Tachiki, M., Matsumoto, H. & Umezawa, H. (1979). *Phys. Rev. B*, **20**, 1915–1927.
Takei, H., Shishido, T., Iwasaki, H. & Muto, T. (1983). *Jpn. J. Appl. Phys.* **22**, 1463.
Tanaka, M., Sekii, H. & Nagasawa, T. (1983) *Acta Cryst.* A**39**, 825–837.
Vandenberg, J. M. & Matthias, B. T. (1977). *Proc. Natl Acad. Sci. USA*, **74**, 1336–1337.
Woolf, L. D., Johnston, D. C., MacKay, H. B., McCallum, R. W. & Maple, M. B. (1979). *J. Low. Temp. Phys.* **35**, 651–669.
Yvon, K. & Johnston, D. C. (1982). *Acta Cryst.* B**38**, 247–250.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1984). C**40**, 1646–1647

Note on the Structure of Ba_2CaMoO_6

By N.-S. Chiu and S. H. Bauer

Department of Chemistry, Cornell University, Ithaca, New York 14853, *USA*

(*Received* 23 *February* 1984; *accepted* 5 *June* 1984)

Abstract. That the O atoms in Ba_2CaMoO_6 are sited at the corners of regular octahedra, centered at Mo atoms, is confirmed by comparing the near-edge shape of its Mo *K*-edge absorption spectrum with those of MoS_2 and $Mo_2O_5(pq)_2$ (pq = 9,10-phenanthrenequinone). The structure parameter of Ba_2CaMoO_6 was then directly determined from its EXAFS spectrum, calibrated by that of K_2MoO_4.

Introduction. To calibrate EXAFS spectra of a series of $Mo/Co/Al_2O_3$ supported catalysts (which are amorphous), we were fortunate in obtaining a sample of Ba_2CaMoO_6 from Dr A. W. Sleight (Du Pont Experimental Station, Wilmington, Delaware). Of the many compounds at our disposal which incorporated 'octahedral' MoO_6 moieties, the Ba/Ca molybdate is the only one in which the O atoms occupy the corners of *regular* octahedra; in all the others the octahedra are grossly distorted. The reported structure of Ba_2CaMoO_6 is based on the similarity of its X-ray powder diffraction pattern to those of a series of homologous tungstates and molybdates (pseudocubic), analyzed by Steward & Rooksby (1951). They reported a value for the cubic cell dimension (8·335 Å), and stated that no detectable deformation from cubic symmetry is apparent in the molybdate. However, no value for the Mo—O distance could be derived other than one based on an *estimate* of the structure parameter ($u = 0{\cdot}23$) for Ba_2CaWO_6. If this is accepted for the molybdate, then $(Mo—O) \approx 1{\cdot}92$ Å. In Ba_2NdMoO_6 the quoted value is 1·86 Å (Brandle & Steinfink, 1971).

Discussion. The X-ray absorption data we recorded at the CHESS facility confirm that in Ba_2CaMoO_6 the octahedra are regular, and we are able to determine directly the magnitude of the Mo—O distance. The first conclusion follows from the shape of the near-edge spectrum, recorded at 1 eV ($1\ \text{eV} = 1{\cdot}60 \times 10^{-19}$J) intervals in the vicinity of the *K* edge of Mo. Refer to Fig. 1 for comparison of the absorption functions for MoS_2 (regular octahedra of S atoms around the Mo atoms) (Takeuchi & Nowacki, 1964), $Mo_2O_5(pq)_2$ (typical for distorted octahedra of oxygens) (Pierpont & Buchanan, 1976), K_2MoO_4 (regular tetrahedra) (Gatehouse & Leverett, 1969), and for Ba_2CaMoO_6. For the tetrahedral and distorted octahedral structures these curves have been resolved into three overlapping Gaussian distributions (as indicated), after the $\{\mu(E).x\}$ values were normalized by dividing them by the magnitude of the total jump from the pre-edge level to the background level, extrapolated from the high-energy side. The assignment sequence for the resolved Gaussian distributions is based on a pseudo-atomic model: $1s \rightarrow 4d$; $1s \rightarrow 5s$; $1s \rightarrow 5p$ (Shulman, Yafet, Eisenberger & Blumberg, 1976). The first transition is dipole forbidden in spherical or regular octahedral symmetry, but the selection rule breaks down when the octahedra are distorted. In Fig. 1, the relative areas for K_2MoO_4 are $A_1 = 16$; $A_2 = 25$; $A_3 = 360$ and for $Mo_2O_5(pq)_2$, $A_1 = 14$; $A_2 = 29$; $A_3 = 353$, whereas for Ba_2CaMoO_6 they are $A_1 = 0$; $A_2 = 8$; $A_3 = 155$, and for MoS_2, $A_1 = 0$; $A_2 = 33$; $A_3 = 308$. A detailed analysis is presented by Chiu, Bauer & Johnson (1984).

A value for the Mo—O distance was derived from a Fourier transform of EXAFS spectra, Fig. 2. K_2MoO_4 was used for the reference species; it incorporates regular tetrahedra of O atoms about the Mo atoms, and thus calibrates the phase-shift correction in the first coordination shell. We previously checked the validity of this procedure for known structures with distorted MoO_6 octahedra (Chiu *et al.*, 1984). Thus in Ba_2CaMoO_6, $(Mo—O) = 1{\cdot}86 \pm 0{\cdot}02$ Å, which is in general agreement with the proposed value for the *u* parameter (0·223). The second peak in the radial distribution curve is due to an unresolved superposition

0108-2701/84/101646-02$01.50

of Mo–Ca and Mo–Ba contributions. It is located at 3·83 Å, assuming a phase shift of 0·35. The Mo–Mo peak in MoS_2 was used to calibrate the phase-shift correction for the second coordination shell. Values derived for $a = 8{\cdot}335$ Å, for the space group $Fm3m$ (O_h^5) give 3·62 Å for (Mo–Ba) and 4·18 Å for (Mo–Ca). The third peak was assigned to Mo–Mo, which when shifted by 0·35 Å appears at 5·9 Å, in agreement with the powder diffraction data.

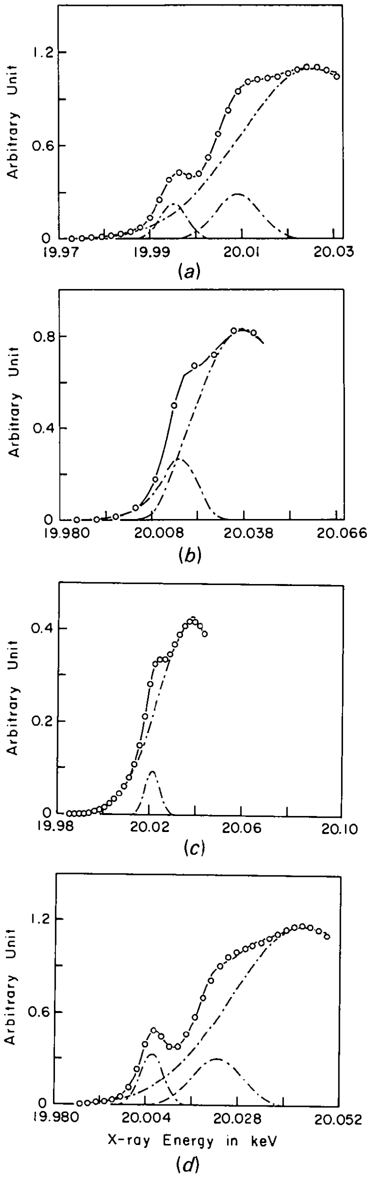

Fig. 1. Near-edge absorption spectra with resolved Gaussian distributions: (*a*) $Mo_2O_5(pq)_2$; (*b*) MoS_2; (*c*) Ba_2CaMoO_6; (*d*) K_2MoO_4. The solid curves are the observed values; the points (○) are the calculated sums of the resolved Gaussian distributions (dotted lines).

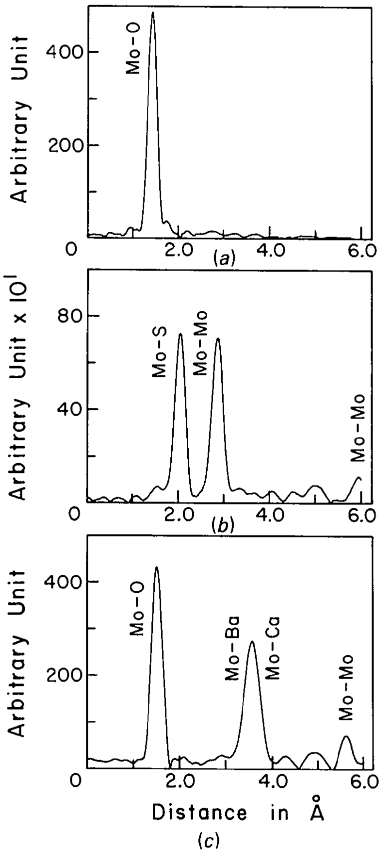

Fig. 2. Radial distribution curves (prior to phase-shift correction and rectification by R^2): (*a*) K_2MoO_4; (*b*) MoS_2; (*c*) Ba_2CaMoO_6. The intensity unit is arbitrary but all graphs are on the same scale.

This work was supported by the National Science Foundation under an Industry/University Collaborative Research Program, Grant No. CPE-80-00025. The EXAFS spectra were recorded at the Cornell High Energy Synchrotron Source supported by NSF Grant No. DMR-780/267. We acknowledge with thanks the calibrating sample furnished by Dr A. W. Sleight and discussions with him of the structure of this interesting compound.

References

Brandle, C. D. & Steinfink, H. (1971). *Inorg. Chem.* **10**, 922–926.

Chiu, N.-S., Bauer, S. H. & Johnson, M. F. L. (1984). *J. Catal.* To be published.

Gatehouse, B. M. & Leverett, P. (1969). *J. Chem. Soc. A*, pp. 849–854.

Pierpont, C. G. & Buchanan, R. E. (1976). *J. Am. Chem. Soc.* **97**, 6450–6455.

Shulman, R. G., Yafet, Y., Eisenberger, P. & Blumberg, W. E. (1976). *Proc. Natl Acad. Sci. USA*, **73**, 1384–1388.

Steward, E. G. & Rooksby, H. P. (1951). *Acta Cryst.* **4**, 503–507.

Takeuchi, U. & Nowacki, W. (1964). *Schweiz. Mineral. Petrogr. Mitt.* **44**, 105–120.