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Synthesis and Crystal Structure of (ThCu$_3$) (Mn$_2^{3+}$Mn$_2^{4+}$) O$_{12}$, a New Ferrimagnetic Perovskite-like Compound

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Single crystals of [ThCu$_3$](Mn$_2^{3+}$Mn$_2^{4+}$]O$_{12}$, a ferrimagnetic perovskite-like compound, have been synthesized by hydrothermal conditions at 600°C and 2 kbar. They have been found to be cubic, of space group *Im*3, with $a = 7.359$ Å, and isostructural with [NaMn$_3$](Mn$_2^{3+}$Mn$_2^{4+}$)O$_{12}$. The crystal structure has been refined by single-crystal X-ray diffraction data. The Th^{4+} cations are surrounded by slightly distorted icosahedra; the Th–O distance is 2.556 Å. The Cu^{2+} cations are also surrounded by 12 oxygens, which are arranged as three mutually perpendicular rectangles of different size, the smallest and the largest of which are almost squares. The three sets of Cu–O distances are 1.973, 2.800, and 3.238 Å. The octahedral Mn–O distance is 1.950 Å. A test based on neutron diffraction powder data indicated that the square sites are occupied by only the Cu^{2+} cations.

Introduction

In recent years, a new series of perovskite-like compounds has been established (*1*–*6*). The prototype of this series is NaMn$_3$ (Mn$_2^{3+}$Mn$_2^{4+}$)O$_{12}$, which is cubic with a unit cell eight times that of the undistorted perovskite structure. The doubling of the lattice parameter is due to two factors: One is the order which occurs between the Na and Mn cations occupying the *A*-sites, and the other is the tilting of the oxygen octahedra. This tilting distorts three-fourths of the 12-coordinated *A*-sites into Jahn–Teller ones with four close oxygen atoms arranged as a square and four further away arranged as a rectangular perpendicular to the square. Consequently, the presence of a Jahn–Teller ion is essential for the existence of this structure.

So far, two subseries have been prepared, one in which the four planar-coordinated sites are occupied by Mn^{3+} and the other by Cu^{2+}. Many compounds of the latter subseries are ferrimagnetic with Curie temperatures greater than 400°K (*6*). In this case, the larger cation occupying one-fourth of the *A*-sites can have any valence between 1+ and 4+ because the difference in charge can be easily compensated by the cations occupying the *B*-sites. If these are occupied by the Mn cations, then the larger cation can be di-, tri-, and tetravalent, the relative formulas being [M^{2+}Cu$_3^{2+}$](Mn$_4^{4+}$)O$_{12}$, [M^{3+}Cu$_3^{2+}$] (Mn^{3+}Mn$_3^{4+}$)O$_{12}$, and [M^{4+}Cu$_3^{2+}$]-(Mn$_2^{3+}$Mn$_2^{4+}$)O$_{12}$. Preliminary results proved that these compounds have different ferromagnetic properties (*6*). This is not surprising because the ferromagnetism probably arises from the interaction between the copper and manganese sublattices, and the latter is different in each compound.

This paper reports the synthesis and the structural refinement of [Th^{4+}Cu$_3^{2+}$](Mn$_2^{3+}$-Mn$_2^{4+}$)O$_{12}$ based on single-crystal X-ray diffraction data and on powder neutron diffraction data. This compound has been found to be ferrimagnetic with a Curie temperature of

~450°K (*6*). Its magnetic structure as determined by powder neutron diffraction will appear in a subsequent paper (*7*).

Experimental

Initially, the compound $[\mathrm{ThCu_3}](\mathrm{Mn_2^{4+}}\text{-}\mathrm{Mn_2^{3+}})\mathrm{O_{12}}$ was synthesized by using high pressure and high temperature conditions. A stoichiometric mixture such as $\mathrm{Th(OH)_4} + 3\,\mathrm{CuO} + 2\,\mathrm{MnO_2} + \mathrm{Mn_2O_3}$ was subjected to 80 kbar at 1200°C in a belt-type apparatus. The quenched material consisted of a single phase whose powder pattern indicated that it was isostructural with the cubic compound $[\mathrm{NaMn_3}](\mathrm{Mn_2^{4+}Mn_2^{3+}})\mathrm{O_{12}}$. A comparison between observed and calculated *d*-spacings along with the observed relative intensities is shown in Table I. A well-crystallized powder, containing very small cubes (~50 μm) was obtained by adding a few drops of water to the starting materials and applying the same pressure and temperature conditions.

$\mathrm{ThCu_3Mn_4O_{12}}$ also can be obtained by hydrothermal synthesis at 600°C and 2 kbar because it is stable in air up to ~600°C. The same starting mixture was used together with a 50% nitric acid solution, whose role was to prevent a possible partial reduction of the $\mathrm{Mn^{4+}}$ cations. A 5–10% excess of CuO had to be used in order to compensate for its greater solubility in the acid. Under these conditions larger single crystals (~200 μm) were obtained.

TABLE I[a]

hkl	I_{obs}	d_{obs}	d_{calc}
110	S	5.204	5.201
200	M	3.676	3.678
211	M	3.001	3.003
220	VS	2.6000	2.6007
310	M	2.3254	2.3262
222	M	2.1238	2.1235
321	S	1.9661	1.9660
400	S	1.8383	1.8390
330 411	W	1.7331	1.7338
420	W	1.6445	1.6448
332	vW	1.5687	1.5683
422	VS	1.5022	1.5015

[a] vW = very weak; W = weak; M = medium; S = strong; VS = very strong. $a = 7.356(2)$ Å.

The powder pattern reported in Table I was obtained with a 360-mm circumference Guinier focusing camera, Fe*K*α radiation ($\lambda = 1.9373$ Å) and KCl as an internal standard. A least-squares refinement based on these data gave $a = 7.356 \pm 0.002$ Å. A fairly close value, $a = 7.359 \pm 0.001$ Å, was obtained from the single crystal mounted on the automatic diffractometer for the intensity data collection. A least-squares refinement was applied on six reflections chosen in the region where complete α_1/α_2 separation occurred. The zero

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS AS DETERMINED BY X-RAY DATA[a]

	Th	Cu	Mn	O
x	0	0	0.25	0.2988(4)
y	0	0.5	0.25	0.1771(4)
z	0	0.5	0.25	0
β_{11}	0.00175(4)	0.0020(1)	0.00192(5)	0.0031(3)
β_{22}	0.00175	0.0023(1)	0.00192	0.0029(4)
β_{33}	0.00175	0.0040(1)	0.00192	0.0032(3)
β_{12}	0	0	−0.00015(6)	0.0006(3)
β_{13}	0	0	−0.00015	0
β_{23}	0	0	−0.00015	0

[a] Temperature factor = $\exp\text{-}(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

TABLE III

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
2 1 3	7.12	6.84	5 3 6	8.95	8.92	1 1 10	6.00	5.97	2 8 8	6.79	6.72
0 0 4	41.19	41.60	2 2 8	23.11	23.27	2 7 7	4.94	4.99	2 3 11	5.93	5.89
1 1 4	9.10	8.95	0 6 6	23.01	22.93	0 2 10	17.44	17.37	3 5 10	4.51	4.49
0 3 3	5.64	5.47	1 3 8	5.38	5.46	2 0 10	15.81	15.80	5 3 10	6.57	6.48
0 2 4	11.26	11.15	3 1 8	8.05	8.13	2 6 8	16.38	16.52	7 2 9	4.79	4.74
2 0 4	7.48	7.53	0 5 7	7.85	7.99	6 2 8	16.77	16.90	6 7 7	5.60	5.53
2 3 3	7.14	7.00	3 4 7	4.98	5.09	0 5 9	6.21	6.22	0 6 10	16.12	16.04
2 2 4	35.93	35.22	4 3 7	5.41	5.35	3 4 9	5.41	5.43	6 0 10	15.58	15.47
0 1 5	5.89	5.84	5 0 7	5.90	5.88	4 3 9	4.28	4.38	6 6 8	13.89	13.77
1 0 5	8.21	8.15	2 6 6	6.58	6.46	2 2 10	5.84	5.77	1 4 11	4.93	5.12
1 3 4	8.89	8.72	2 5 7	4.66	4.50	6 6 6	6.43	6.60	4 1 11	4.33	4.29
3 1 4	8.56	8.40	5 2 7	7.50	7.41	1 3 10	6.23	6.30	7 5 8	6.07	6.04
1 2 5	6.05	5.95	0 4 8	18.24	18.36	3 1 10	4.89	4.91	6 2 10	5.56	5.45
2 1 5	7.80	7.72	4 0 8	19.47	19.49	2 5 9	5.46	5.55	6 5 9	4.98	5.07
0 4 4	31.13	30.55	0 1 9	5.90	5.98	5 2 9	6.31	6.39	0 0 12	14.73	14.51
0 3 5	4.77	4.66	1 0 9	4.65	4.62	5 6 7	4.87	5.00	4 8 8	14.28	14.28
3 0 5	13.28	13.17	3 3 8	5.22	5.31	6 5 7	6.18	6.08	3 4 11	4.89	4.86
3 3 4	5.12	4.91	2 4 8	7.21	7.41	1 7 8	4.39	4.25	4 3 11	4.69	4.52
0 0 6	14.28	14.37	4 2 8	7.57	7.72	5 5 8	4.75	4.84	5 0 11	4.71	4.48
2 4 4	9.60	9.63	1 2 9	6.75	6.83	7 1 8	5.86	6.03	1 8 9	5.17	5.26
1 1 6	7.04	7.05	2 1 9	5.69	5.67	4 7 7	4.99	4.99	7 4 9	4.12	4.11
2 3 5	11.25	11.33	1 6 7	5.93	6.13	0 4 10	6.39	6.36	8 1 9	4.63	4.54
3 2 5	7.31	7.23	6 1 7	6.67	6.75	4 0 10	5.93	5.90	2 0 12	5.10	5.03
0 2 6	25.46	25.85	5 5 6	4.39	4.37	4 6 8	5.77	5.91	1 7 10	4.73	4.83
2 0 6	27.53	27.90	4 6 6	19.28	19.48	6 4 8	4.73	4.79	2 2 12	13.74	13.61
1 4 5	7.28	7.20	3 0 9	6.40	6.26	1 6 9	4.63	4.78	4 6 10	13.43	13.43
4 1 5	7.51	7.54	1 5 8	6.09	6.17	6 1 9	4.92	4.94	6.4.10	13.97	13.97
2 2 6	8.31	8.42	5 1 8	5.06	5.16	2 4 10	15.32	15.32	1 3 12	5.16	4.92
1 3 6	9.17	9.23	4 5 7	5.47	5.66	4 2 10	15.19	15.18	3 1 12	5.46	5.33
3 1 6	6.94	7.01	5 4 7	6.81	6.87	0 1 11	4.57	4.60	3 8 9	4.77	4.79
4 4 4	25.38	25.30	2 3 9	5.61	5.69	1 0 11	5.74	5.72	8 3 9	4.81	4.57
0 1 7	8.66	8.81	3 2 9	6.24	6.34	4 5 9	5.76	5.84	0 4 12	12.50	12.25
1 0 7	7.41	7.38	3 6 7	5.73	5.72	5 4 9	4.76	4.78	4 0 12	13.74	13.80
0 5 5	5.21	5.25	6 3 7	6.10	6.22	3 7 8	5.00	5.06	3 3 12	4.98	4.90
3 4 5	8.90	8.80	4 4 8	17.54	17.72	1 2 11	4.47	4.52	2 4 12	5.11	5.03
4 3 5	7.83	7.85	1 4 9	5.30	5.31	1 5 10	5.03	5.15	3 6 11	5.25	5.23
0 4 6	9.15	9.20	4 1 9	5.71	5.82	5 1 10	5.43	5.44	2 9 9	5.25	5.04
4 0 6	10.51	10.63	3 5 8	7.89	7.96	3 6 9	5.82	5.85	2 8 10	12.43	12.36
1 2 7	7.70	7.74	5 3 8	5.30	5.43	0 8 8	14.19	14.20	8 2 10	12.17	12.05
2 1 7	5.06	5.24	0 7 7	6.40	6.37	3 0 11	6.31	6.58	7 0 11	5.43	5.29
2 0 8	6.22	6.10	0 0 10	8.59	8.39	7 0 9	4.88	4.82	5 8 9	4.98	5.04
4 4 6	7.87	7.92	0 6 8	6.11	6.15	4 4 10	4.92	4.89	6 6 10	5.29	4.99
3 5 6	5.62	5.55	6 0 8	4.97	4.96						

of the ω-circle was obtained by measuring the ω and $-\omega$ values for each reflection.

Precession photographs taken with Mo$K\alpha$ of a small single crystal confirmed the space group $Im3$, a lattice parameter of ~7.3 Å, and 2 molecules per unit cell. The X-ray intensity measurements were taken with an automatic four-circle diffractometer equipped with Ag$K\alpha$ radiation. The specimen was a small cube whose edge measured 0.004 cm. All possible

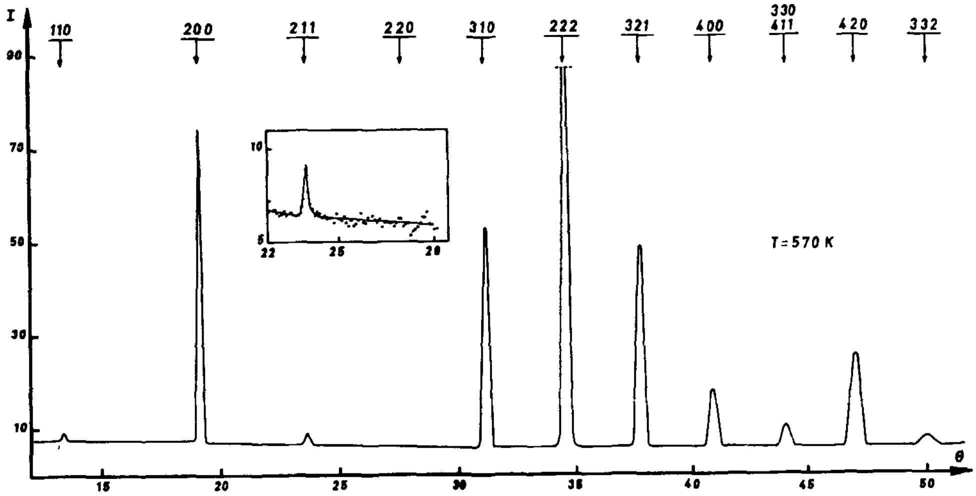

FIG. 1. The neutron diffraction powder pattern $\lambda = 2.4$ Å. The inset shows an enlargement of the region where the 211 and 220 reflections occur.

reflections in the region $8° < \theta < 30°$ were measured by the ω-scan technique with a speed of 0.02°/sec. The measuring procedure was the same as described in (*3*). The Lorentz and polarization corrections were applied to the integrated intensities. Since the absorption effects were very small but not negligible a spherical absorption correction was applied. The radius of the sphere was taken as $r = [3V \text{cube}/(4\pi)]^{1/3}$, which gave an average $\mu R = 0.5$. The total number of independent reflections with $I > 0$ was 186.

The structural refinements based on X-ray data were carried out with the Linex least-squares program. The atomic scattering factors for neutral atoms were used. For the thorium atom the values were taken from the tables given by Cromer and Waber (*8*), while for the other atoms the values reported by Doyle and Turner (*9*) were used.

The anomalous dispersion correction for radiation was applied by using the f' and f'' values published by Cromer and Liberman (*10*). The starting positional and thermal parameters and the weighting scheme were those reported for $CaCu_3Mn_4O_{12}$ (*3*). The scale factor, the isotropic extinction coefficient, 2 positional parameters, and 10 thermal ones were varied. Convergence was attained after a few cycles and the conventional R and wR factors were 0.011 and 0.012, respectively. As expected, the extinction correction was small; in fact, only for two reflections, 400 and 422, was $|F_o|$ corrected by more than 10%. The final positional and thermal parameters are reported in Table II. The observed and calculated structure factors are listed in Table III.

Figure 1 shows a powder neutron diffraction scan ($12 \leqslant 2\theta \leqslant 50°$) taken with a multidetector diffractometer at 570°K, i.e., above the Curie temperature. The multidetector setup consists of 300 detectors located every 0.20° along the 2θ circle. This assembly can be rotated about the goniometer axis in order to explore the entire 2θ region. The wavelength was 2.4 Å and the flux was 10^6 neutrons/cm^2 sec. A structural refinement based on these data was made by using the Rietveld (*11*) program adapted by Hewatt(*12*). In this program the refinement takes into account the intensity and the profile of the reflections (*11*). A value of 0.06 was obtained for the R factor. The oxygen positional parameters were $x = 0.2994(10)$, $y = 0.1789(8)$, $z = 0$, which are in good agreement, within the standard deviation, with the corresponding parameters obtained from X-ray data; however, the temperature factors were not considered reliable. For instance, that of the thorium atom was always negative.

Discussion

A serious problem in these compounds containing copper and manganese is to determine the occupancy of the square sites. Since both Cu^{2+} and Mn^{3+} are Jahn–Teller cations, these sites can be occupied by either of them. Compounds such as $[Th^{4+}Cu^{2+}_{3-x}Mn^{3+}_{x}](Mn^{3+}_{2+x}Mn^{4+}_{2-x})O_{12}$ cannot be distinguished by X-ray data, especially for small values of x, because the difference between the form factors, $f_{Cu} - f_{Mn}$, is less than four electrons. On the contrary, neutron diffraction data can give a good check for the occupancy of the $6b$ sites because the coherent neutron scattering amplitudes for Cu and Mn are very different, +0.76 and −0.39 10^{-12}, respectively. The present neutron data are not accurate enough for carrying out a least-squares refinement including an order parameter; in fact, the structural refinement without the order parameter yielded one negative temperature factor. However, a qualitative text can be made by using two relatively close reflections which are sensitive to the occupancy of the $6b$ sites. For instance, the intensities of the 211 and 220 reflections are proportional to $p_{211}\,(2b_{Th} - 2b_{Cu} - 2.50b_{Ox})^2$-LP and $p_{220}\,(2b_{Th} + 6b_{Cu} + 8b_{Mn} - 7.44b_{Ox})^2$-LP, respectively; p is the reflection multiplicity, b is the neutron scattering amplitude, and LP is the Lorentz polarization factor. The temperature attenuation is not taken into account because it is almost the same for the two reflections. For $x = 0$ one obtains $I_{211} = 0.21$ and $I_{220} = 0.07$, which correspond to $I_{220}/I_{211} = 0.33$. For increasing x these intensities decrease and increase, respectively. For instance, for $x = 0.05$ they are $I_{211} = 0.19$ and $I_{220} = 0.17$, which corresponds to $I_{220}/I_{211} = 0.90$. It can be seen from Fig. 1 that the observed intensity of 211 is small but measurable, whereas that of 220 is nearly zero. Therefore, one can conclude that, within the statistical fluctuations of the two reflections, the x parameter is very close to 0, which indicates that

TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Th Polyhedron	
Th–O × 12	2.556(3)
O(XXI)–O(XVII) × 24	2.709(3)
O(XXI)–O(XVIII) × 6	2.607(4)
O(XV)–Th(II)–O(XVIII) × 6	118.7(1)
O(XXI)–Th(II)–O(XVIII) × 6	62.0(1)
O(XVI)–Th(II)–O(XVIII) × 24	64.0(1)

Cu Polyhedron	
Cu(I)–O(XXII) × 4	1.973(3)
Cu(I)–O(V) × 4	2.800(3)
Cu(I)–O(XXI) × 4	3.238(3)
O(XIX)–O(XXII) × 4	2.607(4)
O(XIII)–O(XXII) × 2	2.962(4)
O(V)–O(XXII) × 8	2.806(3)
O(XI)–Cu(I)–O(V) × 2	116.2(1)
O(VIII)–Cu(I)–O(V) × 2	63.8(1)
O(XIX)–Cu(I)–O(XXII) × 2	85.6(1)
O(XIII)–Cu(I)–O(XXII) × 2	94.4(1)
O(V)–Cu(I)–O(XXII) × 8	69.6(1)

Mn Octahedron	
Mn–O × 6	1.950(1)
O(I)–O(XVII) × 6	2.806(3)
O(I)–O(II) × 6	2.709(3)
O(I)–Mn(I)–O(II)	88.0(1)
O(I)–Mn(I)–O(XVII) × 6	92.0(1)

Important Angles	
Cu(I)–O(XIX)–Mn(I)	108.7(1)
Cu(I)–O(II)–Mn(I)	82.2(1)
Cu(I)–O(XXI)–Mn(I)	70.9(1)
Cu(I)–O(XIX)–Th(I)	108.0(1)
Cu(I)–O(II)–Th(I)	152.6(1)
Cu(I)–O(XXI)–Th(II)	77.9(1)
Mn(I)–O(I)–Th(I)	89.0(1)
Cu(I)–O(XIX)–Cu(II)	99.4(1)
Cu(I)–O(XIX)–Cu(IV)	174.2(1)
Cu(I)–O(VIII)–Cu(II)	74.7(1)
Mn(I)–O(XXI)–Mn(II)	141.3(2)

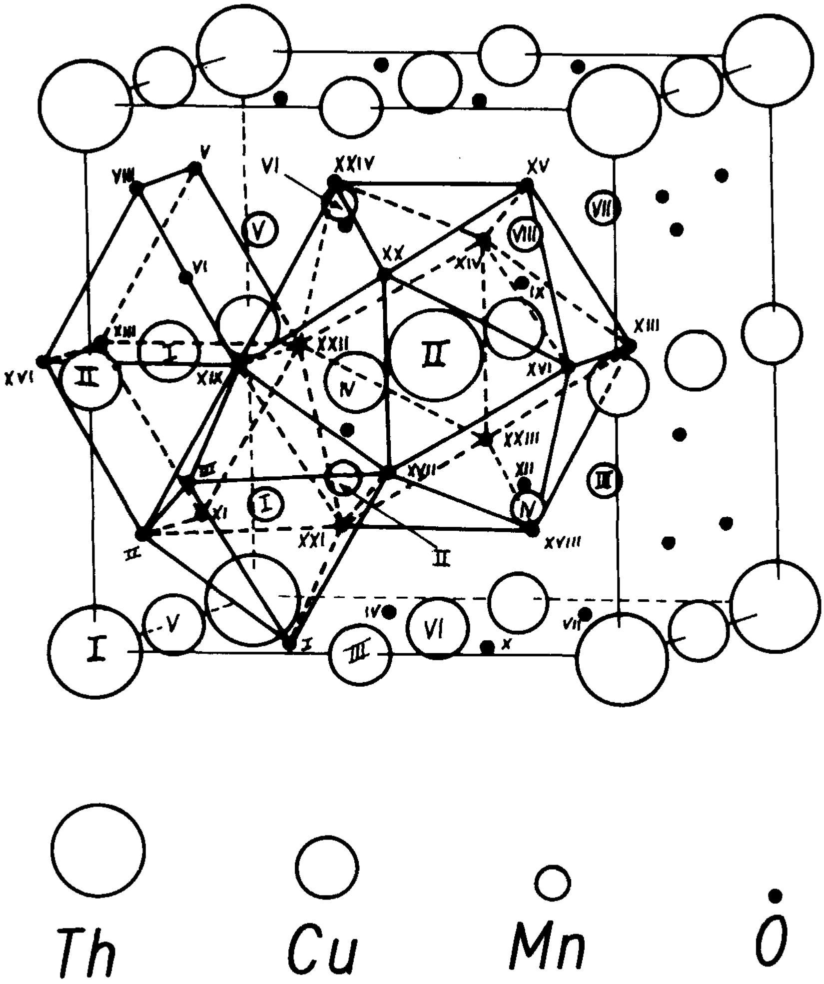

FIG. 2. The three kinds of coordination polyhedra and the way they join together.

the 6*b* sites are entirely occupied by the Cu^{2+} cations.

The interatomic distances and the angles with their standard deviations are reported in Table IV. These values were calculated by the X-ray program by using the final positional parameters obtained from the X-ray data and a lattice constant $a = 7.359$ Å. The coordination polyhedra and the way they join together are shown in Fig. 2. The average cation oxygen distances are Th–O = 2.556 ± 0.003 Å, Cu–O = 1.973 ± 0.003 Å (square coordination), and Mn–O = 1.950 ± 0.001 Å. As far as we know, $ThCu_3Mn_4O_{12}$ is the second compound in which the thorium cations have an icosahedral coordination, the other being $MgTh(NO_3)_6 \cdot 8H_2O$(13). In this compound a larger value (2.63 ± 0.05 Å) was found for the average Th–O distance. The Cu–O distance agrees very well with the average value given (1.97 Å) for a squarely coordinated Cu^{2+} cation (*14*). This result confirms the assumption that the square sites are occupied only by Cu^{2+} cations. In the compound $CaCu_3Mn_4O_{12}$ for the corresponding distance a smaller value, 1.942 ± 0.002 Å, was obtained. This smaller value could be explained by assuming that in $CaCu_3Mn_4O_{12}$ some of the square sites are

TABLE V

THERMAL DATA IN $ThCu_3Mn_4O_{12}$

		Angles with		
	rms	x	y	z
Th	0.069(2)			
Cu	0.074(4)	0	90	90
	0.080(4)	90	0	90
	0.105(4)	90	90	0
Mn	0.067(2)	55	55	55
	0.076(2)	114	114	35
	0.076(2)	45	135	90
O	0.081(8)	130	40	90
	0.094(8)	90	90	0
	0.100(8)	40	50	90

occupied by the Mn^{3+} cations. In fact, the Mn^{3+} distance with square coordination is much smaller than the corresponding Cu^{2+}–O distance. In $NaMn_3Mn_4O_{12}$ for the square sites, we found a value of 1.910 ± 0.003 Å. Preliminary neutron diffraction and magnetic data seem to confirm these assumptions.

The octahedral average distance, $Mn^{3.5+}$–O = 1.950 ± 0.001 Å, found in $ThCu_3Mn_4O_{12}$ agrees very well with the value found in $NaMn_3Mn_4O_{12}$ (1.947 Å). In this latter compound the average effective charge of the cations occupying the octahedral sites is exactly the same as in the thorium compound.

The thermal data, which are reported in Table V, are in agreement with those reported for $NaMn_3Mn_4O_{12}$ and $CaCu_3Mn_4O_{12}$. As was pointed in a previous article (*3*), the sizes of the icosahedra are mainly determined by the sizes of the cations occupying the octahedra. Therefore, if the icosahedra are occupied by smaller cations than the size of the site itself, then an anomalously large thermal vibration should be observed. This was found to be true in $NaMn_3Mn_4O_{12}$, in which the root-mean-square value for the sodium cations was 0.127 Å. As a consequence, the observed Na–O distance was larger than the value calculated from the ionic radius of the 12-coordinated Na^+ cation. The root-mean-square value for the thorium atoms in $ThCu_3Mn_4O_{12}$ is normal, 0.069 Å, which indicates that the Th–O distance found in the present study should be the one corresponding to a 12-equidistant coordinated Th^{4+} cation.

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