MORPHOLOGY AND X-RAY POWDER DIFFRACTION OF Mn-ETHYLENE-DIAMINETETRAACETATE METAL COMPLEXES. I. WITH HEXACOORDINATED METAL IONS (R = Ni, Co, Cu, Zn). $[(H_2O)_4Mn(C_{10}H_{12}N_2O_8R)]_n.2n(H_2O)$; (R = Ni, Co, Cu, Zn).

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INTRODUCTION

The affinity of ethylenediaminetetraacetic acid (H_4EDTA) for Ca was described by F. Hunz. G. Schwarzenbach and his school described this compound as an excellent chelating agent for certain metals (1 to 3) and applied it in chemical and clinical analysis. The compound was used in the textile industry (4) and also as a drug to solve metallic intoxications (5 to 7).

The study of the molecular and crystal structure of EDTA metal complexes was carried out by the J.L. Hoard school (8 to 16) in the Chemical Department of Cornell University (U.S.) and by M.A. Porai-Koshits et al. (17 to 24) in the Chemical Department of the Moscow University «M.V. Lomonosov» (Russia). A large number of papers on the structural analysis of EDTA metal complexes have been published, covering a wide range of elements (25 to 30); studies referring to MnEDTA with four transition elements (Co, Ni, Cu, Zn) were performed in the Departament de Cristal·lografia, Mineralogia i Dipòsits Mineral at the Universitat de Barcelona and published in Acta Crystallographica (25).

In contrast, papers on X-ray powder diffraction of EDTA metal complexes are very few and it is only possible to obtain reduced information in this field. The aim of this paper is to attempt to provide further information and, at the same time, to describe the morphology of the crystals as far as possible.

SAMPLE PREPARATION.

Samples were obtained by reacting metal carbonates ($MnCO_3$ and RCO_3) with ethylenediaminetetraacetic acid (H_4EDTA) in water suspension at a strictly

controlled pH; the acidity produced in the reaction being neutralized by loss of CO_2.

$$H_4EDTA + MnCO_3 = MnH_2EDTA + H_2O + CO_2\uparrow$$
$$MnH_2EDTA + RCO_3 = MnREDTA + H_2O + CO_2\uparrow$$

A water suspension of H_4EDTA was prepared and warmed to 90°C; a known quantity of well-powdered $MnCO_3$ was added, with constant and intense agitation and continuous control of pH and temperature, until its complete reaction. An exact quantity of well powdered RCO_3 was then added very slowly in order to avoid the complex carbonates crystallization (1,2,31). The pH control is important; during the reaction the pH interval must be between 5 and 7.5, in which condition the $EDTA^{-4}$ is stabilized (32). The final solution was slowly cooled and crystals were removed and dried, after being washed in alcohol.

The metal elements were analyzed by acid mineralization (HNO_3 or $HClO_4$) or by calcination of the samples followed by dissolution of the oxides formed. Atomic absorption spectroscopy was used to analyze the composition of the crystals obtained (33,34).

Morphology.

The morphology of the compounds was determined using good selected crystals by measuring the value of the spherical coordinates of their faces by means of a 2-circle goniometer from V. Goldschmidt manufactured by Stoe at Heidelberg.

The crystal forms of the four hexacoordinated complexes were very similar, with the exception of the Mn-Cu complexe. This was isostructural with the other three but had some small variations in the structure referring to the arms of the EDTA, which lead to a slow rate growth of the faces {201} and the appearance of there on the crystals. The other three compounds had the faces {021}, and the faces {120} were common to all hexa-coordinated complexes.

There are three possible orientation of orthorhombic crystals, depending on the choice of the third crystallographic axis from one of the three twofold symmetry axes. In our case, crystals were non-centrosymmetric, belonging to the pyramidal (Groth,1921) or antihemiedry (Friedel,1926) or hemimorphic (Pardillo,1930) crystal class, with only one twofold axis, which must be vertical like the third crystallographic axis and, in accordance with the International Union of Crystallography (35), the first crystallographic axis, a, must be the one with higher parameter, and the axial ratio must be a>b.

The circle angles, the axial ratio and the stereographic projection of the EDTA hexa-coordinated complexes are shown below.

1. $((H_2O)_4.Mn(C_{10}H_{12}N_2O_8Co))_n.2n(H_2O)$.

Good crystals of three-dimensional habit, brown-dark colour, from which six were selected for goniometer measurements.

From the experimental data the axial ratio (90° is the value of interaxial angles since the crystals belong to the orthorhombic system), the circle angles ϕ and ρ of every face and the differences between experimental and calculated values were calculated, which are shown in the following table.

hkl	ϕ_e	ρ_e	ϕ_m	ρ_m	$\phi_e-\phi_m$	$\rho_e-\rho_m$
110	231°44'	90°35'	233°31'	90°00'	-1°47'	+0°35'
120	36°03'	89°59'	34°40'	90°00'	+1°23'	-0°01'
120	145°36'	90°01'	145°20'	90°00'	+0°16'	+0°01'
120	213°24'	89°56'	214°40'	90°00'	-1°16'	+0°04'
120	325°11'	90°05'	325°20'	90°00'	-0°09'	+0°05'
221	55°12'	67°06'	53°31'	66°53'	+1°14'	+0°13'
221	127°49'	67°05'	126°29'	66°53'	+1°20'	+0°12'
221	231°51'	66°55'	233°31'	66°53'	-1°40'	+0°02'
221	305°09'	66°25'	306°29'	66°53'	-1°20'	-0°28'
021	1°25'	53°17'	0°00'	53°49'	+1°25'	-0°32'
021	179°42'	54°21'	180°00'	53°49'	-0°18'	+0°32'
072	182°36'	67°04'	180°00'	66°49'	+2°36'	+0°15'

The axial ratio is 0.73100:1:0.68740.

2. $((H_2O)_4.Mn(C_{10}H_{12}N_2O_8Ni))_n.2n(H_2O)$.

Nice blue-violet crystals of more or less prismatic habit from which six were selected for the goniometer measurements.

hkl	ϕ_e	ρ_e	ϕ_m	ρ_m	$\phi_e-\phi_m$	$\rho_e-\rho_m$
120	33°29'	90°09'	34°03'	90°00'	-0°34'	+0°09'
120	146°25'	89°40'	145°57'	90°00'	+0°28'	-0°20'
120	214°36'	90°19'	214°03'	90°00'	+0°33'	+0°19'
120	325°29'	89°54'	325°57'	90°00'	-0°28'	-0°06'
021	359°29'	53°16'	0°00'	53°34'	-0°31'	-0°18'
021	179°56'	53°52'	180°00'	53°34'	-0°04'	+0°18'

The axial ratio is 0.73989:1:0.67736.

3. $((H_2O)_4.Mn(C_{10}H_{12}N_2O_8Cu))_n.2n(H_2O)$.

Blue three-dimensional crystals of habit different from than those of Mn-Co and Mn-Ni. Six crystals were selected for goniometric measurements.

hkl	ϕ_e	ρ_e	ϕ_m	ρ_m	ϕ_e-ϕ_m	ρ_e-ρ_m
120	34°11'	89°59'	34°12'	90°00'	-0°01'	-0°01'
120	145°44'	90°03'	145°48'	90°00'	+0°04'	+0°03'
120	214°14'	90°03'	214°12'	90°00'	+0°02'	+0°03'
120	325°53'	89°56'	325°48'	90°00'	+0°05'	-0°04'
201	89°42'	59°33'	90°00'	60°24'	-0°18'	-0°51'
201	269°30'	61°15'	270°00'	60°24'	-0°30'	+0°51'
001	46°29'	0°18'	—	0°00'	—	+0°18'

The axial ratio is 0.73573:1:0.64755.

4. $((H_2O)_4.Mn(C_{10}H_{12}N_2O_8Zn))_n.2n(H_2O)$.

Transparent crystals (white in aggregates), with correct conformation habit, some three-dimensional. Six crystals were selected for goniometric measurements.

hkl	ϕ_e	ρ_e	ϕ_m	ρ_m	ϕ_e-ϕ_m	ρ_e-ρ_m
120	34°41'	89°54'	34°27'	90°00'	+0°14'	-0°06'
120	145°29'	90°07'	145°33'	90°00'	-0°06'	+0°07'
120	214°13'	89°45'	214°27'	90°00'	-0°14'	-0°15'
120	325°39'	90°15'	325°33'	90°00'	+0°06'	+0°15'
021	358°24'	53°55'	0°00'	53°44'	-1°36'	-0°12'
021	181°26'	53°32'	180°00'	53°44'	+1°28'	+0°11'

The axial ratio is 0.72886:1:0.68150.

The authors of the structure analysis of these compounds (25), used as space group the $Pn2_1a$, with the twofold axis in the horitzontal position instead of the $Pna2_1$ which is the standard space group for the symmetry of these crystals (35), having the crystallographic axis abc as acb. The morphological constants of the compounds are shown in table 1, together with the axial ratio deduced from the values given in the paper on crystal structure (25).

Table 1. Crystal morphology of ethylenediaminetetracetate metal complexes. I. Mn-Co, Mn-Ni, Mn-Cu, Mn-Zn hexacoordinated ions.

			goniometry morphology
	Hemimorphic		0.73100:1:0.68740
$CoEDTAMn.6H_2O$		mm2	structural analysis
	Orthorhombic		$Pn2_1a$ 1.09113:1:0.73315
			$Pna2_1$ 0.74515:1:0.68200
			goniometric morphology
	Hemimorphic		0.73989:1:0.67736
$NiEDTAMn.6H_2O$		mm2	structural analysis
	Orthorhombic		$Pn2_1a$ 1.09426:1:0.73720
			$Pna2_1$ 0.74216:1:0.67823
			goniometric morphology
	Hemimorphic		0.73573:1:0.64755
$CuEDTAMn.6H_2O$		mm2	structural analysis
	Orthorhombic		$Pn2_1a$ 1.11927:1:0.76284
			$Pna2_1$ 0.73315:1:0.64755
			goniometric morphology
	Hemimorphic		0.72886:1:0.68150
$ZnEDTAMn.6H_2O$		mm2	structural analysis
	Orthorhombic		$Pn2_1a$ 1.09779:1:0.74025
			$Pna2_1$ 0.74149:1:0.67544

POWDER X-RAY DIFFRACTION.

The data of the X-ray powder diffraction were collected with an automatic Philips diffractometer (with PW1130 generator), using CuKα radiation (λ = 1.54178 Å), a focusing beam graphite monochromator and a proportional counter detector, in a 17 cm vertical goniometer. The incident beam aperture (divergence angle 1/2° and 1°) combined with the receiving slit width of 0.05 mm give an instrument profile breadth of 0.11° 2θ (with Si powder of National Bureau of Standards, Standard Reference Material 640a).

Sample data were collected in series of three different diagrams: firstly using an angular speed of the goniometer of 1° minute (figures 1 to 4); secondly, with an angular speed of 1/4° minute; and finally, in some area, with step scanning intervals of 0.01° and 0.02° 2θ, and counting time of 10 seconds per step.

Samples were ground in agate morter and pestle to a particle size of 20-30 μm, and were horizontal powder packed, avoiding possible orientation, in a diffractometer holder which rotated during the data collection.

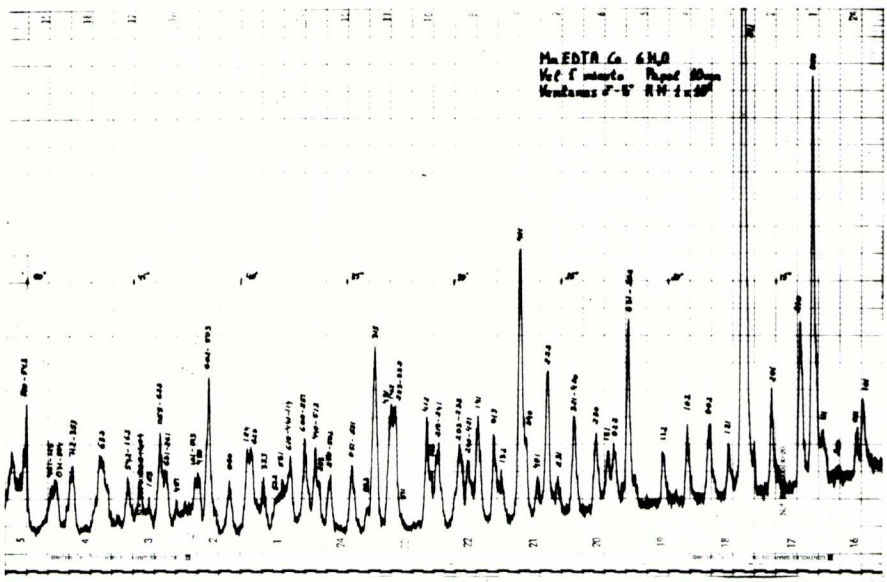

Fig. 1. X-ray powder diagram of Co EDTA Mn complexe (speed 1° minute).

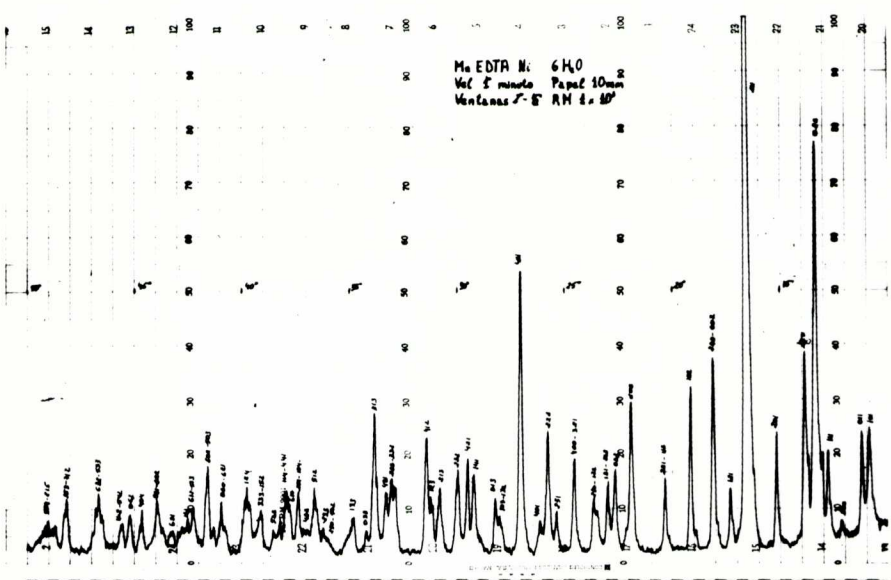

Fig. 2. X-ray powder diagram of Ni EDTA Mn complexe (speed 1° minute).

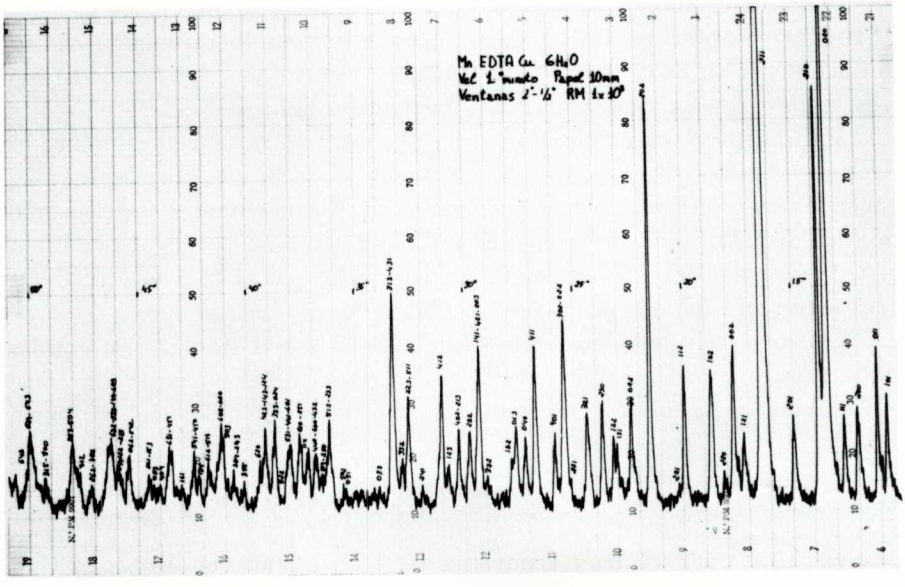

Fig. 3. X-ray powder diagram of Cu EDTA Mn complexe (speed 1° minute).

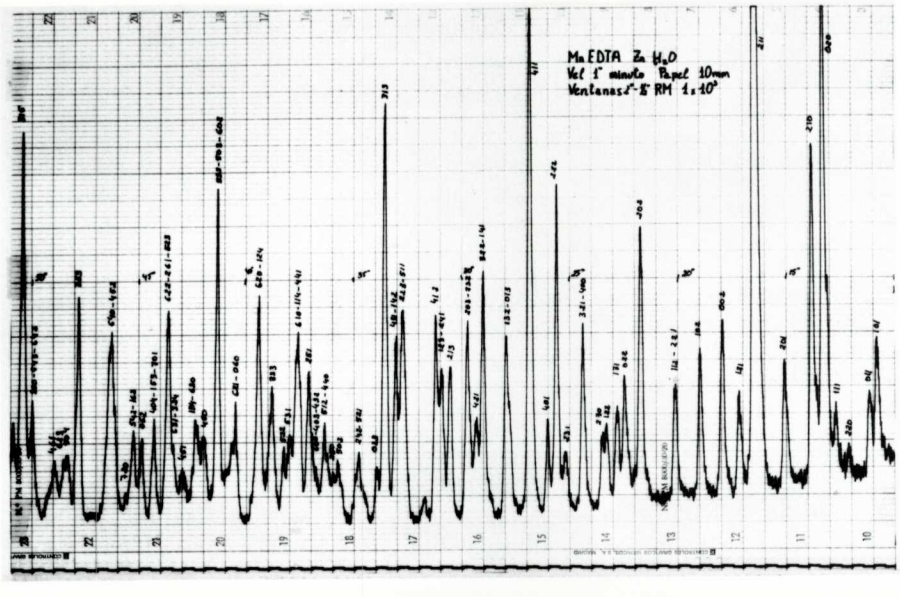

Fig. 4. X-ray powder diagram of Zn EDTA Mn complexe (speed 1° minute).

Intensity measurements were performed from the strip chart recorder (peak height) for diagram of 1/4° angular speed and from the computer of the diffractometer for the step-scanning diagrams; α-Al_2O_3 (JCPDS standard) was used as intensity standard with hkl's of intensity standard 113.

The diagrams were indexed by using the unit cell parameters obtained in the structural analysis of the samples (36 to 38), by computer calculation of 2θ angles of every diffraction line and comparing them with the experimental powder diagram. The Affmail, Steward program, modified by Comberton (1970), Filhol (1972, 1978) and Rodriguez-Carvajal (1982) was used for orientation and refining X-ray powder diffraction by least squares.

The unit cell parameters from single crystals and from X-ray powder diffraction are shown on table 2, with the differences which are near to be equal at the standard deviations, except for the Mn-Ni compound which are much larger.

Table 2. Unit cell parameters from single crystal and powder diffraction.

		single crystal	powder	difference
CoEDTAMn.6H_2O	a_0	14.584(0.003)	14.5837(0.0014)	-0.0003
	b_0	13.366(0.004)	13.3659(0.0012)	-0.0001
	c_0	9,799(0.003)	9.7974(0.0011)	-0.0016
NiEDTAMn.6H_2O	a_0	14.499(0.004)	14.5465(0.0014)	-0.0475
	b_0	13.250(0.004)	13.2434(0.0014)	-0.0066
	c_0	9.768(0.003)	9.7988(0.0010)	0.0338
CuEDTAMn.6H_2O	a_0	14.626(0.003)	14.6230(0.0011)	-0.0030
	b_0	13.068(0.004)	13.0615(0.0010)	-0.0015
	c_0	9.969(0.003)	9.9687(0.0008)	-0.0003
ZnEDTAMn.6H_2O	a_0	14.594(0.004)	14.5951(0.0009)	0.0011
	b_0	13.294(0.004)	13.2922(0.0010)	-0.0018
	c_0	9,841(0.003)	9.8432(0.0008)	0.0022

The diagrams of the X-ray powder diffraction, with 2θ and d experimentals, I/I_0, and the differences between experimental and calculated values are shown at the end of each compound, jointly with figures of merit, unit cell parameters and symmetry. Table 3 shows an abstract of the conditions of X-ray powder technique.

Table 3. X-Ray powder techniques.

Radiation type, source	X-ray, Cu.
Instrument powder	40 Kv, 20 mA.
λ value used	1.54178 Å (K°).
λ discrimination	diffraction beam; focusing graphite crystal monochromator.
λ detector	proportional counter.
Instrument description	17 cm. vertical diffractometer.
Divergence angle	1°.
Receiving slit width	0.05 mm.
Soller slits	2 sets (incident and diffracted beam) aperture q=1.2.
Instrument profile breadth	0.11°(2θ).
Temperature	23°C°1°.
Specimen form	horizontaly powder packed, avoiding possible orientation, in a diffractometer holder.
Particle size	ground in morter and pestle to <30 λm.
Range of 2θ	from 6° to 50°.
Special motion	None.
External 2θ standard	Si (a_0=5.43075 Å) and also a pure quarz with controlled lattice parameters.
2θ error correction procedure	Special factor correction used in any compound.
Intensity measuring procedure	Stript chart recorder (peak heights) and data from the computer of the diffractometer; error 3-5%; on peaks.
Minimum intensity	about 0.4.
Intensity standard used	α-Al_2O_3 standard for intensities measurement with hkl's of intensity standard 113.
Intensity ratio I/I_c	Different for the different compounds; medium one was 2.30.
Resolution (FWHM) for materials	about 0.10°2θ at 33.73°2θ.
2θ reproductibility	about °0.02°2θ at all 2θ.

ETHYLENEDIAMINETETRAACETATE METAL COMPLEXES. I.
Mn-Co, Mn-Ni, Mn-Cu, Mn-Zn, HEXACOORDINATED IONS.

1 . ((H2O)4.Mn(C10H12N2O8Co))n.2n(H2O).

X-ray radiation: CuKα 1.54178 Å. Correction factor: -.04

Nº	2θexp	I/Io	H K L	d exp	dif 2θ	dif d
1	10.88	17	1 0 1	8.1315	0.002	-0.0011
2	11.18	10	0 1 1	7.9139	-0.007	0.0121
3	12.13	2	2 0 0	7.2962	-0.002	0.0043
4	12.73	11	1 1 1	6.9536	-0.004	0.0060
5	13.27	84	0 2 0	6.6718	0.018	-0.0111
6	13.83	23	2 1 0	6.4029	0.000	0.0017
7	15.13	18	2 0 1	5.8556	-0.006	0.0061
8	16.53	100	2 1 1	5.3626	-0.004	0.0038
9	17.16	6	1 2 1	5.1672	-0.005	0.0040
10	18.10	12	0 0 2	4.9009	-0.003	0.0022
11	19.11	11	1 0 2	4.6441	0.001	0.0004

X-ray radiation: CuKα 1.54178 Å. Correction factor: -.04

Nº	2θexp	I/Io	H K L	d exp	dif 2θ	dif d
12	20.24	6	1 1 2	4.3873	0.000	0.0008
13	21.88	30	2 0 2	4.0620	0.013	-0.0043
			0 3 1	4.0620	-0.016	0.0064
14	22.52	11	0 2 2	3.9480	0.010	-0.0029
15	22.75	10	1 3 1	3.9086	0.003	0.0012
16	23.38	17	2 3 0	3.8047	-0.007	0.0029
17	24.41	23	3 2 1	3.6464	0.008	-0.0021
			4 0 0	3.6464	0.000	0.0005
18	25.13	10	2 3 1	3.5436	0.004	-0.0007
19	25.63	24	2 2 2	3.4755	-0.005	0.0017
20	26.08	6	4 0 1	3.4166	0.003	-0.0004
21	26.69	35	0 4 0	3.3399	0.008	-0.0016
22	26.95	58	4 1 1	3.3082	0.001	-0.0023
23	27.75	10	1 3 2	3.2147	0.003	-0.0002
24	28.13	19	0 1 3	3.1721	0.003	-0.0004
25	28.88	18	1 4 1	3.0914	-0.002	0.0006
26	29.34	5	4 2 1	3.0440	-0.006	0.0016
27	29.40	7	2 4 0	3.0379	0.001	0.0002
28	29.76	12	2 3 2	3.0020	0.009	-0.0014
29	29.99	7	2 0 3	2.9795	0.007	-0.0010
30	30.72	24	2 1 3	2.9103	-0.005	0.0012
31	30.81	24	2 4 1	2.9020	-0.002	0.0005
32	31.10	6	1 2 3	2.8756	0.007	-0.0009
33	31.30	28	4 1 2	2.8577	-0.002	0.0005
34	32.73	12	5 1 1	2.7360	0.003	-0.0005
35	32.83	16	3 3 2	2.7279	0.002	-0.0002
36	32.91	17	2 2 3	2.7215	0.005	-0.0006
37	33.01	18	1 4 2	2.7135	-0.006	0.0012
38	33.04	23	4 3 1	2.7111	0.003	-0.0003
39	33.73	40	3 1 3	2.6572	-0.001	0.0004
40	34.03	6	0 3 3	2.6344	-0.002	0.0004
41	34.78	11	0 5 1	2.5793	-0.001	0.0004
			5 2 1	2.5793	-0.001	0.0003
42	35.78	5	2 5 0	2.5095	0.004	-0.0003
43	35.82	5	5 0 2	2.5068	-0.003	0.0007
44	36.26	6	2 3 3	2.4774	0.001	0.0001
45	36.49	11	4 4 0	2.4623	0.010	-0.0011
			5 1 2	2.4623	0.009	-0.0009
46	36.74	8	4 3 2	2.4461	-0.007	0.0011
47	36.97	13	2 5 1	2.4314	0.001	0.0001
			6 0 0	2.4314	-0.005	0.0008
48	37.59	7	6 1 0	2.3927	-0.009	0.0013
49	37.66	7	4 4 1	2.3884	0.006	-0.0006
50	37.84	6	1 1 4	2.3775	-0.003	0.0005
51	37.99	10	5 3 1	2.3684	-0.003	0.0004
52	38.37	10	5 2 2	2.3458	0.008	-0.0008
53	38.89	7	3 3 3	2.3157	0.003	-0.0002
54	39.16	10	0 2 4	2.3003	-0.004	0.0006
55	39.46	12	6 2 0	2.2835	0.008	-0.0007
56	39.68	25	1 2 4	2.2714	0.004	-0.0003
57	40.49	11	0 6 0	2.2278	0.000	0.0002
58	41.48	25	6 0 2	2.1769	0.006	-0.0004
			5 0 3	2.1769	-0.013	0.0015

X-ray radiation: CuKα 1.54178 Å. Correction factor: -.04

Nº	2θexp	I/Io	H	K	L	d exp	dif 2θ	dif d
59	41.86	11	4	5	0	2.1580	-0.011	0.0022
60	42.04	9	1	6	1	2.1492	-0.015	0.0007
61	42.08	7	5	1	3	2.1472	0.001	0.0000
62	42.98	12	4	5	1	2.1043	0.013	-0.0011
63	43.41	10	6	3	1	2.0845	0.006	-0.0004
64	43.48	10	2	6	1	2.0813	0.007	-0.0005
65	43.72	25	6	2	2	2.0704	-0.001	0.0002
			0	5	3	2.0704	-0.019	0.0018
66	44.23	6	1	5	3	2.0477	0.005	-0.0004
67	44.56	6	4	0	4	2.0333	0.000	0.0002
68	44.70	11	0	6	2	2.0273	0.008	-0.0005
69	45.14	7	1	6	2	2.0085	0.001	0.0000
70	45.24	6	5	4	2	2.0043	0.008	-0.0006
71	46.40	42	6	3	2	1.9569	-0.007	0.0007
72	47.77	6	3	5	3	1.9039	-0.005	0.0005
73	47.91	6	7	1	2	1.8987	-0.010	0.0009
74	48.55	10	5	0	4	1.8751	0.009	-0.0006
			0	7	1	1.8751	-0.012	0.0009
75	48.82	7	4	6	1	1.8654	0.012	-0.0007
			1	2	5	1.8654	-0.006	0.0005
76	50.02	11	5	4	3	1.8234	-0.003	0.0003
			8	0	0	1.8234	-0.005	0.0004

FIGURES OF MERIT TYPE:

F 76 = 69.5 (0.006, 176) (G.S. Smith and R.L. Snyder)

M 20 = 55 (P.M. de Wolff)

UNIT CELL DATA:

Crystal structure and cell definition from X. Solans, M. Font-Altaba, J. Oliva and J. Herrera. Acta Cryst. C39(1983)435-438.

Four circle diffractometer unit cell determined by centring and refining orientation matrix and unit cell parameters by least squares.

AFFMAIL, Steward program, Laboratoire de Cristallographie, Université de Bordeaux, modified by Comberton (1970), Filhol (1972,1978) and Rodriguez-Carvajal (1982), for orientation and refining X-ray powder diffraction by least squares.

Crystal system: Orthorhombic. Space group: Pn21a. Z: 4

a	14.5837 (0.0013)	14.584 (0.003)	-0.0003
b	13.3658 (0.0012)	13.366 (0.004)	-0.0002
c	9.7974 (0.0010)	9.799 (0.003)	-0.0016
	a/b = 1.0911	a/b = 1.0911	
	c/b = 0.7330	c/b = 0.7331	

Vp = 1909.737 Vs = 1910.117 Dcal = 1.77 Mgm-3 Wt = 510.3

F(000) = 1048 R = 0.059 Rw = 0.061

2 .((H2O)4.Mn(C10H12N2O8Ni))n.2n(H2O).

X-ray radiation: CuKα 1.54178 Å. Correction factor: 0.00

Nº	2θexp	I/Io	H	K	L	d exp	dif 2θ	dif d
1	10.88	15	1	0	1	8.1315	-0.003	0.0046
2	11.23	11	0	1	1	7.8788	-0.001	0.0017
3	12.18	7	2	0	0	7.2663	0.006	-0.0069
4	12.77	7	1	1	1	6.9319	-0.005	0.0052
5	13.36	43	0	2	0	6.6271	-0.006	0.0054
6	13.88	24	2	1	0	6.3800	-0.005	0.0049
7	15.17	10	2	0	1	5.8402	0.000	0.0000
8	16.59	100	2	1	1	5.3434	-0.002	-0.0003
9	17.27	7	1	2	1	5.1345	-0.002	0.0010
10	18.10	12	0	0	2	4.9009	-0.003	0.0015
			2	2	0	4.9009	-0.008	0.0045
11	19.11	14	1	0	2	4.6441	-0.002	0.0010
12	20.28	8	1	1	2	4.3787	0.007	-0.0029
			2	2	1	4.3787	0.003	-0.0013
13	21.87	23	2	0	2	4.0638	-0.001	0.0003
14	22.58	16	0	2	2	3.9376	0.002	-0.0009
15	22.90	7	2	1	2	3.8833	0.004	-0.0014
16	22.93	7	1	3	1	3.8783	0.002	-0.0008
17	23.41	4	1	2	2	3.7999	0.005	-0.0018
18	23.56	6	2	3	0	3.7760	-0.007	0.0022
19	24.50	10	3	2	1	3.6332	0.000	-0.0001
			4	0	0	3.6332	0.011	-0.0034
20	25.30	3	2	3	1	3.5201	0.005	-0.0015
21	25.73	12	2	2	2	3.4623	0.004	-0.0010
22	26.13	7	4	0	1	3.4102	-0.003	0.0008
23	27.01	25	4	1	1	3.3010	0.003	-0.0007
24	27.87	5	1	3	2	3.2011	-0.008	0.0018
25	28.01	6	1	0	3	3.1854	0.007	-0.0015
26	28.13	9	0	1	3	3.1721	-0.004	0.0009
27	29.14	13	1	4	1	3.0644	0.008	-0.0018
28	29.48	12	4	2	1	3.0298	0.007	-0.0014
29	29.90	12	2	3	2	2.9882	0.007	-0.0015
30	30.76	8	2	1	3	2.9066	0.002	-0.0003
31	30.81	24	2	4	1	2.9020	-0.002	0.0005
32	31.15	8	1	2	3	2.8711	0.003	-0.0005
33	31.36	12	4	1	2	2.8524	-0.004	0.0008
34	32.81	13	5	1	1	2.7295	-0.003	0.0004
35	32.94	12	3	3	2	2.7191	-0.016	0.0025
			2	2	3	2.7191	-0.012	0.0019
36	33.20	10	4	3	1	2.6984	0.000	0.0001
37	33.76	24	3	1	3	2.6549	-0.006	0.0009
38	34.15	5	0	3	3	2.6254	0.006	-0.0003
39	34.73	6	1	3	3	2.5829	0.007	-0.0010
40	35.90	4	5	0	2	2.5014	0.001	-0.0001
41	36.08	5	2	5	0	2.4893	-0.004	0.0005
42	36.36	7	2	3	3	2.4708	-0.009	0.0011
43	36.55	10	5	1	2	2.4584	-0.003	0.0004
44	36.90	4	4	3	2	2.4358	-0.003	0.0003
45	37.22	9	1	0	4	2.4156	0.000	-0.0001
46	37.26	10	2	5	1	2.4131	-0.008	0.0009
47	37.72	8	6	1	0	2.3848	0.000	-0.0000

X-ray radiation: CuKα 1.54178 Å. Correction factor: 0.00

Nº	2θexp	I/Io	H K L	d exp	dif 2θ	dif d
48	37.84	10	1 1 4	2.3775	-0.009	0.0010
49	37.88	10	4 4 1	2.3751	0.001	-0.0001
50	38.18	6	5 3 1	2.3571	0.006	-0.0007
51	38.48	5	5 2 2	2.3394	-0.004	-0.0007
52	39.05	7	3 3 3	2.3065	0.020	-0.0336
53	39.15	6	1 5 2	2.3009	-0.002	0.0002
54	39.58	8	6 2 0	2.2769	-0.002	0.0003
55	39.74	12	1 2 4	2.2681	0.011	-0.0013
56	40.68	6	6 2 1	2.2178	-0.003	0.0002
57	40.89	6	0 6 0	2.2069	0.003	-0.0003
58	41.56	21	6 0 2	2.1729	0.000	-0.0000
			5 0 3	2.1729	-0.004	0.0004
59	42.15	7	6 1 2	2.1438	0.004	-0.0005
			5 1 3	2.1438	0.000	0.0002
60	42.44	6	1 6 1	2.1298	0.002	-0.0003
61	43.58	5	6 3 1	2.0767	0.000	-0.0001
62	43.85	10	2 6 1	2.0646	0.000	-0.0000
			6 2 2	2.0646	0.001	-0.0001
63	44.57	6	4 0 4	2.0329	-0.013	0.0012
64	45.06	6	0 6 2	2.0119	0.006	-0.0005
65	45.47	6	5 4 2	1.9947	0.014	-0.0012
			1 6 2	1.9947	-0.015	0.0012
66	46.58	11	6 3 2	1.9497	-0.003	0.0001
			5 3 3	1.9497	-0.007	0.0005
67	48.05	9	3 5 3	1.8934	0.005	-0.0005
			7 1 2	1.8934	0.000	0.0000
68	48.60	10	5 0 4	1.8733	0.008	-0.0006
			2 1 5	1.8733	-0.001	0.0001

FIGURES OF MERIT TYPE:

F 68 = 72.7 (0.006, 170) (G.S. Smith and R.L. Snyder)

M 20 = 91 (P.M. de Wolff)

UNIT CELL DATA:

Crystal structure and cell definition from X. Solans, M. Font-Altaba, J. Oliva and J. Herrera. Acta Cryst. C39(1983)435-438.

Four circle diffractometer unit cell determined by centring and refining orientation matrix and unit cell parameters by least squares.

AFFMAIL, Steward program, Laboratoire de Cristallographie, Université de Bordeaux, modified by Comberton (1970), Filhol (1972,1978) and Rodriguez-Carvajal (1982), for orientation and refining X-ray powder diffraction by least squares.

Crystal system: Orthorhombic. Space group: Pn21a. Z: 4

a	14.5465 (0.0014)	14.499 (0.004)	0.0475
b	13.2434 (0.0014)	13.250 (0.004)	-0.0066
c	9.7988 (0.0010)	9.765 (0.003)	0.0338

a/b = 1.0984 | a/b = 1.0943
c/b = 0.7399 | c/b = 0.7370

Vp = 1887.691 Vs = 1875.971 Dcal = 1.77 Mgm-3 Wt = 510.1

F(000) = 1046 R = 0.056 Rw = 0.060

3 . ((H2O)4.Mn(C10H12N2O8Cu))n.2n(H2O).

X-ray radiation: CuKα 1.54178 Å. Correction factor: -.01

Nº	2θexp	I/Io	H K L	d exp	dif 2θ	dif d
1	10.79	10	1 0 1	8.1991	0.021	-0.0377
2	11.20	7	0 1 1	7.8998	0.008	-0.0246
3	12.12	7	2 0 0	7.3022	0.004	-0.0093
4	12.73	7	1 1 1	6.9536	0.008	-0.0135
5	13.56	48	0 2 0	6.5298	-0.003	-0.0009
6	13.90	21	2 1 0	6.3708	0.006	-0.0091
7	15.06	14	2 0 1	5.8826	0.013	-0.0131
8	16.51	100	2 1 1	5.3691	0.003	-0.0045
9	17.34	7	1 2 1	5.1139	0.002	-0.0035
10	17.81	16	0 0 2	4.9800	0.004	-0.0043
11	18.24	2	2 2 0	4.8636	0.009	-0.0070
12	18.82	10	1 0 2	4.7150	0.002	-0.0028
13	20.02	11	1 1 2	4.4350	0.001	-0.0022
14	20.31	2	2 2 1	4.3723	0.004	-0.0039
15	21.59	14	2 0 2	4.1159	0.002	-0.0025
16	22.43	17	0 2 2	3.9636	-0.008	0.0014
17	23.12	5	1 3 1	3.8469	0.003	-0.0023
18	23.27	4	1 2 2	3.8224	0.003	-0.0019
19	23.80	5	2 3 0	3.7385	-0.002	-0.0023
20	24.47	8	3 2 1	3.6376	-0.006	0.0006
21	25.44	6	2 3 1	3.5011	0.000	-0.0012
22	25.57	10	3 0 2	3.4836	0.001	-0.0013
			2 2 2	3.4836	-0.004	-0.0000
23	25.95	8	4 0 1	3.4334	-0.009	0.0012
24	26.86	18	4 1 1	3.3191	-0.002	-0.0004
25	27.29	6	0 4 0	3.2678	0.015	0.0024
26	27.73	8	0 1 3	3.2169	0.011	-0.0034
27	27.87	4	1 3 2	3.2011	-0.006	0.0015
28	29.03	3	3 2 2	3.0758	-0.001	0.0012
29	29.41	11	4 2 1	3.0369	0.002	-0.0013
30	29.45	10	1 4 1	3.0329	0.009	-0.0026
31	29.55	6	2 0 3	3.0228	0.007	-0.0023
32	29.87	7	2 3 2	2.9912	0.000	-0.0007
33	30.33	17	4 0 2	2.9468	0.001	-0.0011
			2 1 3	2.9468	-0.003	-0.0003
34	30.82	6	1 2 3	2.9011	0.004	-0.0015
35	31.10	15	4 1 2	2.8756	-0.005	0.0001
36	31.31	10	2 4 1	2.8568	-0.006	0.0003
37	32.64	22	2 2 3	2.7434	0.005	-0.0015
			5 1 1	2.7434	-0.002	-0.0003

X-ray radiation: CuKα 1.54178 Å. Correction factor: -.01

Nº	2θexp	I/Io	H	K	L	d exp	dif 2θ	dif d
38	32.93	6	3	3	2	2.7199	-0.009	-0.0008
39	33.25	30	4	3	1	2.6944	-0.003	-0.0010
40	33.34	32	3	1	3	2.6873	-0.007	0.0004
41	33.94	3	0	3	3	2.6412	-0.004	-0.0003
42	35.54	3	0	5	1	2.5259	0.003	-0.0011
43	35.61	3	5	0	2	2.5211	0.005	-0.0013
44	36.17	8	2	3	3	2.4833	0.003	-0.0010
45	36.26	11	5	1	2	2.4774	-0.009	0.0007
46	36.57	3	2	5	0	2.4571	0.003	-0.0029
47	36.60	6	1	0	4	2.4551	0.008	-0.0016
48	36.83	8	4	3	2	2.4403	0.001	-0.0007
49	36.87	6	6	0	0	2.4378	-0.009	0.0006
50	36.92	3	4	4	0	2.4346	0.002	-0.0007
51	37.24	8	1	1	4	2.4144	-0.004	-0.0000
52	37.56	12	6	1	0	2.3945	0.006	-0.0013
53	37.68	12	2	5	1	2.3872	0.006	-0.0011
54	38.02	13	6	0	1	2.3666	0.001	-0.0008
55	38.04	11	4	4	1	2.3654	-0.002	-0.0004
56	38.13	10	5	3	1	2.3601	0.000	0.0013
57	38.27	4	5	2	2	2.3517	0.007	-0.0013
58	38.67	8	0	2	4	2.3283	-0.004	-0.0001
59	38.79	8	3	3	3	2.3214	0.004	-0.0010
60	39.16	11	4	2	3	2.3003	0.003	-0.0009
			1	4	3	2.3003	0.003	0.0003
61	39.20	11	1	2	4	2.2981	0.008	-0.0013
62	39.45	8	6	2	0	2.2841	-0.006	0.0008
63	40.22	3	3	5	1	2.2421	0.007	-0.0013
64	40.64	5	2	4	3	2.2199	-0.006	0.0007
			3	0	4	2.2199	-0.008	0.0007
65	41.15	9	5	0	3	2.1936	0.004	-0.0018
66	41.24	14	6	0	2	2.1890	0.000	-0.0004
67	41.47	5	0	6	0	2.1774	-0.009	0.0005
68	41.74	6	5	1	3	2.1639	0.007	-0.0011
69	41.84	6	6	1	2	2.1590	0.001	-0.0003
70	42.22	5	1	3	2	2.1404	-0.003	0.0008
71	42.49	8	5	4	1	2.1274	0.009	-0.0009
72	42.56	6	4	5	0	2.1241	0.010	-0.0013
73	42.98	4	1	6	1	2.1043	-0.001	-0.0003
74	43.52	17	6	3	1	2.0794	0.008	-0.0004
75	43.61	10	6	2	2	2.0754	-0.003	-0.0005
76	43.65	10	2	4	3	2.0736	0.001	-0.0004
77	43.97	5	4	0	4	2.0592	-0.004	-0.0000
78	44.11	3	0	5	3	2.0530	0.002	-0.0007
79	44.40	6	2	6	1	2.0403	0.011	-0.0018
80	44.56	3	1	5	2	2.0333	0.000	-0.0004
81	45.44	7	5	4	2	1.9959	-0.002	-0.0003
82	45.47	14	0	6	2	1.9947	-0.001	-0.0002
83	45.87	14	0	4	4	1.9782	0.001	-0.0029
84	45.91	9	2	5	2	1.9766	0.003	-0.0005
			1	6	2	1.9766	-0.004	0.0000
85	46.21	10	6	0	3	1.9645	0.004	-0.0320
86	46.24	11	1	4	4	1.9633	-0.007	0.0001
87	46.35	11	5	3	3	1.9589	0.002	-0.0014

X-ray radiation: CuKα 1.54178 Å. Correction factor: -.01

Nº	2θexp	I/Io	H K L	d exp	dif 2θ	dif d
88	46.44	9	6 3 2	1.9553	0.004	-0.0007
89	47.18	3	7 0 2	1.9263	0.001	-0.0003
90	47.24	3	2 6 2	1.9240	0.003	-0.0006
91	47.71	5	7 1 2	1.9061	-0.007	0.0001
92	47.94	11	5 0 4	1.8975	0.002	0.0006
93	48.09	14	3 5 3	1.8920	0.003	-0.0005
94	49.91	12	8 0 0	1.8272	0.006	-0.0007
			3 1 5	1.8272	-0.004	-0.0000
95	50.11	18	5 4 3	1.8203	-0.006	-0.0016
96	50.18	8	6 4 2	1.8180	-0.002	-0.0005

FIGURES OF MERIT TYPE:

F 96 = 105.9 (0.005, 181) (G.S. Smith and R.L. Snyder)

M 20 = 37 (P.M. de Wolff)

UNIT CELL DATA:

Crystal structure and cell definition from X. Solans, M. Font-Altaba, J. Oliva and J. Herrera. Acta Cryst. C39(1983)435-438.

Four circle diffractometer unit cell determined by centring and refini ng orientation matrix and unit cell parameters by least squares.

AFFMAIL, Steward program, Laboratoire de Cristallographie, Université de Bordeaux, modified by Comberton (1970), Filhol (1972,1978) and Rodr iguez-Carvajal (1982), for orientation and refining X-ray powder diffr action by least squares.

Crystal system: Orthorhombic. Space group: Pn21a. Z: 4

a	14.6230 (0.0011)	14.626 (0.003)	-0.0030
b	13.0614 (0.0010)	13.068 (0.004)	-0.0066
c	9.9687 (0.0008)	9.969 (0.003)	-0.0003
	a/b = 1.1196	a/b = 1.1192	
	c/b = 0.7632	c/b = 0.7629	

Vp = 1903.991 Vs = 1905.401 Dcal = 1.79 Mgm-3 Wt = 514.8

F(000) = 1056 R = 0.044 Rw = 0.047

4 . ((H2O)4.Mn(C10H12N2O8Zn))n.2n(H2O).

X-ray radiation: CuKα 1.54178 Å. Correction factor: .02

Nº	2θexp	I/Io	H K L	d exp	dif 2θ	dif d
1	10.89	19	1 0 1	8.1240	0.003	-0.0367
2	11.24	13	0 1 1	7.8718	0.006	-0.0386

X-ray radiation: CuKα 1.54178 Å. Correction factor: .02

Nº	2θexp	I/Io	H	K	L	d exp	dif 2θ	dif d
3	12.19	4	2	0	0	7.2604	0.010	-0.0371
4	12.79	9	1	1	1	6.9211	0.010	-0.0335
5	13.38	73	0	2	0	6.6172	0.008	-0.0289
6	13.90	40	2	1	0	6.3708	0.007	-0.0261
7	15.17	21	2	0	1	5.8402	0.007	-0.0220
8	16.58	100	2	1	1	5.3466	0.006	-0.0171
9	17.25	14	1	2	1	5.1404	0.001	0.0071
10	18.06	27	0	0	2	4.9116	-0.003	-0.0100
11	19.07	16	1	0	2	4.6537	-0.001	-0.0099
12	20.23	16	1	1	2	4.3894	0.005	-0.0112
			2	2	1	4.3894	-0.005	-0.0070
13	21.83	27	2	0	2	4.0712	0.004	-0.0092
14	22.53	13	0	2	2	3.9463	0.005	-0.0089
15	22.88	13	1	3	1	3.8867	0.000	-0.0071
16	23.34	7	1	2	2	3.8111	0.000	-0.0064
17	23.54	7	2	3	0	3.7792	0.004	-0.0081
18	24.46	10	4	0	0	3.6391	0.012	-0.0097
			3	2	1	3.6391	0.004	-0.0073
19	25.25	6	2	3	1	3.5270	0.007	-0.0077
20	25.67	17	2	2	2	3.4702	0.005	-0.0071
21	26.09	6	4	0	1	3.4153	0.002	-0.0060
22	26.86	20	0	4	0	3.3191	-0.005	-0.0039
23	26.94	30	4	1	1	3.3094	-0.005	-0.0039
24	27.83	9	1	3	2	3.2056	0.008	-0.0066
25	28.07	13	0	1	3	3.1787	0.009	-0.0068
26	29.08	17	1	4	1	3.0706	0.013	-0.0071
27	29.12	17	3	2	2	3.0665	-0.009	-0.0025
28	29.42	9	4	2	1	3.0359	0.009	-0.0060
29	29.82	16	2	3	2	2.9961	0.006	-0.0054
30	29.90	16	2	0	3	2.9882	0.001	-0.0043
31	30.67	39	2	1	3	2.9149	0.003	-0.0045
32	30.99	30	2	4	1	2.8856	0.008	-0.0053
33	31.05	39	1	2	3	2.8801	0.001	-0.0040
34	31.30	43	4	1	2	2.8577	0.005	-0.0046
35	32.74	37	5	1	1	2.7352	-0.001	-0.0033
36	32.86	43	2	2	3	2.7255	-0.002	-0.0032
37	33.13	41	4	3	1	2.7039	0.004	-0.0040
			1	4	2	2.7039	-0.006	-0.0024
38	33.64	97	3	1	3	2.6641	-0.005	-0.0009
39	34.03	14	0	3	3	2.6344	-0.005	-0.0024
40	34.62	10	1	3	3	2.5909	0.006	-0.0039
41	34.83	20	5	2	1	2.5757	0.003	-0.0035
42	34.86	20	2	4	2	2.5736	0.000	-0.0031
43	35.80	11	5	0	2	2.5081	-0.003	-0.0025
44	36.00	11	2	5	0	2.4947	0.003	-0.0032
45	36.27	10	2	3	3	2.4767	0.003	-0.0032
46	36.46	29	5	1	2	2.4642	0.000	-0.0028
47	36.59	14	4	4	0	2.4558	-0.013	-0.0010
48	36.81	20	4	3	2	2.4416	0.002	-0.0030
49	36.87	16	4	0	3	2.4378	-0.006	-0.0019
50	37.00	26	6	0	0	2.4295	0.003	-0.0030
51	37.17	37	2	5	1	2.4188	-0.003	0.0260
52	37.72	37	1	1	4	2.3848	-0.002	-0.0023

X-ray radiation: CuKα 1.54178 Å. Correction factor: .02

Nº	2θexp	I/Io	H	K	L	d exp	dif 2θ	dif d
53	37.77	33	4	4	1	2.3817	-0.005	-0.0018
54	38.08	19	5	3	1	2.3630	0.000	-0.0205
55	38.35	14	5	2	2	2.3470	-0.007	-0.0017
56	38.87	39	3	3	3	2.3168	-0.009	-0.0014
57	39.48	43	6	2	0	2.2824	-0.004	-0.0019
58	39.57	53	1	2	4	2.2774	-0.004	-0.0020
59	40.59	10	6	2	1	2.2225	0.004	-0.0027
60	40.78	17	0	6	0	2.2126	0.005	-0.0028
61	41.09	6	4	4	2	2.1966	-0.006	-0.0016
62	41.37	54	5	3	2	2.1824	0.003	-0.0019
63	41.44	59	5	0	3	2.1789	-0.001	-0.0020
			6	0	2	2.1789	-0.003	-0.0018
64	42.08	24	4	5	0	2.1472	-0.007	-0.0014
65	42.42	24	6	3	0	2.1308	-0.005	-0.0015
66	42.51	24	1	3	4	2.1265	-0.002	-0.0018
67	43.12	10	4	5	1	2.0978	-0.006	-0.0014
68	43.43	28	3	2	4	2.0835	-0.005	-0.0015
69	43.46	30	6	3	1	2.0822	-0.002	-0.0018
70	43.72	56	2	6	1	2.0704	0.000	-0.0019
			6	2	2	2.0704	-0.003	-0.0016
			5	2	3	2.0704	-0.002	-0.0018
71	43.86	30	0	5	3	2.0641	-0.005	-0.0014
72	44.34	14	1	5	3	2.0429	0.005	-0.0023
73	44.44	14	4	0	4	2.0385	-0.002	-0.0017
			7	0	1	2.0385	-0.007	-0.0013
74	44.91	19	0	6	2	2.0183	0.001	-0.0018
75	45.31	23	5	4	2	2.0014	0.000	-0.0018
76	45.35	23	1	6	2	1.9997	-0.005	-0.0014
77	45.64	7	7	2	0	1.9877	0.000	-0.0017
78	46.14	16	4	5	2	1.9673	-0.002	-0.0019
79	46.32	50	6	4	0	1.9601	0.013	-0.0027
80	46.69	11	0	1	5	1.9454	0.004	-0.0020
81	47.88	50	3	5	3	1.8998	-0.001	-0.0015
82	47.90	49	7	1	2	1.8990	-0.007	-0.0011
83	48.42	21	5	0	4	1.8798	0.001	-0.0016
84	48.62	16	6	2	3	1.8726	0.008	-0.0021
85	48.89	13	0	7	1	1.8629	0.002	-0.0016
86	49.01	19	4	6	1	1.8586	-0.008	-0.0010
87	50.04	21	8	0	0	1.8227	0.003	-0.0017
88	50.07	21	5	4	3	1.8217	0.002	-0.0016
89	50.07	21	6	4	2	1.8217	0.000	-0.0015
90	50.52	51	3	1	5	1.8065	0.000	-0.0014

FIGURES OF MERIT TYPE:

F 90 = 105.6 (0.005, 180) (G.S. Smith and R.L. Snyder)

M 20 = 12 (P.M. de Wolff)

UNIT CELL DATA:

Crystal structure and cell definition from X. Solans, M. Font-Altaba, J. Oliva and J. Herrera. Acta Cryst. C39(1983)435-438.

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Four circle diffractometer unit cell determined by centring and refini
ng orientation matrix and unit cell parameters by least squares.

AFFMAIL, Steward program, Laboratoire de Cristallographie, Université
de Bordeaux, modified by Comberton (1970), Filhol (1972,1978) and Rodr
iguez-Carvajal (1982), for orientation and refining X-ray powder diffr
action by least squares.

Crystal system: Orthorhombic.   Space group: Pn21a.   Z:  4

a   14.5951 (0.0009)  |  14.594 (0.004)  |   0.0011
b   13.2922 (0.0010)  |  13.294 (0.004)  |  -0.0018
c    9.8432 (0.0008)  |   9.841 (0.003)  |   0.0022

   a/b = 1.0980       |   a/b = 1.0978
   c/b = 0.7405       |   c/b = 0.7403

Vp = 1909.591    Vs = 1909.278    Dcal = 1.80 Mgm-3   Wt = 516.6

F(000) = 1060   R = 0.054   Rw = 0.057
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ABSTRACT.

Crystal morphology and X-ray powder diffraction data of four Mn-ethylenediaminetetraacetate with hexacoordinated metal ions (Co, Ni, Cu and Zn) have been studied. All of then are orthorhombic hemimorphic, mm2, and with similar crystallization, except the Mn-Cu complexes that have the faces {201} instead of those {021} found in the others. Circle angles and axial ratio are given with a stereographic projection.

Crystal structures have been determined by Solans et al. (1983). Calculated powder diagrams were used to index the experimental ones; the unit cell parameters were refined by the least square method using the Affmail program, and found to be similar to those of the single crystals. Authors reporting the crystal structure give $Pn2_1a$, instead of the equivalent standard one, $Pna2_1$ as space group; in order to avoid differences, we also used the $Pn2_1a$ space group. These four complexes are isostructural, but not isomorphic.

Compounds were obtained from the saturation of ethylenediaminetetraacetic acid by metal carbonates, taking into acount the special conditions of pH and rate of saturation in order to avoid possible carbonatations. Samples were analyzed following mineralization and by absorption atomic spectroscopy.

The unit cell parameters from single crystals and from X-ray powder diffraction are shown on table 2, with the differences which are near to be equal at the standard deviations, except for the Mn-Ni compound which are much larger.

The diagrams of the X-ray powder diffraction, with 2θ and d experimentals, I/I_0, and the differences between experimental and calculated values are shown at the end of each compound, jointly with figures of merit, unit cell parameters and symmetry.

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