

Acta Cryst. (1965). **18**, 582

The crystal structure of $\text{Na}_2\text{Co}_5\text{Mo}_4\text{Cl}_4\text{O}_{16}$. By G. W. SMITH, *The British Petroleum Company Limited, BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, England*

(Received 17 July 1964)

The study of the compound $\text{Na}_2\text{Co}_5\text{Mo}_4\text{Cl}_4\text{O}_{16}$ arose during a general investigation of the crystal structure of CoMoO_4 , whose lattice geometry has already been reported (Smith, 1962). The crystals of CoMoO_4 were extracted from a melt composed of anhydrous cobalt chloride, sodium molybdate and sodium chloride but in addition there were present well formed crystals of two different kinds but both deep blue in colour. Examination of these two crystal types showed one to be orthorhombic and the other monoclinic and in the first instance they were thought to be different crystal forms of a complex cobalt molybdenum oxide. The structure of the orthorhombic crystals, however, has since been determined as a sodium cobalt molybdate (Ibers & Smith, 1964), whilst the structure of the monoclinic crystals, now reported here, shows them to have the complex formula $\text{Na}_2\text{Co}_5\text{Mo}_4\text{Cl}_4\text{O}_{16}$.

The crystals were stubby prisms with the prism axis, $[\bar{1}10]$, exhibiting faces (001), (111), (110), (11 $\bar{1}$) and (00 $\bar{1}$). The cell parameters were calculated from zero-layer Weissenberg photographs about each of the cell axes using $\text{Cu } K\alpha_1 = 1.54050 \text{ \AA}$ and $\text{Cu } K\alpha_2 = 1.54434 \text{ \AA}$.

$$a = 10.706 \pm 0.003, \quad b = 8.852 \pm 0.002, \quad c = 10.663 \pm 0.003 \text{ \AA}$$

$$\beta = 109^\circ 45' \pm 6'$$

$$V = 951 \text{ \AA}^3$$

Reflexions were present only for $h+k=2n$, indicating space groups $C2$, Cm or $C2/m$. A simple test for the pyroelectric effect was negative but the $N(z)$ tests made upon the intensities of $hk0$, $0kl$ and $h0l$ zones and also on the general hkl reflexions all yielded centric distributions and the assumption of $C2/m$ as the space group has subsequently been proved to be correct.

The intensity data were collected with $\text{Mo } K\alpha$ radiation from equi-inclination Weissenberg photographs, using timed exposures. Intensities were estimated visually. For the three principal zones, $hk0$, $0kl$ and $h0l$, reflexions were measured out to the limit of observation, there being 183, 174 and 380 independent non-zero intensities respectively. The three-dimensional data were collected from layers about the b axis for $k=1$ to 12, within a cylinder of reciprocal space whose radius and height were equal to the radius of the sphere for $\text{Cu } K\alpha$. Within this volume an additional total of 1680 independent hkl intensities was collected, of which 215 had an estimated zero intensity. Wilson's method (1942) was used to obtain an approximate scale factor and an isotropic temperature factor $B=0.6 \text{ \AA}^2$. After correction for the Lp factors a 3-D Patterson map was calculated from the complete set of $|F|^2$. No correction for absorption was made.

The density of the crystals was measured by flotation in a thallos malonate/formate solution, and although the values obtained were not very accurate the approximate value of $4.0 \pm 0.1 \text{ g.cm}^{-3}$ may be compared with a theoretical value of 3.92 g.cm^{-3} for two molecules per unit cell. As mentioned previously, in the early stages of the work these results, together with the cell dimen-

sions and the first chemical analyses led to the belief that these crystals were another form of sodium cobalt molybdate (Ibers & Smith, 1964) but detailed examination of the Patterson function revealed that by contrast the unit cell contained 8 molybdenum atoms, 10 cobalt atoms and another set of 8 atoms, which by consideration of peak weights were taken to be chlorine atoms. Another chemical analysis, made for cobalt, molybdenum, chlorine and sodium, agreed well with the expected formula (Found: Na 3.7, Co 25.3, Mo 33.5, Cl 12.0%. Calc. for $\text{Na}_2\text{Co}_5\text{Mo}_4\text{Cl}_4\text{O}_{16}$: Na 4.1, Co 26.3, Mo 34.2, Cl 12.6%). From the Patterson map, coordinates were obtained for:

8 Co(1) in 8(j)
2 Co(2) in 2(c)
4 Mo(1) in 4(i)
4 Mo(2) in 4(i)
8 Cl in 8(j)

The signs of the calculated structure factors were used in a 3-D F_o map which readily showed the positions of the oxygen and sodium atoms. Two sets of oxygen atoms were in the general position 8(j) with four other sets lying in the mirror plane 4(i); the four sodium atoms were also in the mirror plane. A new set of structure factors was calculated, including all the atoms and their revised coordinates which, using a single scale factor and overall isotropic B , gave the value of

$$R = \frac{\sum |KF_o| - |F_c|}{\sum KF_o} = 19.6\%$$

for 2133 reflexions including 288 zero F_o 's. ($R=16.9\%$ if the zero F_o 's are omitted). In this map the Mo, Co and Cl peaks were all nearly spherical, suggesting that their temperature factors were essentially isotropic. However, the O(3), O(4), O(5) and O(6) peaks were elongated, although as these atoms are sited on the second diffraction maximum about the Mo atoms their anisotropy, if any, is obscured. Table 1 gives the coordinates derived from this map. After rescaling with individual scale factors for each layer, but still with an overall isotropic temperature factor, the overall R value fell to 18.1% (15.6% if zero F_o 's are omitted), whilst a third structure factor cycle using individual isotropic temperature factors as well (Table 1) yielded

Table 1. *Atomic coordinates*

Atom	x	y	z	B
Mo(1)	0.0400	0	0.1908	0.50 \AA^2
Mo(2)	0.4467	0	0.1536	0.50
Co(1)	0.2645	0.1780	0.8654	0.69
Co(2)	0	0	0.5000	0.69
O(1)	0.3365	0.1651	0.0776	1.66
O(2)	0.1025	0.1625	0.1375	1.66
O(3)	0.1431	0	0.8734	1.66
O(4)	0.3940	0	0.8850	1.66
O(5)	0.4748	0	0.3275	1.66
O(6)	0.0956	0	0.3270	1.66
Cl	0.1645	0.1977	0.6238	0.90
Na	0.3244	0	0.4881	1.08

an overall $R=17.1\%$ (14.8% if zero F_o 's are omitted). In this final cycle only the layers $k=11$ and 12 had R values greater than 20% whilst the lowest value was 12.0% for $k=5$; all layers have $11.3\% < R < 17.5\%$ if the zero F_o 's are left out. As a least-squares refinement program was not available this is as far as structure factor/Fourier synthesis cycles could be taken.

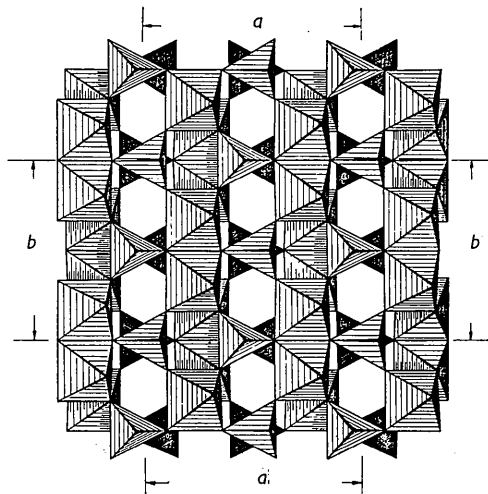


Fig. 1. Complex octahedral/tetrahedral sheet viewed normal to the ab plane.

In this structure, the oxygen atoms form almost regular tetrahedra about both Mo atoms with cation-oxygen distances in the range 1.76 – 1.88 Å. On the other hand the environments of the two cobalt atoms are different from each other and that around $Co(1)$ is unusual. Around $Co(1)$ are grouped one chlorine atom and five oxygen atoms which make a distorted octahe-

dron. Each octahedron shares an edge, along $O(5)$ – $O(4)$ with its reflexion image across the mirror plane, and this pair is then linked to another pair, in the next cell, by sharing one edge along $O(1)$ – $O(1)$ only, to form a two by two zigzag chain parallel to the b axis. The chlorine atoms are on each side of the chain. The C -face centering of the cell produces two such chains per cell which are linked to each other by the MoO_4 tetrahedra, which thus form a complex sheet of octahedra and tetrahedra (Fig. 1).

The coordination polyhedron about $Co(2)$ is another octahedron made up of two oxygen and four chlorine atoms. Such a coordination, which has already been reported for cobalt in the structures of $CoCl_2 \cdot 2H_2O$ (Morosin & Graeber, 1963) and cobalt dipyrindine dichloride (Dunitz, 1957) is closely paralleled in this structure, though there are some important differences. The chlorine atoms are still planar and in a nearly square arrangement, with the $Cl-Co-Cl$ angle of 87.9°

Table 2. Selected interatomic distances

Mo(1)–O(2)	1.76 Å
–O(3)	1.85
–O(6)	1.82
Mo(2)–O(1)	1.88
–O(4)	1.88
–O(5)	1.78
Co(1)–O(1)	1.98, 2.14
–O(2)	2.01
–O(3)	2.06
–O(4)	2.06
–Cl	2.45
Co(2)–O(6)	1.96
–Cl	2.52
Na–O(5)	2.38, 2.71
–O(6)	2.35
–Cl	2.95, 3.12
Cl–Cl	3.50, 3.63

All nearest O–O distances lie in the range 2.65 – 3.10 Å.

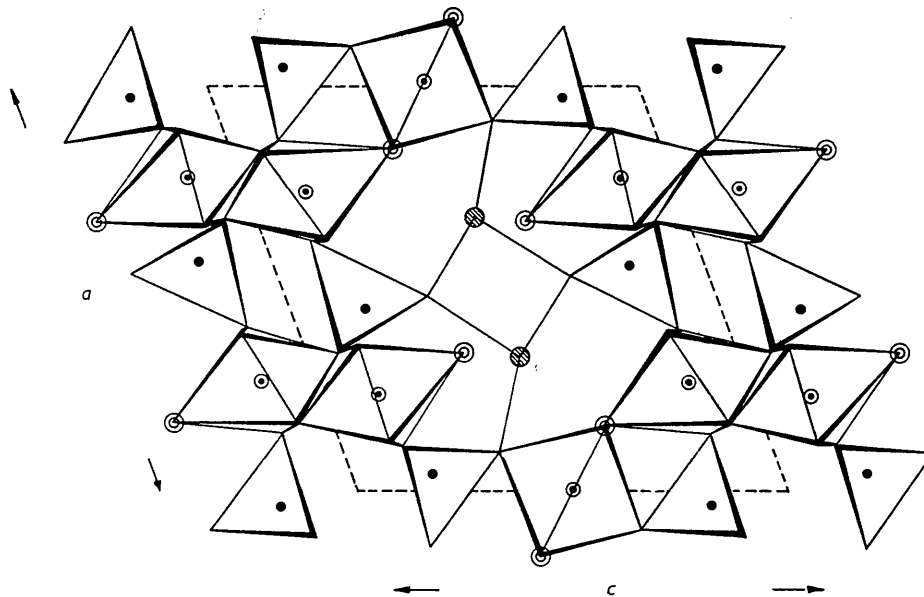


Fig. 2. Plan view of the lower half of the unit cell projected on the ac plane. Black dots, Mo; encircled dots, Co; shaded circles, Na; double circles, Cl

very close to that occurring in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. However, the Co-Cl distances are slightly longer than those reported in the other structures (2.52 Å as against 2.45, 2.48 and 2.49 Å), and are equal, by symmetry. The other important difference is that the other structures contain polymeric chains of Co and Cl, whereas in this structure the octahedron is isolated. It does, however, provide some of the linking between the more complex coordination around Co(1). Additional linking with this complex sheet is provided by the sodium atom which has an environment of three oxygen atoms lying in a planar configuration. Fig. 2 shows the general arrangement for the lower half of the unit cell. A list of selected interatomic distances is given in Table 2.

The Patterson function was calculated on a Deuce computer using programs written by Dr Rollett of Oxford University, but the later F_o maps and structure factor cycles were calculated on the Elliott 803.

The author wishes to thank the Chairman and Directors of The British Petroleum Company Limited, for permission to publish this paper. He also wishes to thank Mr N. Hannon and Mr D. J. Smith of the BP Research Centre who wrote the 3-D Fourier and structure factor programs respectively for the Elliott 803.

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