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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Table 1 (*cont.*)

			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	8	1	1·666	1·657	*ms*				1·495	1·510	*w*	1·490	1·509	*w*	1·639	1·646	*w*
2	8	1	1·610	1·601	*m*				1·464	1·473	*w*	1·462	1·471	*w*	1·610	1·600	*w*
6	3	1	1·589	1·593	*m*	1·605	1·603	*w*									
6	4	1	1·536	1·536	*m*	1·539	1·535	*m*									
4	8	0				1·495	1·500	*w*	1·440	1·434	*w*	1·439	1·433	*w*			
2	10	0	1·464	1·461	*m*										1·480	1·462	*m*
4	8	1	1·445	1·440	*vw*										1·440	1·439	*vw*
8	2	0	1·409	1·409	*w*	1·405	1·406	*w*	1·400	1·390	*w*	1·397	1·391	*w*	1·416	1·406	*vw*
5	1	2	1·394	1·394	*m*										1·372	1·389	*m*
1	7	2				1·361	1·363	*m*	1·322	1·330	*m*	1·318	1·327	*m*			
6	7	1													1·325	1·325	*m*
8	2	1	1·316	1·312	*s*	1·310	1·317	*s*	1·297	1·299	*s*	1·297	1·298	*s*	1·304	1·305	*s*
6	0	8				1·295	1·285	*w*									
9	1	1	1·195	1·195	*w*				1·177	1·180	*vw*	1·163	1·156	*vw*			
5	7	2	1·170	1·174	*vw*	1·181	1·180	*vw*							1·167	1·170	*vw*
0	12	0							1·109	1·109	*vwv*	1·106	1·108	*vvw*			
6	7	2				1·117	1·117	*vw*	1·099	1·096	*w*	1·095	1·095	*w*			
10	4	0	1·094	1·097	*vw*	1·091	1·091	*vw*	1·073	1·070	*vw*	1·059	1·069	*vw*	1·095	1·095	*w*
9	6	1	1·079	1·080	*m*	1·075	1·075	*w*	1·052	1·051	*w*	1·050	1·050	*w*	1·083	1·081	*m*
10	5	0	1·072	1·072	*w*				1·038	1·040	*w*	1·033	1·039	*w*	1·064	1·069	*w*
9	1	2	1·034	1·032	*m*	1·054	1·054	*m*							1·029	1·028	*m*
7	8	2	1·014	1·014	*w*				0·990	0·990	*w*	0·989	0·989	*w*	1·011	1·012	*w*
6	1	3	0·998	1·000	*m*	1·046	1·046	*w*									
5	6	3	0·966	0·967	*m*	0·992	0·996	*m*	0·992	0·992	*m*	0·989	0·989	*w*	0·966	0·965	*m*
12	0	0	0·955	0·955	*m*	0·960	0·958	*m*	0·938	0·940	*m*	0·937	0·940	*m*	0·954	0·953	*m*
10	4	2	0·930	0·932	*w*	0·938	0·940	*w*		0·935			0·933		0·929	0·930	*m*
2	3	4				0·920	0·921	*s*	0·918	0·918	*s*	0·918	0·918	*s*			

Table 2. *Crystallographic constants of* MNb_2S_4

M	*a* (Å)	*b* (Å)	*c* (Å)	X-ray density (g.cm⁻³)
Mn	11·470 ± 0·003	15·096 ± 0·007	3·536 ± 0·001	4·01
Fe	11·481 ± 0·002	14·071 ± 0·003	3·762 ± 0·001	4·05
Co	11·300 ± 0·004	13·315 ± 0·006	3·822 ± 0·002	4·25
Ni	11·299 ± 0·004	13·305 ± 0·004	3·805 ± 0·001	4·35
Cu	11·438 ± 0·005	15·121 ± 0·007	3·524 ± 0·001	4·12

were observed, indicating that the studied materials were single phase.

Magnetic measurements on all of these compounds, as well as Mössbauer effect studies of ^{57}Fe in $FeNb_2S_4$ (Eibschütz, Hermon & Shtrikman, 1966), are also consistent with the existence of one single phase in the compounds reported here.

Lattice constants were calculated by Cohen's (1935) analytical least-squares method (Eibschütz, 1965), and are given in Table 2.

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A method of allowing for thermal anisotropy in evaluating Wilson plots and normalized structure factors.

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A method has been developed for allowing for thermal anisotropy in calculating Wilson plots and evaluating normalized structure factors. The data are first brought to an approximately correct scale by the normal Wilson plot process, and a second series of plots is then made against six products of the Miller indices. The limitations of the method are discussed.

The reliability of direct methods of phase determination (Karle & Karle, 1966) depends to some extent on the accuracy of the calculation of the normalized structure factors, or E values, from the magnitudes of the observed structure factors F. The scaling is normally carried out by a Wilson plot procedure (Wilson, 1942) in which the logarithm of the reciprocal of the mean value of $|F|^2/\sum_{j=1}^{N} f_j^2$, N being the number of atoms in the unit cell and f_j the scat-