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The crystal structures of cobalt molybdate $CoMoO_4$ and nickel molybdate $NiMoO_4$.

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The commercially available compound labelled cobalt molybdate gives the same powder diffraction pattern as the precipitate that is formed when solutions of a cobalt salt and normal sodium molybdate are mixed. On heating this precipitate, a phase change occurs which appears to be complete at about 700 °C., and further prolonged heating to 1100 °C. shows no additional change. Chemical analysis of the final product gives the formula as $CoMoO_4$. This compound can also be prepared by roasting at 750–800 °C. stoichiometric proportions of anhydrous cobalt chloride and normal sodium molybdate. Both preparations yield an apparently black compound, which when ground in a mortar turns to an olive green colour. Under polarized light the colour is blood red.

Analysis of the $\sin^2\theta$ values on a powder photograph yielded a tetragonal unit cell which satisfied many of the reflexions. The compound was also frequently found in the melts from which orthorhombic cobalt molybdate was grown (Smith, 1960) and on occasions, single crystals which were shiny and almost black in appearance were present. The X-ray examination of these crystals revealed unusual lattice geometry which accounted for the simplicity of the powder photographs. The crystals had prismatic habit with ill-formed faces and a rotation photograph about the prism axis, c, showed even layer intensities to be very strong and odd layer intensities weak indicating pseudo-halving. The c spacing was $7{\cdot}71 \pm 0{\cdot}01$ Å. Zero and upper layer equi-inclination Weissenberg photographs taken with Mo $K\alpha$ radiation about c, for $l=0$ to 10, gave the following information.

(i) On zero and even layers the reflexions showed a wide range of intensity but were mostly very strong. On odd layers nearly all reflexions were weak and of almost uniform intensity.

(ii) Even layers showed symmetry $4mm$. with two very prominent central lattice rows, 90° apart, present for $l=0, 4, 8$ but absent for $l=2, 6, 10$. If these are taken as a_1^* directions, the spacings along these rows, as measured with Cu $K\alpha$ radiation from zero-layer photographs about c and each a_1 axis, were not detectably different and corresponded to a spacing of $a_1 = 12{\cdot}53 \pm 0{\cdot}01$ Å. A second but less prominent set of central lattice rows, a_2^*, at 45° to a_1^*, was present on all even layers. $a_2 = 8{\cdot}86 \pm 0{\cdot}01$ Å.

(iii) Odd-layer photographs showed only one central lattice row, along one of the a_2^* directions, about which only mirror-plane symmetry existed.

(iv) Every layer showed the same non-systematic absences and intensity distribution, apart from an overall scale factor, with the fourth layer above it, i.e. layers for which $l=0, 4, 8$ were identical, as were those for $l=1, 5, 9$; $l=2, 6, 10$; and $l=3, 7$.

Thus the structure is pseudo-tetragonal but the true symmetry is only monoclinic with its a^* along one a_2^* axis and its b^* along the other a_2^* axis.

The reappearance of two central lattice rows on all even layers is explained by the staggering of the layers of the reciprocal lattice in such a way that the origin points of the even layers lie directly over the points $h00$ along a^* $(=a_2^*)$ whilst the origin points of the odd

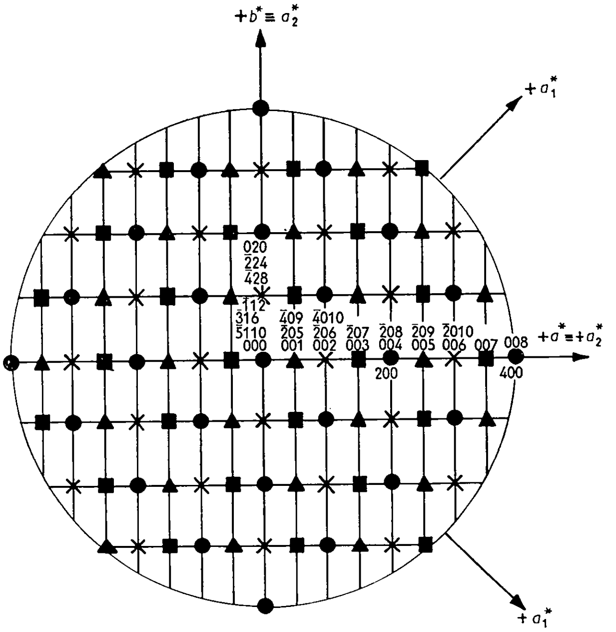

Fig. 1. Reciprocal lattice layers perpendicular to c axis. Only reflexions allowed by space group are indicated.

● R.L. points for layers $l=0, 4, 8$.
× R.L. points for layers $l=2, 6, 10$.
▲ R.L. points for layers $l=1, 5, 9$.
■ R.L. points for layers $l=3, 7$.

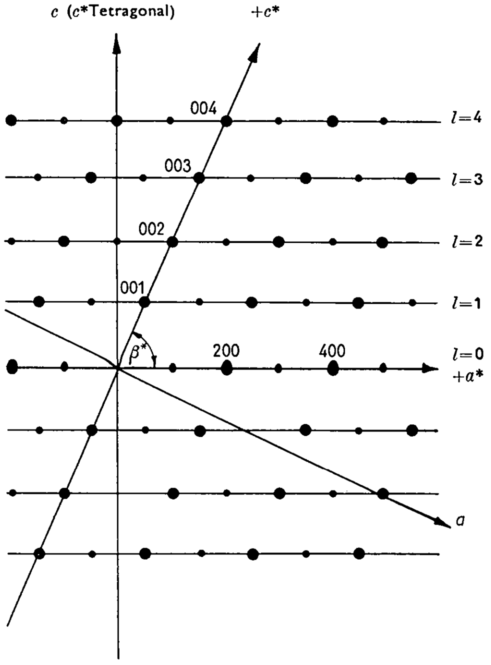

Fig. 2. $h0l$ plane of reciprocal space showing the staggering of hkl layers relative to the $hk0$ layer.

Table 1. *X-ray powder data*
Cu $K\alpha$ radiation

	CoMoO$_4$			NiMoO$_4$		
hkl	$\sin^2\theta_c$	$\sin^2\theta_o$	I_R	$\sin^2\theta_c$	$\sin^2\theta_o$	I_R
110 *	0·0152	0·0154*	70	0·0155	0·0159*	70
11$\bar{1}$ *	0·0194	0·0196*	10	0·0198	0·0202*	5
20$\bar{1}$ *	0·0269	0·0267*	20	0·0275	0·0275*	20
200 *	0·0303	0·0303*	5	0·0311	0·0307*	5
020 *	0·0303			0·0311		
111 *	0·0345	0·0353*	5	0·0353	0·0360*	5
021 *	0·0421	0·0428*	20	0·0431	0·0438*	20
11$\bar{2}$ *	0·0471	0·0478*	50	0·0479	0·0487*	50
20$\bar{2}$ *	0·0471			0·0479		
002	0·0471			0·0479		
201 *	0·0573	0·0585*	5	0·0586	0·0593*	5
22$\bar{1}$ *	0·0573			0·0586		
220 *	0·0607	0·0611*	100	0·0622	0·0628*	100
130 *	0·0758	0·0763*	5			
310 *	0·0758					
022 *	0·0774	0·0777*	40	0·0790	0·0794*	50
112 *	0·0774			0·0790		
22$\bar{2}$ *	0·0774			0·0790		
31$\bar{2}$ *	0·0774			0·0790		
13$\bar{1}$ *	0·0800	0·0792*	40	0·0819	0·0807*	50
131 *	0·0952	0·0966*	5			
20$\bar{3}$	0·0981					
11$\bar{3}$	0·0984					
132 *	0·1078	0·1081*	20	0·1101	0·1105*	20
202 *	0·1078			0·1101		
40$\bar{2}$ *	0·1078			0·1101		
311 *	0·1103	0·1092*	20	0·1130	0·1120*	30
22$\bar{3}$	0·1211	0·1217*	40	0·1234	0·1249*	30
400 *	0·1213			0·1243		
040 *	0·1213			0·1243		
041 *	0·1331	0·1328*	5			
42$\bar{1}$ *	0·1331					
02$\bar{3}$	0·1363	0·1368*	70	0·1390	0·1404*	40
40$\bar{3}$	0·1363			0·1390		
330 *	0·1365			0·1399		
132 *	0·1381			0·1412		
222 *	0·1381			0·1412		
33$\bar{2}$ *	0·1381			0·1412		
24$\bar{1}$	0·1482	0·1483	10	0·1519	0·1518	10
420 *	0·1516	0·1520*	10	0·1554	0·1561*	10
240 *	0·1516			0·1554		
20$\bar{4}$				0·1607	0·1626	30
13$\bar{3}$				0·1623		
401	0·1634	0·1622	30			
042	0·1684	0·1687	5			
24$\bar{2}$	0·1684					
312	0·1684					
51$\bar{2}$	0·1684					
331	0·1710	0·1717	5			
51$\bar{1}$	0·1710					
11$\bar{4}$	0·1732			0·1762	0·1773	10
31$\bar{4}$	0·1732			0·1762		
33$\bar{3}$	0·1742	0·1756	5	0·1778		
241	0·1786	0·1793	5	0·1829	0·1832	10
150 *	0·1971	0·1974*	30	0·2020	0·2024*	25
510 *	0·1971			0·2020		
15$\bar{1}$	0·2013	0·2005	5			
151	0·2165	0·2169	15			
024	0·2187	0·2194	15	0·2229	0·2230	25
42$\bar{4}$	0·2187			0·2229		
44$\bar{1}$	0·2241	0·2249	15			
04$\bar{3}$	0·2273	0·2287*	25	0·2322	0·2337*	30
15$\bar{2}$ *	0·2291			0·2344		
242	0·2291			0·2344		
332	0·2291			0·2344		
402 *	0·2291			0·2344		
44$\bar{2}$	0·2291			0·2344		
53$\bar{2}$	0·2291			0·2344		
60$\bar{2}$ *	0·2291			0·2344		
53$\bar{1}$	0·2316	0·2321	25	0·2373	0·2368	30
11$\bar{4}$	0·2339			0·2384		
13$\bar{4}$	0·2339			0·2384		
33$\bar{4}$	0·2339			0·2384		
51$\bar{4}$	0·2339			0·2384		
60$\bar{1}$				0·2451	0·2432	5
60$\bar{3}$	0·2424	0·2424*	5	0·2477	0·2485	5
440 *	0·2426			0·2487		
20$\bar{5}$	0·2489	0·2501	5			
313	0·2500			0·2555	0·2549	5
53$\bar{3}$	0·2500			0·2555		
31$\bar{5}$	0·2565	0·2577	40			
44$\bar{3}$	0·2576					
350	0·2578			0·2642	0·2650	30
530	0·2578			0·2642		
152	0·2594	0·2593	40	0·2655	0·2677	25
35$\bar{2}$	0·2594			0·2655		
422	0·2594			0·2655		
62$\bar{2}$	0·2594			0·2655		
40$\bar{5}$				0·2686		
11$\bar{5}$	0·2716	0·2736	30			
62$\bar{3}$	0·2728					
600	0·2729			0·2797	0·2801	15
060	0·2729			0·2797		
204				0·2850	0·2859	10
60$\bar{4}$				0·2850		
24$\bar{4}$				0·2850		
15$\bar{3}$				0·2866		
061	0·2847	0·2843	15	0·2917	0·2907	5
441	0·2847			0·2917		
35$\bar{1}$				0·2995	0·2999	20
42$\bar{5}$	0·2944	0·2954	25	0·2996		
134	0·2945			0·3006		
53$\bar{4}$	0·2945			0·3006		
35$\bar{3}$	0·2955					
51$\bar{5}$	0·3020	0·3025	25			
243	0·3031					
260	0·3033			0·3108	0·3103	10
620	0·3033			0·3108		
352	0·3504	0·3517	5			
442	0·3504					
55$\bar{2}$	0·3504					
64$\bar{2}$	0·3504					
55$\bar{1}$	0·3529					

Table 1 (*cont.*)

	CoMoO$_4$			NiMoO$_4$		
hkl	$\sin^2\theta_c$	$\sin^2\theta_o$	I_R	$\sin^2\theta_c$	$\sin^2\theta_o$	I_R
621	0·3605	0·3603	15			
$64\bar{1}$	0·3605					
$53\bar{5}$	0·3626					
$20\bar{6}$	0·3633					
$31\bar{6}$	0·3633					
$40\bar{6}$	0·3633					
063	0·3789	0·3786	25			
550	0·3791					
170	0·3791					
710	0·3791					
205	0·4005	0·3999	10			
$64\bar{4}$	0·4007					
244	0·4007					
602	0·4110	0·4118	25			
$17\bar{2}$	0·4110					
335	0·4384	0·4397	20			
443	0·4396					
730	0·4397					
370	0·4397					

* Reflexions and indices used in least squares analysis.
Bracketed reflexions have identical θ values.
Relative intensities I_R estimated visually.

layers lie over the midpoints between the $h00$ points. From the single-crystal photographs this holds for the ten layers examined. It leads to a special relationship between a, c and β, for, as the layer for $l=4$ superimposes directly upon the zero layer, the reciprocal lattice point 004 lies directly over the 200 point on a^*, i.e.

$$4c^*\cos\beta^* = 2a^* \quad \text{or} \quad a\cos(180-\beta) = c/2\ .$$

Figs. 1 and 2 show the arrangement of the various layers of the reciprocal lattice and Fig. 3 the relationship between the true monoclinic cell and the pseudo-tetragonal cells.

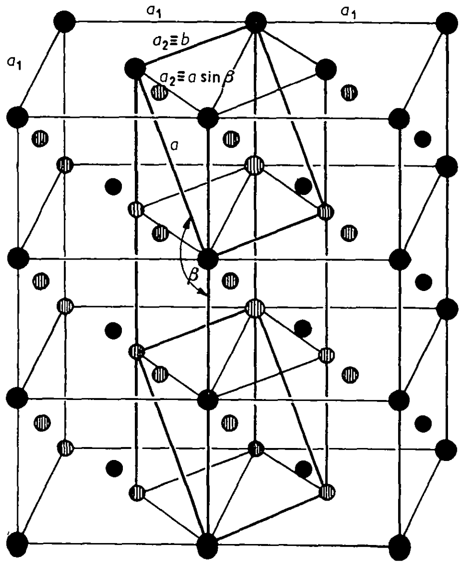

Fig. 3. Relationship between pseudo-tetragonal cells and true monoclinic cell. The c axis has been elongated for clarity.

For the pseudo-tetragonal cell (a_1, a_1, c) the hkl reflexions on the zero and even layers were present only for $(h+k+l)=2n$, whilst for the smaller tetragonal cell (a_1, a_1, $c/2$) the same reflexions were indexed for hkl all even or all odd. This face-centred pseudo-tetragonal cell corresponds to the smaller body centred cell (a_2, a_2, $c/2$). For the monoclinic cell, the hkl reflexions are present only for $(h+k)=2n$ and there are no other systematic absences; the space group is therefore $C2$, Cm, or $C2/m$. No attempt has been made to distinguish between them.

From single-crystal photographs

$$a\sin\beta = b = 8{\cdot}86 \pm 0{\cdot}01,\ a = 9{\cdot}65 \pm 0{\cdot}01,\ c = 7{\cdot}71 \pm 0{\cdot}01\ \text{Å}\ ,$$
$$\beta = 113{\cdot}4 \pm 0{\cdot}2°,\ V = 604\ \text{Å}^3.$$

Chemical analysis: Co 26·10%, Mo 43·95%.
Theoretical analysis for CoMoO$_4$: Co 26·94%, Mo 43·83%.
Highest measured density of powder $=4{\cdot}64$ g.cm.$^{-3}$.
Theoretical density for 8 molecules/cell $=4{\cdot}79$ g.cm.$^{-3}$.

The unusual lattice geometry of the crystal causes great simplification of the general expression for the monoclinic system, $\sin^2\theta = h^2A + k^2B + l^2C + hlD$, where A, B and D are now equal or nearly so. In an attempt to decide whether there were real differences between A, B and D, a least-squares analysis was made of the $\sin^2\theta$ values obtained from powder photographs taken in a 114·6 mm. diameter camera using Cu $K\alpha$ and Cr $K\alpha$ radiations. The greater dispersive power of Cr $K\alpha$ was used to separate several very close reflexions, and the $\sin^2\theta_{\text{Cr}\,K\alpha}$ values were finally converted to $\sin^2\theta_{\text{Cu}\,K\alpha}$. A mean of both sets was used in the analysis. Table 1 sets out the diffraction data; those reflexions marked *, which could be indexed unequivocally from the single-crystal data, were used for the analysis. The twenty-two reflexions so used were indexed with 40 sets of hkl. Three analyses were made under the following conditions (i) $A \neq B \neq D$, (ii) $A = B \neq D$, (iii) $A = B = D$. The derived constants A, B, C and D, shown in Table 2, are very close for each case but the residual standard error is least when $A = B = D$. In the absence of more accurate data, such as might be provided by a focusing camera, the relations $a\sin\beta = b$ and $a\cos(180-\beta) = c/2$ have been taken to be exact and the list of $\sin^2\theta_c$ compiled on this assumption. Because of the equivalent values of $\sin^2\theta$ for several sets of hkl not all the planes whose indices are listed would necessarily contribute to a reflexion on the powder photograph.

The X-ray data for nickel molybdate, NiMoO$_4$ (Brenner, 1955) have been quoted as being best fitted by a tetragonal cell and a comparison of the data for CoMoO$_4$ with that for NiMoO$_4$ (ASTM 9–175) suggested that the structures might be isomorphous. A sample of NiMoO$_4$ was therefore prepared by roasting together stoichiometric proportions of nickel oxide and molybdenum trioxide. At least

Table 2.

Cu $K\alpha = 1{\cdot}5418$ Å

	CoMoO$_4$			NiMoO$_4$		
	$A \neq B \neq D$	$A = B \neq D$	$A = B = D$	$A \neq B \neq D$	$A = B \neq D$	$A = B = D$
A	0·007570	0·007581	0·007581	0·007767	0·007771	0·007771
B	0·007586			0·007775		
D	0·007589	0·007593		0·007770	0·007773	
C	0·011784	0·011782	0·011775	0·011988	0·011987	0·011986
a	9·675 Å	9·668 Å	9·666 Å	9·555 Å	9·555 Å	9·555 Å
$a \sin \beta$	8·860	8·854	8·854	8·747	8·745	8·745
b	8·851	8·854	8·854	8·743	8·745	8·745
$c \sin \beta$	7·102	7·102	7·104	7·041	7·041	7·042
c	7·755	7·755	7·755	7·691	7·693	7·694
β	113° 41′	113° 41′	113° 39′	113° 44′	113° 45′	113° 45′

4 hr. heating at 750 °C. or 2 hr. at 800–820 °C. was found to be necessary. The powder pattern was almost identical with that of cobalt molybdate apart from a slight increase in θ values. The same least-squares analysis of the $\sin^2 \theta$ values again indicated that the constants A, B and D were equal. The data are tabulated in Tables 1 and 2. The calculated and measured densities of nickel molybdate are 4·94 g.cm.$^{-3}$ and 4·91 g.cm.$^{-3}$ respectively.

These two molybdates have a different crystal structure from the tungstate analogues, which belong to an isomorphous series RWO$_4$, where R = Co, Fe, Mg, Ni and Zn. Until the iron, magnesium and zinc molybdates have been formed it is not possible to conclude whether a similar isomorphous molybdate series does exist. (The data are being sent to Prof. A. J. C. Wilson (Cardiff) for inclusion in the X-ray Powder Data File).

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Crystallographic data for *N*-Benzyldithiocyanopyrrole.

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Preliminary X-ray crystallographic data were gathered for *N*-Benzyldithiocyanopyrrole during the search for a dithiocyanated pyrrole whose unit cell dimensions and symmetry would allow a rapid determination by two-dimensional Patterson and Fourier methods of the substitution position of the thiocyanate groups on the pyrrole ring. Chemical proof of structure (Matteson & Snyder, 1957) has indicated the substitution to be β, that is two carbons removed from the nitrogen, whereas *NMR* spectra (Gronowitz, Hörnfeldt, Gestblom & Hoffman, 1961) point strongly to α substitution.

Crystals were grown by slow cooling of a saturated 95% ethanol solution. They appeared as transparent light brown colored orthorhombic prisms, elongated in the direction subsequently designated as the b axis. Rotation, Weissenberg and precession photographs (Cu $K\alpha$ radiation) showed the crystals to be orthorhombic and having the following cell dimensions:

$$a_0 = 17{\cdot}26 \pm 0{\cdot}01,\ b_0 = 10{\cdot}22 \pm 0{\cdot}01,\ c_0 = 14{\cdot}54 \pm 0{\cdot}01 \text{ Å}.$$

The space group was unambiguously determined to be $Pbca\text{–}D_{2h}^{15}$ by noting the systematic absences of reflection on Weissenberg and precession photographs. The density was experimentally determined by flotation to be 1·396 g.cm.$^{-3}$ which agrees closely with a calculated density of 1·405 g.cm.$^{-3}$ for a unit cell containing 8 molecules. The molecules are thus in general positions.

During the course of the X-ray investigation, it was observed that all photographs exhibited a very sharp fall-off in the diffracted intensities, with virtually no recorded diffraction occurring at interplanar spacings shorter than 1·2 Å. It was thought that this was indicative of rather large temperature motions, however intensity measurements made at −140 °C. using the General Electric Single Crystal Orienter (Cu $K\alpha$ radiation) and Precession Photographs (Mo $K\alpha$ radiation) showed only a small amount of sharpening, thus ruling out the possibility of large thermal motions. On the basis of the low temperature data, it must be concluded that the observed sharp fall-off in intensities is not due to excessive thermal motions but rather very likely due to stacking disorders.

No further work on this compound is contemplated at this time.

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