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The crystal structure of the orthorhombic form of bis-(*N*-methylsalicylaldiminato)nickel.

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The crystal structure of the orthorhombic form of bis-(*N*-methylsalicylaldiminato)nickel has been determined. The space group is *Ibam* and the cell has dimensions $a=9·22$, $b=24·46$, $c=6·58$ Å and contains 4 molecules. The crystal structure is essentially identical with that of the corresponding copper compound.

The crystal structure of the monoclinic form of bis-(*N*-methylsalicylaldiminato)nickel has been reported by Frasson, Panattoni & Sacconi (1959). We have now determined the crystal structure of the orthorhombic form, which is isomorphous with the α form of the corresponding copper compound (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961).

Green orthorhombic needles grown along [001] were obtained from Dr James Ferguson. Cell dimensions, determined from rotation and zero-level Weissenberg photographs, taken with Cu $K\alpha$ radiation and calibrated by superimposing the rotation pattern of sodium chloride ($a_0=5·6894$ Å) on each photograph, are $a=9·22(3)$, $b=24·46(1)$, $c=6·58(1)$ Å. Systematic absences of hkl for $h+k+l\neq 2n$, of $h0l$ for $h\neq 2n$, and of $0kl$ for $k\neq 2n$, indicate the space groups *Ibam* or *Iba*2. There are four molecules in the cell.

A crystal of dimensions 0·1 mm × 0·06 mm × 0·8 mm was used for collection of intensities of $hk0$ through $hk3$. Because of the great similarity of the distribution of intensities between $hk0$ and $hk2$ and between $hk1$ and $hk3$, only the $hk0$ and $hk1$ intensities were measured. The photographs were taken on a Nonius integrating-Weissenberg camera and the intensities were measured as previously described (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961). 219 independent reflections were examined, of which 48 were found to be too weak to be measured. Lorentz and polarization factors were applied, but no corrections were made for absorption or anomalous dispersion.

The structure was refined by full-matrix least-squares calculations using the program of Busing & Levy (1959) as adapted by Stewart (1964). The function minimized was $\Sigma\, w(F_o-F_c)^2$ and all reflections were given equal weight except that, in each cycle, unobserved reflections with $F_c<F_o$ were given zero weight. The initial parameters used for the non-hydrogen atoms were those from the copper compound (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961). After five cycles, R was 0·080, where $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, with summation over the observed reflections only. At this point, hydrogen atom positions were calculated, and a plot of log F_o/F_c *vs* I_c indicated that the 110, 121 and 141 reflections were affected by secondary extinction. A set of four additional least-squares cycles, including the contributions of the hydrogen atoms but not refining their parameters, and omitting the reflections 110, 121 and 141, reduced R to its final value of 0·070. In the final cycle, all parameter shifts were less than one standard deviation. The final values of the parameters and their estimated standard deviations are listed in Table 1, while the bond lengths and angles are listed in Table 2.

Table 1. *Final values of parameters*

	$x/a\times 10^4$	$y/b\times 10^4$	$z/c\times 10^4$	$B\times 10$
Ni	0	0	0	32 (1)
N	−1222 (13)	635 (4)	0	32 (3)
O	1694 (9)	406 (3)	0	27 (2)
C(1)	1892 (20)	948 (5)	0	32 (4)
C(2)	3287 (16)	1146 (6)	0	36 (4)
C(3)	3539 (18)	1708 (6)	0	49 (5)
C(4)	2456 (17)	2063 (6)	0	39 (4)
C(5)	1036 (17)	1889 (6)	0	39 (4)
C(6)	705 (16)	1312 (6)	0	35 (4)
C(7)	−778 (14)	1145 (5)	0	28 (3)
C(8)	−2836 (14)	563 (5)	0	26 (3)
H(1)	4125	887	0	36
H(2)	4561	1846	0	49
H(3)	2673	2464	0	39
H(4)	232	2164	0	39
H(5)	1535	1438	0	28
H(6)	3175	175	0	26
H(7)	−3233	746	1241	26

Table 2. *Bond distances and angles*

Ni—O	1·85 (1) Å	O—Ni—N	93·4 (4)°
Ni—N	1·92 (1)	Ni—N—C(7)	125·9 (8)
N—C(7)	1·31 (2)	Ni—N—C(8)	119·1 (8)
N—C(8)	1·50 (2)	C(8)–N—C(7)	114·9 (8)
C(7)–C(6)	1·43 (2)	N—C(7)–C(6)	124·9 (8)
C(6)–C(5)	1·45 (2)	Ni—O—C(1)	130·3 (8)
C(5)–C(4)	1·38 (2)	O—C(1)–C(6)	121·4 (9)
C(4)–C(3)	1·32 (2)	O—C(1)–C(2)	118·4 (10)
C(3)–C(2)	1·40 (2)	C(7)–C(6)–C(1)	124·2 (9)
C(2)–C(1)	1·37 (2)	C(7)–C(6)–C(5)	118·9 (10)
C(1)–C(6)	1·41 (2)	C(6)–C(1)–C(2)	120·2 (9)
C(1)–O	1·34 (2)	C(1)–C(2)–C(3)	120·2 (10)
		C(2)–C(3)–C(4)	121·4 (10)
		C(3)–C(4)–C(5)	120·9 (10)
		C(4)–C(5)–C(6)	120·2 (9)
		C(5)–C(6)–C(1)	116·9 (10)

The crystal structure is essentially identical with that of the copper compound and there are no significant differences between the molecular dimensions of the two compounds except for the bond distances to the metal ions.

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Synthesis and lattice constants of transition metal thioniobates with berthierite structure.*

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Compounds with chemical formula MNb_2S_4 where M is one of the divalent transition metals Mn, Fe, Co, Ni, Cu were synthesized. The lattice constants of these compounds, isomorphous with berthierite ($FeSb_2S_4$), were determined from the powder diffraction data, using Cohen's analytical method.

As a part of a research program on ternary sulphides, a new family of compounds has been synthesized. The chemical formula is MNb_2S_4, where M = Mn, Fe, Co, Ni and Cu. We began with the idea that niobium is chemically analogous to antimony and thus substituted Nb for Sb in the natural mineral $FeSb_2S_4$. The second step was to substitute other transition metals for the Fe ion, in particular Mn, Co, Ni and Cu.

All the materials were prepared by the ceramic method: molar ratios of the elements were intimately mixed, pressed into pellets, and after sealing under vacuum in silica tubes, fired for 18–20 hours at 1050–1080°C and cooled. The materials were dark grey in color and were odorless. It is interesting to note that in these sulphides the niobium is trivalent, in contrast to the known niobates (Turnock, 1966) in which it is pentavalent.

The X-ray powder photographs were taken with a Norelco Straumanis camera having a diameter of 114·6 mm and Co radiation filtered through an iron foil. The powder photographs were indexed on the basis of the orthorhombic unit cell, using the crystallographic constants of berthierite (Buerger & Hahn, 1955). The indexed diffraction data are given in Table 1. The systematic absences observed in the patterns are consistent with the space group of berthierite, *i.e. Pnam* (D_{2h}^{16}), (Buerger & Hahn, 1955). Results of density measurements carried out with a pycnometer for $FeNb_2S_4$, $d = 4{\cdot}02$ g.cm^{-3}, were consistent with the assumption that there are 4 molecules per unit cell, as in $FeSb_2S_4$. Note that no lines alien to those allowed by the *Pnam* space group

Table 1. *Powder diffraction data for* MNb_2S_4 (*space group Pnam*)

	Mn			Fe			Co			Ni			Cu		
$h\ k\ l$	d_o	d_c	I_o	d_o	d_c	I_o	d_o	d_c	I_o	d_o	d_c	I_o	d_o	d_c	I_o
1 2 0	6·25	6·31	*s*	6·11	6·01	*s*	5·85	5·74	*s*	5·77	5·73	*s*	6·40	6·31	*s*
0 3 1							2·950	2·945	*m*	2·939	2·942	*m*			
2 4 0	3·156	3·153	*m*				2·870	2·868	*m*	2·853	2·860	*m*			
2 1 1				3·062	3·070	*m*									
4 0 0	2·872	2·867	*m*	2·870	2·870	*m*							2·870	2·862	*m*
4 1 0	2·803	2·812	*m*	2·800	2·810	*m*	2·780	2·763	*m*	2·765	2·763	*m*	2·811	2·810	*m*
2 3 1	2·592	2·583	*ms*	2·604	2·613	*ms*	2·581	2·577	*ms*	2·567	2·571	*ms*	2·601	2·580	*ms*
2 4 1	2·370	2·360	*m*	2·351	2·345	*m*	2·318	2·300	*m*	2·300	2·290	*m*	2·376	2·350	*m*
2 5 1	2·133	2·132	*vs*	2·100	2·097	*vs*	2·060	2·048	*vs*	2·050	2·038	*vs*	2·148	2·130	*vs*
4 3 1				2·049	2·052	*m*									
2 6 1				1·873	1·880	*w*	1·829	1·820	*w*	1·822	1·815	*w*	1·930	1·930	*w*
0 8 0	1·899	1·890	*w*				1·662	1·664	*m*	1·669	1·663	*m*			
6 4 0	1·706	1·705	*m*	1·673	1·681	*m*	1·630	1·639	*m*	1·630	1·639	*m*	1·690	1·700	*m*
2 8 0							1·600	1·597	*s*	1·597	1·595	*s*			

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