Synthesis and Structural Analysis of the New Layered Compound [$FeWO_4Cl$]

Jin-Ho Choy,* Dong-Youn Noh, Hyung-Ho Park and Jeong-Chul Park
Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea

The compound [$FeWO_4Cl$] has been prepared under a temperature gradient of 400–450 °C by the chemical vapour transport technique. The crystal symmetry is tetragonal with unit-cell dimensions of $a = 6.677(5)$ and $c = 5.270(5)$ Å (space group $P4/nmm$ and $Z = 2$). The structure was refined by the least-squares method to a conventional reliability factor of $R = 0.06$.

Recently we have intensively studied the intercalation reaction of two-dimensional [$FeMoO_4Cl$][1–3] and also explored the properties of the new layered compounds. In this paper, we report the synthesis and crystal-structure analysis of the new layered compound [$FeWO_4Cl$].

Results and Discussion

The compound [$FeWO_4Cl$] was prepared by heating a mixture of WO_3, Fe_2O_3 and a slight excess of anhydrous $FeCl_3$ (mol ratio 3:1:1.05), which acts not only as a reactant but also as a transport agent in this reaction, in an evacuated quartz tube at 420 °C for 30 d according to the chemical vapour transport (CVT) technique. After air-quenching at room temperature, yellowish plate-like crystals with dimensions 4 × 4 × 1 mm were obtained in the cold zone of the ampoule in very low yield: most of the starting materials remained unreacted in the hot zone. For the structural determination, crystals were separated and washed with absolute ethanol in order to remove the excess of $FeCl_3$. In the CVT technique the molecular weights of the reactants as well as the nature of the transport agent seem to be very important in determining the reaction conditions and the yield.[4] The reason for the relatively long reaction time and the low yield in this reaction might be due to the difficulty in vapour transport of WO_3 (M 231.85) which is about 1.5 times heavier than Fe_2O_3 (M 159.69). It might also be the reason why Torardi *et al.*[5] did not succeed in preparing this compound.

X-Ray powder diffraction data for [$FeWO_4Cl$] (Table 1) were obtained using Cu-Kα radiation and a multi-channel analyser. Silicon powder ($a = 5.4305$ Å) was used as an external standard. The observed intensities calculated by the area integration method were corrected for absorption using the shape factor from ref. 6. Comparison of the X-ray powder diffraction patterns of [$FeWO_4Cl$] and [$FeMoO_4Cl$] shows that they are isostructural. For indexation of the X-ray pattern with a tetragonal system, the $1/d^2$ values observed were compared with those calculated using a trial-and-error computer program (DICVOL).[7] The resulting refined parameters obtained from 29 reflections by a least-squares method are $a = 6.677(5)$ and $c = 5.270(5)$ Å. For $Z = 2$, the calculated density is 4.79 g cm^{-3}. The refinement of the X-ray powder diffraction data was carried out with the computer program AFPOUD.[8] Ionic scattering factors for Fe^{3+}, W^{6+}, O^{2-} and Cl^- were taken from ref. 6. A final calculation in space group $P4/nmm$ (no. 129) with average isotropic B factors for identical ions converged to $R = 0.06$ (Table 2).

Table 1 X-Ray powder diffraction data for [$FeWO_4Cl$]

h	k	l	d_{obs}/Å	d_{calc}/Å	I_{obs}	I_{calc}
0	0	1	5.26	5.27	560	603
1	1	0	4.72	4.72	213	264
1	0	1	4.14	4.14	94	88
1	1	1	3.521	3.517	1000	1129
2	0	0	3.344	3.339	900	917
2	0	1	2.822	2.820	330	384
2	2	0	2.363	2.361	231	204
1	1	2	2.303	2.301	536	530
2	2	1	2.156	2.155	131	138
3	1	0	2.113	2.112	31	38
2	0	2	2.069	2.069	69	55
3	0	1	2.053	2.050	41	29
3	1	1	1.962	1.960	392	386
2	2	2	1.758	1.758	106	70
0	0	3		1.757		31
4	0	0	1.670	1.669	168	143
3	1	2	1.649	1.648	466	405
1	1	3		1.647		41
4	0	1	1.592	1.591	90	79
2	0	3	1.555	1.555	148	122
3	3	1	1.509	1.508	59	75
4	2	0	1.494	1.493	172	135
4	2	1	1.437	1.437	112	93
2	2	3	1.410	1.409	155	116
3	3	2	1.351	1.351	173	109
3	1	3		1.351		56
0	0	4	1.318	1.318	39	20
5	1	0	1.310	1.310	29	20
4	2	2	1.299	1.299	61	32
5	1	1	1.271	1.271	133	97
1	1	4		1.269		20
2	0	4	1.226	1.226	56	56
4	0	3	1.211	1.210	36	39

The main interatomic distances and angles in [$FeWO_4Cl$] are given in Table 3. The structure of this compound is composed of a FeO_4Cl square pyramid and a WO_4 tetrahedron linked as shown in Fig. 1. In the WO_4 tetrahedral unit the W–O distance [1.77(6) Å] is well consistent with the sum of ionic radii for four-co-ordinated W^{6+} and two-co-ordinated O^{2-} (1.77 Å).[9] As for the FeO_4Cl square-pyramidal unit, the Fe–O

Table 2 Atomic coordinates and isotropic thermal parameters for [$FeWO_4Cl$]

Atom	Wyckoff position	*x*	*y*	*z*	$B/Å^2$
Fe	(2c)	0.25	0.25	0.281(3)	0.63(4)
W	(2a)	0.25	0.75	0	0.46(0)
O	(8i)	0.25	0.96(5)	0.19(8)	0.94(7)
Cl	(2c)	0.75	0.75	0.288(2)	1.32(4)

The values shown in parentheses here and in the text represent the last decimal place of the respective value.

Table 3 Main interatomic distances (Å) and angles (°) in [$FeWO_4Cl$]

Intralayer			
Fe–O(1)	1.95(2)	Cl–Fe–O(1)	102.9(7)
Fe–Cl	2.26(9)	Fe–O(1)–W	156.9(4)
W–O(1)	1.77(6)	O(1)–Fe–O(2)	87.1(2)
O(1) ••• O(2)	2.69(0)	O(1)–W–O(5)	107.9(5)
O(1) ••• O(5)	2.87(3)	O(1)–Fe–O(3)	154.0(7)
O(1) ••• O(6)	2.91(4)	O(1)–W–O(6)	110.2(4)
O(1) ••• Cl	3.30(9)		
Interlayer			
Fe ••• Cl′	3.00(2)	O(1) ••• Cl′	3.19(2)

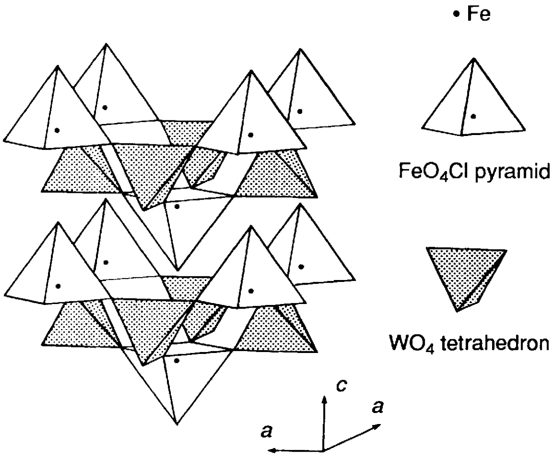

Fig. 1 Perspective view of the polyhedra linking the [$FeWO_4Cl$] structure

distance [1.95(2) Å] is in between the sum of ionic radii for high-spin Fe^{3+} and O^{2-} (1.930 for five- and 1.995 Å for six-co-ordinated Fe^{3+}). In this analysis, however, the error could be somewhat higher particularly for the light atom oxygen compared to the heavy atom. Therefore the possibility of error in the Fe–O bond distance would not be avoidable. The intralayer bond distance Fe–Cl [2.26(9) Å] is shorter than the Shannon radii (2.390 for five- and 2.455 Å for six-co-ordinated Fe^{3+}), as also observed in molecular square-pyramidal complexes such as [$Fe(S_2CNH_2)_2Cl$] (2.270 Å)[10] and [$Fe(acac)_2Cl$] (acac = acetylacetonate) (2.213 Å).[11] The interlayer Fe ••• Cl′ bond distance [3.00(2) Å] is longer than the Shannon radii mentioned above due to the van der Waals interaction between the layers. Thus some degree of ionic–covalent bonding character could be expected in Fe ••• Cl′ from the fact that in the *c* direction of the square pyramid of FeO_4Cl an increase in co-ordination number could occur by adopting the Cl′ ligand from $Cl'O_4Fe$ in an adjacent layer, forming a FeO_4ClCl' distorted octahedron through the overlap of $e_g(Fe)$–$p_\sigma(Cl')$. The degree of distortion from an ideal octahedron (90°) can be seen from the angles of 87.1(2)° for O(1)–Fe–O(2) and 102.9(7)° for Cl–Fe–O(1), as well as the interlayer Fe ••• Cl′ [3.00(2) Å] and intralayer Fe–Cl [2.26(9) Å] bond distances along the *c* direction (Table 3 and Fig. 2).

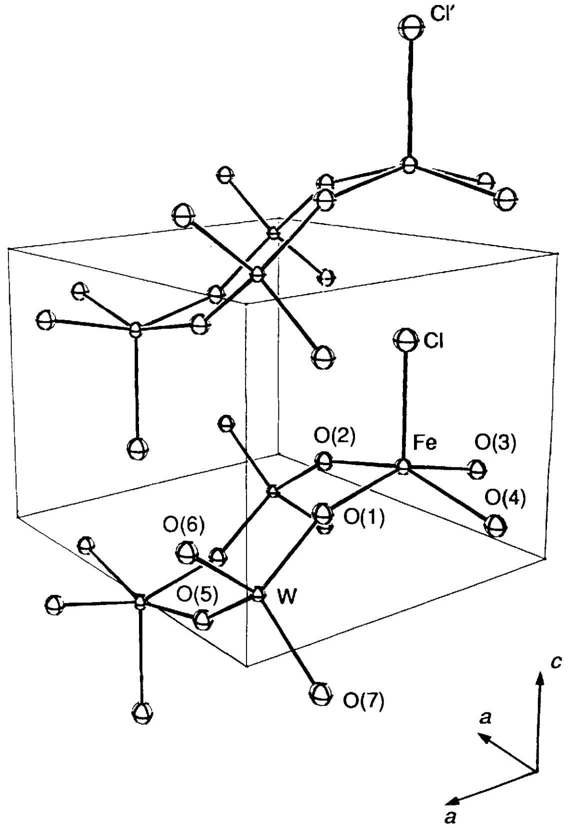

Fig. 2 The structure of [$FeWO_4Cl$] showing two stacked layers along the *c* axis

The possibility of the intercalation reaction of this compound with small ionic species (Li^+ and Na^+) and organic molecules is now under investigation.

Acknowledgements

This research was supported by the Korea Science and Engineering Foundation and H.-H. P. would like to thank the Korean Ministry of Education for a Postdoctoral fellowship.

References

1 J. H. Choy, D. Y. Noh, J. C. Park, S. H. Chang, C. Delmas and P. Hagenmuller, *Mater. Res. Bull.*, 1988, **23**, 73; J. H. Choy, S. H. Chang, D. Y. Noh and K. A. Son, *Bull. Korean Chem. Soc.*, 1989, **10**, 27; J. H. Choy, D. Y. Noh, K. A. Son and D. Y. Seung, *Bull. Korean Chem. Soc.*, 1989, **10**, 210; J. H. Choy, D. Y. Noh, S. H. Chang and C. Delmas, *Eur. J. Solid State Inorg. Chem.*, 1990, **27**, 391; C. Delmas, S. H. Chang, D. Y. Noh and J. H. Choy, *Solid State Ionics*, 1990, **40/41**, 563.
2 J. H. Choy, J. W. Uh, J. K. Kang, A. Weiss and M. Rey-Lafon, *J. Solid State Chem.*, 1988, **77**, 60.
3 J. H. Choy, Y. G. Kim and A. Weiss, *Mater. Res. Bull.*, 1985, **20**, 1401.
4 K. E. Spear, *J. Chem. Educ.*, 1972, **49**, 81.
5 C. C. Torardi, J. C. Calabrese, K. Lazar and W. M. Reiff, *J. Solid State Chem.*, 1984, **51**, 376.
6 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
7 D. Louer and R. Vargas, *J. Appl. Crystallogr.*, 1982, **15**, 542.
8 G. Perez and M. Saux, *Bull. Soc. Chim, Fr.*, 1970, **10**, 3478.
9 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
10 R. L. Martin and A. H. White, *Inorg. Chem.*, 1967, **6**, 712.
11 P. F. Lindley and A. W. Smith, *Chem. Commun.*, 1970, 1355.

Received 7th February 1991; *Paper* 1/00588J