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The Structure of a Carbon Monoxide Adduct of Zeolite 5A

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The structure of Ca_5Na_2–A : 5CO has been determined at room temperature using Rietveld profile refinement in space group *Fm*3*c* with *a* refined to 24.6558(2) Å. The final R_{pw} was 3.5%. As in the case of dehydrated zeolite 5A, the exchangeable cations are located in S1 (6-ring) sites, with Ca–O and Na–O distances of 2.32 and 2.37 Å. The carbon atoms of the carbon monoxide molecules have been located on the three-fold axis in the α-cage in a position analogous to that found in the CO complex of cobalt-exchanged zeolite A. However, the oxygen atoms are either undergoing considerable thermal motion or are disordered over several off-axis locations. The Ca–C distance is 2.83 Å. Inside the β-cage, with site occupancy approximately three-fourths, there are AlO_4H_3 tetrahedral species evenly distributed between two orientations, as has been found previously in studies of divalent exchanged samples of zeolite A. This aluminum complex bonds to the framework via Al–O–H . . . O(3) hydrogen bonds and there is coordination of the non-hydrogen-bearing oxygen atom to exchangeable calcium ions (Al–O . . . Ca).

Introduction

Some time ago, Angell and Schaffer (*1*) found, rather surprisingly, that carbon monoxide was sorbed by X and Y zeolites containing divalent ions. The C–O stretching frequency was higher than that found for gas-phase CO and this was interpreted as being due to polarization of the carbon monoxide molecules in the electric field near the exchangeable cations.

More recently, Förster *et al.* (*2*) found that carbon monoxide was sorbed fairly strongly by alkaline earth-exchanged samples of zeolite A, especially at low temperatures and, indeed, this gas was oxidized in the zeolite at temperatures as low as 150 K. Bose *et al.* (*3*) confirmed these results and suggested on the basis of infrared evidence that CO is held near the calcium ions on S1 sites and near sodium ions on S1, S2, and S3 sites in $Na_{12-2x}Ca_x$-exchanged zeolite A. Bose *et al.* (*3*) considered that there were linear cation–C–O and cation–O–C arrangements, the former predominating, which were aligned (for cations in S1 sites) along [111], although a significant degree of librational motion occurred.

The interaction between alkali or alkaline earth cations and carbon monoxide in zeolites must have little in common with the so-called carbonyls of the alkali and alkaline earth metals which are prepared from the metal and CO in solution in liquid ammonia or from the molten metal and gas directly. These materials contain $^-OC{=}CO^-$ or $C_6O_6^{6-}$ units (*4–6*). In zeolites we start with M^+ or M^{2+} ions rather than M^0; the situation is much closer to that found for carbonyl derivatives of metal

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halides, e.g., $CoI_2 + CO \rightarrow Co(CO)I_2$, but these are only formed by transition metals (*7*).

The present investigation of the structure of a CO complex of Ca_5Na_2–A was carried out to compare the arrangement of the guest molecules in the cavity with that found in partially cobalt-exchanged samples of zeolite A studied previously (*8, 9*). In particular, the disposition of the CO molecules with respect to the exchangeable cations is of interest. It is known that the oxidation activity of Ca_5Na_2–A is much greater than that of Co_4Na_4–A(2), yet, in zeolite X and Y at least, the infrared evidence suggests very similar bonding situations in a variety of divalent exchanged samples, there being a good correlation between the C–O stretching frequencies and the field strength around the cations (*1*). For each of the zeolites, A, X, and Y, only a 10-cm^{-1} difference in stretching frequency separates Ca- and Co-exchanged samples (*1, 3*); there is nothing in the infrared data to suggest why Ca_5Na_2–A should have special oxidative properties.

Experimental

The zeolite used in this work was a commercially available 5A zeolite manufactured by Union Carbide Corporation and supplied by BDH. It was from the same batch as that used by Adams and Haselden (*10*) to refine the structure of dehydrated zeolite 5A. The composition was $Ca_{40}Na_{16}Si_{96}Al_{96}O_{384} \cdot 33H_2O$ (*10*).

Neutron powder diffraction data were collected with the high-resolution diffractometer D1A at the Institut Laue-Langevin, Grenoble (*11*). Five grams of the zeolite was used in a 16-mm-diameter vanadium sample can. Dehydration was carried out in a vacuum furnace *in situ* (600 K, 2×10^{-6} Torr, 12 hr), after which the sample was allowed to cool to 300 K and exposed to carbon monoxide gas at a pressure of 1.2 bar. Data were collected for 20 hr and covered a range of 19.00–158.03° (2θ) using 1.909-Å neutrons. The background was estimated from regions where no Bragg peaks occurred. Structure refinement was carried out using the Rietveld method (*12, 13*) with the program of Wiles (*14*): the peak-shape function used was Gaussian and contributions to the intensity were made up to 1.5 half-widths from the peak centers. The XTAL System (*15*) was employed for all other calculations and the scattering lengths used were those given in the "International Tables for X-Ray Crystallography" (*16*). Throughout this study the space group $Fm3c$ was used as the best approximation (*10, 17*).

Structure Refinement

Since it is known that carbon monoxide is not sorbed strongly by zeolite A, it was considered that the framework structure of the dehydrated 5A zeolite (*10*) could be used as a starting model. The initial R_{pw} was 16.5%.

Regarding the exchangeable cation positions, in the dehydrated material the calcium and sodium ions were located near the 6-ring at $x = y = z = 0.089$ and 0.109, respectively. A difference Fourier map, calculated after anisotropic refinement of the framework atoms, showed that the situation was similar, even after sorption of CO. Again the scattering density trace near the plane of the 6-ring appeared to consist of two components along [111], one containing most of the scattering density, just inside the β-cage (at $x = y = z \sim 0.09$), and the other at $x = y = \ \sim 0.11$ (Fig. 1). Since the zeolite sample contained considerably more calcium than sodium, and since the neutron scattering length of calcium is greater than that of sodium, the assignment of Ca to the former and Na to the latter site was made, in a fashion analogous to that adopted for dehydrated zeolite 5A (*10*). An-

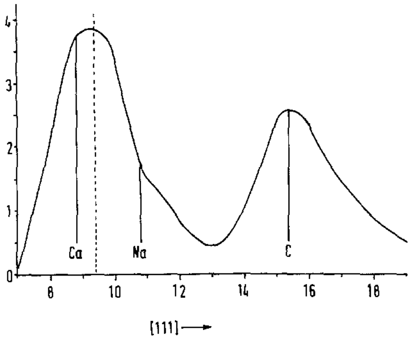

FIG. 1. Difference ($F_o - F_c$) Fourier trace along [111] calculated when using only the framework parameters taken for the related study on dehydrated zeolite 5A (*10*). The dashed line represents the plane of the 6-ring. On the horizontal axis, the scale is in hundredths of a unit cell, i.e., $x = y = z = 0.01 \times$ scale.

isotropic refinement including Ca(1) and Na(1) reduced R_{pw} to 10.4%.

The presence of the guest molecules in the α-cage of the zeolite could also be deduced from Fig. 1; there was a large peak on the threefold axis, with a maximum at $x = y = z \sim 0.155$. As was also the case for the CO complex of cobalt-exchanged zeolite A (*9*), the oxygen atom could not be resolved on the difference plot on the threefold axis. However, addition of the carbon atom, C(1), and further anisotropic refinement gave R_{pw}= 7.2%.

In some studies of divalent cation-exchanged samples of zeolite A, tetrahedral species of AlO_4 type have been found in the center of the sodalite cages. For reasons of charge balance, at least some of these oxygen atoms are likely to be protonated, and in each case the O . . . O (3, framework) distance has been consistent with H-bond formation (*9, 18, 19*). Difference Fourier calculations certainly showed, in the present structure, peaks at 0, 0, 0 and 0.04, 0.04, 0.04, which were considered to be due to two disordered orientations of AlO_4 tetrahedra. Inclusion of these atoms and refining them isotropically gave R_{pw} of 5.5%, an Al–O distance of ~1.80 Å, and O . . . O (3, framework) of 3.20 Å. Approximately three-quarters of the β-cages appeared to contain such species.

Evidence for the presence of hydrogen atoms bonded to the AlO_4 oxygen atoms was also found. There was a negative disk of scattering density around the $\bar{3}$ axis, centered at ~0.063, 0.063, 0.063, i.e., ~1 Å from the oxygen atom. It was considered that this was a composite peak, resulting from the contributions of three equivalent, off-axis, hydrogen positions, each involved in a weak O . . . O (3, framework) hydrogen bond. Now in every β-cage there are eight 6-rings. Just inside these cages we have five of the rings occupied by Ca ions, and for these rings it is unlikely that we could have AlO–H . . . O (framework) hydrogen bonds of the type suggested above; a H–Ca distance of only 1.1 Å would result. Hydrogen atoms were therefore added to the model at positions just over 1 Å from the AlO_4 oxygen atom and along the line between this atom and O(3); the occupancy of these atoms was set at three-quarters of that of the oxygen atoms to which they were bound, so that in any β-cage which contained an AlO_4 unit, no more than three 6-rings would accept H bonds. Independent refinement of this hydrogen atom did not prove possible, and it was allowed to ride on the oxygen atoms to which it was attached. R_{pw} fell to 4.4%.

We now returned to consider the carbon monoxide guest species. A Fourier synthesis gave no evidence of an oxygen atom 1.1 or 1.2 Å from C(1) along the $\bar{3}$ axis, while there were three equivalent peaks of scattering density in an off-axis position at this distance (Fig. 2). An oxygen atom was introduced ~1.12 Å from C(1), slightly shorter than the gas-phase value of 1.128 Å (*20*) to be consistent with the infrared data (*3*)—though the bond was then rather shorter than that found in typical transition metal carbonyls (1.15 Å, (*7*))—and was allowed to refine. For comparison, a second

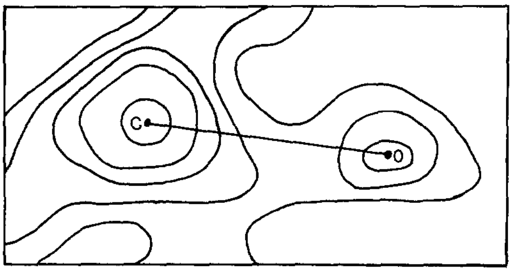

FIG. 2. F_{obs} Fourier map calculated at R_{pw} = 4.4% showing one of the three equivalent regions of scattering density just off the $\bar{3}$ axis, considered to be due to oxygen atoms of disordered CO molecules. The carbon atom is in the $\bar{3}$ axis at ~0.154, 0.154, 0.154 and the off-axis peak (denoted O) is at ~0.156, 0.156, 0.200. The C–O distance taken directly from this map is ~1.2 Å.

model was constructed with its C–O bond lying along the threefold axis.

Free refinement of the oxygen position in the first (off-axis) model resulted in a slow drift of the oxygen atom over many cycles, until it settled down 1.6 Å from C(1) at ~0.152, 0.152, 0.216. This distance was not realistic for any likely type of C–O bond, and a further refinement was made with the C–O distance constrained. The temperature factor of the oxygen atom was high at B_{iso}(equiv) ~ 29, but was stable and similar to that of the carbon atom. The final R_{pw} was 3.5% and the derived Bragg R factor (R_B) was 1.4%. With the second model, the temperature factor of the oxygen atom increased to above 40 (B_{iso}(equiv)) but the final R factors were similar to those above: R_{pw} = 3.6%, R_B = 1.3%. For both models, totally free refinements of the occupancies of the CO molecules, together with their isotropic thermal parameters, proved impossible, but populations approximated the number of calcium ions and in the final refinement cycles they were fixed at this value.

The non-CO atomic parameters from the two refinements were in good agreement. Those from the first (off-axis) refinement are given in Table I together with both sets of CO parameters. Geometric information is given in Table II and observed in calculated diffraction patterns in Fig. 3. The

TABLE I

ATOMIC COORDINATES, OCCUPANCIES, AND TEMPERATURE FACTORS FOR THE CARBON MONOXIDE COMPLEX OF ZEOLITE 5A

Site	Position	Population	x	y	z	β_{11} (or B)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	96(i)	96	0	0.0926(4)	0.1851(4)	7(2)	4(2)	9(2)	0	0	0(1)
Al(1)	96(i)	96	0	0.1869(6)	0.0884(5)	8(2)	13(2)	9(2)	0	0	11(2)
O(1)	96(i)	96	0	0.1098(2)	0.02472(4)	15(1)	15(1)	9(1)	0	0	4(1)
O(2)	96(i)	96	0	0.1402(2)	0.1421(3)	34(1)	14(2)	−1(1)	0	0	6(1)
O(3)	192(j)	192	0.0538(2)	0.0575(2)	0.1699(1)	10(1)	14(1)	16(1)	6(1)	4(1)	2(1)
Ca(1)	64(g)	40	0.0877(3)	0.0877(3)	0.0877(3)	20(1)	20(1)	20(1)	6(1)	6(1)	6(1)
Na(1)	64(g)	16	0.1078(2)	0.1078(12)	0.1078(12)	20	20	20	6	6	6
C(1)	64(g)	40	0.1541(8)	0.1541(8)	0.1541(8)	120(6)	120(6)	120(6)	−32(9)	−32(9)	−32(9)
O(4)	192(j)	40	0.1558(19)	0.1558(19)	0.1995(16)	129(13)	133(13)	147(15)	67(7)	43(6)	35(6)
Al	8(b)	6.2(2)	0	0	0	6.5(2)					
O*	64(g)	24.8(7)	0.0422(8)	0.0422(8)	0.0422(8)	21(1)					
H*	192(j)	18.7(5)	0.0470	0.0480	0.0837	21					
C(1)[a]	64(g)	40	0.1553(5)	0.1553(5)	0.1553(5)	117(9)	117(9)	117(9)	−30(6)	−30(6)	−30(6)
O(4)[a]	64(g)	40	0.1815(5)	0.1815(5)	0.1815(5)	334(13)	334(13)	334(13)	−72(8)	−72(8)	−72(8)

Note. Anisotropic displacement factor given by $10^4 \exp\text{-}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. $R_{pw} = 100[\Sigma w(y_{obs} - (1/c)y_{calc})^2/\Sigma(y_{obs})^2]^{1/2}$ and $R_{Bragg} = 100\Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs}$, where w is the weight at each 2θ data point and y_{obs} and y_{calc} are the observed and calculated intensities at that point; c is the scale factor. I_{calc} is the calculated intensity of the appropriate peak. The program divides the observed counts between overlapping reflections according to the relative contributions of the calculated reflections, applies a Lorentz correction, and then calculates "I_{obs}" in each case.

[a] Alternative positions for CO molecule obtained after refinement assuming that there is a linear M–C–O arrangement with the CO molecules lying in the $\bar{3}$ axis.

TABLE II

BAND DISTANCES (Å) AND ANGLES (°) FOR THE CARBON MONOXIDE COMPLEX OF ZEOLITE 5A[a]

Si(1)–O(1)	1.588(14)	O(1)–Si(1)–O(2)	116.6(9)
Si(1)–O(2)	1.582(15)	O(1)–Si(1)–O(3)	111.3(4)
Si(1)–O(3), O(3^{i})	1.628(9)	O(2)–Si(1)–O(3)	103.9(5)
Al(1)–O(1^{ii})	1.708(17)	O(3)–Si(1)–O(3^{i})	109.2(8)
Al(1)–O(2)	1.755(15)	O(1^{ii})–Al(1)–O(2)	113.0(8)
Al(1)–O(3^{i}), O(3^{iii})	1.707(9)	O(1^{ii})–Al(1)–O(3^{i})	112.8(5)
Ca(1)–O(3), O(3^{i}), O(3^{iv})	2.315(8)	O(2)–Al(1)–O(3^{i})	102.5(6)
Ca(1)–O(2), O(2^{i}), O($^{\mathrm{iv}}$)	2.855(9)	O(3^{i})–Al(1)–O(3^{iii})	112.3(7)
Na(1)–O(3), O(3^{i}), O(3^{iv})	2.378(30)	Si(1)–O(1)–Al(1^{viii})	146.5(7)
Na(1)–O(2), O(2^{io}), O(2^{iv})	2.901(30)	Si(1)–O(2)–Al(1)	173.1(8)
Ca(1)–C(1)	2.84(2)	Si(1)–O(3)–Al(1^{iv})	142.4(7)
C(1)–O(4)	1.12	O(3)–Ca(1)–O(3^{i})	118.8(7)
Al*–O*, O$^{*\mathrm{v}}$, O$^{*\mathrm{vii}}$, O$^{*\mathrm{vii}}$	1.80(2)	O(3)–Na(1)–O(3^{i})	113.8(7)
O*–H*	1.04	O(3)–Ca(1)–C(1)	83.6(6)
O*–O(3), O(3^{i}), O(3^{iv})	3.18(2)	O*–Al*–O*	109(5)
H*–O(3)	2.14(1)	Al*–O*–H*	136.2
O*–Ca(1)	1.94(2)	O*–H*–O(3)	180.0

Note. Symmetry codes: (i) y, z, x; (ii) $x, \frac{1}{2} - z, y$; (iii) $-y, z, x$; (iv) z, x, y; (v) $x, -y, -z$; (vi) $-x, y, -z$; (vii) $-x, -y, z$; (viii) $-x, z, \frac{1}{2} - y$.

[a] The esd's in the last column are given in parentheses.

overall unit cell formulation, derived from the refinement, is $[\mathrm{AlO(OH)_3}]_{6.2} \cdot \mathrm{Ca_{40}Na_{16}} \cdot \mathrm{Al_{96}Si_{96}O_{384}} \cdot \mathrm{(CO)_{40}}$. The lack of charge balance is due in the main to lack of precision in defining the aluminum complex.

Discussion

Framework

It is apparent from the similarity of bond lengths and angles found for the present

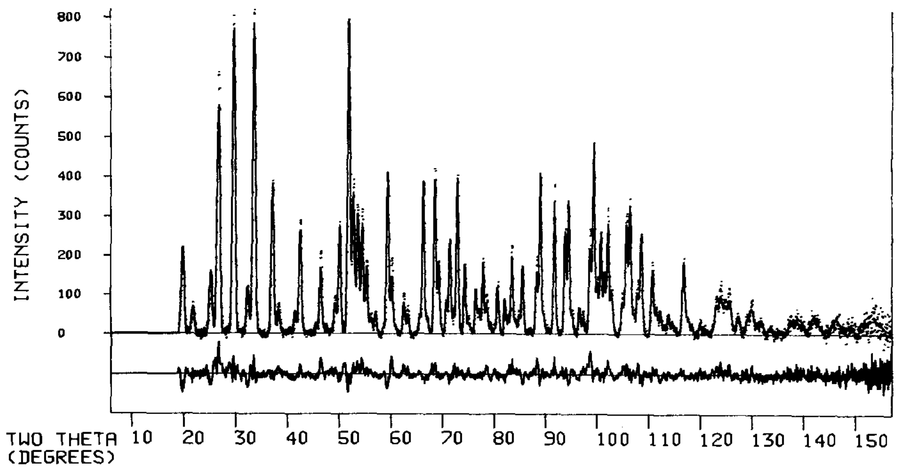

FIG. 3. Observed (dotted line) and calculated (solid line) diffraction patterns for zeolite 5A : CO complex at 300 K, together with a difference plot.

sample and for the parent, dehydrated zeolite 5A that there is no strong interaction between the guest molecules and the framework. The average Si–O and Al–O bond lengths are 1.599 and 1.726 Å compared with 1.607 and 1.715 Å found for dehydrated 5A (*10*); moreover the degree of tetrahedral rotation found in that structure is also mirrored here with Si(1)–O(3)–Al(1) and Si(1)–O(2)–Al(1) angles of 142.5 and 172.7° in the CO complex compared with 140.6 and 174.5° for dehydrated 5A (*10*).

Exchangeable Cation Positions

As was also the case for the dehydrated zeolite 5A from which it was derived, the nuclear scattering density peak near the center of the 6-ring was found to have two components, the larger being just inside the β-cage and the smaller one just inside the α-cage. Since the sample contained five calcium ions for every two sodium ions and since the scattering length of calcium is greater than that of sodium, we followed the procedure used in our earlier study (*10*) and assigned Ca to the site just inside the β-cage, with Na in the site projecting into the α-cage.

Other studies of dehydrated zeolites containing exchangeable calcium ions—Ca_4Na_4–A(21) and Ca_6–A(19)—have placed the majority of the calcium ions in sites projecting slightly into the α-cage. The reason why the present zeolite sample should differ is not clear. It should be noted that the two sites are about equidistant from the 6-ring, and it is possible that there is statistical occupancy of both types of atom in both positions. However, studies of 3A and 4A zeolites (*22–26*) place the sodium ions in sites consistent with those given in our present study.

Tetrahedral AlO_4 Species in β-Cage

The AlO_4 species, disordered over two orientations, has now been found in several divalent cation-exchanged samples of zeolite A (*9, 18, 19*), and in dealuminated zeolite Y (*27*), though not in univalent ion-exchanged materials. Only in the neutron study of the cobalt-exchanged zeolite A : CO complex did it prove possible to locate the hydrogen atoms. They were found to be involved in Al–O* . . . O (3, framework) hydrogen bonds, with some apparently bonded to O* and some to O(3). Here the Fourier maps indicate clearly that the hydrogen atoms are only bonded to O*.

Since only some of the O* atoms are protonated, it is apparent that two possibilities exist. For a particular 6-ring which does not contain calcium ions we can have Al–O*–H . . . O(3) bonds. However, when a calcium ion is present we have Al–O* . . . Ca^{2+} interactions (Fig. 4). This possibility was suggested by Pluth and Smith (*18, 19*) in their studies of Ca^{2+}- and Sr^{2+}-exchanged A. The O* . . . O(3) and O* . . . Ca^{2+} distances are ~3.2 and 1.9 Å rather than the 2.9 and 2.3 Å expected. Pluth and Smith rationalized a similar effect in Sr^{2+}–A (*18*) by pointing out that the O* peak is a composite, and a small displacement off [111] in any particular bonding situation would mean that suitable local bond lengths could be achieved.

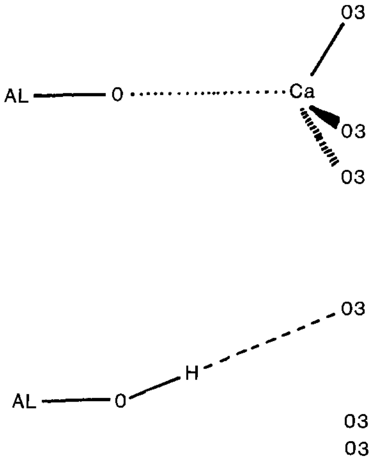

FIG. 4. Bonding of the AlO_4 complex to Ca ions and framework oxygen atoms.

Carbon Monoxide Position (Fig. 5)

In the refinement itself, and in the section below, we have only considered the possibility of *M* . . . C–O arrangements rather than *M* . . . O–C, since the infrared evidence suggests that this is the overwhelming arrangement (*3*).

The most interesting point to note about the CO coordinates is that the carbon atom is at about the same position in the unit cell as that found for cobalt-exchanged zeolite A (*6*). The infrared evidence (*3*) is of carbon monoxide held in the field of the calcium ion rather than sodium, yet the distance from the peak we have designated Ca^{2+} to the carbon atom is 2.83 Å. This distance seems rather long in view of the fact that the corresponding Co^{2+}–C distance in cobalt-exchanged A is 2.03 Å (*6*) and the difference in infrared C–O stretching frequencies in the two cases is only 5 cm^{-1} (*2*). To reconcile these two pieces of data it might be that we should reconsider the likelihood that the two exchangeable cation peak components could result from

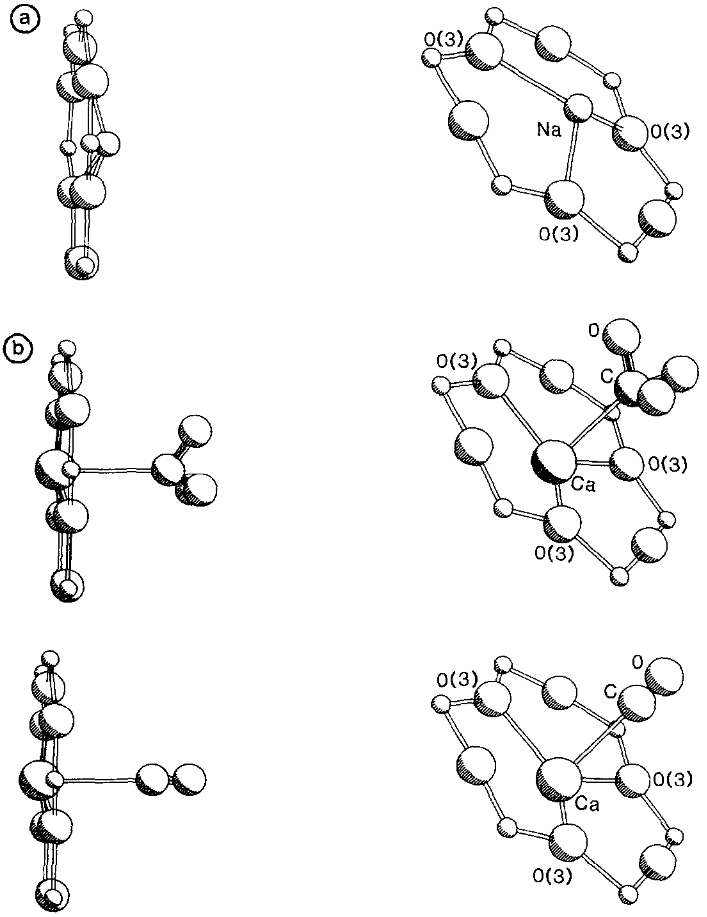

FIG. 5. Plot of the nearest-neighbor atoms for the exchangeable cations in 6-ring sites: (a) Na site in 5A : CO complex and (b) Ca ion and CO molecule. In (b), both possible types of carbonyl orientation have been shown; in the off-axis case (b, top) only one of the three equivalent orientations would be occupied at any instant.

statistical occupancy by Ca and Na. The "Na"–C distance of only 1.98 Å is much closer to that found in the transition metal case. However, it seems unlikely that bonding from CO to Ca^{2+} should be as strong as that from CO to transition metals and, moreover, the number of CO molecules per large cavity is much greater than the number of ions in the "Na" site. We incline to the view that the guest molecules do not form strong bonds to either type of exchangeable cation in 5A zeolite, but merely have their stretching frequency perturbed by the electrostatic field. Indeed the fact that the carbon monoxide *is* strongly bonded to cobalt ions in cobalt-exchanged A (*6*) but is not so bonded in Ca_5Na_2–A, while still having energy levels modified by the field in the zeolite pores, might account for the differences noted in oxidation activity (*2*).

Regarding the actual orientation of the CO molecule, neither of the two proposed models is considered entirely adequate. It is not possible to decide whether the molecules have a mean orientation along the threefold axis, but with a high degree of libration, or whether they really are disordered between three equivalent off-axis C–O orientations, mimicking closely the situation previously found in the CO complex of offretite (*28*).

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