

# Cuprammine ion-exchanged NaX zeolite and crystal structure analysis

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## *Cuprammine / Zeolites / Structure analysis / Heavy atom approximation procedure*

**Abstract.** The Cuprammine exchanged NaX zeolite ( $M = 17846$ , cubic, space group  $Fd\bar{3}m$ ,  $a = 24,915(1) \text{ \AA}$ ,  $V = 15466 \text{ \AA}^3$ ) is investigated for site occupancy by the cuprammonium ions. Intensity data are resolved into component  $hkl$  contributions by treating the known framework sites as conventional heavy atoms. Difference Fourier and least square methods were used to reveal and refine the interstitial Cu, Na,  $\text{NH}_3$  and water in hydrated samples. Final  $R = 0,09$  for 75 F and  $\sigma$ -criterion for the refinement  $F > 3\sigma(F)$  were used.

It is found that 25% of the cuprammine species are located in  $I'_{(U)}$  site [ $xxx$  with  $x = 0,100(2)$ ], origin at centre ( $\bar{3}m$ ) which is close to the centre of the sodalite cage while the rest is labile in the supercages.

## Introduction

Molecular sieves are support materials that provide sites for metal-ion localization with a variety of coordination symmetries (Dwyer, 1984; Maes and Cramers, 1973; Mortier, 1978; Ogawa, Nitta and Aoumora, 1979; Nitta, Ogawa and Aoumora, 1980). The occupancy of sites by metal-ion complexes that possess catalytic properties is of great interest since in zeolitic structures the complexes are found in a variety of coordination symmetries. Furthermore, by controlling site-occupancy of the metal-com-

plex one can investigate the catalytic activity of metal-ions of various coordination symmetries. Additionally, it is possible to immobilize homogeneous catalysts or activate small molecules by incorporating them in zeolitic structures (Mortier and Schoonheydt, 1985). Also, the zeolitic structure of a particular zeolitic crystalline material consists of cavities and channels of finite size. Therefore, some reagent molecules with greater size are not able to enter the zeolitic structure, those with intermediate size reach the sites adjacent to walls of the large cavities and the small size molecules reach almost all sites, thus providing selectivity in catalytic activity. For all these reasons it is important to have methods for preparing such complexes in zeolites and methods for determining the site-occupancy in their crystalline structure.

Fortunately, there are several well-established methods for preparing complexes of metal ions in zeolitic structures, both of general or of specialized-types (Peigneur, Lunsford and Schoonheydt, 1977; Schoonheydt, Peigneur and Uytterhoven, 1978; Bein and Jacobs, 1983; Rhee, Rao, Stencel, et al., 1983; De Wilde, Peeterns and Lunsford, 1980). The conventional ion-exchange method is used effectively just for small size cationic complexes. The methods for determination of site occupancy qualitatively and quantitatively are few and all are based on computer approximations. The method of "heavy atom approximation" is one that treats the intensities of the X-ray powder data and is most recently used in the field of zeolites (Evmerides, Beagley and Dwyer, 1976; Beagley, Dwyer, Evmerides, et al., 1982; Al-Ajdah, 1981; Al-Ajdah, Al-Rished, Beagley, et al., 1985).

It has been established that the metal ions are localized in sites in relation to their size of coordination sphere radius, their charge-size and the chemical nature of metal-ion involved (Dwyer, 1984; Maes and Cramers, 1973; Mortier, 1978; Ogawa, Nitta and Aoumora, 1979; Nitta, Ogawa and Aoumora, 1980). However, there is a lack of research on the influence of the ligand of a complex on the site selectivity of the metal-ion between complexes of approximately the same coordination sphere radius.

In this work, we have prepared a cuprammine complex of NaX zeolite and obtained its X-ray powder pattern. The intensity data were treated by the "heavy atom approximation" method and the site-occupancy was determined qualitatively and quantitatively.

## Experimental

All chemicals were of analytical reagent grade and the water used throughout was distilled. Commercial NaX molecular sieves were purchased from SIGMA in powder form. The 0.005 M Cuprammine aqueous stock solution was prepared by ion-exchanging 0.3455 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (MERCK)

Table 1. Final coordinates and population parameters for the exchanged zeolite.

Atom	Site <sup>a</sup>	x			Occupancy	No./Cell
T	192 i	0.2137(5)	0.1209(7)	0.3024(5)	1.0	192
O(1)	96 h	0.107(1)	0.2500	0.356(1)	1.0	96
O(2)	96 g	0.005(1)	x	0.120(2)	1.0	96
O(3)	96 g	0.071(1)	x	-0.027(2)	1.0	96
O(4)	96 g	0.070(2)	x	0.331(2)	1.0	96
Cu	I <sub>(U)</sub> 32 e	0.100(2)	x	x	0.22(3)	7.1(9)
Cu/Na	II 32 e	0.241(2)	x	x	0.23(3)	8(1)
N/O	U' 48 f	1/8	1/8	0.044(3)	1.0(1)	50(5)
O(H <sub>2</sub> O)	IIIA' 96 g	0.163(3)	x	0.439(4)	0.40(8)	38(8)

<sup>a</sup> Wyckoff positions.

Note

i. The uncertainties in each value are given in brackets.

ii. The number per unit cell is calculated by multiplying the occupancy by the number of symmetry sites.

in 0.2 M ammonia solution and was further standardized by atomic absorption spectroscopy. The 0.2 M ammonia stock solution was prepared by diluting 13.30 ml 25% w/V ammonia solution (MERCK) to 1:1.

The ion-exchanged NaX sample was prepared by ion-exchanging 1.0 g of NaX (in hydrated form) with 500.0 ml portions of solutions 0.005 M in Cu<sup>2+</sup>, at room temperature for 48 hours. The samples were washed and dried in a vacuum desiccator with CaCl<sub>2</sub> for long period of time and were moved to another desiccator containing a saturated solution of ammonium chloride or sodium nitrate.

The chemical analysis of the Cuprammine-exchanged NaX for water, silicon, aluminum, copper and sodium content gave 23.58% by weight (evaporation at 500°C), 219.50 mg/g (gravimetric method), 173.90 mg/g (gravimetric method with oxine), 81.20 mg/g (by A.A.S.), 43.28 mg/g (by Flame photometry), respectively (Vogel, 1978).

Powder diffraction patterns were recorded with a Scintag powder diffractometer using CuK $\alpha$  radiation. The crystal structures were analysed in the space group  $Fd\bar{3}m$  and the unit cell constant of the sample was found to be  $a_0 = 24.915(2)$  Å, with unit cell volume 15466.2 Å<sup>3</sup>. Full details of the method of structure determination are given in earlier papers (Evmerides, Beagley and Dwyer, 1976; Beagley, Dwyer, Evmerides, et al., 1982).

The computation of: (a) structure factors, (b) difference Fourier Maps, (c) least-squares refinement and (d) bond lengths and angles were performed using the SHELX X-ray package with the complementary TKI-program (Beagley, Dwyer, Evmerides, et al., 1982; Al-Ajdah, Al-Rished, Beagley, et al., 1985) for subdividing the intensities of the non-unique reflections. Finally, the figures showing the arrangement of the atoms of the complex

**Table 2.** Bond lengths and angles for the framework atoms (estimated standard deviations).

Atoms	Distance (Å)
T-O(1)	1.66(2)
T-O(2)	1.63(2)
T-O(3)	1.64(2)
T-O(4)	1.84(3)
average	1.69
O(1)-O(2)	2.81(3)
O(1)-O(3)	2.80(2)
O(1)-O(4)	2.61(2)
O(2)-O(3)	2.20(4)
O(2)-O(4)	3.08(3)
O(3)-O(4)	3.02(2)
average	2.75
Atoms	Angles (deg.)
O(1)-T-O(2)	117(2)°
O(1)-T-O(3)	116(2)°
O(1)-T-O(4)	98(2)°
O(2)-T-O(3)	84(2)°
O(2)-T-O(4)	125(3)°
O(3)-T-O(4)	120(2)°
average	110°

in the zeolitic structure were made using the PLUTO (Motherwell and Clegg, 1978) package.

## Results

The difference Fourier methods revealed the nonframework sites and least-squares refinement steps provided partial occupancy parameters and atomic coordinates (Table 1) for the atoms of Cu, N, and H<sub>2</sub>O of the incoming cuprammine ions.

The first 52 lines of the powder diffraction pattern of the cuprammine ion exchanged NaX zeolite were used for the "heavy atom approximation" calculations. The refinement calculations (final  $R = 0.09$ ) resulted in calculated structure factors which are comparable to the experimentally observed.<sup>1</sup>

<sup>1</sup> Additional material to this paper can be ordered referring to the no. CSD 55761, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Informationen mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

**Table 3.** Bond lengths, multiplicity and angles for the non framework atoms (estimated standard deviations).

Atoms	Distance (Å)	Multiplicity
CuI <sub>(U)</sub> -N	1.66(6)	3
CuI <sub>(U)</sub> -N,O	2.78(6)	3
Cu II-O(2)	3.01(8)	3
Cu II-O(4)	3.12(4)	3
N-N	2.87(4)	
N-N	4.06(3)	
N-O(2)	3.13(4)	2
N-O(3)	2.58(4)	2
OW-OW	2.69(4)	
OW-O(4)	2.75(5)	
OW-O(1)	3.30(4)	
Atoms	Angles (deg.)	
N-CuU-N	119.5(7)°	
O(4)-Cu II-O(3)	60.3(7)°	
O(4)-Cu II-T	32.2(5)°	
O(2)-Cu II-T	28.5(5)°	
CuU-N-UCu	63(6)°	

(Further distances are given in the text).

The bond lengths and angles for all atoms are tabulated in Table 2 and Table 3 respectively.

## Discussion

Consistent with previous work (Al-Ajdah, 1981), no cations were located at the centre of the hexagonal prism SI (coordinates: 0, 0, 0). This has been ascribed to the size of the Cu<sup>2+</sup> ion and/or electrostatic repulsion from the I' site. With the Cu(NH<sub>3</sub>)<sub>x</sub><sup>2+</sup> ion used in this determination, occupancy would be very unlikely on steric grounds alone.

Cations were located in a I'<sub>(U)</sub> (coordinates in Table 1) site however. These have been assigned as copper ions on the basis of their environment. Each cation has three atoms associated with it at a distance of 1.66 Å and another three at 2.78 Å. These six atoms were in an U' (coordinates in Table 1) site, and in view of the 1.66 Å bond length can reasonably be attributed to a Cu–N bond, and are thus ammonia molecules coordinated to the copper ion. The non symmetrical arrangement might well be the result of a Jahn-Teller distortion, which is common in Cu<sup>2+</sup> complexes (Barrer and Townsend, 1976). However, from Table 1 there is approximately

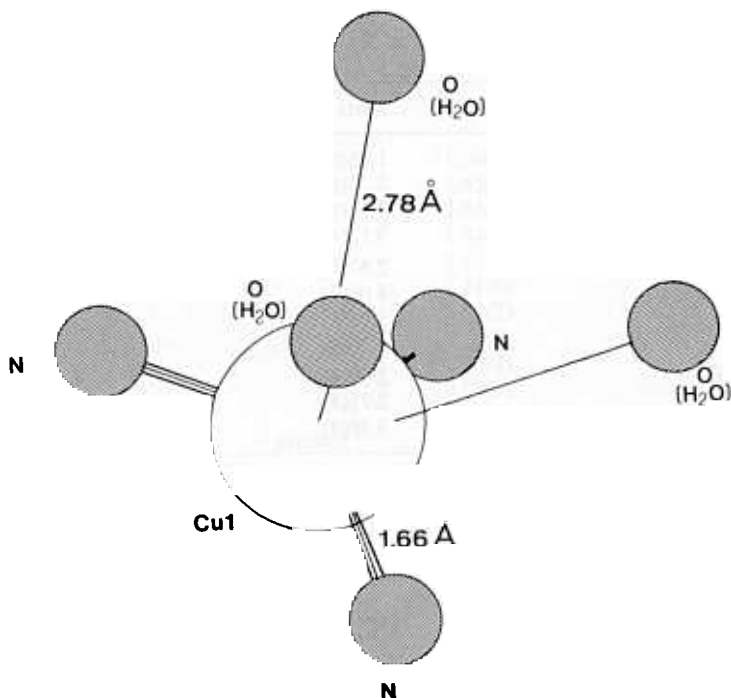


Fig. 1. The Cuprammine species located in the sodalite unit.

one Cu atom in each  $\beta$ -cage (8  $\beta$ -cages/cell) and due to the three ligand bond lengths of 1.66 Å and of 2.78 Å it is more likely to suggest a  $\text{Cu}(\text{NH}_3)_3^{2+} \cdot 3\text{H}_2\text{O}$  complex rather than a  $\text{Cu}(\text{NH}_3)_6^{2+}$  since the latter complex is not evidenced even in the aqueous solutions. The arrangement of the atoms is shown in Fig. 1.

The N–Cu–N angle of the closer ammonia nitrogens ( $\sim 120^\circ$ ) suggest that the  $\text{Cu}^{2+}$  ion is in a trigonal planar coordination. There is a  $\text{Cu}(I'_{(U)})$ – $\text{Cu}(I'_{(U)})$  distance of 1.73 Å which corresponds to the  $\text{Cu}(I'_{(U)})$  site at the centre of the three more distant ligands. Only one of these  $\text{Cu}(I'_{(U)})$  sites can be occupied at one time, as the distance between the  $\text{Cu}^{2+}$  ions would be too short.

The nearest framework atoms to the  $\text{Cu}(I'_{(U)})$  site are three O(3)'s at 3.34 Å and three O(2)'s at 3.84 Å. Fig. 2 shows part of the sodalite cage enclosing the cuprammine unit.

The three nearest ammonia nitrogens to the  $\text{Cu}(I'_{(U)})$  site were coordinated to an O(3) at 2.58 Å and an O(2) at 3.13 Å (Fig. 2). The distances implying the co-ordination being through hydrogen bonds (Greenwood and Earnshaw, 1984).

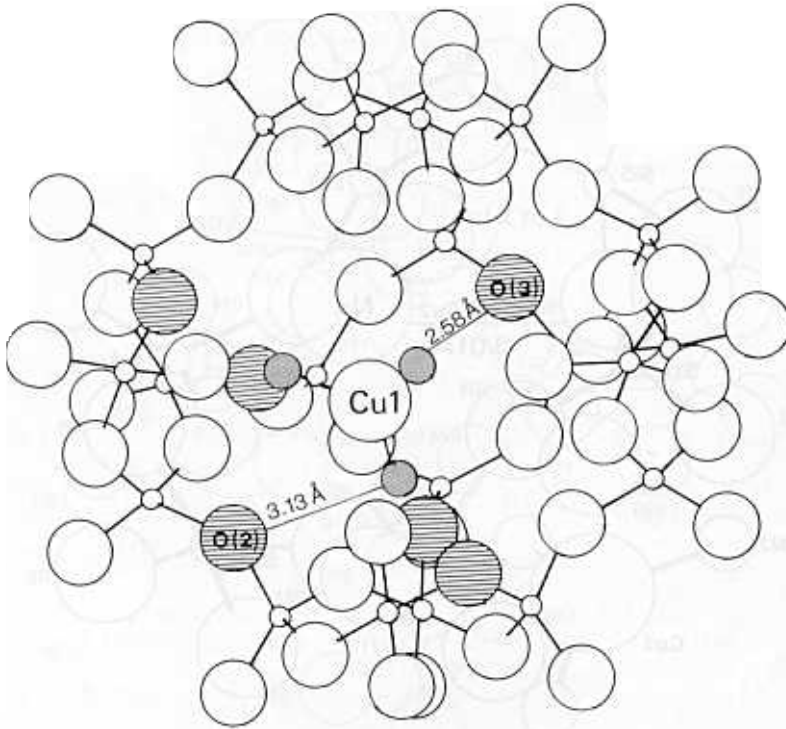


Fig. 2. The Cuprammine species (only closest three nitrogens shown), in the sodalite unit with the front four  $\text{TO}_4$  units removed.

The occupancy value of 7.1 for the  $\text{Cu}(I'_{(U)})$  site, would suggest that there is one of the cuprammine units associated with the majority of the sodalite units in the structure ( $\sim 87\%$ ). Due to the size of the species, the sodalite having a diameter of  $\sim 7.5 \text{ \AA}$  could only accommodate one ion.

Previous work (Al-Ajdah, 1981) on  $\text{Cu}^{2+}$  exchanged NaX had found  $\text{Cu}^{2+}$  ions in a  $I'$  site. In this structure determination the position of the Cu ion is displaced from  $I'$  site towards the U site. It is undoubtedly the bulk of the cuprammine species, and hence its interaction with the framework atoms, that causes it to occupy a  $I'_{(U)}$  site nearer to the centre of the sodalite unit. These findings do not agree with those of some workers (Fletcher and Townsend, 1980) who have suggested that such cuprammonium ions are restricted to the supercages in zeolites X and Y.

The other cation site located was a II site, coordinated to the 6-ring of a sodalite unit facing a supercage. In view of the fact that the cations in the site are only co-ordinated to the framework oxygens, and again in view of

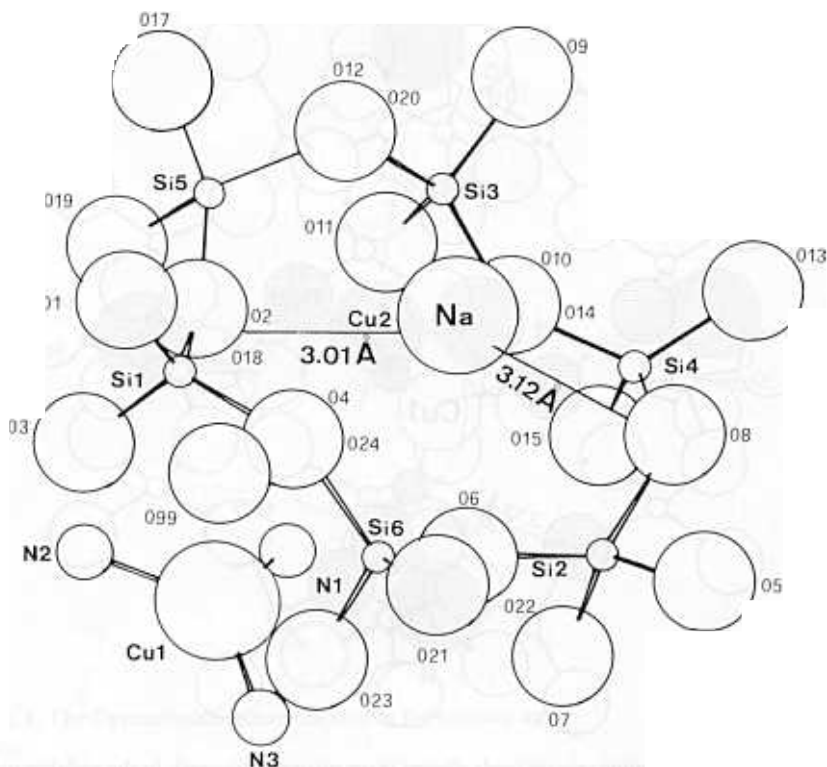


Fig. 3. The co-ordination of the sodium (labeled Cu2), in the II site

previous results (Al-Ajdah, 1981), some of these are likely to be sodium ions.

The cations are 3.01 Å from three O(2)'s and 3.12 Å from three O(4)'s. Previous results (Al-Ajdah, 1981) seem to suggest  $\sim 2.6$  Å for the O(2)-cation distance, but the longer distance found might well be a result of the large species in the sodalite unit. This arrangement is shown in Fig. 3, (Note that the cation of interest is actually labeled Cu2).

That last site located was IIIA' site. There was initially some confusion as to the content of the site, as the structure determination gave identical results for a copper or oxygen (water) containing site. In view of the low coordination and the framework distances in relation to previous work (Beagley, Dwyer, Evmiridis, et al., 1982; Al-Ajdah, 1981; Al-Ajdah, Al-Rished, Beagley, et al., 1985) the site was attributed to water molecules. The position of the water molecule relative to the 4-ring of the sodalite unit is shown in Fig. 4, the water molecule being labeled 099.



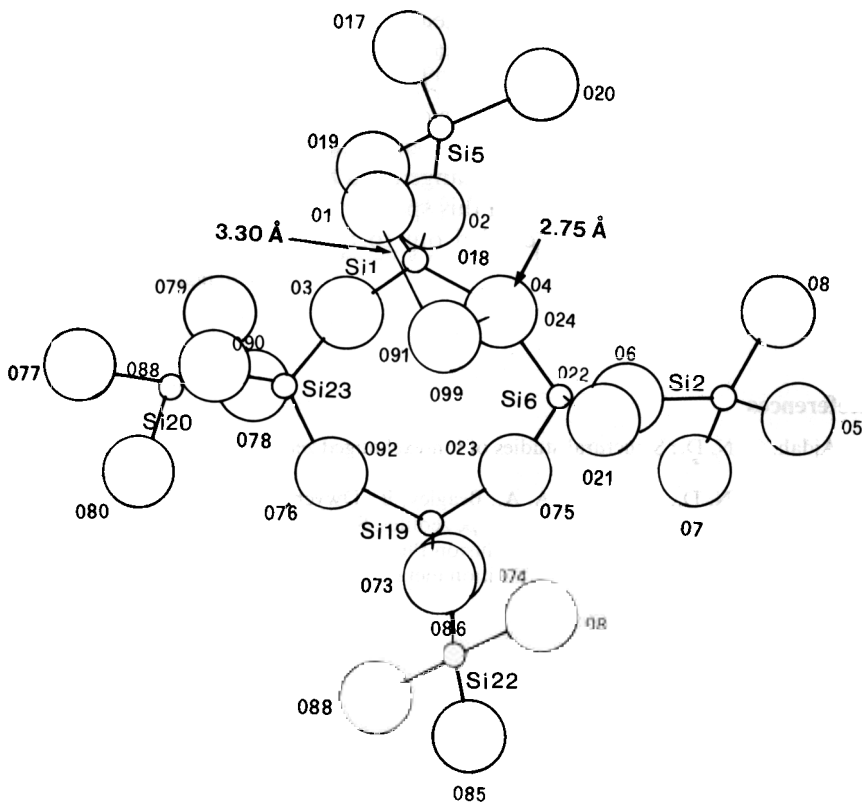


Fig. 4. The co-ordination of the water molecule (labeled 099) in the IIIA' site.

The water molecule is hydrogen bonded to the framework via an O(1) at 3.30 Å and O(4) at 2.75 Å. The calculated occupancy of 38.4 implies that around 40% of the available sites have water molecules associated with them.

The overall cation occupancy in the located sites only amounts to a charge of around  $21^+$ . The other cation species providing the remainder of the  $\sim 86^+$  charge required for zeolite X, must be located in the supercages, not coordinated to the framework, or in sites of low occupancy. They are likely to be associated in the supercages, with water molecules and possibly ammonia molecules, as mobile cationic complexes.

## Conclusions

To conclude, the structure determination was carried out successfully for the ion exchanged NaX zeolite, using the data provided. A distorted ar-

rangement of  $\text{Cu}(\text{NH}_3)_x^{2+}$  was located towards the centre of the sodalite units. Further cations were located at the site II and some possibly assignable to  $\text{Na}^+$  ions. Water molecules were located at site IIIA'.

Many of the deductions from this determination are in agreement with previous work. This work yielded some data on the behaviour of the cuprammine species, when ion exchanged in a zeolite X. In view of the little amount of work carried out with this species in ion exchange experiments, more work will have to be carried out to determine if these results are typical.

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