upon complexation a considerable part of Co^{II} is no longer in the original tetrahedral coordination. For both materials, the weak band around 8500 cm^{-1} may be associated with a weak band at the

---

(9) (a) Newsam, J. M.; Treacy, M. M. J.; Vaughan, D. E. W.; Strohmaier, K. G.; Mortier, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 493. (b) Annen, M. J.; Young, D.; Arhancet, J. P.; Davis, M. E.; Schramm, S. *Zeolites* **1991**, *11*, 98.

(10) Delprato, F.; Delmotte, L.; Guth, L. J.; Huve, L. *Zeolites* **1990**, *10*, 546.

(11) Hutta, P. J.; Lunsford, J. H. *J. Chem. Phys.* **1977**, *66*, 4716.

Table 2. EPR Parameters of Low-Spin Square-Planar Cobalt(II) Schiff Base Complexes

complex	g_x	g_y	g_z	$\lvert A_x\rvert^a$	$\lvert A_y\rvert^a$	$\lvert A_z\rvert^a$	ref
[Co^{II}(acacen)] in [Ni^{II}(acacen)]	3.26	1.88	2.00	115.8	37.5	34.5	14
[Co^{II}(acacen)]NaY	2.85	1.969	2.097	29	30	45	this work
[Co(amben)(–)(chxn)] in nematic phase	2.737	1.987	2.132	27	28.6	23	15

^{a} Cobalt hyperfine splittings in 10^{-4} cm^{-1}. ^{b} (amben)(–)(chxn) = bis(*o*-aminobenzylidene)-(*R*,*R*)-(–)-1,2-cyclohexanediamine).

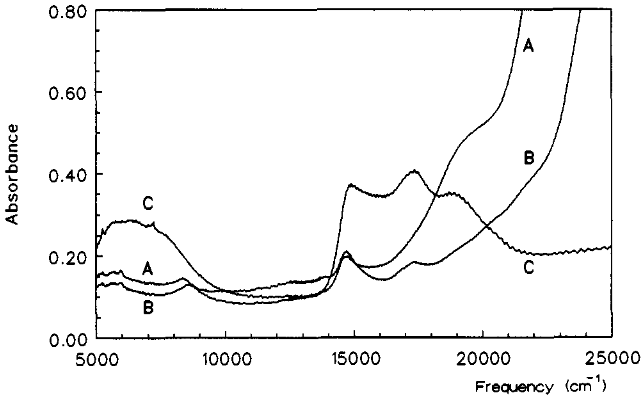


Figure 2. Vis–near-IR spectra of (A) [Co^{II}(salen)]NaY before soxhlet extraction, (B) [Co^{II}(acacen)]NaY before soxhlet extraction, and (C) the starting dehydrated CoNaY.

same frequency in the near-IR spectra of [Co^{II}(acacen)] and [Co^{II}(salen)] in noncoordinating solvents.[12] This band has been considered as typical for a square-planar organization of the ligand around Co^{II} and is now generally assigned to the transition from the $^2A_2(d_{yz})$ state to the $^2A_1(d_{x^2-y^2})$ state in low-spin four-coordinate Co^{II} complexes.[13] However, EPR fails to prove clearly the existence of square-planar species in [Co^{II}(salen)]NaY; the observed, temperature-dependent spectra without clear hyperfine structure cannot be related directly to those reported for low-spin [Co^{II}(salen)][6] in solution. Thus there is not sufficient spectral evidence for formation of planar [Co^{II}(salen)] in [Co^{II}(salen)]-NaY.

In case of [Co^{II}(acacen)]NaY, however, the presence of low-spin square-planar Co^{II} species was suggested by the near-IR spectrum and is confirmed in EPR. In Table 2, the parameters of [Co^{II}(acacen)]NaY are compared with those of [Co^{II}(acacen)] diluted in [Ni^{II}(acacen)][14] and with those of [Co^{II}(amben)-(–)(chxn)][15] (amben(–)(chxn = bis(*o*-aminobenzylidene)-(*R*,*R*)-(–)-1,2-cyclohexanediamine). The interpretation of our data is based on the analysis of Hitchman and of Nishida and Kida.[13] They found that the *g* and *A* values in low-spin Co^{II} Schiff base complexes are determined mainly by the energy of the $^2A_2(d_{yz}) \rightarrow {}^2A_1(d_{z^2})$ transition. The EPR parameters of [Co^{II}(acacen)]-NaY fit well into the values predicted for low-spin Co^{II} complexes by Hitchman's model, but the energy separation between the $(d_{yz})^1$ ground state and the $(d_{z^2})^1$ state, calculated from the observed EPR parameters, is considerably higher for [Co^{II}(acacen)] in NaY (2500 cm^{-1}) than for the same complex diluted in [Ni^{II}(acacen)] (only 1800 cm^{-1}). The EPR parameters of [Co^{II}(acacen)]NaY and the corresponding transition energy come even close to those of [Co^{II}(amben)(–)(chxn)], in which 4 N donors provide a very strong in-plane field (see Table 2). This may reflect that for [Co^{II}(acacen)] in NaY axial coordination is extremely weak, excluding any coordination of the complex by the zeolite or by residual OH^- or H_2O.

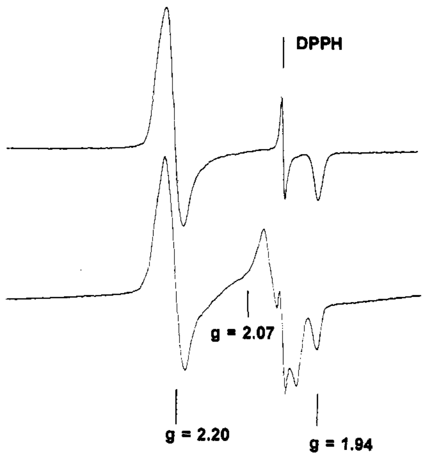


Figure 3. X-band EPR spectra (130 K) of CH_2Cl_2-extracted [Co(salen)]-NaY (top) under N_2 and (bottom) under 760 Torr of oxygen.

A low-spin Schiff base Co^{II} complex has an optimum reactivity toward incoming O_2 when the unpaired electron resides mainly in the d_{z^2} orbital, perpendicular to the plane of the complex. The electronic configuration which corresponds to the EPR parameters of [Co^{II}(acacen)]NaY is however $(d_{xz})^2(d_{x^2-y^2})^2(d_{z^2})^2(d_{yz})^1$; the inertness of the low-spin [Co^{II}(acacen)] species toward O_2 matches well the location of the unpaired electron in an orbital with partial in-plane character, d_{yz}.

Characterization of [Co(salen)]NaY and [Co(acacen)]NaY after Soxhlet Extraction. In solution, oxygen activation on tetradentate Schiff base Co^{II} complexes is largely promoted by the addition of a supplementary, axially coordinating base.[8] Therefore, the samples were extracted with dichloromethane or with pyridine; dichloromethane-extracted samples were afterward exposed to pyridine vapor at room temperature or were studied as such. The extraction is thus not only meant to remove the excess ligand but may also influence the Co^{II} coordination.

For all extracted [Co^{II}(salen)]NaY and [Co^{II}(acacen)]NaY samples, the 8500-cm^{-1} band in the vis–near-IR spectra was strongly weakened. In addition, pyridine extraction also affected the 14 700-cm^{-1} band, which remained important for samples extracted with dichloromethane. The reflectance spectra were not noticeably influenced by exposure to O_2 or by evacuation.

The EPR spectra of soxhet-extracted [Co^{II}(salen)]NaY are no longer temperature dependent as they were before extraction. For all samples, they consist of two Co^{II}-dependent, superimposed signals (Figure 3): (i) a nearly axially symmetric signal, with $g_\perp$ = 2.20 and $g_\parallel$ = 1.94, which is not sensitive to O_2, and (ii) an asymmetric signal, with approximately $g_\perp$ = 2.00 and $g_\parallel$ = 2.07. Species ii can be generated by exposure to O_2 and disappears upon evacuation. It is more intense on pyridine-treated samples and can therefore be identified with the [Co^{III}(salen)(pyridine)·O_2^-] superoxo species observed by Herron.[4] However, double integration revealed that less than 1% of the total Co^{II} is involved in the dioxygen binding. In agreement with earlier work,[4] the deoxygenated precursor of the superoxo complex, which should be five-coordinate and low spin,[16] could not be observed on this zeolite sample. Species i was not previously observed. It is insensitive to oxygen and does not incorporate pyridine, as it is formed also on CH_2Cl_2-extracted samples. In view of the sample composition

---

(12) (a) Nishikawa, H.; Yamada, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 8. (b) Crumbliss, A. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 55.

(13) (a) Hitchman, M. A. *Inorg. Chem.* **1977**, *16*, 1985. (b) Nishida, Y.; Kida, S. *Coord. Chem. Rev.* **1979**, *27*, 275. For the location of the axes in square-planar complexes, this paper adopts the convention of Hitchman (ref 13a).

(14) Cariati, F.; Morazzoni, F.; Busetto, C.; Del Piero, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1976**, 343.

(15) Urbach, F. L.; Bereman, R. D.; Topich, J. A.; Hariharan, M.; Kalbacher, B. J. *J. Am. Chem. Soc.* **1974**, *96*, 5063.

(16) Ochiai, E. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1727.

and the observed *g*-values, species i is to be ascribed to a low-spin Co^{II} species. The apparent $A_{\parallel}$ hyperfine constant is though anomalously small, and this prevents further understanding of species i.

On extracted [Co^{II}(acacen)]NaY, only a weak superoxo signal, similar to signal ii of [Co^{II}(salen)NaY], was observed; the four-coordinate low-spin species, present before solvent treatment, was not stable in any of the extractions. Again, the concentration of the oxygen-binding species was low (maximally about 1% of Co^{II}) and a low-spin precursor for the superoxo species, which was observed in frozen solution,[17] could not be found.

The high-spin character of the oxygen-free form of the active Co^{II} complex in [Co^{II}(salen)]NaY and [Co^{II}(acacen)]NaY is somewhat unexpected but may tentatively be ascribed to a nonplanar organization of the ligand around Co^{II}.[18] However, the successive loading of the Co^{II} zeolite with a tetradentate Schiff base ligand and a supplementary base does not seem to be effective in mobilizing a considerable part of the intrazeolitic Co^{II} for O_2 binding. This may be due to the limited formation of low-spin four-coordinate Schiff base complexes in the zeolites. In solution, the four-coordinate complexes are intermediates in the formation of the five-coordinate, oxygen-binding complexes, but in zeolites, the four-coordinate chelates are only formed in low concentrations (in [Co^{II}(acacen)]NaY) or are not even detected in their typical form (in [Co^{II}(salen)]NaY).

It is not very clear what the coordination of the larger part of the Co^{II} in these zeolites is. The 14 700-cm^{-1} band, present for all samples (except those extracted with pyridine), is also found with a nearly identical width in a CoNaY which has been successively dehydrated and partially rehydrated. Therefore, we suggest that this band may represent Co^{II} in a 5- or 6-fold coordination; the Co^{II} may still be partially chelated by the zeolite but also interacts with some extra donor atoms supplied by the ligand. Such pseudo-octahedral Co^{II} complexes with a nonplanar salen ligand have also been proposed for mixed Co chelates of salen and acetylacetone.[18] The limited formation of square-planar [Co^{II}(salen)] in NaY may therefore be attributed to the presence of the zeolite which competes for coordination with Co^{II}. An analogous preposition has been made by Bedioui et al. on the basis of voltammetric observations.[7]

Characterization of [Co^{II}(smdpt)]NaY, [Co^{II}(smdpt)]NaEMT, and [Co^{II}(amdpt)]NaY. As [Co^{II}(smdpt)] is much larger than, for example, [Co^{II}(salen)], the steric interactions between [Co^{II}(smdpt)] and the cages of cubic NaY or hexagonal NaEMT were simulated.[19] The analysis indicated that [Co^{III}(smdpt)·O_2^-] may assume various positions in the hypercage of NaEMT, without overlap with the zeolite framework. In a NaY supercage, formation of [Co^{III}(smdpt)·O_2^-] may be possible, but the motion of the chelate within the supercage seems to be restricted as the van der Waals envelopes of lattice and complex atoms approach closely. Inclusion of [Co^{II}(amdpt)] in NaY was not found to be critical from a steric viewpoint.

EPR signals of deoxygenated Co^{II} complexes are not observed on [Co^{II}(smdpt)]NaY and [Co^{II}(smdpt)]NaEMT, not even at 130 K. This is in agreement with the reported high-spin character of [Co^{II}(smdpt)].[20] However, if the formed Co^{II} complexes bind O_2, these oxygen adducts should be visible in the EPR spectra. Oxygen exposure of [Co^{II}(smdpt)] faujasites indeed resulted in strong rhombic signals (Figure 4). The intensity of these signals grows upon raising the O_2 pressure and decreases under vacuum pumping. The reversibility of the oxygen binding may already be sufficient to assign these signals to mononuclear Co^{II} superoxo complexes. The reversibility is observed before and after extraction, but the response to O_2 or vacuum is considerably faster on extracted samples. The maximal intensities, reported in Table 1, were observed at 130 K under an O_2 pressure of 760 Torr.

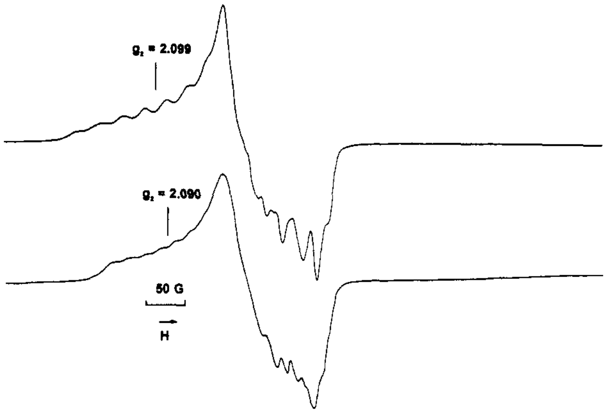


Figure 4. X-band EPR spectra (130 K, 760 Torr of O_2) of (top) [Co^{II}-(smdpt)]NaY before soxhlet extraction (g_z = 2.099, A_z = 27 G) and (bottom) [Co^{II}(smdpt)]NaEMT after CH_2Cl_2 extraction (g_z = 2.090, A_z = 19.5 G).

[Co^{III}(smdpt)·O_2^-]NaY has a well-resolved EPR spectrum (Figure 4). By simulation, the following parameters were obtained: $g_z = 2.099 \pm 0.001$, g_y and $g_x = 2.000 \pm 0.005$, $A_z = 27.0 \pm 0.5$ G, A_y and $A_x = 15 \pm 3$ G. Relatively large errors accompany the *x* and *y* parameters. For a more precise parametrization, one should take into account at least two supplementary effects: (i) linewidths may be field dependent (as suggested by the aspect of the *z* component of the spectrum) and (ii) the *x*, *y*, and *z* axes probably do not coincide for the **A** tensor and the **g** tensor.[21] Our simulation program however does not allow for these effects, but the precise A_z and g_z values are sufficiently informative, as these are the parameters which are most sensitive to complex structure in superoxo adducts.[8] Before the soxhlet extraction, the intensity of the [Co^{III}(smdpt)·O_2^-] signals is mostly comparable for NaEMT and NaY, but the spectral resolution on NaEMT is insufficient for determination of the EPR parameters. This already suggests that the structure of [Co^{III}(smdpt)·O_2^-] in both zeolites may be different.

The CH_2Cl_2 extraction produced no effect on the EPR parameters for [Co^{III}(smdpt)·O_2^-]NaY; the only effect observed in the EPR spectrum was a slight decrease of the signal intensity upon prolonged extraction. On the contrary, application of the standard CH_2Cl_2 extraction procedure to [Co^{II}(smdpt)]NaEMT raised the signal intensity (to a maximum of 38 μmol g^{-1} or 25% of the total Co^{II}) and resulted in new EPR parameters: $g_z = 2.090 \pm 0.001$, $A_z = 19.5 \pm 0.5$ G, g_x and $g_y = 2.000 \pm 0.005$, A_x and $A_y = 14 \pm 2$ G. Replacing the cubic NaY zeolite by its hexagonal variant NaEMT thus generates new EPR parameters as well as an increased signal intensity.

Two elements may be important for understanding the differences between the complexation in cubic NaY and hexagonal NaEMT: (i) the different cage architecture and (ii) the different Si:Al ratio of the framework of the zeolite. The Si:Al ratio of the NaEMT sample is 3.5, whereas it is only 2.46 for NaY. For

---

(17) Hoffman, B. M.; Diemente, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 61.

(18) For dioxygen binding on a Co^{II} complex, the strongest donor group need not be *trans* to the bound O_2, as proved crystallographically for the superoxo adduct of [bis(salicylaldehyde)nitrilodipropylenediimide]cobalt(II), where the secondary nitrogen group is *cis* to O_2 (ref 25b). If in zeolite-encapsulated [Co(salen)(pyridine)·O_2] the pyridine ligand is *cis* to O_2, the deoxygenated complex would probably be high spin. The nonplanar organization of the salen ligand required for such a geometry has been found, for example, in mixed Co complexes of salen and acetylacetone: Calligaris, M.; Manzini, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1972**, 543.

(19) The interactions between the zeolite host and the complex were simulated with ChemX software (Chemical Design, Ltd., Oxford, England). For crystallographic coordinates of [Co(smdpt)·O_2], see ref 25a. Coordinates for the zeolite structures were obtained from Rietveld refinements: Lievens, J. Ph.D. Thesis, Leuven University, 1992.

(20) Tovrog, B. S.; Drago, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 6765.

(21) de Bolfo, J. A.; Smith, T. D.; Boas, J. F.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* **1976**, 1495.

Table 3. EPR Parameters for Some Reversible Cobalt–Dioxygen Complexes

	g_z	g_y	g_x	A_z[a]	A_y[a]	A_x[a]
$[Co^{II}(smdpt)]NaY$	2.099 ± 0.001	2.000 ± 0.005	2.000 ± 0.005	27.0 ± 0.5	15 ± 3	15 ± 3
$[Co^{II}(smdpt)]NaEMT$	2.090 ± 0.001	2.000 ± 0.005	2.000 ± 0.005	19.5 ± 0.5	14 ± 2	14 ± 2
$[Co(smdpt)\cdot O_2]$[b]	2.092 ± 0.003	2.00 ± 0.01	2.00 ± 0.01	19.3 ± 0.5	11 ± 1	14 ± 1
$[Co(smpdt)\cdot O_2]$[c]	2.086 ± 0.001	2.005 ± 0.001	1.999 ± 0.001	18.7 ± 0.3	12.0 ± 0.3	13.6 ± 0.3
$[Co(X\text{-}salDAPE)\cdot O_2]$[b]						
X = 5-H	2.103 ± 0.003	1.996 ± 0.01	1.994 ± 0.01	33.0 ± 0.5	14.5 ± 1	22.5 ± 1
X = 5-OMe	2.099 ± 0.003	2.000 ± 0.01	1.997 ± 0.01	28.5 ± 0.5	13.0 ± 1	19 ± 1

[a] Cobalt hyperfine coupling constants in G. [b] Data from ref 24a. [c] Data from ref 24b.

an identical zeolite topology, a higher Al content of the lattice may hamper expulsion of the zeolite from the primary coordination sphere of the transition metal ion. This was proved, for example, for the formation of $[Cu(en)_n]^{2+}$ in zeolites NaX and NaY (with Si:Al ratios of 1.25 and 2.5, respectively).[22] The quantitative differences observed between $[Co^{III}(smdpt)\cdot O_2^-]$ formation in NaY and NaEMT may be a consequence of a different Si:Al ratio. However, a substantial difference in Co^{II} siting and availability for complexation should be reflected in differences in the visible spectra of the dehydrated zeolites, which is not the case: the starting dehydrated CoNaY and CoNaEMT have identical reflectance spectra.

Thus factors other than cation availability have to be invoked, especially to explain the different EPR parameters. The EPR parameters of the zeolite species are compared in Table 3 to those of $[Co^{III}(smdpt)\cdot O_2^-]$ and some related complexes in frozen solution. The parameters for $[Co^{III}(smdpt)\cdot O_2^-]$ in NaEMT are very close to those observed in frozen solutions.[23,24] In the cages of NaEMT, $[Co^{III}(smdpt)\cdot O_2^-]$ apparently can assume exactly the same conformation as in solution. This does not seem possible in the supercage of NaY. As $[Co^{III}(smdpt)\cdot O_2^-]$ superoxo complexes are six-coordinate, intervention of zeolite Y in the primary coordination sphere is improbable. In view of the results of the molecular graphics analysis, the only reasonable explanation is that the supercage of NaY sterically hinders the $[Co^{III}(smdpt)\cdot O_2^-]$ complex in assuming its most stable and normal configuration, which is found in NaEMT and in solution; in the usual form of the complex, the tertiary nitrogen effectively coordinates Co^{III} *trans* to the O_2^- ligand, as proved by crystallographic studies.[25a]

At least two propositions can be made for the anomalous, distorted structure of $[Co^{III}(smdpt)\cdot O_2^-]$ in NaY. Large A_z values, like found for $[Co^{III}(smdpt)\cdot O_2^-]NaY$, have been associated with a decreased donor strength around Co^{II}.[24a] For instance, in $[Co^{III}(saldape)\cdot O_2^-]$ (saldape = bis(salicylaldehyde) 4-oxaheptane-1,7-diyldiimine), the tertiary nitrogen has been replaced by a noncoordinating ether linkage and this yields A_z = 33 G. This suggests that, in the distorted $[Co^{II}(smdpt)]NaY$, the coordination of the tertiary nitrogen to Co^{II} may be weaker. An alternative explanation is the existence of isomerism around Co^{II}. Normally the tertiary nitrogen is *trans* to the bound O_2, but for the related $[Co^{III}(sdpt)\cdot O_2^-]$ (sdpt = bis(salicylaldehyde) nitrilodipropylenediimine), the nitrogen base was found to be *cis* to O_2.[25b] Such stereoisomerism may also be responsible for the anomalous EPR parameters and the structure of $[Co^{III}(smdpt)\cdot O_2^-]NaY$.

The approach of using a pentadentate ligand for oxygen activation was also successful in case of the acetylacetone-derived ligands. When $[Co^{II}(amdpt)]NaY$ is exposed to dioxygen, a Co superoxo signal is observed; parameters are $g_z = 2.080 \pm 0.005$, $A_z = 24 \pm 2$ G, g_x and $g_y = 2.000 \pm 0.005$, and A_x and $A_y = 14 \pm 3$ G. The maximum signal intensity was about 6 $\mu mol\cdot g^{-1}$, which markedly exceeds the concentration obtained with the tetradentate $acacenH_2$. However, the intensity of the superoxo signals was clearly lower with $amdptH_2$ than with $smdptH_2$; the differing donor properties of the $smdptH_2$ and $amdptH_2$ ligands are probably coming into play. Detailed comparison of $[Co^{II}(amdpt)]$ and $[Co^{II}(smdpt)]$ zeolites is however hampered by the absence of literature data about $[Co^{II}(amdpt)]$ complexes and their oxygen adducts. The zeolite-hosted $[Co^{III}(amdpt)\cdot O_2^-]$ complexes were not noticeably influenced by the extraction treatment or by a change of the zeolite topology (EMT instead of FAU). It should however be noted that the resolution of the spectra obtained for $[Co^{II}(amdpt)]$-containing zeolites was lower than for $[Co^{II}(smdpt)]$ zeolites; this certainly hinders observation of subtle changes of the EPR spectra.

The diffuse reflectance spectra of $[Co^{II}(smdpt)]NaY$, $[Co^{II}(smdpt)]NaEMT$, and $[Co^{II}(amdpt)]NaY$ prove again that the original tetrahedral Co^{II} coordination is disturbed by ligand adsorption. Only a single band at 14 700 cm^{-1} out of the typical triplet pattern of zeolite-coordinated Co^{II} resists complexation by the pentadentate ligands. As for $[Co^{II}(salen)]NaY$ and $[Co^{II}(acacen)]NaY$, this band can tentatively be ascribed to Co^{II}, partially chelated by the zeolite and by the ligand. Considerable broadening and intensification of the 14 700-cm^{-1} band was observed for $[Co^{II}(smdpt)]NaY$ and $[Co^{II}(smdpt)]NaEMT$; in the last sample, extraction caused a further broadening. Therefore, the 14 700-cm^{-1} band may in this case very well be identical to the band observed at the same frequency for $[Co^{II}(smdpt)]$. Sacconi and Bertini[26] ascribed this band to d–d transitions in five-coordinate Co^{II} complexes with a structure intermediate between a trigonal bipyramid and a square pyramid. The formation of superoxo complexes cannot be derived from changes in the reflectance spectra. The rather weak charge transfers between Co^{3+} and O_2^- are probably heavily obscured by the intense ligand and ligand–metal charge transfer absorptions beyond 18 000 cm^{-1}.

Characterization of $[Co^{II}(pyren)NaY$. Two species were detected in the EPR spectra of $[Co^{II}(pyren)]NaY$. Soxhlet extraction with CH_2Cl_2 did not influence the spectra. At room temperature and under vacuum, the sample is EPR silent. This seems to exclude a planar ligand disposition around Co^{II}.[27] However, under O_2, a superoxo species is observed (Figure 5), for which the EPR parameters are $g_z = 2.058 \pm 0.002$, $A_z = 13.8 \pm 0.3$ G, $g_x = 2.001 \pm 0.002$, $A_x = 12.0 \pm 0.3$ G, $g_y = 2.00 \pm 0.01$, and $A_y = 12 \pm 2$ G. These parameters are close to those of zeolite Y entrapped $[Co^{III}(bipyridine)(terpyridine)\cdot O_2^-]^{2+}$ (which has $g_z = 2.057$ and $A_z = 15$ G).[1c] The maximal amount of Co^{II} involved in O_2 binding at room temperature was 9 $\mu mol\cdot g^{-1}$.

When the sample is cooled under vacuum, a new orthorhombic signal appears (Figure 5), of which estimated parameters are $g_1 = 2.26 \pm 0.02$, $g_2 = 2.152 \pm 0.002$, $g_3 = 2.04 \pm 0.02$, $A_1 = 25 \pm 10$ G, $A_2 = 52 \pm 1$ G, and $A_3 = 25 \pm 10$ G. As spin crossover

---

[22] Peigneur, P.; Lunsford, J. H.; De Wilde, W.; Schoonheydt, R. A. *J. Phys. Chem.* **1977**, *81*, 1179.

[23] De Vos, D. E.; Thibault-Starzyk, F.; Jacobs, P. A. *Angew. Chem.* **1994**, *106*, 447–450.

[24] (a) Tovrog, B. S.; Kitko, D. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 5144. (b) Niswander, R. H.; Taylor, L. T. *J. Magn. Reson.* **1977**, *26*, 491.

[25] (a) Cini, R.; Orioli, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2563. (b) Lindblom, L. A.; Schaefer, W. P.; Marsh, R. E. *Acta Crystallogr.* **1971**, *B27*, 1461.

[26] Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* **1966**, *88*, 5180.

[27] The distances between the nitrogen donors in pyren are probably too small to allow a planar disposition of the ligand around Co^{II}. Planar complexes of Co^{II} with ligands containing unsaturated nitrogen donors are mostly low spin and EPR visible; see, for instance: Nishida, Y.; Hayashida, K.; Sumita, A.; Kida, S. *Inorg. Chim. Acta* **1978**, *31*, 19.

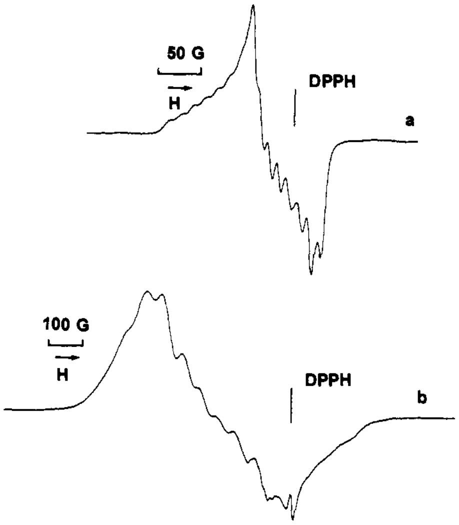


Figure 5. X-band EPR spectra of [Co^{II}(pyren)]NaY (top) at 293 K under 100 hPa of O_2 pressure and (bottom) at 110 K under N_2; before cooling, the sample was evacuated for 10 min at 323 K to remove as much O_2 as possible.

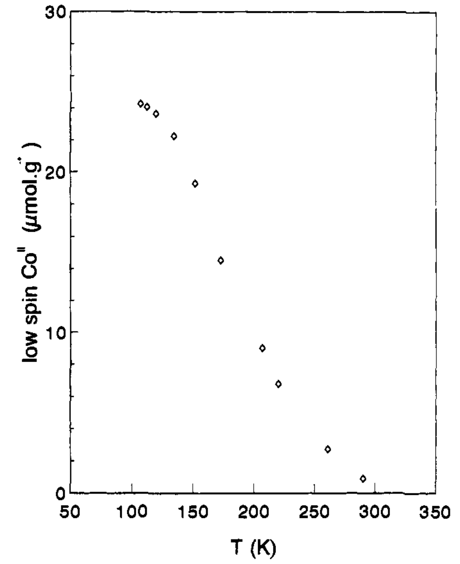


Figure 6. Concentration of the low-spin Co^{II} species in [Co^{II}(pyren)]NaY (μmol·g^{-1}) as a function of temperature (K). Concentrations were calculated by double integration of the EPR spectra and were corrected for temperature (on the assumption that signal intensity ≈ $1/T$).

phenomena are common for Co^{II} and Fe^{III} complexes containing α-diimine ligands,[28] this observation can reasonably be ascribed to a Co^{II} low-spin–high-spin equilibrium. The temperature-corrected EPR intensity of the low-spin [Co^{II}(pyren)]NaY signal is plotted in Figure 6 against the absolute temperature. The continuous character of the transition proves that the zeolite-entrapped species behave like those in a solid solution, *i.e.* there is no cooperative interaction between the Co^{II} centers having a variable spin-multiplicity. Around 115 K, the concentration of low-spin Co^{II} levels off to a maximum of 26 μmol·g^{-1}. If this number represents all Co^{II} participating in the spin transition, the equilibrium constant K for the low-spin $\rightleftharpoons$ high-spin transition can be calculated as a function of temperature. The enthalpy change calculated from the dependence of ln K *vs* T is a direct measure of the energy separation between the low-spin and the high-spin states. The observed value of 625 cm^{-1} agrees well with, for example, 550–600 cm^{-1} found for [Co^{II}(terpyridine)$_2$]$^{2+}$ [29] and confirms that a spin equilibrium occurs in

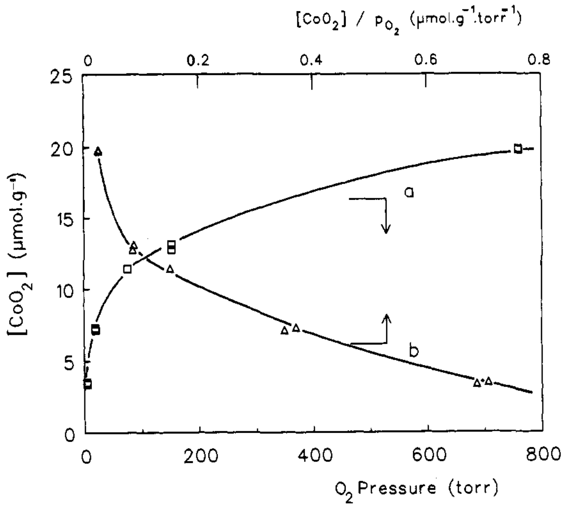


Figure 7. Concentration of the cobalt superoxo complex ([CoO$_2$], μmol·g^{-1}) in a CH_2Cl_2-extracted [Co^{II}(smdpt)]NaEMT sample (a) plotted as a function of the oxygen pressure p_{O_2} over the sample (Torr) and (b) plotted *vs* [CoO$_2$]/p_{O_2} (μmol·g^{-1}·Torr^{-1}).

[Co^{II}(pyren)]NaY. The spin crossover of the Co^{II} species was observed not only under N_2 but also under O_2 atmospheres. Apparently, the Co^{II} species which display a spin equilibrium do not participate in O_2 binding. This shows that pyren adsorption on zeolite CoNaY produces at least two distinct species: a complex with a spin transition and an oxygen-binding chelate.

The interaction of pyren with a considerable part of the Co^{II} was confirmed by the vis spectrum of the material, which showed a transition at 18 000 cm^{-1}, with an intensity far exceeding that of Co^{II} d–d transitions. As we observed analogous absorptions on Mn^{2+} and Ni^{2+} zeolites loaded with pyren, we ascribe this band to a charge transfer between Co^{II} and pyren.

Many characteristics of [Co^{II}(pyren)]NaY (*e.g.* charge-transfer band, Co^{II} spin transition, and EPR parameters of the superoxo complex) are similar to those of the bipyridine and terpyridine systems studied by Lunsford.[1c,2,30] However, in the case of pyren, only one single ligand molecule is needed to create a complex with a vacant site for incoming O_2.

Oxygen Sorption Characteristics of Zeolite-Entrapped Co^{II} Schiff Base Complexes. The amount of chemisorbed oxygen was derived from the EPR spectra at O_2 pressures between 5 and 760 Torr for soxhlet-extracted [Co^{II}(smdpt)]NaY, [Co^{II}(smdpt)]NaEMT, [Co^{II}(amdpt)]NaY, and [Co^{II}(pyren)]NaY. The maximal concentrations of oxygen-binding sites varied considerably for these samples and were already reported in Table 1. The pressure was increased stepwise and decreased again; as in no case was hysteresis observed, equilibrium must have been reached at each point. Figure 7 shows the sorption isotherm for a [Co^{II}(smdpt)]NaEMT sample. For the binding of O_2 on a [Co(CN)$_n$]$^{2-n}$ complex in zeolite Y, Taylor et al.[3] calculated the dioxygen affinities by plotting [CoO$_2$], the concentration of chemisorbed dioxygen (μmol·g^{-1}), *vs* [CoO$_2$]/p_{O_2}, p_{O_2} being the pressure of O_2 above the zeolite. The slope of this plot, $p_{1/2}$, equals the pressure at which half of the oxygen-binding sites are saturated.[3] The lower this pressure, the higher the O_2 affinity.

For the present zeolite-encapsulated complexes, plots of [CoO$_2$] *vs* [CoO$_2$]/p_{O_2} were not always linear (Figure 7). At higher dioxygen pressures, the affinity decreases and this effect seems to be more pronounced when the number of active sites in the zeolites is larger. Below an oxygen pressure of 50 Torr, approximate $p_{1/2}$ values, calculated from the slope of the tangent to the curve [CoO$_2$] *vs* [CoO$_2$]/p_{O_2}, are 12 ± 3 Torr for

---

(28) Dose, E. V.; Hoselton, M. A.; Sutin, N.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1141.

(29) Kremer, S.; Henke, W.; Reinen, D. *Inorg. Chem.* **1982**, *21*, 3013.

(30) (a) Mizuno, K.; Lunsford, J. H. *Inorg. Chem.* **1983**, *22*, 3484. (b) Quayle, W. H.; Peeters, G.; De Roy, G. L.; Vansant, E. F.; Lunsford, J. H. *Inorg. Chem.* **1982**, *21*, 2226.

[Co^{II}(smdpt)]NaY and [Co^{II}(smdpt)]NaEMT, 9 ± 1 Torr for [Co^{II}(amdpt)]NaY, and 7 ± 1 Torr for [Co^{II}(pyren)]NaY. The negative cooperativity between the active sites was also observed by Herron[4] for [Co^{II}(salen)(pyridine)]NaY. As the EPR spectra seem to indicate that all O_2-binding complexes are equivalent, the negative cooperativity in O_2 sorption may well be a pure zeolite effect, as suggested by Herron.[4] It cannot be derived from the literature whether this effect is somewhat general or whether it may occur also with, for example, bipyridine–terpyridine ligands.[2]

Conclusions

Changing the polydentate Schiff base ligand used for chelation of Co^{II} in faujasite type zeolites shows that there are important differences between the formation of Schiff base complexes in solution and that in a zeolite cage.

With tetradentate ligands like salen and acacen, four-coordinate low-spin Co^{II} complexes are only formed in low yield in zeolite Y. By starting with these tetradentate ligands, it is also difficult to form considerable amounts of five-coordinate complexes of the type [Co^{II}(acacen)(pyridine)]. For these reasons, oxygen activation on salen or acacen containing zeolites is limited. In solution, Schiff base complex formation is mostly a smooth process. Although there is a widespread belief that the same still holds for a zeolite cage, the present results indicate that this is not true.

With pentadentate ligands, the axial base is part of the ligand. Not only is the synthesis procedure of zeolite-encapsulated complexes now reduced to adsorption of a single ligand molecule but the pentadentate ligands are also more effective in withdrawing charge-compensating Co^{II} from zeolite coordination and forming encaged O_2-binding complexes. It is well-known that the yields of superoxo complexes in NaY are often limited. Sometimes changing the cocation has been a successful approach in raising the active Co fraction,[3] but the reasons for this are not always well understood.[2] Changing the ligand structure is a valid alternative for increasing active Co concentrations. A hexagonal NaEMT zeolite with entrapped [Co^{II}(smdpt)] complexes contained 25% of active cobalt, which compares favorably to the best optimized literature systems.

All this proves that preorganization of a coordination sphere in a single polydentate ligand can be an effective method for controlling intrazeolitic chelation.

Experimental Section

Materials. The following compounds, all reagent grade, were used without further purification: salen(bis(salicylaldehyde) ethylenediimine (**1**) and Cu–acetylacetone (Cu(acac)$_2$) from Strem, cobalt acetate (CoAc$_2$·4H$_2$O), acetylacetone, 2-pyridinecarboxaldehyde, and 3,3′-diamino-*N*-methyldipropylamine all from Aldrich, NaOH pellets, salicylaldehyde, and ethylenediamine from Merck, 18-crown-6 (Janssen Chimica), Ludox HS-40 (Du Pont), and sodium aluminate (Riedel de Hahn).

The cubic faujasite NaY was a sample from the PQ Corp., with a Si:Al ratio of 2.46. Hexagonal faujasite, with a Si:Al ratio of 3.5, was synthesized in the presence of 18-crown-6 ether by modification of the procedure of Delprato et al.[10] The molar composition of the synthesis gel was 10:1:2.4:0.97:135 $SiO_2:Al_2O_3:Na_2O$:18-crown-6:H_2O. The gel was aged at 293 K for 3 days and crystallized at 372 K for 9 days. The synthesis product was washed, dried, and calcined at 823 K for 20 h. The exclusive presence of the EMT phase was confirmed by X-ray diffraction.

Acacen (**2**) was obtained by condensation of acetylacetone and ethylenediamine by following the method of Martell et al.[31] White crystals were obtained: mp 115 °C; ^{1}H NMR (CDCl$_3$) 10.9 (b, 2H, NH), 5.00 (s, 2H, C—CH=C), 3.43 (d, 4H, CH$_2$), 2.00 (s, 6H, CH$_3$), 1.91 (s, 6H, CH$_3$).

Smdpt (**3**) was prepared by mixing 3.37 g of salicylaldehyde and 2 g of 3,3′-diamino-*N*-methyldipropylamine. Water escaped by boiling, and upon standing, the viscous mixture yielded bright yellow crystals: mp 40 °C; ^{1}H NMR (CDCl$_3$) 13.60 (b, 2H, OH), 8.32 (s, 2H, CH=N), 7.30 (d, d, 2H, ArH), 7.20 (d, 2H, ArH), 6.94 (d, 2 H, ArH), 6.84 (d, d, 2H, ArH), 3.62 (t, 4H, CH$_2$), 2.43 (t, 4H, CH$_2$), 2.22 (s, 3H, CH$_3$), 1.85 (m, 4H, CH$_2$).

Amdpt (**4**) was prepared by dropwise addition of 5.8 g of 3,3′-diamino-*N*-methyldipropylamine, dissolved in 10 mL of dry diethyl ether, to 8 g of acetylacetone in 20 mL of dry diethyl ether in an ice bath. The white precipitate was recrystallized from diethyl ether. The final product consisted of white crystals which were stored under vacuum: mp 34 °C; ^{1}H NMR (CDCl$_3$) 5.51 (s, 2H, C—CH=C), 2.74 (t, 4H, CH$_2$), 2.39 (t, 4H, CH$_2$), 2.21 (s, 3H, CH$_3$), 2.05 (s, 12H, CH$_3$), 1.62 (m, 4H, CH$_2$).

Pyren (**5**) was prepared by mixing 8 g of 2-pyridinecarboxaldehyde and 2.24 g of ethylenediamine in 30 mL of absolute ethanol. This mixture was stirred for 30 min, and the solvent was evaporated. The product was an orange oil which was crystallized from cold and dry diethyl ether to yield yellow crystals: mp 67 °C; ^{1}H NMR (CDCl$_3$) 8.62 (d, 2H, ArH), 8.42 (s, 2H, CH=N), 7.98 (d, 2H, ArH), 7.73 (d, d, 2H, ArH), 7.30 (d, d, 2H, ArH), 4.07 (s, 4H, CH$_2$).

Preparation of Zeolite Samples with Complexed Co. Na$^+$ forms of cubic (NaY) and hexagonal faujasite (NaEMT) were partially exchanged with Co^{II} by stirring overnight 4 g of zeolite (moisture saturated in a relative humidity of 80%) in 300 mL of a 2 mM Co(CH$_3$COO)$_2$ aqueous solution at pH 5. The Co content of the zeolites, determined by elemental analysis, was 0.9 wt %, corresponding to one Co ion per four supercages for CoNaY or to one Co per four cages (two hypercages + two hypocages) for NaEMT. The zeolite samples were dried by gradual heating (1 K/min) under an oxygen flow (50 mL/min) to 473 K and were kept there for 10 h; finally, they were cooled to room temperature under a nitrogen flow and eventually evacuated.

These dry zeolite samples were mixed under an inert atmosphere with a 2-fold excess (with respect to Co) of the dry, crystalline ligands and heated for 10 h under an atmosphere of 0.1 MPa of nitrogen at a temperature well above the melting point of the ligands (413 K for **1** and **2**, 373 K for **3**, **4**, and **5**). At this stage the samples were either used or soxhlet extracted with dichloromethane or pyridine. Pyridine was only applied to salen- and acacen-containing samples. After extraction, the samples were stored under vacuum for further use. The resulting samples are denoted as [Co^{II}(salen)]NaY, [Co^{II}(smdpt)]NaY, [Co^{II}(smdpt)]-NaEMT, [Co^{II}(acacen)]NaY, [Co^{II}(amdpt)]NaY, and [Co^{II}(pyren)]-NaY.

Spectroscopic characterization. Measurements were performed on the ligand-containing Co zeolites before and after removal of excess ligand by soxhlet extraction. Vis–near-IR diffuse reflectance spectra were recorded between 5000 and 30 000 cm^{-1} with a Cary 5 photometer with an integration sphere. EPR spectra were recorded at X-band (9.50 GHz) in a TE$_{104}$ cavity with a Bruker 200 or 300 apparatus equipped with a liquid air cooling accessory. Spin concentrations were estimated by double integration using KBr-diluted Cu(acac)$_2$ for calibration. For determination of the fraction of Co^{II} which binds O_2, the superoxo concentration obtained from the double integration was divided by the total Co^{II} concentration (0.9 wt %), determined by elemental analysis. Spectra were simulated by a self-written program suited for rhombic spectra with hyperfine structure; first-order approximations were used for the resonance field positions. Line widths could be chosen independently in each direction. ^{1}H NMR spectra were taken with a Bruker AMX 300 at 300 MHz.

Acknowledgment. This work was supported by the Belgian Federal Government in the Frame of an Interuniversitary Attraction Pole on Supramolecular Catalysis. D.D.V. and E.F. thank the Flemish NFWO and IWONL, respectively, for positions as research assistants. We thank P. J. Grobet for recording ^{1}H NMR spectra.

---

[31] Martell, A. E.; Linn Belford, R. L.; Calvin, M. *J. Inorg. Nucl. Chem.* **1958**, *5*, 170.