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SOLID-STATE CHEMISTRY OF NICKEL(II)–OXALATE–AMINE SYSTEMS. SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF THE BIS(2,2′-BIPYRIDINE)(OXALATO-O,O′)NICKEL(II) TETRAHYDRATE

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Abstract—Purple single crystals of the mononuclear mixed-ligand complex [Ni(ox)(bipy)$_2$]·4H$_2$O, where ox is oxalate and bipy is 2,2′-bipyridine, were obtained by slow evaporation of a solution previously prepared by adding an ethanolic bipy solution to an aqueous solution of nickel(II) chloride hexahydrate and potassium oxalate monohydrate (molar ratio 1 : 2). The compound was characterized by elemental analysis, FT-IR spectroscopy and single-crystal X-ray diffraction. The crystal structure consists of neutral mononuclear [Ni(ox)(bipy)$_2$] units and crystallization water molecules which are held together by an extensive three-dimensional network of O—H···O and C—H···O hydrogen bonds and face-to-face stacking interactions between the π-systems of the bipy aromatic rings. The nickel atom is coordinated by two oxygen atoms of a bidentate oxalate ligand and four nitrogen atoms belonging to two bipy in an octahedral *cis* arrangement. Thermal decomposition of the complex was studied by TG–DTA techniques in synthetic air and argon atmospheres.

A lot of work has been devoted to the study of mixed-ligand complexes because of their key role in biological processes[1] and their properties in areas such as analytical chemistry, catalysis and magnetochemistry.[2] Of these, two of the best studied groups, both in solution[3] and solid-state,[4] are copper(II) and nickel(II) complexes with N-donor ligands and the oxalate (ox) anion. In spite of these exhaustive studies, dimeric[5] and polymeric chain[6] structures are predominant in the solid-state chemistry of oxalato-nickel(II) complexes, and very little has been published to date about the structures of mononuclear complexes. Up to now, the CSD (version 5.8, October 1994) database[7] only shows the crystal structure of a monomeric oxalato-nickel(II) complex, the potassium *trans*-diaquabis(oxalato-O,O′)nickelate(II)-water (1/4).[8] This is due to the versatility of the oxalate ion which can act as a mono-, di-, tri- or tetradentate ligand capable of forming bridged polynuclear complexes[5,6,9] and extended molecular assemblies with very interesting magnetic behaviour.[10]

In view of this interest, and as a part of our research programme on solid-state reactivity of first-row transition metal oxalato complexes with polydentate N-donor ligands, we report here the preparation, chemical characterization and crystal structure of the mononuclear mixed-ligand complex, [Ni(ox)(bipy)$_2$]·4H$_2$O (**1**) (bipy and ox being 2,2′-bipyridine and the dianion of oxalic acid).

The choice of the 2,2′-bipyridine was determined first by the assumption that such a ligand is capable of giving very stable species in solution[11] due to the π back-bonding from the metal to the aromatic amine. Second, solid-state structures of chemical species containing π-aromatic systems are stabilized

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by stacking interactions involving the π-systems. These non-covalent interactions control many molecular recognition and self-assembly processes in solution and solid-state, and exercise important effects on the organization and properties of many materials in areas as biology, crystal engineering and materials science.[12]

EXPERIMENTAL

Reagents and techniques

Nickel(II) chloride hexahydrate, potassium oxalate monohydrate and 2,2′-bipyridine were of reagent grade and used without further purification. Carbon, nitrogen and hydrogen analyses were performed on a Perkin–Elmer 240 C-, H-, N-analyser. The concentration of nickel was determined using a Perkin–Elmer 360 Atomic Absorption/Flame Emission Spectrometer. Density was measured by flotation in a mixture of acetone–bromoform. An IR absorption spectrum was recorded on a Nicolet FT-IR 740 using KBr disks over the wavenumber range 4000–400 cm^{-1}. A Setaram TAG 24 S 16 simultaneous thermal analyser was used to obtain the differential thermal analysis (DTA) and thermogravimetric analysis (TG and DTG) curves, in synthetic air and argon at a heating rate of 5° min^{-1}. All thermal decompositions were recorded in a dynamic atmosphere with a flow rate of 50 cm^3 min^{-1}. X-ray powder diffraction patterns of microcrystalline final products of the thermal decompositions were recorded at room temperature with a Philips PW 1710 instrument equipped with graphite monochromated Cu-K_α radiation, and they were compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards, JCPDS.[13]

Synthesis of the complex

Nickel(II) chloride hexahydrate (0.67 g, 2.82 mmol) dissolved in distilled water (10 cm^3) was added dropwise to an aqueous solution (15 cm^3) of potassium oxalate monohydrate (1.04 g, 5.64 mmol) at room temperature with continuous stirring. To the resulting dark green solution, 2,2′-bipyridine (1.32 g, 8.45 mmol) dissolved in ethanol (15 cm^3) was dropped. Initially, some blue solid was formed which subsequently dissolved to give a red–purple solution. This solution was allowed to evaporate slowly until purple single crystals were formed. The crystals were collected on a glass frit, washed several times with cold water followed by ether and dried in opened air. The crystals were found to be stable to air and X-ray exposure. Yield: 70% based on Ni. Found: C, 50.0; H, 4.4; N, 10.7; Ni, 11.0. Calc. for $C_{22}H_{24}N_4NiO_8$: C, 49.7; H, 4.5; N, 10.5; Ni, 11.0%. IR (KBr, cm^{-1}): 3600–3200 br; 3110m, 3070m, 1720sh, 1670m, 1645vs, 1610m, 1605m, 1570m, 1480m, 1470m, 1450m, 1440m, 1425s, 1310m, 1290vs, 1250m, 1180m, 1050m, 1025m and 770s.

Crystallographic data collection and structural refinement

A single crystal of **1** ($0.20 \times 0.18 \times 0.14$ mm) was mounted with epoxy resin on a glass fiber and used for data collection on an Enraf–Nonius CAD4 four circle diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 well centred reflections in the range $8 < \theta < 14^\circ$. Crystallographic data and some features of the structure refinement are given in Table 1.

Intensity data were collected at 293 K in the range $1 \leqslant \theta \leqslant 30^\circ$ ($0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 25$, $-20 \leqslant l \leqslant 20$), using graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) and ω–2θ scan technique. Two standard reflections were monitored every hour and revealed no significant fluctuations in intensity and orientation which indicated crystal and electronic stability. The intensities were corrected for Lorentz–polarization effects and an empirical absorption correction[14] was applied ($T_{max} = 1.098$, $T_{min} = 0.981$). Scattering factors for neutral atoms and anomalous dispersion corrections for all non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography* (1974).[15] The structure was solved by direct methods[16] and succesive Fourier difference synthesis, and refined by the full-matrix least-squares method using X-RAY76.[17] Anisotropic thermal parameters were given to all the non-hydrogen atoms. A convenient weighting scheme was used to give no trends in $\langle w\Delta^2F\rangle$ vs $\langle F_o\rangle$ and vs $\langle \sin\theta/\lambda\rangle$.[18] A Fourier difference synthesis revealed the positions of all hydrogen atoms which were introduced in the refinement as fixed isotropic contributors. Most calculations were carried out on a Micro VAX II computer. Final atomic positional and thermal parameters, together with anisotropic thermal parameters for non-hydrogen atoms, full list of bond distances and angles, dihedral angles, least-squares planes, and a list of observed and calculated structure factors have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.

Table 1. Crystal and refinement data of $[Ni(ox)(bipy)_2] \cdot 4H_2O$

Formula	$C_{22}H_{24}N_4NiO_8$	$F(000)$	1104
Formula weight	531.15	μ (Mo-K_α) (cm^{-1})	8.469
Crystal system	Monoclinic	Number of measured refl.	7103
Space group	$P2_1/n$	Number of observed refl.	1181 $[I > 2\sigma(I)]$
a (Å)	9.657(2)	Number of parameters	316
b (Å)	17.862(2)	S^a	1.13
c (Å)	14.269(1)	$(\Delta/\sigma)_{\text{max, aver}}$	0.06, 0.001
β (°)	97.11(2)	$\Delta\rho_{\text{max, min}}$ (e Å^{-3})	0.70, −0.60
V (Å^3)	2442.4(6)	$R^b(F_o)$	0.042
Z	4	$R_w^c(F_o)$	0.043
D_{calc} (g cm^{-3})	1.445		
D_{obs} (g cm^{-3})	1.45(1)		

[a] $S = [\Sigma w(|F_o| - |F_c|)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

RESULTS AND DISCUSSION

Description of the structure

The crystal structure of the complex is made up of neutral mononuclear $[Ni(ox)(bipy)_2]$ units and uncoordinated water molecules linked together by an extensive network of hydrogen bonds and stacking π–π intermolecular interactions. A perspective view of the neutral entity, with the atomic numbering scheme, is given in Fig. 1. Main bond lengths and angles are listed in Table 2.

The nickel atom has an octahedral coordination comprised of two carboxylate-oxygen atoms from a bidentate oxalate ligand and four nitrogen atoms from two chelating bipy groups. All the ligands show a *cis* arrangement of the two donor atoms around the nickel(II) ion. The Ni—O(oxalate) bond distances (mean value 2.05 Å) are slightly shorter than the Ni—N(bipy) bond lengths (mean value 2.09 Å). The bite angles N—Ni—N [78.0(4) and 78.7(4)°] and O—Ni—O [79.9(3)°] are far from the ideal one of 90° because of the constrained geometry of the bipyridine rings system[19] and the usual small bite size of the five-membered planar chelate rings formed by the bidentate oxalate ligand. These values agree well with previously reported for other nickel(II) complexes containing bipy[20,21] or oxalate.[5,8,22] The best equatorial plane of the NiN_4O_2 chromophore is defined by atoms N(12), N(18), N(22) and O(2) [largest deviation from the mean plane 0.09 Å for N(12)] and the nickel atom is 0.03 Å out of this plane. The distortion of the NiN_4O_2 environment from the octahedral geometry has been evaluated by application of the Muetterties and Guggenberger's method[23] involving dihedral angles between the various faces of the polyhedron. The value obtained, $\Delta = 0.07$, is indicative of a slight distortion from the ideal topology ($\Delta = 0$ octahedron, $\Delta = 1$ trigonal prism) and is close to those observed for analogous six-coordinated complexes such as $[Ni(bipy)_2(NCO)_2]$.[24]

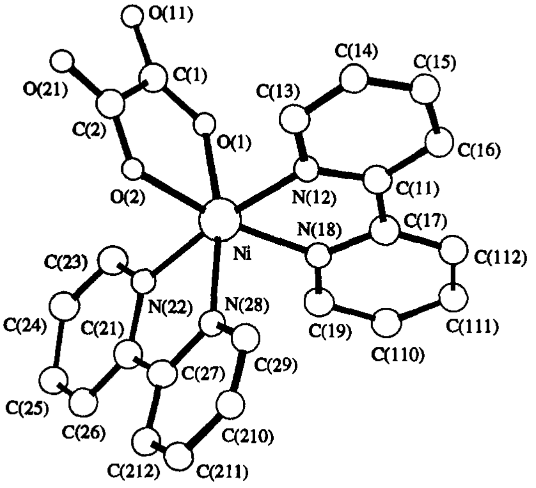

Fig. 1. Molecular structure of mononuclear entity [Ni(ox)(bipy)$_2$] showing the labelling scheme. Hydrogen atoms are not included.

As expected, the individual pyridine rings of the two bipy are nearly planar [the largest deviation from the mean planes is 0.04 Å at C(24)]. However, the bipy ligands as a whole are far from being planar, and the dihedral angles between the six-membered pyridyl rings in each bipy are 7.6(3) and 8.0(4)°. Such dihedral twist motion is perfectly normal for a coordinated bipy although angles up to 18° have been previously observed in bipy complexes.[25] Average C—C (1.38 Å) and C—N (1.35 Å) bond lengths within the rings and inter-ring

Table 2. Selected interatomic distances (Å) and bond angles (°) for $[Ni(ox)(bipy)_2]\cdot 4H_2O$

Nickel environment			
Ni—O(1)	2.036(8)	Ni—N(18)	2.103(9)
Ni—O(2)	2.070(8)	Ni—N(22)	2.072(8)
Ni—N(12)	2.081(8)	Ni—N(28)	2.113(9)
O(1)—Ni—O(2)	79.9(3)	N(12)—Ni—N(18)	78.0(4)
O(1)—Ni—N(12)	91.2(3)	N(12)—Ni—N(22)	172.4(4)
O(1)—Ni—N(18)	94.6(3)	N(12)—Ni—N(28)	98.4(4)
O(1)—Ni—N(22)	92.5(3)	N(18)—Ni—N(22)	95.1(4)
O(1)—Ni—N(28)	168.3(3)	N(18)—Ni—N(28)	93.8(4)
O(2)—Ni—N(12)	94.6(3)	N(22)—Ni—N(28)	78.7(4)
O(2)—Ni—N(18)	170.8(3)	Ni—O(1)—C(1)	115.3(8)
O(2)—Ni—N(22)	92.5(3)	Ni—O(2)—C(2)	114.7(7)
O(2)—Ni—N(28)	92.7(3)		
Oxalato			
C(1)—O(1)	1.259(15)	C(2)—O(2)	1.288(15)
C(1)—O(11)	1.246(15)	C(2)—O(21)	1.241(16)
C(1)—C(2)	1.559(19)		
O(1)—C(1)—O(11)	127(1)	O(2)—C(2)—C(1)	114(1)
O(1)—C(1)—C(2)	116(1)	C(1)—C(2)—O(21)	121(1)
C(2)—C(1)—O(11)	117(1)	O(2)—C(2)—O(21)	125(1)

2,2-*Bipyridine*

	X = 1	X = 2		X = 1	X = 2
C(X1)—N(X2)	1.341(16)	1.368(14)	C(X7)—N(X8)	1.356(14)	1.352(14)
C(X1)—C(X6)	1.399(17)	1.387(16)	C(X7)—C(X12)	1.380(18)	1.395(17)
C(X1)—C(X7)	1.441(17)	1.475(16)	N(X8)—C(X9)	1.361(15)	1.341(16)
N(X2)—C(X3)	1.370(16)	1.340(17)	C(X9)—C(X10)	1.409(18)	1.382(22)
C(X3)—C(X4)	1.363(18)	1.393(20)	C(X10)—C(X11)	1.368(21)	1.381(22)
C(X4)—C(X5)	1.333(24)	1.385(23)	C(X11)—C(X12)	1.393(19)	1.374(21)
C(X5)—C(X6)	1.421(22)	1.382(21)			

C—C bonds (1.46 Å) are in good agreement with those currently given in the literature for the non-coordinated[19] and coordinated 2,2′-bipyridine.[20,21,26] Although the mean angle within the individual pyridine rings is the expected 120°, deviations from this angle are observed for inter-ring angles C_{ring1}—C_{ring2}—N_{ring2} [around 116°] and C_{ring1}—C_{ring2}—C_{ring2} [around 124°].

Concerning the oxalate dianion, it is essentially planar [the largest deviation being 0.03 Å at O(11)]. The nickel atom is 0.05 Å out of this plane. Usually, in structural works dealing with bidentate oxalato-containing first-row transition metal complexes, the coordinated C—O bond distances are longer than those observed for the uncoordinated oxygen atoms. However, in the title compound carbon–oxygen bonds lengths are quite similar (1.24–1.29 Å) due to the hydrogen-bonds strength established between the water molecules and uncoordinated oxygen atoms. The C—C bond length [1.56 Å] is indicative of a single bond and is in accord with previously reported values.[5,8,22]

The three ligands around the nickel atoms are almost perpendicular to each other. The dihedral angles between the oxalate plane and the bipy mean planes are 87 and 84°, respectively; whereas that between the bipy mean planes is 85°.

Figure 2 shows the crystal packing of the compound. The neutral complex units stack to form infinite zig-zag chains along the [100] direction in which are held together by face to face interactions among the π-aromatic systems of the bipy (X = 1) ligand. These intermolecular stacking interactions are established between one neutral A unit (x, y, z) and two next-neighbouring units, B $(-x, -y, -z)$ and B* $(-x+1, -y, -z)$. The A—B interaction implies to the two rings of the bipy ligand with a dihedral angle between the mean planes of 7.7°, interplanar distance of 3.57 Å, lateral offset 1.37 Å and the shortest interatomic contact 3.50 Å. The shortest nickel–nickel distance in the crystal structure [Ni(A) $\cdots$ Ni(B) = 7.504(2) Å] is established between these neighbouring units. The second interaction A—B* is strictly parallel but is only established by partial overlap of one of the two pyridyl rings with interplanar distances of 3.50 Å, offset

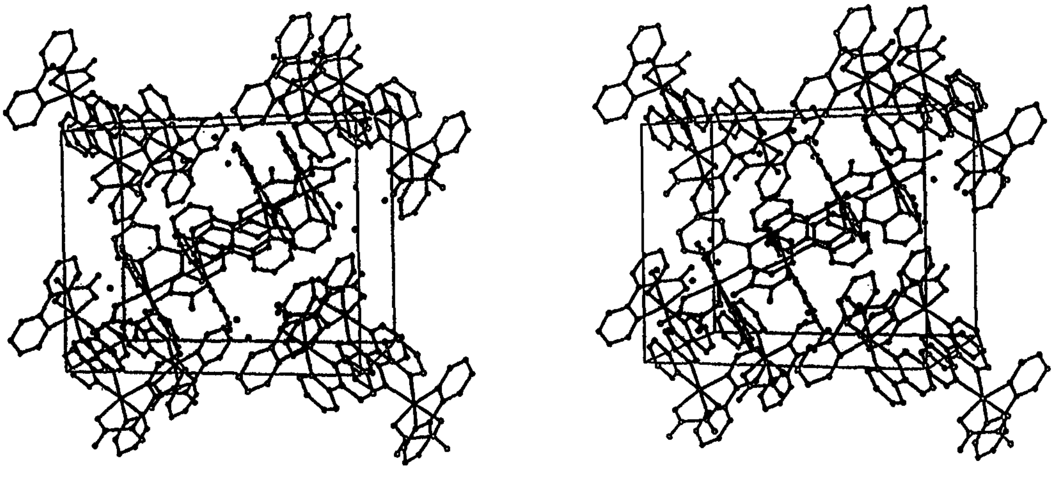

Fig. 2. Crystal packing viewed down the a-axis (c-axis is vertical) of $[Ni(ox)(bipy)_2] \cdot 4H_2O$.

1.77 Å and contacts ranging from 3.55 to 3.75 Å. The Ni(A) ··· Ni(B*) distance is 8.966(2) Å. These π–π stacking interactions, aproximately along the a-axis, are observed in Fig. 3.

The water molecules occupy the interstitial space between the neutral complexes and display hydrogen contacts to each other and to the oxalate oxygen atoms (Table 3).

There are also some weak C—H ··· O contacts which involve the carbon atoms of the bipy ligands as hydrogen-donors and the oxalate and water molecule oxygen atoms as acceptors. There is no doubt that not all the C—H ··· O contacts can be considered as hydrogen bonds, but are indicative of some polarization. The importance of C—H ··· O and C—H ··· O_w hydrogen bonds has long been known to spectroscopists and crystallographers, but definitive evidence for their structural significance was given only a few years ago.[27] In nitrogen-containing molecules, the inductive effect of neutral or charged nitrogen atoms decrease the electron density of immediately adjacent CH groups (C_α atoms) and enhances the facility with which they participate in C—H ··· X hydrogen bonds, being usually the shortest ones. However, in our sample, all of the C_α atoms are not available due to the bipy coordination geometry and only the C(23) atom forms a C—H ··· O contact. The remaining contacts involve the β-carbon atoms to nitrogen ones (C_α to the intering carbon atoms) whose hydrogen atoms are outer and have been determined to be the most acidic protons on the ring.[28] This behaviour also takes place in other bipy complexes.[29]

IR spectroscopy and thermal studies

The IR spectrum of the complex is consistent with the structural data presented above. It shows a continuous absorption at 3600–3200 cm^{-1} due to the presence of lattice water molecules. The sharp bands of medium intensity located in the 1610–1440 cm^{-1} region are assignable to the C–C and C–N stretching vibrations of the coordinated 2,2′-bipyridine. These bands are split into two components with respect to the same vibrations observed for

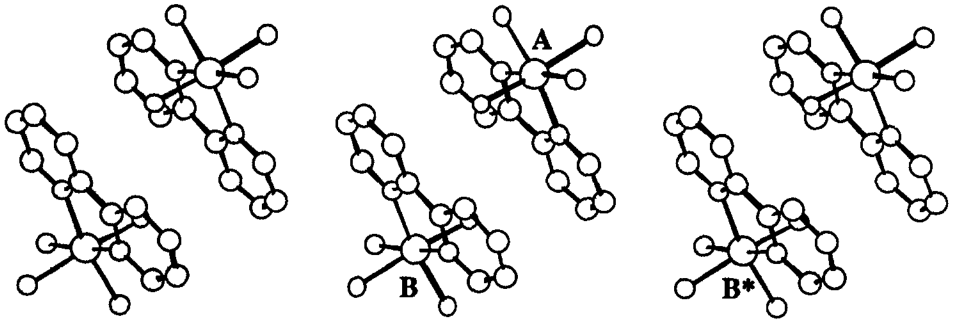

Fig. 3. An illustration of a zigzag chain of units $[Ni(ox)(bipy)_2]$, along the a-axis, linked by stacking π–π interactions. Part of the bipy (X = 2) and oxalate ligands have been omitted for clarity.

Table 3. Hydrogen-bonding system (Å, °)

Bond	Symm.	D···A	H···A	<D—H···A
O(1)$_w$—H(11)$_w$···O(4)$_w$	(1)	2.77(1)	1.85	149
O(1)$_w$—H(12)$_w$···O(2)		2.85(1)	1.84	179
O(2)$_w$—H(21)$_w$···O(11)	(2)	2.75(1)	1.75	177
O(2)$_w$—H(22)$_w$···O(4)$_w$	(3)	2.80(1)	1.81	165
O(3)$_w$—H(31)$_w$···O(2)$_w$	(4)	2.84(1)	1.99	147
O(3)$_w$—H(32)$_w$···O(1)$_w$		2.76(1)	1.75	179
O(4)$_w$—H(41)$_w$···O(21)	(2)	2.80(1)	2.01	135
C(16)—H(16)···O(1)	(5)	3.37(2)	2.35	152
C(23)—H(23)···O(3)$_w$	(6)	3.37(2)	2.50	140
C(26)—H(26)···O(11)	(2)	3.02(1)	2.44	120
C(212)—H(212)···O(21)	(2)	3.39(1)	2.45	154

Symmetry codes
(1) $x-1, y, z$ (2) $x+1, y, z$ (3) $-x+3/2, y-1/2, -z+1/2$
(4) $-x+3/2, y+1/2, -z+1/2$ (5) $-x, -y, -z$ (6) $-x+1/2, y-1/2, -z+1/2$

free 2,2′-bipyridine and undergo shifts to lower frequencies,[30] which indicate that the bipy nitrogen atoms are involved in the coordination to the nickel(II). One of the most relevant features of the IR spectra of oxalate-containing complexes concerns the carbon–oxygen stretching frequencies of the oxalato group because they can be diagnostic of the coordination modes of this ligand. The occurrence of bidentate oxalate is clearly observed in the IR spectrum of the title compound: the ν_{asym}(CO) [1720, 1670 and 1645 cm^{-1}], ν_{sym}(CO) [1425 and 1290 cm^{-1}] and δ (OCO) [770 cm^{-1}] bands are characteristic of this coordination mode and agree very well with those reported for bidentate oxalate-containing nickel(II) complexes.[22]

The thermal behaviour of the compound has been deduced from its TG and DTA curves in both air and argon atmospheres. As it is observed in other oxalato-complexes,[31] the thermal stability does not show significant dependence with the nature of the environmental gas and thermal degradation starts with the elimination of the four crystallization water molecules during one endothermic process which has a temperature range slightly shifted towards lower temperatures in air (50–120°C) than in argon (60–130°C). Although the crystals conserve their form, their crystalline properties are destroyed during the dehydration process and the crystals of the anhydrous compounds are opaque. As they are mounted on an X-ray Weissenberg camera, the photographic film does not show diffraction spots. The anhydrous compound is thermally stable up to around 210°C at which temperature the pyrolytic decomposition starts. The final residues are affected by the surrounding atmosphere,[32] NiO [ASTM 4-0835] and metallic nickel [ASTM 4-0850] are obtained in air and argon atmospheres, respectively.

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