Synthesis and Crystal Structure of $MCu(edta)\cdot 4H_2O$: Molecular Precursors for $MCuO_2$ (M = Ca, Sr, Ba)

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The compounds $MCu(edta)\cdot 4H_2O$ (edta = ethylenediaminetetraacetic acid; M = Ca, Sr, Ba) have been synthesized and characterized by analytical and spectroscopic techniques. The structures of the strontium and barium complexes have been determined by X-ray diffraction methods. Both compounds are isostructural and crystallize in the monoclinic system, space group $P2_1/c$, with four formula weights in a cell measuring $a = 8.717(1)$, $b = 10.568(3)$, $c = 19.374(3)$ Å, $\beta = 100.39(1)°$ for $[SrCu(edta)(H_2O)_3]\cdot H_2O$ and $a = 8.818(1)$, $b = 10.200(2)$, $c = 19.737(2)$ Å, $\beta = 102.40(1)°$ for $[BaCu(edta)(H_2O)_3]\cdot H_2O$. The structures were refined to $R = 0.046$ ($R_w = 0.051$) and $R = 0.034$ ($R_w = 0.037$) for strontium and barium compounds, respectively. The geometry of the complexes consists of an intricate network of ligand-bridged coordination polyhedra, where the arrangement of the copper(II) ion exhibits a distorted octahedral topology. The geometry of the alkaline-earth metal cations is near to the bicapped trigonal prism, being bound to three water molecules and to five oxygen atoms from different edta molecules. In comparison with the structural results of the $[CaCu(edta)(H_2O)_2]\cdot 2H_2O$, a change in the coordination polyhedron of calcium ion has been established. Thermal treatment of the complexes using TGA involves three consecutive steps: dehydration, ligand pyrolysis and the formation of inorganic residue. Taking these results into account, further thermal treatments have been performed in order to obtain $MCuO_2$ phases (M = Ba, Sr, Ca).

Introduction

As the existence of the copper oxide plane structure plays an important role in mechanisms of high-T_c superconductivity,[1] a study of the different properties in ternary copper–oxygen systems is important even on materials which show no superconductivity.[2] Among a large number of ternary copper–oxygen systems, the $MCuO_2$ (M = Ba, Sr, Ca) compounds have very interesting structures. These oxides are traditionally prepared by the ceramic method which does not always yield single-phase products of the required stoichiometry. Taking into account the alternative strategies that can be used to improve the final products, metalloorganic precursors hold much promise.[3,4] This method not only allows mixing of the different metal species on an atomic scale but also reduces the diffusion distance to ~10 Å. Thus, suitable precursors would result in significant modifications in the microstructure of the final products.

The aminocarboxylates have been long known and studied as binding agents, not only with respect to practical applications but also as classic research models for polydentate chelation.[5] Accordingly, ethylenediaminetetraacetate (edta) may be considered an adequate ligand to complex two divalent cations in the aim of obtaining precursors of mixed oxides. In this way, the complexes with formula $MCu(edta)\cdot 4H_2O$ (M = Ca, Sr, and Ba) have been prepared and characterized by spectroscopic techniques. Two of them, the derivatives of strontium and barium, have been obtained as pale blue crystals, and their structures are reported in the present work. As the structure of the compound, $[CaCu(edta)(H_2O)_2]\cdot 2H_2O$, was previously described,[6] our results have been compared in some detail with those obtained from this resolution.

In addition, the present study shows the usefulness of these compounds for the clean and soft synthesis of pure $MCuO_2$ (M = Ca, Sr, and Ba) oxides. For this purpose the decomposition of $MCu(edta)\cdot 4H_2O$ has been extensively studied by TGA. In consideration of these data, the complexes were heated at different temperatures to get the respective oxides.

Experimental Section

Synthesis and Characterization of the Compounds. An aqueous solution of $Cu(edta)Na_2$ (1 mmol, Aldrich Chemical Co.) was added to solutions of $MCl_2\cdot nH_2O$ (1 mmol, M = Ca, Sr, Ba) in hot water and the mixture stirred for 1 h. After 2 days, blue crystalline compounds were obtained, they were filtered off and washed with ether. Recrystallization from water/ethanol (1:1) mixture yielded rhombohedric and needle-like crystals, for the strontium and barium compounds, respectively. Elemental analysis of the compounds together with the percentage of dehydration are shown in Table 1. The powder patterns fit well with unique phases, so physical properties have been performed. For $[CaCu(edta)(H_2O)_2]\cdot 2H_2O$ the diffraction peaks were indexed with the unit-cell parameters and space group from the literature.[6]

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Table 1. Elemental and Copper Analyses together with Thermal Analysis Data for the Dehydration Steps for $MCu(edta)\cdot4H_2O$ Compounds (M = Ca, Sr, and Ba)

	found (calcd) (%)						
compound	C	H	N	Cu	T^a range (°C)	wt loss (%)	activation energy (kJ mol^{-1})
$CaCu(edta)\cdot4H_2O$	25.8 (25.9)	4.2 (4.4)	6.0 (6.1)	13.5 (13.7)	43–97	16.1 (15.53)	318.6
$SrCu(edta)\cdot4H_2O$	23.1 (23.5)	3.3 (3.9)	5.4 (5.8)	12.4 (12.1)	35–70	14.8 (14.07)	448.2
$BaCu(edta)\cdot4H_2O$	21.6 (21.4)	3.1 (3.6)	5.1 (5.0)	11.4 (11.3)	35–85	13.7 (14.42)	351.2

Table 2. Data Collection and Structure Refinement of $[MCu(edta)(H_2O)_3]\cdot H_2O$ (M = Sr and Ba)

formula	$C_{10}N_2O_{12}H_{20}SrCu$	$C_{10}N_2O_{12}H_{20}BaCu$
dimensions/mm	0.9 × 1.1 × 0.2	0.1 × 0.1 × 1.0
formula wt	511.4	561.16
system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	8.717(1)	8.818(1)
b/Å	10.568(3)	10.200(2)
c/Å	19.374(3)	19.737(2)
β/deg	100.39(1)	102.40(1)
V/Å^3	1755.5(6)	1733.8(4)
Z	4	4
D_m/g cm^{-3}	1.99(5)	2.13(4)
D_c/g cm^{-3}	1.935	2.149
μ (Mo Kα) cm^{-1}	42.24	35.51
F(000)	1028	1100
measurements		
λ (Mo Kα)/Å	0.7107	0.7107
scan type	$\omega/2\theta$	$\omega/2\theta$
θ Range/deg	1–30	1–30
check reflns	1-4-6, -2-29, -2-3-1, -1-3-3	-136, 42-5, -320, 32-7
no. of measd reflns	5102	5039
interval h, k, l	12, 14, ±27	12, 14, ±27
refinements		
no. of variables	281	273
selection criterion	$I \geq 3\sigma(I)$	$I \geq 2.5\sigma(I)$
no. of unique reflns	3002	3688
weighting scheme		
$w = 1/[\sigma^2\lvert F_o\rvert + p\lvert F_o\rvert^2]$	$p = 0.005\,056$	$p = 0.001\,884$
$R = (\sum\lVert F_o\rvert - \lvert F_c\rVert)/(\sum\lvert F_o\rvert)$	0.046	0.034
$wR = [\sum_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum_w\lvert F_o\rvert^2]^{1/2}$	0.051	0.037

X-ray Diffraction Study. Preliminary oscillation and Weissenberg photographs for the strontium (named SrCu) and barium (named BaCu) compounds showed monoclinic symmetry with space group $P2_1/c$. Well-formed prismatic crystals with dimensions 0.9 × 1.1 × 0.2 mm and 0.1 × 0.1 × 1.0 mm for SrCu and BaCu, respectively were mounted on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Unit-cell dimensions were determined from 25 reflections ($6 < \theta < 12°$). Crystal data are shown in Table 2. Lorentz and polarization corrections were applied to all reflections. Scattering factors were taken from the International Tables of X-ray Crystallography.[7] In each case, the metal atoms were located through Patterson methods.[8] A Fourier map, calculated with phases based on these ions, revealed the non-hydrogen atoms of the complexes.[9] Empirical absorption correction was applied using the program DIFABS.[10] Several cycles of anisotropic refinement were carried out. H atoms were located by difference electron density maps and refined with common overall isotropic thermal parameters and restricted distances (1.01 Å) to the bonded carbon atoms.

The final R factors were $R = 0.046$, $R_w = 0.051$ for $[SrCu(edta)(H_2O)_3]\cdot H_2O$ and $R = 0.034$ $R_w = 0.037$ for $[BaCu(edta)(H_2O)_3]\cdot H_2O$. The maximum peaks in the final DF maps were 0.978 and 2.10 e Å^{-3}, respectively. The geometric calculations were performed with PARST[11] and BONDLA;[12] molecular illustrations were drawn with ORTEP.[13] Further details are presented as supplementary data (see paragraph at end of paper) together with thermal parameters, bond lengths, and angles, mean average planes, and structure factors.

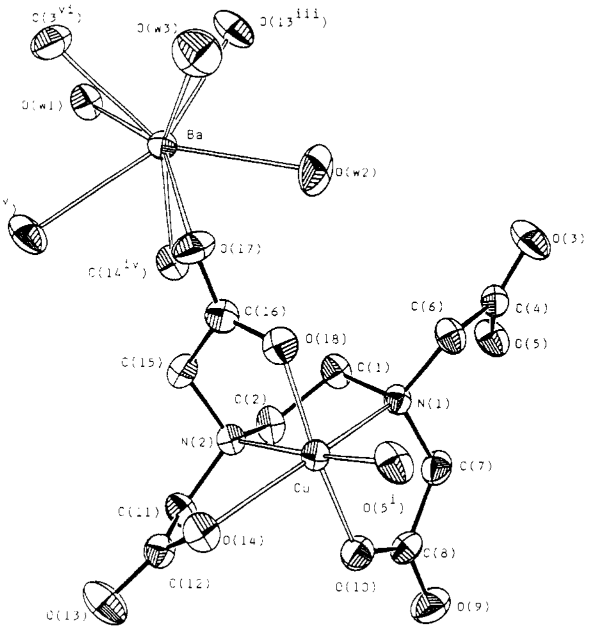

Figure 1. View of the $[BaCu(edta)(H_2O)_3]\cdot H_2O$ molecule with atom numbering (ORTEP II, Johnson, 1976).

Physical Measurements. TGA measurements were carried out with Perkin-Elmer System-7 DSC-TGA and SETARAM TAG 24 S 16 units. Crucibles containing 20 mg were heated at 2 °C min^{-1} under nitrogen and air atmospheres. The obtained products were examined by X-ray powder diffraction with a STOE diffractometer, equipped with a germanium monochromator, at temperature of 293 ± 1 K. Infrared spectra were obtained using KBr disks (2%) on a Perkin-Elmer 1430 spectrophotometer. A Bruker ESP 300 spectrometer, operating at the X- and Q-bands, was used to record the ESR powdered spectra. The temperature was stabilized by an Oxford Instrument (ITC4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter, and the frequency inside the cavity was determined by the signal of the DPPH radical. Scanning electron microscopic (SEM) observations were also carried out to give some indication of the oxide compactness; for that purpose a Philips 501B equipment was used.

Results and Discussion

Description of the Structure. A perspective drawing of $[BaCu(edta)(H_2O)_3]\cdot H_2O$ compound, as well as the labeling of the atoms, is shown in Figure 1. Atomic coordinates and some selected bond distances and angles are given in Tables 3 and 4, together with those for the $[CaCu(edta)(H_2O)_2]\cdot2H_2O$ complex. The relative arrangement of anions and cations in the structure is

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Table 3. Fractional Atomic Coordinates (×10⁴ for Sr and Ba and ×10⁵ for Cu) and Equivalent Isotropic Temperature Factors (Å²) for Non-Hydrogen Atoms with Esd's in Parentheses for [MCu(edta)(H₂O)₃]·H₂O [M = Ba, Sr (Italics)]

atom	*x*	*y*	*z*	B_{eq}[a]
Ba	34342(3)	18965(2)	3226(1)	2.33(1)
Sr	*32856*(6)	*15100*(5)	*4967*(2)	*2.58*(*1*)
Cu	76377(5)	43382(4)	29623(2)	1.99(1)
Cu	*7683*(*7*)	*37093*(5)	*30664*(3)	*2.38*(*1*)
N(1)	9183(4)	2630(3)	2574(2)	2.10(6)
N(*1*)	*9358*(5)	*2023*(4)	*2751*(2)	*2.52*(9)
N(2)	6095(4)	2819(3)	2938(2)	2.02(6)
N(2)	*6353*(6)	*2251*(4)	*3256*(3)	*3.4*(*1*)
O(3)	11179(5)	2050(4)	1149(2)	4.2(1)
O(3)	*11012*(5)	*1304*(4)	*1185*(2)	*3.13*(9)
O(5)	11089(4)	853(3)	2090(2)	3.23(8)
O(5)	*11224*(4)	*229*(3)	*2197*(2)	*2.81*(8)
O(9)	10798(4)	2441(4)	4425(2)	3.66(9)
O(9)	*11220*(5)	*2452*(4)	*4562*(2)	*3.8*(*1*)
O(10)	8939(4)	3709(3)	3847(1)	2.74(7)
O(*10*)	*9156*(5)	*3405*(3)	*3953*(2)	*3.14*(9)
O(13)	4348(5)	4324(3)	4241(2)	4.2(1)
O(*13*)	*4320*(*7*)	*3948*(5)	*4382*(3)	*6.3*(2)
O(14)	5791(4)	5145(3)	3560(2)	2.90(8)
O(*14*)	*5905*(4)	*4570*(3)	*3681*(2)	*3.3*(*1*)
O(17)	4466(4)	4004(4)	1206(2)	3.37(8)
O(*17*)	*4018*(6)	*2978*(5)	*1577*(3)	*4.8*(*1*)
O(18)	6474(4)	4698(3)	2007(2)	2.70(7)
O(*18*)	*6220*(5)	*3790*(4)	*2177*(2)	*3.4*(*1*)
O(w1)	1622(4)	−416(4)	−81(2)	3.47(8)
O(*w1*)	*1640*(4)	*−464*(4)	*−93*(2)	*3.03*(9)
O(w2)	6561(4)	2323(4)	536(2)	5.0(1)
O(*w2*)	*6286*(6)	*1723*(6)	*844*(3)	*6.2*(2)
O(w3)	3680(6)	4266(4)	−459(2)	5.1(1)
O(*w3*)	*3860*(9)	*3910*(6)	*225*(4)	*7.7*(2)
O(w4)	8934(18)	4063(1)	296(8)	23.7(8)
O(*w4*)*A*	*7009*(9)	*4481*(*7*)	*913*(3)	*5.3*(2)
O(*w4*)*B*	*−48*(*21*)	*958*(*16*)	*5612*(8)	*5.2*(5)
C(1)	7961(5)	1629(4)	2375(2)	2.60(9)
C(*1*)	*8319*(8)	*928*(6)	*2758*(4)	*4.3*(2)
C(2)	6907(5)	1560(4)	2883(2)	2.47(9)
C(2)	*7360*(8)	*1000*(5)	*3325*(4)	*3.9*(2)
C(4)	10787(5)	1857(4)	1712(2)	2.43(8)
C(4)	*10774*(6)	*1159*(5)	*1797*(3)	*2.4*(*1*)
C(6)	9880(5)	2956(4)	1984(2)	2.62(9)
C(6)	*9845*(6)	*2200*(5)	*2078*(3)	*2.7*(*1*)
C(7)	10320(5)	2296(5)	3207(2)	2.94(9)
C(*7*)	*10659*(*7*)	*2014*(6)	*3349*(3)	*3.6*(*1*)
C(8)	9996(5)	2848(4)	3876(2)	2.51(9)
C(8)	*10316*(6)	*2671*(4)	*4006*(3)	*2.6*(*1*)
C(11)	5447(5)	2828(4)	3571(2)	2.53(9)
C(*11*)	*5760*(8)	*2368*(5)	*3927*(3)	*3.9*(2)
C(12)	5145(5)	4214(4)	3804(2)	2.38(9)
C(*12*)	*5263*(6)	*3739*(5)	*3990*(3)	*3.0*(*1*)
C(15)	4831(5)	3040(4)	2315(2)	2.43(8)
C(*15*)	*5032*(*7*)	*2058*(6)	*2658*(3)	*4.0*(*1*)
C(16)	5302(5)	3966(4)	1794(2)	2.51(9)
C(*16*)	*5089*(6)	*3006*(6)	*2087*(3)	*3.5*(*1*)

[a] $B_{eq} = {}^{8}/_{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

determined by a complex three-dimensional network of ligand bridges.

In these structures, the potentially hexadentate ethylenediaminetetraacetate ligand is only acting as pentadentate with the O(5^i) atom of a symmetry-related ligand taking up the sixth position, giving rise to a distorted octahedron around the copper(II) ion [$i = 2-x, {}^1/_2 + y, {}^1/_2 - z$)], with four coplanar bonds (N(2)–O(18)–O(5^i)–O(10)) of nearly equivalent length (Table 4). The copper ion displacement from the mean plane is −0.0311(7) Å for the SrCu and −0.0672(6) Å for the BaCu compounds. The two longer tetragonal bonds are Cu–O(14) 2.305(4) and 2.355(4) Å, Cu–N(1) 2.449(4) and 2.435(3) Å for the SrCu and BaCu complexes, respectively.

Table 4. Some Selected Bond Distances (angstroms) and Angles (degree) with Esd's in Parentheses for [MCu(edta)(H₂O)₃]·H₂O (M = Sr and Ba). Corresponding Data for the Calcium Compound Are Also Given for Comparison[6]

	M		
	Sr	Ba	Ca
Coordination Spheres for Metals			
O(18)–Cu	1.953(4)	1.978(3)	1.971
N(2)–Cu	2.084(5)	2.056(3)	2.076
O(10)–Cu	1.976(4)	1.979(3)	2.008
O(5^i)–Cu	1.981(4)	1.926(3)	1.968
O(14)–Cu	2.305(4)	2.355(4)	2.709
N(1)–Cu	2.449(4)	2.435(3)	2.344
O(3^{vi})–M	2.590(4)	2.834(4)	2.395
O(9^{v})–M	2.559(4)	2.688(3)	2.452
O(17)–M	2.591(5)	2.794(3)	2.413
O(w3)–M	2.656(7)	2.900(4)	2.395
O(14^{iv})–M	2.614(4)	2.806(3)	2.315
O(w1)–M	2.669(4)	2.864(3)	2.133
O(w2)–M	2.590(5)	2.733(4)	
O(13^{iii})–M	2.533(6)	2.737(4)	
$i = (2-x, {}^1/_2+y, {}^1/_2-z)$ $iv = (1-x, y-{}^1/_2, {}^1/_2-z)$ $vi = (x-1, y, z)$	$iii = (x, {}^1/_2-y, z-{}^1/_2)$ $v = (x-1, {}^1/_2-y, z-{}^1/_2)$		
EDTA Molecule			
C(1)–C(2)	1.499(11)	1.509(7)	1.538
C(1)–N(1)	1.471(8)	1.475(5)	1.460
C(2)–N(2)	1.491(7)	1.485(5)	1.477
N(1)–C(6)	1.454(7)	1.466(6)	1.459
N(1)–C(7)	1.468(6)	1.463(5)	1.483
C(7)–C(8)	1.525(8)	1.518(6)	1.506
C(6)–C(4)	1.524(7)	1.539(6)	1.519
N(2)–C(11)	1.502(9)	1.481(6)	1.456
C(11)–C(12)	1.523(8)	1.528(6)	1.499
N(2)–C(15)	1.481(7)	1.489(5)	1.478
C(15)–C(16)	1.500(9)	1.519(6)	1.516
C(1)–N(1)–Cu	100.1(4)	98.8(2)	101.0
C(15)–N(2)–Cu	107.1(4)	106.2(2)	105.3
C(16)–O(18)–Cu	117.2(4)	115.2(3)	116.7
C(12)–O(14)–Cu	111.8(3)	110.3(3)	105.4
C(8)–O(10)–Cu	123.8(3)	122.9(3)	117.5
N(1)–C(1)–C(2)	113.1(5)	112.0(3)	110.7
C(16)–C(15)–N(2)	114.0(5)	112.9(3)	112.5
N(2)–C(11)–C(12)	111.3(5)	112.6(3)	113.6
N(1)–C(7)–C(8)	114.5(5)	115.7(4)	111.6
O(18)–Cu–O(14)	92.6(2)	98.0(1)	106.9

The low octahedron distortions around the copper ion, $\Delta = 0.1$ for SrCu and $\Delta = 0.08$ for BaCu, have been calculated by quantification of the Muetterties and Guggenberger description.[14] These deviations from the ideal geometry are probably due to the perturbations produced by the distortion presented by the EDTA ligand and the Jahn–Teller effect of copper(II) ion. The EDTA is bonded to other symmetry-related metals (Cu or M = Sr, Ba) by O(3), O(5), O(9), O(13), O(14), and O(17), so that they serve as bridges to hold the three-dimensional network. For O(14) three different links have been found, Cu, C(12), and Ba^{ii} which form practically an even plane [$ii = 1-x, {}^1/_2 + y, {}^1/_2 - z$)]. The copper polyhedron in [CaCu(edta)(H₂O)₂]·2H₂O is also a symmetric elongated tetragonal bipyramid, but slightly distorted with axial distances, Cu–O(5) 2.709 Å and Cu–N(1) 2.344 Å.[6]

For the structures of the title compounds, the possibility of a conformation of five-membered chelated rings is reduced to four rings and the three glycinate rings are fused equatorially, G_1 [Cu–N(2)–C(11)–C(12)–O(14)] or axially R_1 [Cu–N(2)–C(15)–C(16)–O(18)] and R_2 [Cu–O(10)–C(8)–C(7)–N(1)] to the central ethylenediamine

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(14) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.*, **1988**, *7*, 1383.

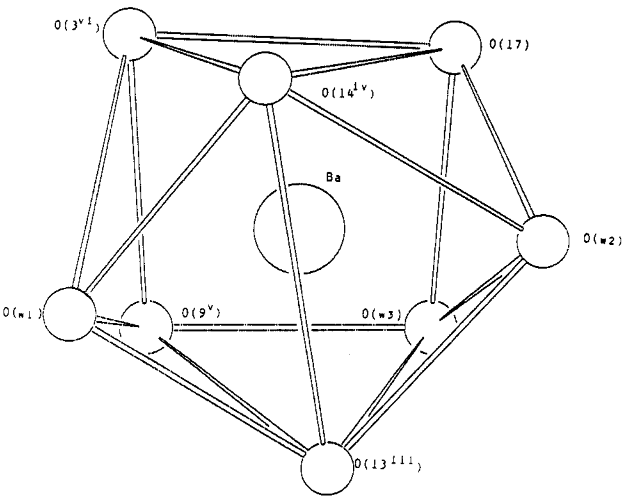

Figure 2. View of the coordination polyhedron for barium with atom numbering (SCHAKAL88, Ketler, 1988).

ring, E [Cu–N(2)–C(2)–C(1)–N(1)]. As in the calcium compound, the orientation of the ligand in both complexes is E, G/R, characteristic of different hexacoordinated complexes with edta.[15–17]

The coordination polyhedra for the alkaline-earth-metal atoms have been analyzed using Muetterties and Guggenberger's description,[14] considering the square antiprism and bicapped trigonal prism configurations as ideal geometries. The topology of the coordination polyhedra is near to the bicapped trigonal prism with the atoms O(w3), O(3^{vi}), O(17), and O(9^{v}) on the same plane (Figure 2) [maximum distances from it are –0.032(7) and –0.007(5) Å for O(w3) and minimum ones –0.010(4) and 0.004(4) for O(3^{vi}) and O(17), for SrCu and BaCu, respectively]. (See supplementary material.) One nonlinked water molecule, O(w4), is present in both compounds. In the strontium one it is unlocalized in two different positions with an occupation factor of 70% and 30%.

In the [CaCu(edta)$(H_2O)_2$]·$2H_2O$ compound, the coordination polyhedron for the calcium ion is a distorted octahedron, as in other complexes with transition-metal cations and this ligand,[18] probably due to a lower atomic radius compared to the strontium and barium ones. Nevertheless, it can be pointed out that the calcium ion in other edta compounds is octacoordinated when it links to the ligand, due to the steric requirements of five-membered chelate rings,[19] which leave vacant sites to be occupied by other oxygen atoms to complete the coordination.

It is important to notice the symmetry observed in the carboxylate groups. The average C–C–O angles are of 117(1)° and 117.5(8)°, while the C–O average bond distance is 1.25(2) and 1.24(2) Å, for the SrCu and BaCu compounds, respectively. These data show that the configuration of the carboxylate groups have not been greatly influenced by the perturbations produced by the different M–O bonds. According to the standard notation described by Porai-Koshits[20] for bridging carboxylates, the classification for the four oxalates is s–2–s C(4), a–2–s C(8), a–3–sa (C12), and a–2–a for C(16).

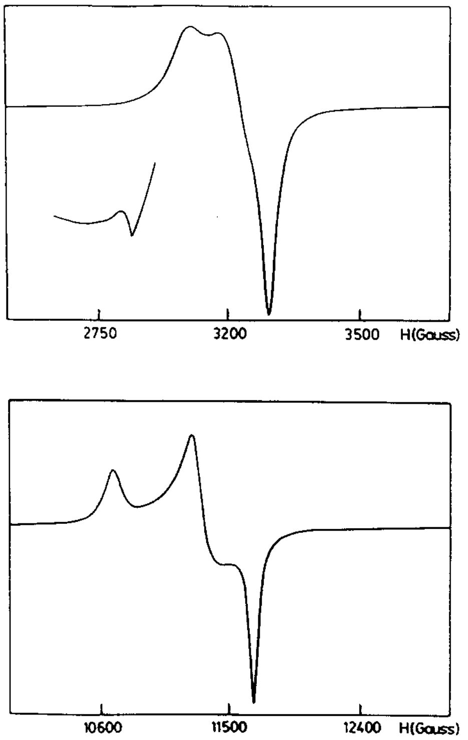

Figure 3. X- and Q-band ESR spectra at 273 K of a powdered sample of [BaCu(edta)$(H_2O)_3$]·H_2O.

IR and ESR Spectroscopies. The interest of the infrared spectra of the compounds lies in the bands due to the C–O group. The spectra of the compounds show important analogies with those obtained from the ethylenediaminetetraacetic acid. The variations observed in the position of a determined number of bands are indicative of the complexation of this ligand.

The broad bands observed in the 3100–3700-cm^{-1} region can be assigned to the stretching vibration of the –OH groups of the water molecules because of the absence of bands corresponding to the δ_{ip}(OH) absorption of the alcohol groups (it appears at 1450 cm^{-1} in the free ligand). A band appearing at 1600 cm^{-1}, due to the stretching vibration of the carbonyl group ν(C=O), together with the absence of absorption around 1700 cm^{-1}, indicates that no $-CO_2H$ groups are present in the complexes, in agreement with the previous structural results and with the literature for these kind of compounds.[21] On the other hand, the splitting of the band at 1110 and 1125 cm^{-1} suggests the coordination of the nitrogen atoms to copper, as can be observed in the crystal structure of the title compounds.

The X-band ESR spectra of the polycrystalline samples show axial-type signals with a slightly orthorhombic component, which remain unchanged from room temperature down to 100 K. To obtain a better resolution of the spectra, new measurements were performed at the Q-band. As no significant differences among the spectra have been established, the spectrum of only one of them, the barium derivative, is shown in Figure 3.

At the Q-band, an orthorhombic resolution for the **g** tensor is observed, because of the splitting of the band

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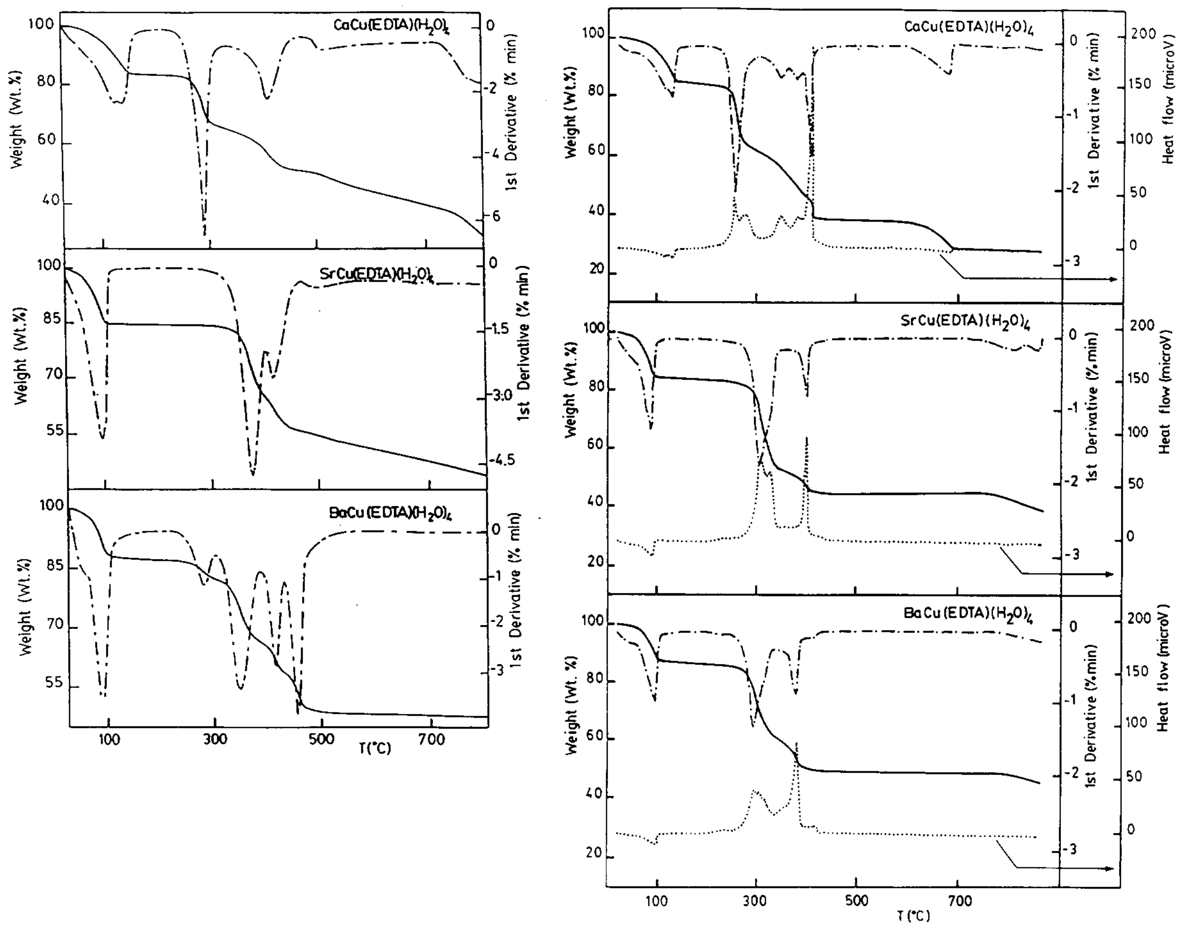

Figure 4. TGA curves of MCu(edta)·4H$_2$O compounds (M = Ca, Sr, and Ba): (a, left) nitrogen; (b, right) air atmosphere.

corresponding to perpendicular directions of the magnetic field. The **g** values for the strontium compound are g_1 = 2.263, g_2 = 2.149, and g_3 = 2.065 and for the barium compound are g_1 = 2.269, g_2 = 2.141, and g_3 = 2.079. In the case of [CaCu(edta)(H$_2$O)$_2$]·2H$_2$O, the spectrum also shows an orthorhombic signal with values g_1 = 2.244, g_2 = 2.148, and g_3 = 2.062. In all cases, the data are in good accord with distorted octahedral geometries for the copper coordination polyhedra.

Note the appearance of weak signals at "half-field" positions in the X-band ESR spectra of the three compounds. These absorptions correspond to the ΔM_s = 2 forbidden transition and could be indicative of possible dipolar interactions between the nearest copper(II) ions. These type of signals have also been observed in other copper compounds with similar distances between the two copper ions.[22]

Thermal Analysis. The decomposition steps of the complexes were obtained from their TG curves (Figure 4), which show the occurrence of three consecutive processes, dehydration, ligand pyrolysis, and inorganic residue formation.

The first process corresponds to the loss of the four water molecules (Table 1), and it seems to take place in only one step for strontium and barium compounds. For the calcium compound, as can be observed in DTA performed in an air atmosphere, two endothermic peaks appear, which may be attributed to the liberation of two hydration and two coordination molecules present in the crystal structure.[6] Dehydration supposes a lowering in the coordination number of the alkaline-earth-metal ion, which could probably result in a rearrangement of the ligand between the two metallic centers. Kinetic analysis of the dehydration curves in nitrogen atmosphere was first performed using Satava's integral method.[23] In the cases in which different kinetic equations of the same process led to similar correlation factors, the Sharp differential method[24] was employed to obtain the best least-squares fit. The function which gave the best fit was random nucleation, Avrami 2 (Table 1).

Decomposition of the anhydrous compounds follows immediately after dehydration in the temperature range 250–400 °C. This process generally involves two overlapping steps, namely, decarboxylation (in one or more stages) and breakdown of the ethylenediamine structure; furthermore, the great diversity of possible products, carbonates, oxides, etc., precludes exhaustive interpretations. The following reaction schemes are the most reasonable to describe the decomposition process:

$$\text{(a)}\quad \mathrm{MM'(EDTA)(s) \rightarrow MCO_3(s) + M'CO_3(s) + R(g)}$$

$$\text{(b)}\quad \mathrm{MM'(EDTA)(s) \rightarrow MO(s) + M'CO_3(s) + R(g)}$$

$$\text{(c)}\quad \mathrm{MM'(EDTA)(s) \rightarrow MO(s) + M'O(s) + R(g)}$$

In the control of these pyrolysis results, the nature of the cation coordinated to the ligand may be the main

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factor.[25] Depending on the stability of the metal carbonates, reactions a, b, or c can occur. In our case, as alkaline-earth-metal carbonates are stable, the ligand pyrolysis can be described by the second reaction, which is in good accord with the theoretical weight losses accompanying the degradation and with X-ray diffraction data.

An understanding of the stage in which the inorganic residue undergoes after ligand pyrolysis is required for a study of the final products. In this step, several differences have been observed in TGA analysis depending on the atmosphere conditions. The experiments performed in air show stable steps over an interval between 400 and 800 °C, for the barium and strontium compounds. They correspond to the presence of MCO_3 and CuO (M = Sr, Ba) which decompose at higher temperatures to form mixed oxides. For calcium compound, the flat baseline is observed until 600 °C, at this temperature $CaCO_3$ and CuO yield $Ca_{1-x}CuO_2$. This compound decomposes into Ca_2CuO_3 and CuO above 750 °C, as demonstrated by the X-ray diffraction pattern of the inorganic residue. However, for decompositions performed in nitrogen atmosphere, the ligand degradation does not seem to finish, as substantial slopes appear in TGA data. So, final products are formed by MCO_3 and CuO (M = Ca, Sr, Ba). In this sense, it can be considered that the air atmosphere favors forming CO and CO_2, and ethylenediamine structure breaks down more rapidly with less intermediate products.

Taking these results into account other experiments in tubular furnaces have been performed in the aim of obtaining pure phases of $MCuO_2$ (M = Ca, Sr and Ba). In this way, all the complexes have been heated first at 400 °C for 10 h to separate the organic part, followed by treatments at 650 °C for 24 h for the calcium compound and 10 h at 800 °C for the strontium and barium compounds. X-ray diffraction patterns of the products were obtained and indexation was performed by LSUCRE[26] or FULLPROF (pattern matching analysis)[27] in the range of 2θ = 10–70°.

The $Ca_{1-x}CuO_2$ oxide was obtained from the decomposition of the $[CaCu(edta)(H_2O)_2]\cdot 2H_2O$ at 650 °C. The diffraction pattern was indexed on the basis of an orthorhombic cell with a = 10.569(1), b = 2.803(1), c = 6.320(1) Å, and space group *Fmmm* (Figure 5a). This oxide is quite interesting due to a remarkable modulated structure with a complicated stoichiometry.[28] Moreover, it is one of the simple phases occurring in the phase diagrams of the complex superconductors of the bismuth and thallium family. Although a stoichiometric phase has recently been found,[29] remaining minor peaks from the CaO phase could indicate, in our case, the presence of the calcium-deficient major phase.

From the decomposition of the strontium complex at 800 °C, the phase $SrCuO_2$[30] has been obtained, with unit cell parameters, a = 3.575(1), b = 16.370(7), c = 3.915(1) Å, and space group *Cmcm* (Figure 5b). The structure can be described as an intergrowth of simple rock salt layers and an oxygen deficient ReO_3-type shear structure. It is interesting to note the improvement in the reaction times obtained from the complex, whereas according to the literature,[31] calcination at temperatures between 700 and 900 °C for several hours, two or three times, was required to obtain the pure oxides from the ceramic method.

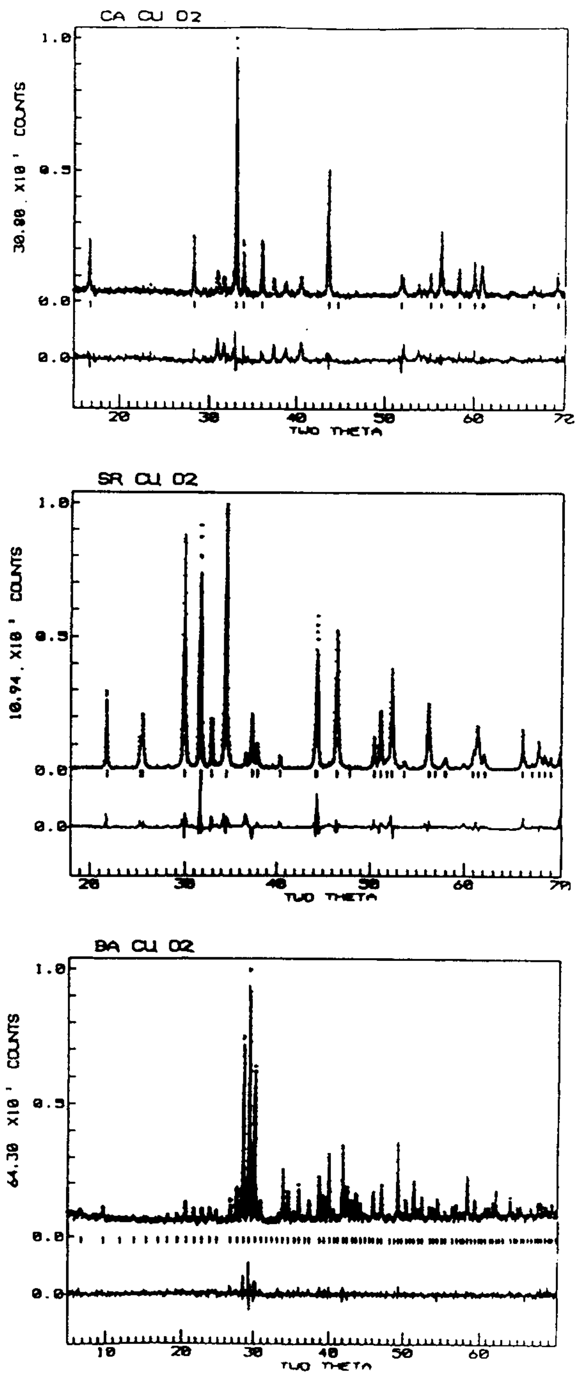

Figure 5. Pattern matching analysis of X-ray powder diffraction spectra of the $MCuO_2$ compounds (M = Ca, Sr and Ba).

After thermal treatment of the $[BaCu(edta)(H_2O)_3]\cdot H_2O$ at 800 °C the $BaCuO_2$ phase was obtianed (Figure 5c), with space group *Im*3*m* and cell parameter, a = 18.272(1) Å. This last compound probably shows the most complicated crystal structure which has been described for an oxocuprate, in which four different equivalent positions

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for barium, four for copper, and six for oxygen have been found.[32] This oxide is also nonstoichiometric, with large deviations from the ideal composition. In this case, the short reaction times needed to get these oxides from the complexes (around 10 h) is also remarkable, whereas from the ceramic method longer treatments have to be performed.[32] These results are in accord with those obtained by heating other metalloorganic compounds.[4]

IR experiments have been performed in order to detect the presence of carbonates in these final oxides. The calcium and strontium compounds show very weak bands at 1430, 875 and 1450, 869 cm^{-1}, respectively, corresponding to impurities of $CaCO_3$ and $SrCO_3$, in good agreement with the elemental analysis (% C 0.28 and 0.35 for calcium and strontium carbonates). However, for the barium compound, the bands appear at 1400 and 860 cm^{-1}, in accord with the results observed by Aranda and Attfield[33] for an oxocarbonate of barium in which the carbonate is occupying the disordered region of the structure.

Scanning Electron Microscopy. Scanning electron microscopic photographs of the $MCuO_2$ (M = Ca, Sr, and Ba) pellets are shown in Figure 6. As can be osberved, powders consisting of small particles with a diameter around 1–9 μm have been obtained. In the calcium compound, minor crystals were observed which could correspond to the impurity that appears in the X-ray diffraction pattern.

It should be noticed the analogous morphology between the calcium and strontium oxides, in both cases prismatic-round crystals of size around 2 μm are observed. Notwithstanding, in the barium compound two different shapes appear, long and narrowly sized crystals about 8 μm in length and polycrystaline aggregates between 2 and 9 μm. To check the composition of this kind of crystals, quantitative analysis was performed, and a relation 1:1 of barium and copper was corroborated for both cases.

Concluding Remarks

The structures of two new EDTA derivatives have been determined by X-ray diffraction methods, which consist of an intricate network of ligand-bridged coordination polyhedra. An octacoordinated arrangement around the alkaline-earth-metals and a distorted octahedral geometry for the copper(II) ion have been observed. Comparison with $[CaCu(edta)(H_2O)_2]\cdot 2H_2O$ has shown a difference in the coordination polyhedron of the calcium ion which exhibits a distorted octahedral geometry. Thermal degradation of these complexes yield mixed oxides of formula $MCuO_2$ (M = Sr, Ba, Ca) at comparatively short reaction times and low temperatures, as could also be obtained from other metalloorganic complexes.[4] Taking into account the fact that the new compounds are isostructural, several solid solutions with formula $Ba_{1-x}Sr_xCu(edta)\cdot 4H_2O$ have been prepared to obtain $Ba_{1-x}Sr_xCuO_2$ oxides after the corresponding thermal treatments. Preliminary experiments display good results which, together with the magnetic properties of these oxides, will be published shortly.

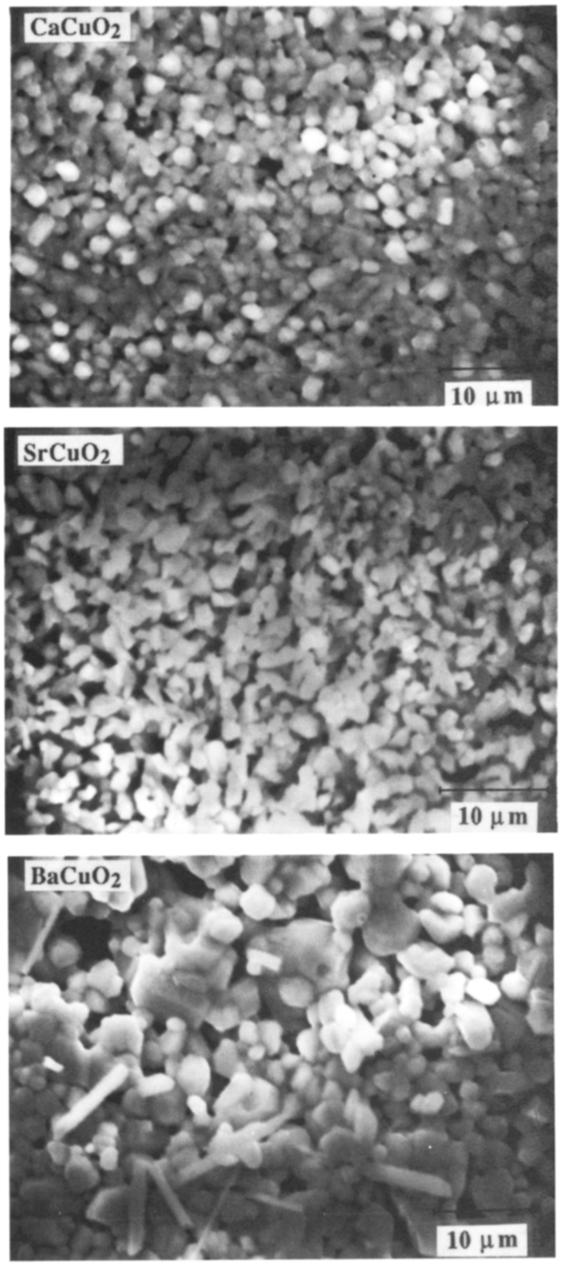

Figure 6. SEM photographs of the $MCuO_2$ oxides (M = Ca, Sr, and Ba).

Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, bond lengths and angles, and mean average planes (42 pages); observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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