shape. In the tetracarbon species (structures II–V), this may become particularly important (we have already pointed out the extremely short bond between C(7) and C(8) in V).

Obviously, the method of synthesis also plays a major role in determining the cage geometry, as is clearly evident in the structure described in this paper. It will be interesting to see how the interplay of these various factors develops as additional metalloboron nido cage structures are determined.

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Supplementary Material Available: A listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 3: J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **17**, 6 (1978).
(2) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972); (c) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).
(3) A survey illustrating the broad applicability of the theory is given by R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).
(4) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970), and references cited therein.
(5) (a) W. M. Maxwell, R. F. Bryan, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4008 (1977); (b) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *ibid.*, **99**, 4016 (1977).
(6) W. M. Maxwell, K-S. Wong, and R. N. Grimes, *Inorg. Chem.*, **18**, 3094 (1977).
(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(8) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(10) D. T. Cromer and J. A. Ibers in ref 8.
(11) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(12) See paragraph at end of paper regarding supplementary material.
(13) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976).
(14) The essential geometry which was proposed earlier[13] for the iron complex has been confirmed in a recent x-ray study: J. R. Pipal and R. N. Grimes, to be submitted for publication. The two C_2B_4 units are aligned so that the two $CH_3C–CCH_3$ units are not completely eclipsed, but are partially rotated away from each other at an angle of 87°.
(15) D. P. Freyberg, R. Weiss, E. Sinn, and R. N. Grimes, *Inorg. Chem.*, **18**, 1847 (1977).
(16) The C–C distances in pyramidal or bipyramidal carboranes and metallo-carboranes range from 1.410 (4) Å in $1,2,3-(CO)_3FeC_2B_3H_7$[17] to 1.485 (4) Å in $\mu-C_3H_4-1,7,2,3-(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$.[18] For a tabulation of these and related data, see ref 18.
(17) J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **12**, 2266 (1973).
(18) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **17**, 10 (1978).
(19) V. S. Mastryukov, L. V. Vilkov, and O. V. Dorofeeva, *J. Mol. Struct.*, **24**, 217 (1975).
(20) (a) M. R. Churchill and B. G. Deboer, *Inorg. Chem.*, **13**, 1411 (1974); (b) F. Y. Lo, C. E. Strouse, K. P. Callahan, C. G. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 428 (1975).
(21) (a) E. I. Tolpin and W. N. Lipscomb, *Inorg. Chem.*, **12**, 2257 (1973); (b) M. R. Churchill and B. G. DeBoer, *ibid.*, **12**, 2674 (1973).
(22) K-S. Wong, J. R. Bowser, J. R. Pipal, and R. N. Grimes, *J. Am. Chem. Soc.*, in press.
(23) R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, **18**, 67 (1976).
(24) (a) A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2270 (1975); 962 (1977); (b) W. E. Carroll, M. Green, F. G. A. Stone, and A. J. Welch, *ibid.*, 2263 (1975); (c) G. K. Barker, M. Green, J. L. Spencer, F. G. A. Stone, B. F. Taylor, and A. J. Welch, *J. Chem. Soc., Chem. Command.*, 804 (1975).
(25) D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 602 (1977).
(26) By this we mean that the bridge carbon atom is calculated to be less than 0.8 Å from a point over the open face which would correspond to the 12th vertex of the icosahedron.
(27) NOTE ADDED IN PROOF. A recent crystallographic study of another 12-vertex, 28-electron system, $(\eta^5-C_5H_5)_2Co_2(CH_3)_4C_4B_6H_8$, revealed it to have a geometry like that of V, with the cobalt atoms occupying the 1, 12 vertices: J. R. Pipal and R. N. Grimes, in preparation.

Electronic and Resonance Raman Spectra of the [Mo2Br8]4- Ion

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Abstract: The electronic and resonance Raman spectra of [Mo2Br8]4- ion have been recorded at room temperature and at ca. 80 K. The strong band at ca. 18 000 cm^{-1} is assigned to the $^1A_{2u} \leftarrow {}^1A_{1g}$, $\delta^*(b_{1u}) \leftarrow \delta(b_{2g})$ transition; its wavenumber is in accord with that expected from the relation between the MoMo bond length, $r(MM)$, and the $\delta^* \leftarrow \delta$ wavenumber for $[M_2X_8]^{n-}$ ions. The 18 000-cm^{-1} band displays a ten-membered progression at ca. 80 K in $\nu_1(MoMo)a_{1g}$ (320 cm^{-1}). Resonance Raman spectra, excited by use of radiation with a wavenumber corresponding to that of the $\delta^* \leftarrow \delta$ transition, consists of an intense progression in $\nu_1(MoMo)a_{1g}$ reaching to 6 ν_1 at room temperature and 11 ν_1 at ca. 80 K, together with a much weaker progression $\nu_2(MoBr)a_{1g} + \nu_1\nu_1$. The spectroscopic constants ω_1 and x_{11} are calculated to be 336.9 and -0.48 cm^{-1} respectively. The MM bond dissociation energies of the $[Mo_2X_8]^{4-}$ and $[Re_2X_8]^{2-}$ ions (X = Cl or Br) are estimated to be ca. 500 kJ mol^{-1}.

Recent studies of the Raman spectra of metal–metal (MM) bonded species, particularly those for which the metal–metal bond is multiple, have shown that under resonance conditions very large enhancements take place to the ν (MM) band and its overtones.[1] Particularly spectacular in this respect have been the studies on species which belong, or to a first approximation belong, to the D_{4h} point group, viz., the $[Mo_2Cl_8]^{4-}$,[2,3] $[Re_2Cl_8]^{2-}$,[4] and $[Re_2Br_8]^{2-}$ ions,[4] the carboxylate-bridged species $Ru_2(O_2CR)_4Cl$ (R = CH_3 or n-C_4H_9),[5] the oxygen-bridged species $[Ru_2OCl_{10}]^{4-}$, and other structurally identical ions.[6] The recent synthesis of the $[Mo_2Br_8]^{4-}$ ion[7] opens the way to the possible study of its electronic and resonance Raman (rR) spectra, and thus to

detailed comparisons of its spectroscopic properties with those of other structurally related $[M_2X_8]^{n-}$ ions. The results of this study allow the relation between the MM bond length and the $^1A_{2u} \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \delta$) transition energy to be delineated for $[M_2X_8]^{n-}$ ions, and also permit approximate MM bond dissociation energies to be calculated.

Experimental Section

The $[Mo_2Br_8]^{4-}$ ion was prepared according to the method of Brenčič et al.[7] Anal. Calcd for $(NH_4)_4[Mo_2Br_8]$: N, 6.20; Br, 70.77. Found: N, 6.16; Br, 70.5.

Raman spectra were recorded using a Spex 1401 double spectrometer in conjunction with Coherent Radiation Models 12 and 52
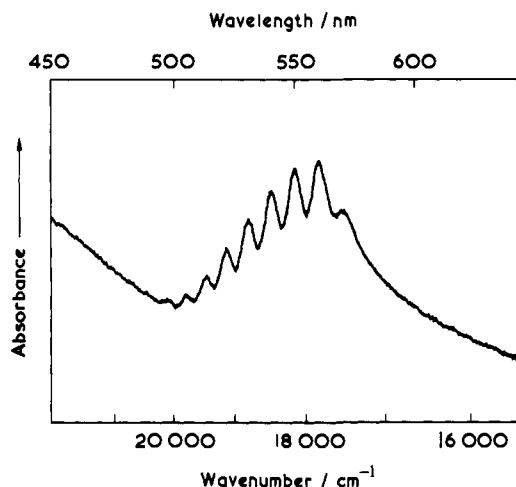
Figure 1. Transmission spectrum of $(NH_4)_4[Mo_2Br_8]$ as a KBr disk at ca. 80 K.

Table I. Vibrational Structure Observed in the KBr Transmission Spectrum of $(NH_4)_4[Mo_2Br_8]$ at ca. 80 K in the 18 000 cm^{-1} Region

Peak position, cm^{-1}	Peak separation, cm^{-1}
17 564	320
17 884	319
18 203	330
18 533	332
18 865	311
19 176	312
19 488	311
19 799	299
20 098	

Ar^+ lasers, a Model 52 Kr^+ laser, and a Model 490 dye laser (sodium fluorescein with cyclooctatetraene). The powers of the lasing lines were in the range 100 mW to 1.5 W. Detection was by means of RCA C31034 and FW 130 phototubes operating on the linear response mode. Further details are given elsewhere.[3,4] The rotating sample technique was used.[1,8] Band areas were determined by the cut and weigh procedure and then corrected for the spectral response of the instrument.

Diffuse reflectance and KBr transmission spectra were recorded using a Cary 14 spectrometer, fitted with a liquid nitrogen Dewar.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer as Nujol mulls, and on a Grubb-Parsons IRIS interferometer as polyethene disks, the measurements on the latter being made by courtesy of Dr. P. Goggin. The infrared spectrum of the anion consists of a very strong, broad band at 186 cm^{-1} and a medium band at 171 cm^{-1} (both assigned to $\nu(MoBr)$) together with a weak-medium band at 90 cm^{-1} assigned to $\delta(BrMoBr)$.

Results and Discussion

Electronic Spectra. The electronic spectrum of the $[Mo_2Br_8]^{4-}$ ion consists of a strong band at 18 000 cm^{-1} (Figure 1) which, by analogy with the assignments for the corresponding band of other $[M_2X_8]^{n-}$ ions, can be assigned confidently to the $^1A_{2u} \leftarrow {}^1A_{1g}$, $\delta^*(b_{1u}) \leftarrow \delta(b_{2g})$ transition. The band displays a progression in $\nu_1(a_{1g})$, the MoMo stretching mode, which extends to ten members. The average value for the wavenumber of the fundamental in this excited state is 320 cm^{-1} (Table I). This value is only 16 cm^{-1} less than that (335.8 cm^{-1}, see later) in the ground state, suggesting that the δ contribution to the bonding is small. The situation in this respect is entirely analogous to that for the $[Mo_2Cl_8]^{4-}$ ion, for which the $^1A_{2u} \leftarrow {}^1A_{1g}$ transition is centered at 18 700 cm^{-1} and for which a long progression in the $\nu_1(a_{1g})$ mode is clearly evident at ca. 80 K (excited state wavenumber of ν_1 is 337.5
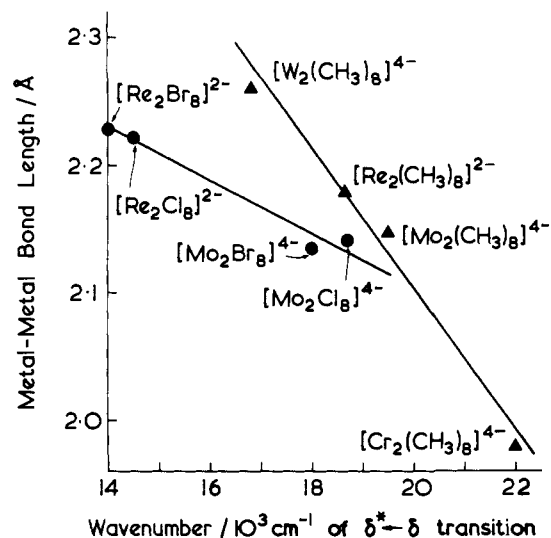

Figure 2. Plot of metal–metal distance vs. $^1A_{2u} \leftarrow {}^1A_{1g}$, $\delta^* \leftarrow \delta$ transition energy for M_2X_8-type species.

cm^{-1}, ground state value 345.9 cm^{-1}, for the potassium salt).[3]

The low-temperature disk spectrum of the $[Mo_2Br_8]^{4-}$ ion, like that of the $[Mo_2Cl_8]^{4-}$ ion,[3] shows a weak, broad feature ca. 2000 cm^{-1} on the low frequency side of the band maximum. This feature, on the basis of recent Raman, electronic, and luminescence spectral studies, seems likely to be the spin-forbidden transition $^3A_{2u} \leftarrow {}^1A_{1g}$, $\delta^* \leftarrow \delta$.[3,9,10]

A weak structured band appearing in the spectra of some salts of the $[Mo_2Cl_8]^{4-}$ at ca. 6000 cm^{-1} was originally thought to arise from this $^3A_{2u} \leftarrow {}^1A_{1g}$ transition, but it now appears more likely to arise from the $^1A_{2u} \leftarrow {}^1A_{1g}$, $\delta^* \leftarrow \delta$ transition of a surface-oxidized impurity, possibly the $[Mo_2Cl_8]^{3-}$ ion (cf. the corresponding transition for the $[Tc_2Cl_8]^{3-}$ and $[Mo_2(SO_4)_4]^{3-}$ ions[11,12] also occurs at ca. 6000 cm^{-1}).

There thus now exists a tetrad of $[M_2X_8]^{n-}$ ions for which both x-ray[7,13] and electronic spectral[3,4,14,15] information is available. A plot of the MM bond length vs. the $\delta^* \leftarrow \delta$ transition energy for these ions is given in Figure 2. This plot suggests a similar correlation between these two quantities as has been noted[16,17] for the corresponding $[M_2(CH_3)_8]^{n-}$ ions, viz., that as the MM bond distance decreases, and in consequence the overlap of the δ orbitals increases, so the energy difference between the δ and δ^* orbitals increases. The small blue shift in the $\delta^* \leftarrow \delta$ transition energy on going from an $[M_2X_8]^{n-}$ ion to the corresponding $[M_2(CH_3)_8]^{n-}$ ion is thought to arise from increased δ–δ orbital overlap for the latter type of ion, consequent on its δ orbitals, unlike those of the halogeno ions, having virtually no ligand π character.

Resonance Raman Spectra. The rR spectrum of $(NH_4)_4$-$[Mo_2Br_8]$ at both room (Figure 3) and liquid nitrogen temperature is characterized by an enormous enhancement to the intensity of the $\nu_1(MoMo)$, a_{1g} band at 335.8 cm^{-1}, the excitation profile of which reached a maximum at approximately the Franck-Condon maximum of the $^1A_{2u} \leftarrow {}^1A_{1g}$, $\delta^* \leftarrow \delta$ transition. The situation for this ion is thus directly analogous to that for the other $[M_2X_8]^{n-}$ ions[3,4] studied in this way; i.e., the coordinate primarily responsible for converting the ion from the ground- to the $^1A_{2u}$ excited-state geometry is the one which has its intensity enhanced under rR conditions.[18]

In addition to the enhancement to the intensity of the $\nu_1(a_{1g})$ mode, the other major effect of recording the Raman spectrum of this salt under rR conditions is the appearance of two long progressions, in each of which it is the $\nu_1(a_{1g})$ mode which acts as the progression-forming mode. The progressions observed

Table II. Wavenumbers and Assignments of the Bands Obtained in the Resonance Raman Spectrum of $(NH_4)_4[Mo_2Br_8]$ at ca. 80 K

|	v_1v_1 progression			$v_2 + v_1v_1$ progression	
Band	Max, cm^{-1}	Rel intensity[a]	Band	Max, cm^{-1}	Rel intensity[a]
v_1	335.8 ± 0.5	1.00	v_2	168.8 ± 1	0.05
$2v_1$	669.9 ± 0.5	0.70	$v_2 + v_1$	503.7 ± 1	0.03
$3v_1$	1006.4 ± 1	0.53	$v_2 + 2v_1$	839.9 ± 1	0.03
$4v_1$	1337.8 ± 0.5	0.33	$v_2 + 3v_1$	1174.7 ± 2	0.03
$5v_1$	1674.0 ± 0.5	0.15			
$6v_1$	2003.8 ± 0.5	0.05			
$7v_1$	2329.4 ± 3				
$8v_1$	(2669.5 ± 5)				

[a] Wavelength of exciting radiation 568.2 nm; data are corrected for the spectral response of the instrument.

Table III. Results of rR Studies on $M_2X_8{}^{n-}$ Ions at 300 K

Complex	v_1, cm^{-1} (MM)	v_2, cm^{-1} (MX)	Main progression	Second progression	ω_1 cm^{-1}	x_{11}, cm^{-1}	v_e(band max), cm^{-1} ($\delta^* \leftarrow \delta$)	D_0,[f] kJ mol^{-1}
$[NH_4]_5[Mo_2Cl_8]Cl$	338.0	274.0	$9v_1{}^a$	$v_2 + 4v_1$	339.6	−0.76 ± 0.07	18 700	638
$[NH_4]_4[Mo_2Br_8]$	335.8	168.8	$6v_1{}^b$	$v_2 + 4v_1$	336.9	−0.48 ± 0.09	18 000	705
$[n\text{-}Bu_4N]_2[Re_2Cl_8]$	271.9^c	356.5^d	$4v_1$	$v_2 + 2v_1$	272.6	−0.35 ± 0.05	14 500^e	636
$[n\text{-}Bu_4N]_2[Re_2Br_8]$	275.4^c	209.8^d	$4v_1$	$v_2 + 2v_1$	276.2	−0.39 ± 0.06	14 100	

[a] With cesium salt. [b] $11v_1$ at liquid nitrogen temperature. [c] $\rho \approx 0$. [d] $\rho = 0.01$ in acetone. [e] ϵ 1530 M^{-1} cm^{-1} in methanol. [f] Bond dissociation energy, estimated from the Birge–Sponer extrapolation. The value for the $[Mo_2Cl_8]^{4-}$ ion is the average of the values calculated for each of the five salts of the ion for which rR studies have been made (ref 3).
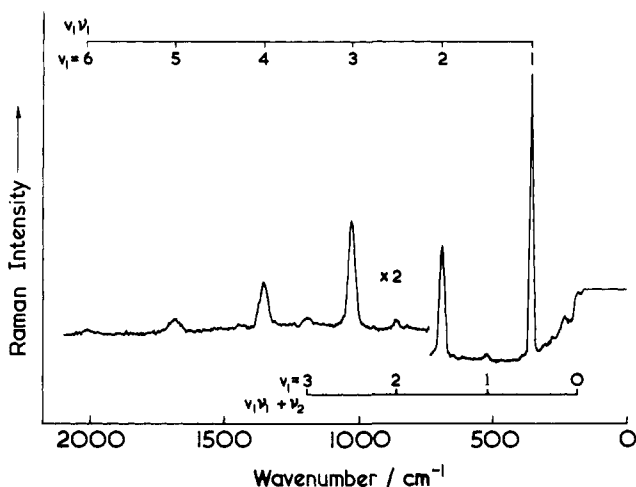
Figure 3. Resonance Raman spectrum of $(NH_4)_4[Mo_2Br_8]$ at 300 K.

are v_1v_1 to $v_1 = 6$ at 300 K and to $v_1 = 11$ at ca. 80 K, and $v_2 + v_1v_1$ to $v_1 = 3$ at 300 K. The fundamental v_2 occurs at 168.8 cm^{-1}, and is assigned to the $v_2(a_{1g})$MoBr stretching mode; cf. the corresponding MoCl stretching mode of the $[Mo_2Cl_8]^{4-}$ ion at 274 cm^{-1}.[3] The observed band maximum for the members of the two progressions are listed in Table II. The members of each progression display the characteristic features of the rR effect of continuous increase in half-bandwidth and continuous decrease in band areas with increase in the vibrational quantum number.

The observation of a large number of overtones of the v_1 fundamental makes it possible, by standard procedures,[1,19] to calculate the harmonic frequency ω_1 and the anharmonicity constant x_{11}. The results, together with previously obtained results on other $[M_2X_8]^{n-}$ ions, are drawn together in Table III. In all four cases the $v_1(a_{1g})$ mode is close to being a harmonic oscillator, the x_{11}/ω_1 value averaging −0.0016.

Bond dissociation energies (D_0) of diatomic molecules can be estimated from the Birge–Sponer extrapolation

$$D_0 = (\omega_e{}^2/4x_{11}) - \omega_e/2$$

which commonly gives values ca. 20% high. Additional difficulties arise when attempting to apply this expression to polyatomic molecules, owing to possible coupling between different modes of the same symmetries. Any such coupling should, however, be very similar for all four complex ions under discussion because the geometries are closely similar to one another, the MMX angle being 104.8 ± 1.5° in all cases. The values calculated for the $[M_2X_8]^{n-}$ ions, on the basis of the above expression and zero coupling, are given in the final column of Table II; the average value of D_0 for MoMo is 670 kJ mol^{-1} and for ReRe is 610 kJ mol^{-1}. After making allowance for the ca. 20% overestimate typical of this method, one can conclude that these metal–metal quadruple bands have $D_0 \approx$ 500 kJ mol^{-1}, which is a very substantial value, exceeded (as indicated by Trogler et al.)[10] among homonuclear units only by those of $C\equiv C$ and $N\equiv N$. Thus these data provide crude semiquantitative evidence for the high strength of MoMo and ReRe quadruple bonds, a fact which has long been appreciated by synthetic chemists.

References and Notes

(1) R. J. H. Clark in "Advances in Infrared and Raman Spectroscopy", Vol. 1, R. J. H. Clark and R. E. Hester, Ed., Heyden, London, 1975, p 143.
(2) R. J. H. Clark and M. L. Franks, *J. Chem. Soc., Chem. Commun.*, 316 (1974); C. L. Angell, F. A. Cotton, B. A. Frenz, and T. R. Webb, *ibid.*, 339 (1973).
(3) R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, **97**, 2691 (1975); R. J. H. Clark and B. Stewart, to be published.
(4) R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, **98**, 2763 (1976).
(5) R. J. H. Clark and M. L. Franks, *J. Chem. Soc., Dalton Trans.*, 1825 (1976).
(6) R. J. H. Clark, M. L. Franks, and P. C. Turtle, *J. Am. Chem. Soc.*, **99**, 2473 (1977); J. R. Campbell and R. J. H. Clark, *Mol. Phys.* in press.
(7) J. V. Brenčič, I. Leban, and P. Segedin, *Z. Anorg. Allg. Chem.*, **427**, 85 (1976).
(8) W. Kiefer, in ref 1, Vol. 3, 1977, p 1.
(9) P. E. Fanwick, D. S. Martin, F. A. Cotton, and T. R. Webb, *Inorg. Chem.*, **16**, 210 (1977).

(10) W. C. Trogler, C. D. Cowman, H. B. Gray, and F. A. Cotton, *J. Am. Chem. Soc.*, **99**, 2993 (1977).
(11) F. A. Cotton, P. E. Fanwick, L. D. Gage, B. Kalbacher, and D. S. Martin, *J. Am. Chem. Soc.*, **99**, 5642 (1977).
(12) D. K. Erwin, G. L. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler, and A. A. Zagars, *J. Am. Chem. Soc.*, **99**, 3620 (1977).
(13) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).
(14) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973).
(15) F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Am. Chem. Soc.*,

98, 2768 (1976).
(16) A. P. Sattelberger and J. P. Fackler, *J. Am. Chem. Soc.*, **99**, 1258 (1977).
(17) F. A. Cotton, S. Koch, K. Mertis, M. Millar, and G. Wilkinson, *J. Am. Chem. Soc.*, **99**, 4989 (1977).
(18) M. Tsuboi and A. Y. Hirakawa, *Science*, **188**, 359 (1975); ref 1, Vol. 5, 1978, in press.
(19) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. I, Van Nostrand, Princeton, N.J., 1950, pp 205, 438.

Near Zero Coordinate Ca^{2+} and Sr^{2+} in Zeolite A. Crystal Structures of Dehydrated Ca_6-A and Sr_6-A

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Abstract: The crystal structures of vacuum-dehydrated fully Ca^{2+}-exchanged zeolite A ($a = 12.278$ (2) Å) and vacuum-dehydrated fully Sr^{2+}-exchanged zeolite A ($a = 12.316$ (2) Å) have been determined by single-crystal x-ray diffraction methods in the cubic space group $Pm3m$. The structures were refined to final R (weighted) indices of 0.066 and 0.096, respectively. In each structure, five divalent cations are located on threefold axes near the centers of 6-oxygen rings. In Ca_6-A, the five Ca^{2+} ions are located at three unique equipoints: three equivalent ions are recessed 0.51 Å into the large cavity; one is nearly in the plane of a 6-oxygen ring; the fifth is 0.63 Å into the sodalite unit. The five threefold-axis Sr^{2+} ions occupy two equipoints: three equivalent ions are recessed 0.28 Å into the large cavity, and two are 0.78 Å into the sodalite unit, on opposite sides of the origin. The sixth Ca^{2+} ion is located at an unusual position in the plane of an 8-oxygen ring, and the sixth Sr^{2+} ion occupies a similar site near this plane. This Ca^{2+} ion is 3.08 (4) Å from its nearest neighbor, a single oxide ion of the aluminosilicate framework—this exceeds the sum of the respective ionic radii by 0.77 Å. (Two other oxide ions are 3.13 (6) Å from this Ca^{2+} ion.) The corresponding Sr^{2+} ion is 2.96 (12) Å from its nearest neighbor, a framework oxide ion—this distance is 0.52 Å longer than the sum of the corresponding ionic radii. (Two other oxide ions are 2.98 (13) Å from this Sr^{2+} ion.) These discrepancies are especially significant because the conventional ionic radii used are appropriate for larger coordination numbers and should be too long to describe the low-coordinate situation of the 8-ring cation. Presumably, one ion is located in an 8-ring in each structure because this allows a more satisfactory distribution of positive charge than would be possible if all six cations per unit cell occupied threefold-axis sites.

Introduction

The crystal structure of dehydrated Ca_4Na_4-A,[1,2] determined using x-ray powder diffraction data, shows that the eight exchangeable cations per unit cell occupy the eight 6-ring[3] sites. These sites are apparently preferred by Ca^{2+} and Na^+, and it was anticipated that all exchangeable cations in dehydrated further Ca^{2+}-exchanged zeolite A, Ca_xNa_{12-2x}-A, $4 < x \leq 6$, would locate at 6-ring sites. Subsequent work with $Mn(II)$,[4,5] $CO(II)$,[5,6] and $Zn(II)$[5,7] incompletely exchanged into zeolite A also shows all divalent cations to be located at 6-ring sites upon vacuum dehydration.

The crystal structure of dehydrated Eu_xNa_{12-2x}-A,[8] $5.5 \leq x \leq 6.0$, possibly a fully $Eu(II)$-exchanged material, shows that, although most $Eu(II)$ ions are located at 6-ring sites, both 8-ring and 4-ring sites are also occupied, even though additional 6-ring sites are available. Most interesting is the presence of one $Eu(II)$ ion per unit cell at the very center of an 8-oxygen ring, 3.4 Å from the four nearest oxide ions of the aluminosilicate framework of the zeolite—*this distance is approximately 1.0 Å more than the sum of the corresponding ionic radii.*[9] This result suggested immediately that similar unusual coordination geometries might occur commonly in dehydrated fully divalent-cation-exchanged zeolite A.

Large monovalent cations that are zero coordinate[10-13] (K^+ and Rb^+) or near zero coordinate[14] (Tl^+) have been found in various exchanged forms of zeolite A. The principles involved have been discussed.[11-14] Qualitatively different principles would describe the zero coordination of divalent cations. *A far more diverse and interesting chemistry can be envisioned for*

zero and near zero coordinate divalent cations, which could include many transition metal ions, than might be expected for the large alkali-metal monovalent cations.

In order to explain the sorption of gases by Ca^{2+}-exchanged zeolite A as a function of its calcium content, Takaishi and co-workers[15] concluded, using percolation theory, that one Ca^{2+} ion per unit cell in dehydrated Ca_6-A is located at an 8-ring site. They were also able to learn that this 8-ring Ca^{2+} ion is relatively easily displaced from its window-blocking position, indicating it to be weakly held and to have a high thermal parameter. This unexpected finding is very much in accord with the structural results on $Eu(II)$-exchanged zeolite A.[8]

The locations of the Ca^{2+} ions in hydrated Ca_6-A are surprisingly irregular.[16] Three Ca^{2+} ions are recessed far into the sodalite cavity, and three lie relatively far into the large cavity, positions quite different from those found for Ca^{2+} ions in hydrated Ca_4Na_4-A.[17] By showing that six divalent cations occupy sites dissimilar to those in a four-divalent-cation exchanged hydrated structure, this work[11] encouraged hopes that dehydrated structures as unusual as that of Eu_xNa_{12-2x}-A,[8] $5.5 \leq x \leq 6.0$, would be found upon full exchange with other divalent cations.

To establish the existence of zero or near zero coordinate divalent cations in addition to $Eu(II)$ in zeolite A, and to better define the principles involved, work on the structures of dehydrated Ca_6-A and Sr_6-A was initiated. Ion exchange using these alkali-earth cations was expected to be facile and complete.[18] The ionic radii[8] of Ca^{2+} (0.99 Å) and Sr^{2+} (1.12 Å) are similar to that of $Eu(II)$ (1.09 Å). Finally, the preparation