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Synthesis, Characterization, and ab Initio Structure Determination from Powder Diffraction Data of a New X' Form of Anhydrous Copper(II) 8-Hydroxyquinolinate Doped with Amine. Modeling of the Polymorphic Transformation to the Stable Anhydrous β'' Form

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A new X' form of anhydrous copper(II) 8-hydroxyquinolinato complex doped with amine has been prepared and characterized. The structure has been solved from X-ray powder diffraction and refined by the Rietveld method. The unit cell is monoclinic, space group $P2_1/c$, with the following parameters: a = 10.930(2) Å, b = 4.885(1) Å, c = 15.184(3) Å, β = 121.21(1)°, V = 693.4(1) Å^3. The structure is close to that of palladium(II) 8-hydroxyquinolinate, with the copper atom lying in a planar square coordination. The molecules are held by van der Waals bonds only. Thermodynamic and kinetic parameters of the $X' \rightarrow \beta''$ transformation are determined and compared with other irreversible transformations to the β'' form. A two-step mechanism is proposed as a model for this polymorphic transition.

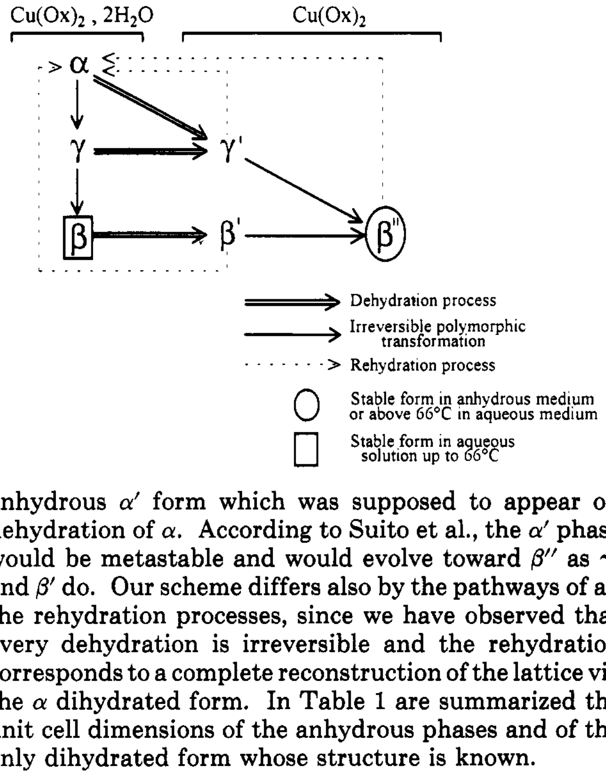
Introduction

8-Hydroxyquinoline (i.e., oxine) is a well-known ligand used as a complexing agent for extraction and separation of cations.[1,2] The deprotonated form (Ox hereafter), acting as a bidentate ligand on most M^{2+} or M^{3+} metallic ions, induces the precipitation of low solubility complexes in aqueous solutions.[3]

The complexes obtained with the cupric ion (Cu^{2+}) present various polymorphic dihydrated and anhydrous forms. Several of these varieties are of special interest because of their extensive use in phytoprotection.[4,5] Since the biological activity is closely dependent on metastability, the current study is part of a wide research program devoted to the preparation of new metastable copper(II) oxinates and the understanding of their chemical behavior.[6] The first exhaustive study of the transformations between those series was reported in 1966 by Suito et al.,[7] whose notation is adopted hereafter.

Scheme 1 illustrates all the possible transformations between dihydrated $Cu(Ox)_2$, $2H_2O$, and anhydrous $Cu(Ox)_2$ copper oxinates observed so far by our team. This scheme differs from Suito's scheme[7] by the absence of the anhydrous α' form which was supposed to appear on dehydration of α. According to Suito et al., the α' phase would be metastable and would evolve toward β'' as γ' and β' do. Our scheme differs also by the pathways of all the rehydration processes, since we have observed that every dehydration is irreversible and the rehydration corresponds to a complete reconstruction of the lattice via the α dihydrated form. In Table 1 are summarized the unit cell dimensions of the anhydrous phases and of the only dihydrated form whose structure is known.

Scheme 1



All the kinetics of the transformations observed (Scheme 1) are strongly influenced by the presence of impurities. For example, the successive rehydration and transformation processes $\beta' \rightarrow \alpha \rightarrow \gamma \rightarrow \beta$ can be slowed down from half an hour to several months by introducing a specific

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Table 1. Crystallographic Parameters of Copper Oxinates and Anhydrous Palladium Oxinate

	$Cu(Ox)_2 \cdot 2H_2O$ (β form)	$Cu(Ox)_2$ (β' form)	$Cu(Ox)_2$ (β'' form)	$Cu(Ox)_2$ (γ' form)	$Cu(Ox)_2$ (X′ form)	$Pd(Ox)_2$
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	2	2	4	2	2	2
a (Å)	13.01(4)	7.40(3)	10.644(4)	10.213(2)	10.930(2)	11.49(3)
b (Å)	5.56(2)	3.84(2)	8.593(3)	5.075(1)	4.885(1)	4.77(2)
c (Å)	11.34(4)	24.37(9)	15.239(4)	15.325(2)	15.184(3)	15.31(3)
β (deg)	106.1(2)	98.1(2)	102.18(2)	120.48(2)	121.21(1)	121.90(3)
V/Z (Å^3)	394.1	342.8	340.6	342.3	346.7	356.2
ref	32	24	23	6	this work	25

additive in the crystal during the dehydration of the β phase.[8] In the same way, the preparation of single crystals of the γ' form (and its structural determination) has been realized by introducing 8-hydroxyquinoline-5-sulfonic acid as a blocking agent of the transformation toward β''.[6]

Moreover, we ascertained that the full activity of impurities is obtained by introducing these additives at a precise moment, mainly during a phase transformation (i.e., crystallization, dehydration, or rehydration). This led us to the assumption that these impurities could operate if incorporated in the new crystal.

We also observed that the addition of small quantities (<1%) of additives could bring about the crystallization of new phases. Unfortunately, the phases obtained are usually poorly crystallized; the X-ray powder diffraction pattern shows only a few broadened lines.

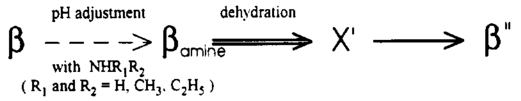
Nevertheless, if the crystallinity of a new phase is good enough, and single crystals of sufficient size are not available, the use of data obtained from powder diffraction can be a powerful tool in order to improve the crystallographic and structural knowledge of new metastable varieties, provided the crystal structure is not too complex. Indeed, after the ab initio structural determination of $(NH_4)_4[(MoO_2)_4O_3](C_4H_3O_5)_2 \cdot H_2O$ by Berg and Werner,[9] several ab initio structure solutions of inorganic and molecular compounds obtained from powder diffraction data have been reported in recent years, e.g. cimetidine $C_{10}H_{16}N_6S$,[10] $ZrKH(PO_4)_2$,[11] $Nd(OH)_2(NO_3) \cdot H_2O$,[12] and dihydrated copper(II) sulfoxinate (form I) $C_9H_5NO_4SCu \cdot 2H_2O$.[13] Except for the case of cimetidine, solved from X-ray synchrotron data, the other examples were studied by using conventional X-ray sources.

The present paper deals with the use of these recent developments for the structural analysis of a new anhydrous phase of copper(II) 8-hydroxyquinolinate $Cu(Ox)_2$ (X′ form). In addition to the preparative route, the characterization and the structural resolution from powder diffraction data, we present here a study of the irreversible transformation from X′ to the stable β'' form of copper(II) oxinate.

Experimental Section

Preparation and Identification. The pure dihydrated copper(II) oxinate ($Cu(Ox)_2, 2H_2O$) is prepared at 20 °C by adding solid oxine to an aqueous solution of copper sulfate, according to the molar ratio Cu/Ox = 2. A quantitative yield (>99%) is obtained by adjusting the pH of the suspension to 4 or above with any mineral base such as NaOH, KOH, or $Ca(OH)_2$. To obtain the pure β form with a good crystallinity, a 60-min waiting time with continuous stirring is found to be necessary to ensure that each of the successive transformations $\alpha \rightarrow \gamma \rightarrow \beta$ is completed. The dehydration of $Cu(Ox)_2, 2H_2O$ (β form) can be achieved by several routes: heating above 80 °C, dehydrating for a week in the presence of P_2O_5 at room temperature, or by agitation in acetone or methanol for 30 min. Whatever the route, it leads to formation of the metastable anhydrous β' form which evolves toward β'', with kinetic parameters depending on physical conditions.

Scheme 2



When the pH of the aqueous suspension containing the β dihydrated form is adjusted with an amine derivative NHR_1R_2 (R_1 and R_2 = H, CH_3, C_2H_5), the X-ray diffraction pattern of the β form obtained is unchanged. Nevertheless, the dehydration of this β_{amine} form by any of the routes indicated above does not lead to the β' anhydrous form, but induces the formation of a polycrystalline sample of a new anhydrous complex $Cu(Ox)_2$ (X′ phase), often mixed with a small amount of the other β' and β'' forms (Scheme 2).

When the pH adjustment is performed with ammonia, careful analyses of a several-gram sample using Kjeldahl's method show that about 0.5 mol % of amine, contained in the β_{amine} phase, remains in the powder of the X′ phase. Application of a vacuum does not allow release of the ammonia; like other adducts, the amine is likely to be inserted within the crystals, although it could not be identified in the structure study reported below. Thus, the X′ form is not a proper polymorphic form of $Cu(Ox)_2$ but rather a doped structure with the amine acting as an adduct. Nevertheless, we shall use hereafter the term "form" for the X′ phase, the Latin letter distinguishing it from the other true polymorphic varieties.

This X′ variety can be isolated in nearly pure form (>95%, a small quantity of β' or β'' forms appeared difficult to avoid) and is identified by its powder diffraction pattern and infrared spectra (Table 2). Like β' and γ', it is a metastable phase and tends to transform irreversibly into the stable β'' form by heating at 180 °C.

The impossibility of obtaining single crystals led us to use X-ray powder diffraction data and the Rietveld method for an ab initio determination and refinement of the structure. The granularity of the powder has a nearly Gaussian distribution with the following characteristics: 13 μm; σ = 4.5.

X-ray Powder Diffraction Analysis. *Data Collection.* A D500 Siemens powder diffractometer, using Bragg-Brentano geometry, was used for data collection. Pure Cu Kα_1 radiation (λ = 1.540 598 Å) was produced with an incident beam curved-crystal germanium monochromator and asymmetric focusing (short focal distance 124 mm, long focal distance 216 mm). Complete illumination of the sample was effective from 12° (2θ). Consequently, intensity data below this angle were corrected. The alignment of the diffractometer was checked by means of standard reference materials. The zero error was measured as less than 0.01° (2θ). The powder diffraction pattern was scanned in steps of 0.02° (2θ) and fixed-time counting (56 s) was employed. Finally, when all data had been collected, the stability of the intensity of the incident beam was checked by measuring again the first few lines of the pattern. A precise determination of

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Table 2. X-ray Powder Diffraction Data and Infrared Spectra of $Cu(OX)_2$ (X′ form)

hkl	$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	d_{obs} (Å)	$I/I_0 \times 100$	ν (cm^{-1})	transmittance %
100	9.436	9.453	9.37	88	1597	31
$\bar{1}02$	11.885	11.893	7.44	100	1570	8
002	13.622	13.626	6.50	37	1547	56
$\bar{2}02$	16.642	16.653	5.32	8	1495	2
200	18.962	18.971	4.676	4	1464	1
111	23.133	23.143	3.842	72	1427	23
$\bar{2}04$	23.909	23.916	3.719	2	1379	1
$\bar{3}02$	24.447	24.436	3.638	13	1325	3
$\bar{2}11$	24.601	24.608	3.616	13	1284	18
$\bar{1}13$	25.326	25.344	3.514	14	1236	31
$\bar{2}10$	26.353	26.369	3.379	46	1221	16
$\bar{2}13$	26.680	26.695	3.339	16	1173	43
112	27.343	27.341	3.259	34	1137	46
$\bar{3}04$	27.520	27.531	3.239	2	1114	8
202	28.702	28.716	3.108	10	1053	50
211	29.703	29.697	3.005	31	1031	45
$\bar{3}13$	31.144	31.141	2.869	1	954	63
$\bar{3}11$	31.626	31.634	2.827	5	922	71
113	32.536	32.545	2.750	4	858	68
014	33.121	33.104	2.703	3	829	17
104	33.574	33.560	2.667	3	802	36
310	34.106	34.100	2.627	3	741	7
$\bar{2}15$	34.779	34.781	2.577	1	631	41
$\bar{1}15$	35.756	35.764	2.509	3	582	70
$\bar{3}06$	36.226	36.215	2.478	3	519	25
$\bar{4}13$	37.720	37.669	2.383	5	471	77
$\bar{1}20$	38.051	38.046	2.362	1	444	80
$\bar{4}00$	38.482	38.489	2.338	4	406	60
$\bar{4}06$	39.422	39.418	2.284	8	323	45
$\bar{4}11$	39.980	39.960	2.253	1	281	70
$\bar{4}15$	40.566	40.563	2.222	6		
312	42.335	42.343	2.133	5		
221	43.983	43.989	2.057	3		
$\bar{2}24$	44.334	44.338	2.042	5		
$\bar{5}06$	44.696	44.675	2.026	3		
$\bar{2}17$	46.170	46.134	1.964	4		
$\bar{3}24$	46.531	46.540	1.950	5		
$\bar{3}20$	47.268	47.244	1.922	1		

Table 3. Crystallographic Data and Details of the Rietveld Refinement[a]

crystal name	X′ form of copper(II) 8-hydroxyquinolinato doped with amine
formula	$C_{18}H_{12}O_2N_2Cu$
formula wt	351.84
crystal system and space group	Monoclinic $P2_1/c$
Z	2
a (Å)	10.930(2)
b (Å)	4.885(1)
c (Å)	15.184(3)
β (°)	121.21(1)
V (Å^3)	693.4(1)
D_x (g·cm^{-3})	1.69 (calc.)
wavelength (Å)	1.540598
2θ range (deg)	8–85
step increment (deg 2θ)	0.02
no. of reflections	496
no. of structural parameters	35
no. of profile parameters	15
number of non-hydrogen atoms	12
R_F	0.05
R_B	0.05
R_p	0.12
R_{wp}	0.18

[a] Note: the R factors are defined as $R_F = \sum|I(\text{“obs”})^{1/2} - I(\text{calc})^{1/2}|/\sum I(\text{“obs”})^{1/2}$; $R_B = \sum|I(\text{“obs”}) - I(\text{calc})|/\sum I(\text{“obs”})$; $R_{wp} = \sum w_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2/\sum w_i[y_i(\text{obs})]^2$; $R_p = \sum|y_i(obs) - (1/c)y_i(\text{calc})]/\sum y_i(\text{obs})$.

peak positions and integrated intensities of Bragg components was carried out by means of the fitting program, FIT, available in the Socabim PC software package DIFFRAC-AT, supplied by Siemens.

Powder Pattern Indexing. The indexing of the powder diffraction data was performed by means of the successive dichotomy method.[14] The program DICVOL91[15] which tackles any system, including triclinic, was used for indexing the pattern. The first 20 lines were completely indexed on the basis of a monoclinic cell. The reliability of the unit cell and indexing was indicated by the figures of merit $M_{20} = 28$[16] and $F_{20} = 46$ (0.0073, 60).[17] From this solution, the powder diffraction data (first 38 lines) were reviewed by means of the computer program NBS*AIDS83.[18] From this evaluation of data quality, the unit-cell parameters were refined from the complete dataset and are given in Table 3. The final figures of merit are $M_{20} = 32$ and $F_{30} = 44$ (0.0106, 64). The list of observed and calculated peaks is given in Table 2. From the pattern indexed with this unit cell, there is evidence for systematic absences consistent with the space group $P2_1/c$. For comparison purposes, the unit-cell dimensions of the X′ form are also listed in Table 1. The parameters of the new X′ phase are significantly different, although analogies exist between the unit cells and volume per molecular unit of all anhydrous phases.

Structure Solution and Refinement. The extraction of the integrated intensities has been carried out by means of an automatic fitting procedure implemented in the program FULLPROF[19] which is derived from the Rietveld program DBW3.2S.[20,21] The 496 $|F_{obs}|$ so obtained were used in the program PATSEE[22] running on a PC computer. This program, which combines both Patterson and direct methods for locating a fragment of known geometry was particularly suitable in this case. Indeed, the known fragment introduced was the half-molecule of the β'' form[23] and, with the additional constraint that Cu must be located at the origin ($Z = 2$), the complete solution was easily found. The coordinates of the atoms were input to the Rietveld profile refinement program. Integrated intensities were distributed over 5 fwhm on either side of a diffraction line represented by a modified Lorentzian function. To describe the angular dependence of peak half-widths, the usual quadratic form in tan θ was used, and the initial values of the constants U, V, and W were derived from the fitting of some individual lines. Five coefficients were used and refined to describe the functional dependence of the background. One overall isotropic temperature factor parameter for all atoms was refined ($B = 4.2$ Å^2) instead of individual temperature factors. At the final stage of the refinement, the idealized geometry of the organic fragment was used to reduce the risk of false minima, and all 33 positional parameters for the non-hydrogen atoms were independently refined. The conditions of the refinement are compiled in Table 3. A few lines with low intensity belonging to the β'' phase were detected in the powder diffraction pattern, together with five lines of the sample holder (Al). These additional phases, whose structure is known, were taken into account in the final stage of the refinement. From the overall scale factor values for the two phases of copper(II) oxinates (i.e., 0.0311 for X′ form and 0.0004 for β'' form), the abundance of β'' phase can be estimated approximately to 1.5%. Figure 1 shows the observed and calculated powder diffraction patterns. The final Rietveld fit corresponds to satisfactory crystal structure model indicators ($R_F = 0.05$ and $R_B = 0.05$) and profile factors ($R_p = 0.12$ and $R_{wp} = 0.18$). A list of the atomic positions of the model is given in Table 4. Hydrogen atom positions have been calculated with respect to a bond length between carbon and hydrogen atoms of

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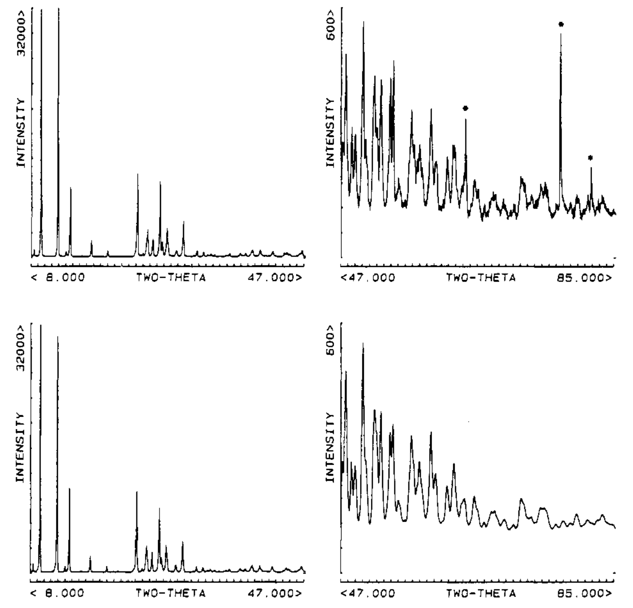

Figure 1. Observed powder diffraction pattern (upper figures) and calculated pattern from the Rietveld refinement (lower figures) for copper(II) oxinate (X′ form). Note the change in intensity scale for the higher angle range. (Three lines in the observed pattern, indicated by an asterix, belongs to the Al sample holder; they are not represented in the calculated plot.)

Table 4. Atomic Coordinates for $Cu(Ox)_2$ (X′ Form)

atom	x/a	y/b	z/c
Cu	0.000(0)	0.000(0)	0.000(0)
O	0.099(3)	0.153(4)	−0.065(2)
N	0.104(4)	0.274(7)	0.111(3)
C2	0.110(5)	0.315(8)	0.196(4)
C3	0.199(4)	0.529(10)	0.268(3)
C4	0.288(4)	0.657(7)	0.248(3)
C5	0.381(4)	0.754(7)	0.130(3)
C6	0.370(4)	0.681(9)	0.040(4)
C7	0.288(5)	0.463(9)	−0.027(3)
C8	0.193(5)	0.328(9)	0.001(3)
C9	0.193(5)	0.406(8)	0.086(4)
C10	0.294(5)	0.616(9)	0.156(4)
H2	0.058	0.201	0.215
H3	0.195	0.576	0.328
H4	0.353	0.785	0.297
H5	0.447	0.892	0.173
H6	0.421	0.792	0.017
H7	0.296	0.409	−0.083

0.95 Å. The complete lists of bond lengths, angles and calculated and observed integrated intensities may be obtained on request.

Results and Discussion

Description of the Structure. Figure 2 depicts the quasi-square-planar coordination of Cu^{2+}, with bond lengths Cu—O=1.95(2) Å, Cu—N=1.99(3) Å, and the angle O—Cu—N=93(1)°. No additional apical bond exists. The planar geometry of the oxine moiety is in agreement with previously reported structures for anhydrous copper(II) oxinates.[6,23,24] There are no significant deviations of atoms from the mean plane since all deviations are less than 0.08 Å.

The molecular planes are nearly parallel to (210), and form a dihedral angle of 87° with one another. Along the b axis, the structure consists of a stack of parallel molecules (Figure 2), with a distance of 3.36 Å between two successive molecular planes. This value is in agreement with previously reported distances (3.21 Å in the γ′ form,[6] 3.45 Å in the β′ form[24]) and corresponds to the greater stability for parallel π systems. No hydrogen bonds exist, and thus the cohesion of the crystal is due to van der Waals interactions only.

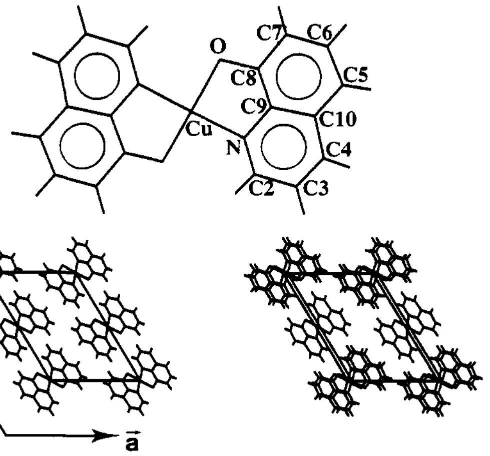

Figure 2. Labels of atoms and stereoscopic view down b of copper(II) oxinate (X′ form).

Once the crystal structure of $Cu(Ox)_2$ (X′ form) had been solved, it was found to be isomorphous to the structure of palladium(II) 8-hydroxyquinolinate (hereafter $Pd(Ox)_2$; see Table 1), with the center of symmetry of the molecule coinciding with the crystallographic centre of the lattice ($P2_1/c$, $Z = 2$) as in the β′ and γ′ structures. The structural relationship between $Pd(Ox)_2$ and $Cu(Ox)_2$ (γ′ form) has been reported[6] and consists mainly of a transposition of the roles of O and N atoms. The same relationship is therefore valid between $Cu(Ox)_2$ (γ′ form) and $Cu(Ox)_2$ (X′ form).

The structure of $Pd(Ox)_2$ was solved in 1966 by Prout and Wheeler[25] from single-crystal diffraction data collected by means of the film technique in which intensities were visually estimated. It is, therefore, of interest to comment briefly on the accuracy of the results reached in both studies. It appears that crystallographic parameters a, b, c obtained from the powder method are much more precise (×10) than those deduced from Weissenberg photographs. Nevertheless, the mean values of the esd's on atomic coordinates are twice as high with the powder method. Although the comparison between the two methods must be undertaken carefully, it has to be noted that the structure solution obtained from powder diffraction is based on the half number and overlapping reflections, since the angular range is limited to $\sin\theta/\lambda = 0.438$ Å^{-1}.

EPR Study

According to Sivy et al.,[26] the observed g^c values lead to molecular g parameters in quasi-axial symmetry:

$$g_\parallel = g_1^c + g_2^c - g_3^c \qquad g_\perp = g_3^c$$

Moreover, the canting angle 2γ, between the mean square planes of two copper atoms, is given by

$$\cos 2\gamma = \frac{g_1^c - g_2^c}{g_1^c + g_2^c - 2g_3^c}$$

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Table 5. Enthalpies and Activation Energies of the Irreversible Transformations toward β''

phase	enthalpy ΔH (kJ mol^{-1})	σ	activation energy (kJ mol^{-1})
β'	-3.7	0.26	131 ± 9
β'_{stab}	-3.4	0.25	172 ± 13
γ'_{stab}	-3.8	0.31	126 ± 8
X′	-2.3	0.36	158 ± 12

The validity of this model has been checked for structures where the copper atom has a pyramidal and even a distorted octahedral coordination polyhedron.[27] Nevertheless, in the absence of an apical bond (β', γ'), the model cannot be applied.

The observed values ($g_1{}^c = 2.155, g_2{}^c = 2.105, g_3{}^c = 2.060$) lead to the calculated canting angle $2\gamma = 69°$. The large discrepancy with respect to the real value (82°) gives an indirect confirmation of the pure square-planar coordination of the Cu^{2+} cation.

Study of Phase Transformation X′ → β''

As indicated above, $Cu(Ox)_2$ (X′ form) is a metastable phase and undergoes an irreversible evolution toward the β'' form.

Enthalpy and Activation Energy. To complete previous results concerning transformations of anhydrous forms toward the stable β'' form,[6] we have determined the enthalpy and the activation energy of the transformation X′ → β''.

The experimental values of enthalpies (see Table 5) are obtained by means of differential scanning calorimetry (Setaram DSC 101) measurements. The absolute value of ΔH for the transition β'' is lower for X′ than for $\gamma'_{stab.}$ or $\beta'_{stab.}$. This is consistent with the closer structural relation between X′ and β'' with regard to the other metastable phases.

According to Kissinger,[28] the activation energy can be estimated by considering the slope of the straight line which corresponds to the following relation:

$$\ln\left(\frac{V}{T_m{}^2}\right) = -\frac{\Delta E}{R}\left(\frac{1}{T_m}\right)$$

where T_m is the temperature of maximum deflection of the exothermic peak, V the heating rate and ΔE the activation energy. Values of T_m and V were obtained from DSC results, according to the following conditions: weight of sample from 50.5 to 51.3 mg heating rate from 0.5 to 32 °C/min. Figure 3 displays the good agreement between the experimental results and Kissinger's relation, showing that irreversible (solid–solid) phenomena can also be described by this relation. The corresponding activation energies are reported in Table 5.

The significant difference between the values of activation energy for transitions of β' and $\beta'_{stab.}$ highlights the influence of specific additives on the stability of metastable phases. From this point of view, the activation energy for the X′ phase has to be compared with that for $\gamma'_{stab.}$ and $\beta'_{stab.}$ because the formation of the X′ phase requires the presence of an adduct. Although the three values are of the same order, the activation energies for formation of X′ and $\beta'_{stab.}$ are close, showing that both forms are better stabilized than $\gamma'_{stab.}$ with regard to the transition toward the stable β'' form.

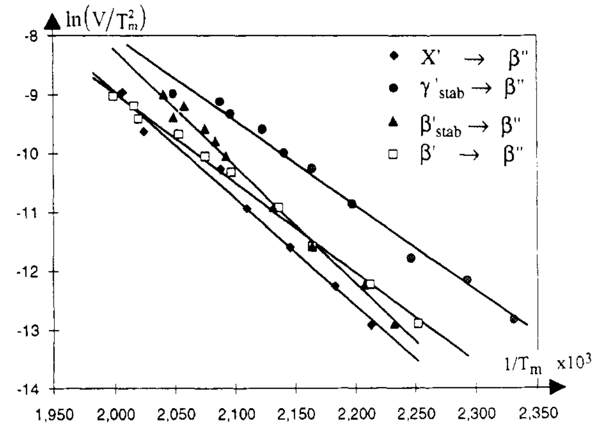

Figure 3. Kissinger's relation between the heating rate (V) and the reciprocal temperature ($1/T_m$) of the transformation toward β''.

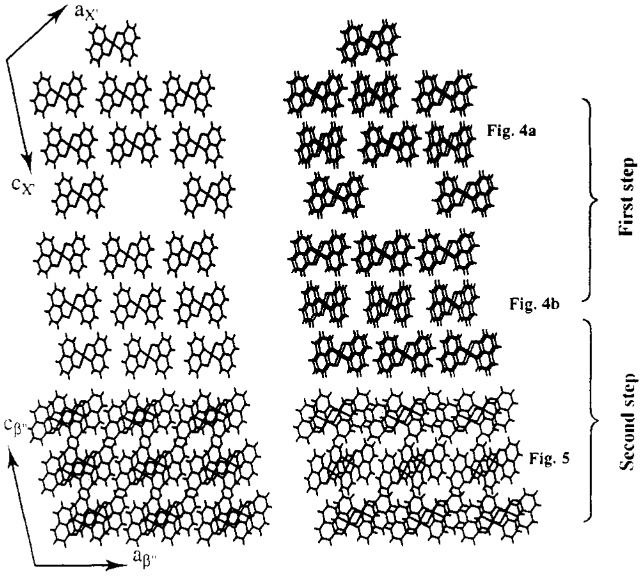

Figure 4. Stereoscopic view down b of $Cu(Ox)_2$ (X′ form) showing the glide along c. **Figure 5.** Stereoscopic view down b of $Cu(Ox)_2$ (β'' form).

Modeling of the Transformation X′ → β''. Crystallographic parameters of the β'' form[23] present analogies with those of X′ (Table 1). Comparison of densities shows that β'' is only slightly more compact; the sharp increase in stability seems mainly due to the formation of dimers.

The transformation X′ → β'' has been modeled with respect to the following hypotheses: (1) The transformation is achieved with the lowest possible activation energy, that is to say with a limited series of cooperative movements of small magnitude. (2) These movements maintain contacts continuously between complexes included in planes or at least in rows.

The systematic search of all possible pathways respecting these hypotheses and the evaluation of docking enery[29] during the glide of planes and rows lead to the only possible solution, which consists of two successive steps:

1: a $^1/_2\vec{c}$ glide of one in two $(100)_{X'}$ slices (Figure 4)

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(28) Kissinger, H. E. *J. Res. N.B.S.* **1956**, *57*, 217; *Anal. Chem.* **1957**, *29*, 1702.

(29) SYBYL, Molecular Modeling Software (version 5.5, 1992) TRIPOS Associates, St. Louis, MO.

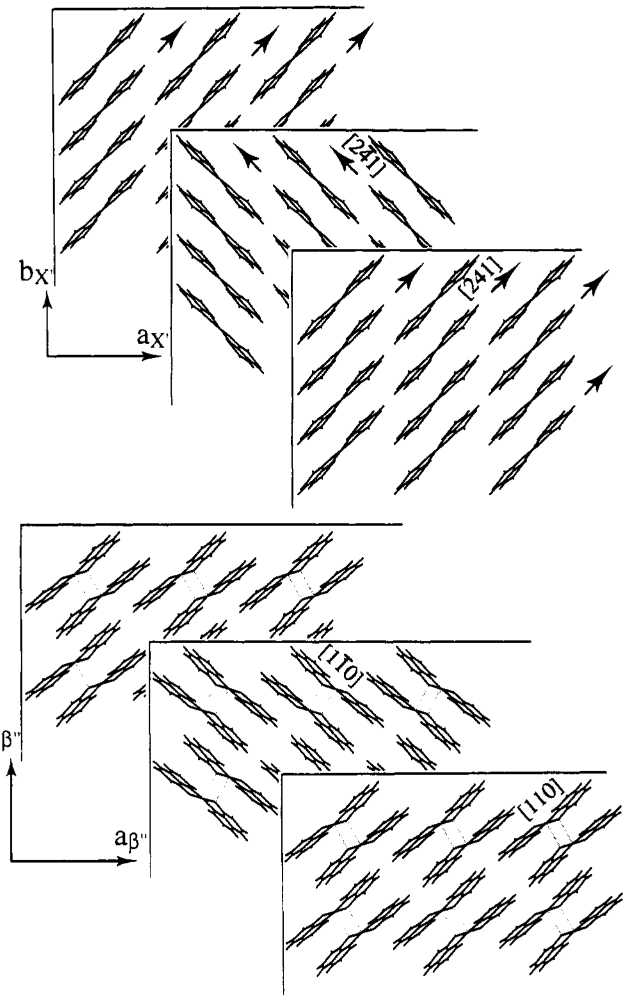

Figure 6. Projections along *c* showing the glides of $[241]_{X'}$ and $[2\bar{4}1]_{X'}$ rows contained in successive $(\bar{1}02)_{X'}$ slices, leading to the dimer units of $Cu(Ox)_2$ (β'' form).

2: a 4.2-Å glide of one in two $[241]_{X'} = [110]_{\beta''}$ rows contained in the $(\bar{1}02)_{X'} = (002)_{\beta''}$ slice (and a glide of $[2\bar{4}1]_{X'} = [1\bar{1}0]_{\beta''}$ rows for the neighboring slices), leading to the formation of dimers (Figures 4b, 5, and 6).

The two gliding movements are 82° apart, and this implies topological constraints; the second step can only begin after the first one is completed. The sequence of the two steps also results from the hypotheses which impose a permanent molecular cohesion and only cooperative movements. The first step is decisive since the docking energy during its realization peaks at 200 kJ mol^{-1} above the initial state taken at level 0. Because only rigid complexes were considered in our simulation and because we did not take into account any defect in the crystal,[30,31] this overestimated value seems quite consistent with the experimental value of activation energy 158 ± 12 kJ mol^{-1}.

Conclusion

The preparation of a dihydrated copper(II) oxinate doped with amine induces, on dehydration, the formation of a new packing of copper(II) oxinate (X′ form) in which a small proportion of adduct remains.

The efficiency of the X-ray diffraction powder method in determining crystal structures, even in the case of a mixture of polymorphic forms, is assessed. The accuracy of the method is discussed and found to be roughly equivalent to the determination of structure by means of visual estimation of diffracted intensities from Weissenberg films. The structure reveals a square-planar coordination for the copper atom, confirmed by EPR spectra. The main feature consists of compact stacks of parallel complexes along the *b* direction, with a dihedral angle of 87° between neighbouring molecular planes.

Comparisons of ΔH and activation energy with other irreversible transitions toward β'' lead to consistent results. The mechanism for the transition $X' \rightarrow \beta''$ is shown to be a two-step process, with a preliminary glide of $(100)_{X'}$ slices along *c* direction with a magnitude of 7.6 Å, followed by the formation of the dimer units observed in the structure of β'' by means of a glide of rows contained in $(\bar{1}02)_{X'} = (002)_{\beta''}$ slices.

Despite a very simple molecular geometry, copper(II) oxinates exhibit a great variety of packing. The effects of small concentrations of additives highlight the versatilities of the system by inducing and stabilizing new crystal structures. Other organic adducts bring about new packings, but simultaneously create a lot of defects in the structure, leading to poorly crystallized phases. This could lead to a limitation in the X-ray structure determination, even by means of the powder method.

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Supplementary Material Available: Tables of crystallographic parameters, fractional coordinates, bond distances and angles, deviations from the mean plane for copper(II) 8-hydroxyquinolinate (X′ form) (8 pages); calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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