Electron Paramagnetic Resonance Studies of Some Cobalt Amine Oxygen Adducts in Zeolite Y

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Abstract: The reversible formation of low-spin $[Co^{III}L_xO_2^-]^{2+}$ adducts within the large cavities of a Co^{II}–Y zeolite is demonstrated by EPR, where L = NH_3, CH_3NH_2, or *n*-$CH_3CH_2CH_2NH_2$, and *x* is probably equal to 5. Dimeric μ-superoxo $[L_xCo^{III}O_2^-Co^{III}L_x]^{5+}$ adducts can also be formed with L = NH_3 or CH_3NH_2, but not with *n*-$CH_3CH_2CH_2NH_2$. The EPR parameters of the 1:1 and 1:2 adducts in Co–Y are similar to those of analogous adducts in solution. The observation of nonaxial *g* tensors for both the monomeric and dimeric adducts is consistent with a bent Co–O–O structure.

The reversible uptake of oxygen by cobalt(II) complexes in solution has been extensively studied, particularly with a view to understanding the bonding and activation of oxygen in biological oxygen carriers.[1] Several recent electron paramagnetic resonance (EPR) studies have shown that transition metal cations in the faujasite-type zeolite Y can form well-defined complexes with added ligands within the large cavities of the zeolite framework, which are approximately 13 Å in diameter.[2-4] Cobalt oxygen adducts formed within the zeolite structure may be expected to show interesting differences in properties from those of the analogous adducts in solution. Our study of these adducts in zeolite Y has also been prompted by the possibility of activating oxygen in a heterogeneous system.

A preliminary account has been given of the formation of the monomeric oxygen adduct of a cobalt(II) ammonia complex in zeolite Y.[5] This paper describes a more detailed study of the formation and stability of oxygen adducts of cobalt with ammonia, methylamine, and *n*-propylamine as ligands. It is shown that with ammonia and methylamine both monomeric 1:1 and dimeric 1:2 oxygen adducts can be formed, whereas with *n*-propylamine only the 1:1 adduct is observed.

Experimental Section

Three $Co^{II}Y$ zeolites with different cobalt contents were prepared from a Linde NaY zeolite (Lot no. 13544-76, unit cell composition $Na_{56}Al_{56}Si_{136}O_{384}\cdot 264H_2O$) by conventional ion exchange. Cation analysis of the exchanged zeolites indicated the following concentrations: CoY(1), 15 Co^{2+} per unit cell; CoY(2), 10 Co^{2+} per unit cell; CoY(3), 0.7 Co^{2+} per unit cell. These correspond to an average of 1.9, 1.25, and 0.09 Co^{2+} ions per supercage, respectively. Ammonia, methylamine, and *n*-propylamine from commercial sources were dried over dehydrated NaY zeolite and outgassed by repeated freeze-pumping before use.

Zeolite samples were dehydrated by heating to 400° in increments of 100° per hour under a vacuum of 10^{-5} Torr and transferred to a quartz side arm for EPR measurements. Amine ligands were adsorbed by exposing samples to successive doses of amine vapor until no further adsorption occurred. The EPR spectra were recorded at −196 or 25° with Varian E6S and V4502 spectrometers for X-band (9.1 GHz) and Q-band (35 GHz) measurements, respectively. The *g* values were obtained using a 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard (*g* = 2.0036). Spin concentrations were calculated by numerical double integration of the recorded derivative spectra and comparison with a phosphorus doped silicon standard of known spin concentration; the uncertainty in the spin concentration measurements is estimated to be ±30%.

Simulated spectra were calculated using the computer program SIM13 written by George Lozos, Brian Hoffman, and Charles Franz of Northwestern University.

Results

Adsorption of ammonia at 25° into dehydrated CoY, followed by exposure to about 10 Torr of oxygen at −78°, causes the appearance of the EPR signal previously attributed[5] to a 1:1 cobalt oxygen adduct. A maximum signal intensity is obtained by exposing to oxygen at −78° for at least 3 hr before recording the spectrum at −196°. The presence of excess ammonia also appears to be important. If, after adsorption of ammonia, the zeolite is outgassed at 25° for more than 30 min before exposing to oxygen, a much reduced signal is obtained. The maximum signal intensities recorded correspond to about two adducts per unit cell in both CoY(1) and CoY(2), which is significantly less than the spin concentrations reported by Vansant and Lunsford[5] for zeolites of comparable cobalt content.

Brief evacuation at 25° causes immediate removal of the oxygen adduct, but the EPR signal may be restored by further exposure to oxygen at −78°. A spectrum of the adduct can be recorded at room temperature, but the signal is not stable in the presence of oxygen at 25° and decays rapidly to less than 10% of its original intensity within 5 min. The signal decay is accompanied by a change in color of the sample from green to light brown. The original spectrum and the green color can be restored by cooling again to −78° (in oxygen).

Prolonged exposure of the ammoniated CoY to oxygen at 25° (typically for 12-15 hr) followed by evacuation at 25° causes the appearance of a new signal, shown in Figure 1. As discussed below, we attribute this signal to a dimeric 1:2 cobalt oxygen adduct. A maximum concentration of the dimeric adduct is formed by exposing the ammoniated CoY to oxygen (20-50 Torr) at 25° for at least 12 hr, followed by evacuation at 25° for an additional 12 hr. The spectrum of the dimer is first detected after about 30 min evacuation and grows in intensity on further pumping. The formation of the dimer is accompanied by a color change from brown to violet. The maximum signal intensities observed correspond to about 0.25 dimeric adducts per unit cell in CoY(1), but less than 0.02 per unit cell in CoY(2).

Once formed, the dimeric adduct is stable to evacuation at 25°, but is slowly removed upon raising the temperature to 100°. The adduct is stable in the presence of oxygen at 25° but is immediately destroyed upon exposure to ammonia. Further addition of oxygen at −78° after exposure of the dimer to ammonia restores the spectrum of the 1:1 monomeric adduct.

A 1:1 cobalt oxygen adduct is formed with methylamine as the ligand in the same manner as with ammonia, i.e., by adsorbing oxygen at −78° into CoY containing methylamine. The methylamine adduct has an EPR spectrum similar to that of the corresponding ammonia adduct (the EPR parameters of the 1:1 adducts are summarized in Table I). The maximum spin concentrations observed with methyl-

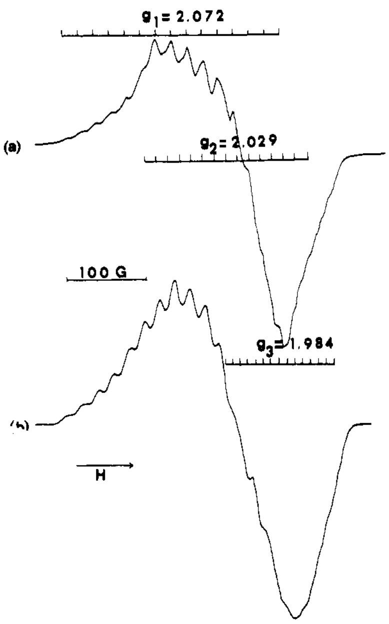


Figure 1. X-Band spectra (derivative) of $[Co^{III}(NH_3)_x-O_2^--Co^{III}(NH_3)_x]^{5+}$ in CoY: (a) experimental spectrum, (b) spectrum simulated with parameters listed in Table II.

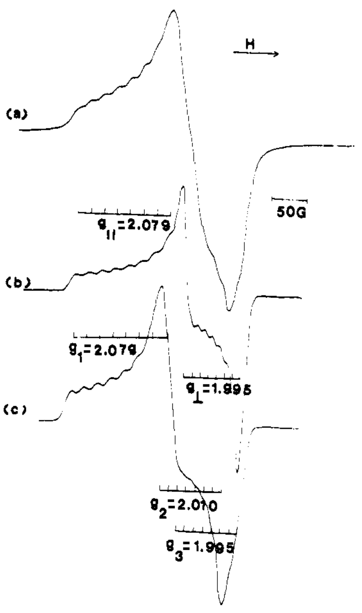


Figure 2. X-Band spectra (derivative) of $[Co^{III}(PrNH_2)_xO_2^-]^{2+}$ in CoY: (a) experimental spectrum, (b) spectrum simulated assuming axial symmetry, (c) spectrum simulated assuming nonaxial symmetry, $g_2 - g_3 = 0.015$. Parameters are as listed in Table I.

amine as the ligand were about 6.5, 6.5, and 0.5 adducts per unit cell in CoY(1), CoY(2), and CoY(3), respectively. The EPR signal disappears rapidly on warming in oxygen to 25°, but only in the low exchanged CoY(3) can the signal be restored by cooling again to −78°. In the higher exchanged zeolites CoY(1) and CoY(2) it is necessary to remove the oxygen at 25° by brief evacuation, cool to −78° in vacuo, and add further oxygen to restore the original signal.

If the CoY zeolite containing methylamine is exposed to oxygen (20–50 Torr) at 25° the monomeric signal is not observed, but a second signal similar to that in Figure 1 appears slowly over a period of up to 12 hr, and the sample turns brown. Subsequent evacuation at 25° causes no further change in the spectrum; this behavior may be contrasted with that of the corresponding ammonia adduct. The same signal is obtained from the 1:1 methylamine cobalt oxygen adduct by warming from −78 to 25° in oxygen for several hours. The EPR parameters of the dimeric oxygen adducts are summarized in Table II. The maximum signal intensities observed correspond to about 1.5 and 0.6 methylamine cobalt oxygen dimers per unit cell in CoY(1) and CoY(2), respectively. The dimeric adduct could not be observed in CoY(3).

Figure 2 shows the EPR signal obtained by adsorbing oxygen at −78° into CoY containing *n*-propylamine. This spectrum is similar to those observed with ammonia and methylamine as ligands, although less well resolved in the high-field region. The maximum intensities observed correspond to about two adducts per unit cell in CoY(1) and CoY(2). At no time have we observed a dimeric 1:2 cobalt oxygen adduct in CoY with *n*-propylamine as the ligand, either after allowing the 1:1 adduct to stand in oxygen (100 Torr) at 25° or on subsequent evacuation.

Discussion

Monomeric 1:1 Cobalt Oxygen Adducts. X-Ray diffraction studies have shown that most of the divalent cations in a dehydrated faujasite reside within the sodalite cages and hexagonal prisms.[6] Adsorption of suitable ligands may, however, cause migration of the cations into the large cavities. In particular, Vansant and Lunsford[3] and Mikheikin et al.[4] have shown by EPR that six-coordinate cobalt(II) complexes are formed in the large cavities of zeolite Y with methylisocyanide and water as ligands. Adsorption of ammonia, methylamine, or *n*-propylamine into dehydrated CoY at 25° causes a pronounced color change from blue to various shades of violet, indicating that these molecules are entering the coordination sphere of cobalt. It thus seems likely that in the presence of amine ligands cobalt(II) ions migrate into the large cavities to form six-coordinate complexes, although the high-spin character of the hexamine complexes precludes their observation by EPR at −196°, and we cannot directly determine the number of amine ligands coordinated. A six-coordinate complex of *n*-propylamine would have a diameter of about 13 Å, approximately equal to the internal diameter of the large cavities in the faujasite structure, while with ammonia and methylamine two or more six-coordinate complexes per large cavity are sterically possible. The 1:1 oxygen adducts are then formed on subsequent adsorption of oxygen at −78°.

Vansant and Lunsford[5] interpreted the spectrum of the monomeric cobalt(II) ammonia oxygen adduct in terms of an axially symmetric spin Hamiltonian, the two sets of eight hyperfine lines observed being attributed to the parallel and perpendicular directions of the symmetry axis with respect to the magnetic field. Such an interpretation appears to be consistent with the X-band spectrum. We now find, however, that the spectra of the 1:1 oxygen adducts with ammonia, methylamine, and *n*-propylamine as ligands cannot be satisfactorily computer simulated unless nonaxial symmetry is assumed; i.e., $g_{xx} \neq g_{yy}$, where the x and y axes are perpendicular to the symmetry axis. Figure 2 shows typical computed spectra for the *n*-propylamine oxygen monomer, assuming axial symmetry ($g_{\perp} = 1.995$, trace b) and nonaxial symmetry ($g_{xx} = 1.995$, $g_{yy} = 2.010$, trace c). The lack of complete agreement with the experimental spectrum (trace a) in the high field region is, we believe, due to the line width associated with g_{yy} being greater than that associated with g_{xx}, which also removes the hyperfine structure around g_{yy}. Our computer program does not allow for such line width variations. Exact values of g_{xx} and g_{yy} cannot be determined in this manner, but for all three oxygen adducts in CoY ($g_{yy} - g_{xx}$) lies within the range

Table I. EPR Parameters[a] of CoO_2 Adducts

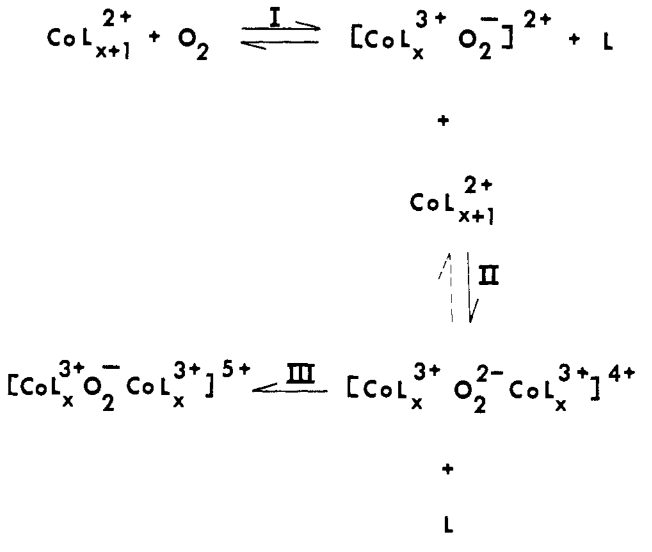
Adduct	g_1	g_2[b]	g_3	A_1^{Co}, G	A_2^{Co}, G[b]	A_3^{Co}, G
$Co(NH_3)_xO_2$-Y	2.084	2.01	2.000	17.8	12	12.5
$Co(CH_3NH_2)_xO_2$-Y	2.075	2.01	1.999	21.0	12	12.0
$Co(PrNH_2)_xO_2$-Y[c]	2.079	2.01	1.995	18.5	12	12.0
$Co(NH_3)_5O_2$[d]	2.081	1.995	1.995	17.7	12.2	12.2
$Co(TPP)(CH_3CN)O_2$[e]	2.076	2.004	1.995	15.6	17.7	17.7

[a] Estimated errors for g values, ±0.002; for hyperfine splittings, ±0.5 G, unless otherwise stated. [b] Estimated from computer simulation. [c] Pr = $CH_3CH_2CH_2$. [d] Formed in γ-irradiated $[Co(NH_3)_5(NO_3)](NO_3)_2$ (solid state), ref 9. [e] In frozen toluene solution, TPP = tetraphenylporphyrin, ref 8.

0.010-0.020, and A_{yy}^{Co} is approximately equal to A_{xx}^{Co}. Figure 3a shows the Q-band spectrum of the n-propylamine oxygen adduct in CoY. The low field maximum corresponding to g_{zz} is well resolved, but g_{yy} and g_{xx} cannot be clearly separated, although the presence of a shoulder on the high field minimum supports our contention that the symmetry is best described as orthorhombic rather than axial.

A nonaxial g tensor is expected if the 1:1 adducts in CoY have the same nonlinear structure as in the complex $[Co(bzacen)pyO_2]$,[7] for which the Co-O-O bond angle has been found to be 126°. Nonaxial g tensors have been reported for oxygen adducts of cobalt(II) tetraphenylporphyrin in frozen solution.[8] The close similarity between the EPR parameters of the 1:1 adducts in CoY and in frozen solution or the solid state (Table I) suggests that the structures are the same. As discussed previously,[5,10] the small ^{59}Co hyperfine splitting constants indicate that the unpaired electron is largely localized on the oxygen molecule; thus the oxygen adducts are best formulated as $[Co^{III}(RNH_2)_xO_2^-]^{2+}$, where x is probably equal to 5.

The stability, and hence the maximum observable concentrations of the 1:1 adducts in CoY, is limited by the reversibility of the formation step and the tendency to dimerize, as discussed below. With n-propylamine as the ligand, dimerization within the large cavities is not possible for steric reasons, so that disappearance of the monomer signal on warming in oxygen to 25° represents a shift of the equilibrium I in favor of the uncomplexed oxygen, which is reversed on cooling again to −78°. Dimerization of the methylamine cobalt oxygen adduct is not possible in CoY(3), which contains an average of 0.1 cobalt ions per large cavity, and the disappearance of the signal on warming to room temperature is thus similarly reversible. In CoY(2) and CoY(1), on the other hand, dimerization can occur (reaction II), evidently irreversibly, and it is necessary to decompose the dimer by evacuating at 25° before adding further oxygen at −78° to restore the monomer signal. Dimerization of the ammonia oxygen adduct also occurs in CoY(1) and CoY(2) at 25°, but in this case reaction II can be reversed by cooling again to −78° in oxygen, without prior evacuation.



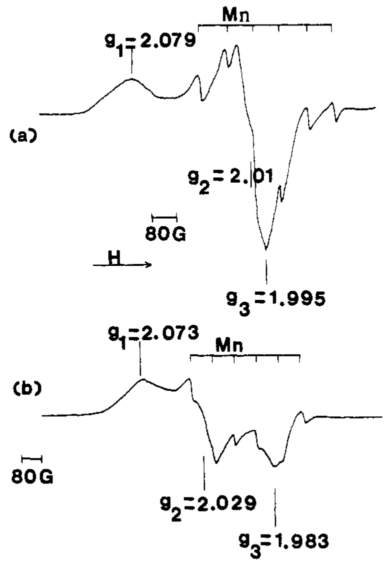


Figure 3. Q-Band spectra (derivative): (a) $[Co^{III}(PrNH_2)_xO_2^-]^{2+}$, (b) $[Co^{III}(NH_3)_xO_2^-Co^{III}(NH_3)_x]^{5+}$. Lines marked Mn are due to an Mn^{2+} impurity in the zeolite.

Dimeric 1:2 Cobalt Oxygen Adducts. The formation of 1:2 cobalt oxygen adducts in solution has long been known. In general, dimerization of 1:1 adducts leads to μ-peroxodicobalt species, $[Co^{III}L_xO_2^{2-}Co^{III}L_x]^{4+}$, where L represents a nitrogen-containing ligand, which may be oxidized to give μ-superoxodicobalt adducts, $[Co^{III}L_xO_2^-Co^{III}L_x]^{5+}$. The paramagnetic μ-superoxo adducts in solution show a characteristic 15-line EPR spectrum due to interaction of the unpaired electron with two equivalent ^{59}Co nuclei.[11] The zeolite spectrum in Figure 1a has at least two sets of 15 lines, which may at first sight be attributed to the parallel and perpendicular components of an axially symmetric g tensor. However, as with the monomeric adducts, the observed spectrum cannot be simulated unless nonaxial symmetry is assumed. Figure 1b shows a typical computed spectrum. The nonaxial symmetry of the dimeric adducts is clearly revealed in the Q-band spectra, as shown for example in Figure 3b.

Well-resolved polycrystalline spectra of μ-superoxodicobalt adducts have not been previously reported, but the average $\langle g \rangle$ and $\langle A \rangle$ values of the dimeric adducts in CoY with ammonia and methylamine as ligands compare closely with those of μ-superoxo adducts in solution. Thus the paramagnetic dimers in CoY are almost certainly μ-superoxo adducts with the same planar CoO_2Co structure that has been reported for $[NH_3)_5CoO_2Co(NH_3)_5]^{5+}$.[12] The number of amine ligands coordinated to each cobalt is probably five, although the possibility of the terminal coordination sites being occupied by zeolitic oxide anions cannot be ruled out. The anisotropy of the g tensor arises from the asymmetric location of the cobalt ions about the O-O bond. Paramagnetic dibridged μ-amido-μ-superoxodicobalt ad-

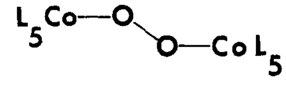


Table II. EPR Parameters of CoO_2Co Adducts[a]

Adduct	g_1	g_2	g_3	$\langle g_{iso} \rangle$[c]	A_1Co, G	A_2Co, G[b]	A_3Co, G	$\langle A_{iso}$Co$\rangle$[c]
$[Co(NH_3)_x]_2O_2$-Y	2.072	2.029	1.983	2.028	20.0	15	10.0	15
$[Co(CH_3NH_2)_x]_2O_2$-Y	2.077	2.038	1.984	2.033	20.0	15	10.0	15
$[Co(NH_3)_5]_2O_2(NO_3)_5$[d]				2.025				11.4
$K_5[Co(CN)_5]_2O_2$[d]				2.020				8

[a] Estimated errors for g values, ±0.002; for hyperfine splitting, ±0.5 G, unless otherwise stated. [b] Estimated from computer simulation, ±5 G. [c] Average of principal values. [d] Solution spectra, ref 12.

ducts are also known,[9] but are usually formed via the monobridged species, and have significantly larger average g values. We have not observed any such species in CoY.

No detailed description of the bonding in μ-superoxodicobalt adducts is yet available. The unpaired electron will be located in a molecular orbital involving an antibonding $2p\pi_g$ oxygen molecular orbital and two cobalt $3d_t$ orbitals, but may also have some s orbital character as a result of spin polarization. If the principal axes of the hyperfine and g tensors are assumed to be parallel, it can be shown by the usual methods that for the μ-superoxo adducts in CoY the unpaired electron is about 4% localized on cobalt 3d orbitals and about 1% on cobalt 4s orbitals, the s orbital population being close to that expected for simple spin polarization. These values must, however, be treated with caution, since the assumption of parallel g and hyperfine tensors may be invalid.

We envisage the formation of μ-superoxo adducts within the large cavities of zeolite Y occurring in much the same manner as in solution via μ-peroxo species, although the diamagnetic μ-peroxo adducts cannot be directly observed by EPR. With ammonia as the ligand, the μ-peroxo adduct is formed from the 1:1 monomer on warming in oxygen to 25°, but only on subsequent evacuation is this slowly oxidized to give the paramagnetic μ-superoxo species. With methylamine as the ligand, on the other hand, the peroxo species is much less stable and is oxidized to the superoxo species on standing in oxygen at 25°.

The highest concentrations of the μ-superoxo adducts are formed in CoY(1), but amount to only 10 and 20% respectively of the concentrations expected for complete reaction of the ammonia and methylamine monomeric adducts according to reactions II and III. In CoY(2), the dimer concentrations are up to an order of magnitude lower, although there are still sufficient cobalt ions present (1.25 per large cavity) to allow dimerization of at least one-fourth of the monomeric adducts. This suggests that the oxidation step (III) in the zeolite is very dependent on the cobalt exchange level. Schrauzer and Lee[13] have suggested that formation of the superoxo radical in solution may be initiated by a disproportionation of the μ-peroxo adduct. Such a reaction seems unlikely to occur within the zeolite for steric reasons. In solution, the reversibility of oxygen uptake by cobalt(II) complexes is limited by the eventual irreversible oxidation to cobalt(III) through side reactions which are not well understood.[9] We prefer to attribute the oxidation of μ-peroxo adducts in CoY to the presence of small amounts of Co^{III} (up to about 1.5 and 0.6 ions per unit cell in CoY(1) and CoY(2), respectively), which is not complexed with oxygen, although this explanation must remain speculative in the absence of direct observation of cobalt(III) in the Co^{II} exchanged zeolite.

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