Bismuth derivatives of 2,3-dicarboxypyrazine and 3,5-dicarboxypyrazole as precursors for bismuth oxide based materials†

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Depending on the experimental conditions, different bismuth derivatives of 2,3-dicarboxypyrazine (2,3-H_2pzdc) were obtained, corresponding to the compositions Bi(2,3-Hpzdc)$_3 \cdot 2H_2O$ (**4**) and Bi(2,3-Hpzdc)$_2 \cdot$ OH (**5**). In line with the analytical results and the infrared spectra, high resolution NMR studies (DMSO — d^6) of anhydrous Bi(2,3Hpzdc)$_3$ (**4a**) confirmed unequivocally the presence of one free carboxylic acid in the structure. Thermal degradation of **4a** in air proceeds in three steps and results in the formation of α-Bi_2O_3 at moderate temperature (451 °C). A bismuth derivative of 3,5-dicarboxypyrazole (3,5-H_3Dcp) corresponding to the formula Bi_2(3,5-Dcp)$_2 \cdot nH_2O$ (**3**) was obtained from bismuth nitrate and the dicarboxylic acid in hot water. It decomposes into α-Bi_2O_3 when heated in air at 385 °C. The starting compounds and their thermal degradation products were also examined with X-ray photoelectron spectroscopy.

Coordination compounds generate considerable interest as precursors for the preparation of homogeneously dispersed solid state materials like oxides, sulfides, carbides and nitrides. They are thought to be particularly helpful in the design of multimetallic or multiphasic systems with controlled architecture, leading to interesting applications in the fields of superconductivity and heterogeneous catalysis. With respect to this, bismuth is an attractive element because of its widely recognized potential as a promoter in selective oxidation catalysts[1,2] and as an additive in 1-2-3 YBaCuO superconductors.[3] Less advertised applications of this element concern the manufacture of new chemical sensors based on the Bi–Sn association for the detection of formaldehyde[4] and the obtention of photosensitive layers in the 'silver-free physical development' process.[5]

The general use of carboxylates as precursors of highly dispersed oxide-based materials offers several advantages: (*i*) these compounds exhibit usually well-defined structures and stoichiometries depending on the nature of the carboxylate chain; (*ii*) they can be designed in order to contain no heteroelements other than carbon, nitrogen, oxygen and hydrogen, thus preventing eventual poisoning or alteration of the final material by elements like sulfur or halogens; (*iii*) their multidentate structure often favours the formation of polymeric patterns, which can help to control the distribution of the active metals on the surface, and (*iv*) the thermal decomposition of these ligands into well-defined and finely dispersed powdered samples occurs at moderate temperatures that limit sintering effects. We recently used this approach for the preparation of Bi-based ternary oxides and heterometallic bismuth–lanthanide molybdate catalysts for the selective oxidation of alkenes.[6,7]

Polycarboxylic systems based on heterocyclic skeletons arouse great interest for that purpose. Because of their aromatic structure, these compounds seem to be particularly adapted for the preparation of carbon-supported heterogeneous catalysts, if one wishes to take advantage of the π–π stacking interactions between the precursor molecule and the graphitic planes of the support. This could help in controlling more appropriately the incorporation of the active metals in the catalysts and, consequently, ensure more homogeneous dispersions. Some bismuth(III) salts of pyridine-, pyrazine- and pyridazine- mono- or dicarboxylic acids have been described in the literature.[8,9] The present work deals with the synthesis and spectroscopic characterization (IR, ^{1}H and ^{13}C NMR, XPS) of new bismuth(III) derivatives of two nitrogen-containing dicarboxyheterocycles, namely 3,5-dicarboxypyrazole (3,5-H_3Dcp), **1**, and 2,3-dicarboxypyrazine (2,3-H_2pzdc), **2**, in view of their use as precursors for the preparation of bismuth-based oxides.

Results and Discussion

Synthesis and spectroscopic (IR, NMR) characterization of the bismuth derivatives

Bis(3,5-pyrazoledicarboxylato)dibismuth(III) polyhydrate: Bi_2(3,5-Dcp)$_2 \cdot nH_2O$, 3. Characteristic IR wavenumber values are listed for the different complexes in Table 1. The absorption bands of the carboxylic groups at 1696 cm^{-1} and those associated with the N—H bonds at 3228 and 3436 cm^{-1} in the free ligand **1** have disappeared in the infrared spectrum of complex **3**, suggesting the formation of a trianionic species consisting of one pyrazolate and two carboxylate functions. The shifts observed with the carboxylic and C═N vibrations in the range 1700–1500 cm^{-1} also confirm that the heterocyclic ligand coordinates the central atom through both the oxygen of the carboxylic group and the heterocyclic nitrogen atom. The wavenumber values measured in the Bi complex **3** are close to those obtained with the corresponding potassium salt, K_3Dcp. The large Δν value observed between the frequencies associated with the symmetric and antisymmetric stretching modes of the carboxylate group [$\Delta\nu = \nu_{as}(COO) - \nu_s(COO) = 277$ cm^{-1}] in **3** is in line with a monodentate type of coordination.[11] Dinuclear Pd^{II}, Pt^{II}, Ni^{II} and Cu^{II} complexes of the same ligand displaying square planar

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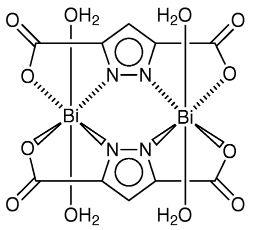
† Non-SI unit employed: 1 eV ≈ 1.60 × 10^{-19} J.

Table 1 Characteristic IR data in cm^{-1}

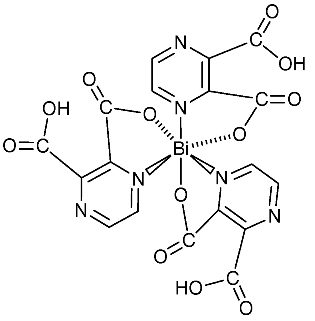
Compound	ν(N—H)	ν(ArC=O)	$\nu_{as}(COO^-)$	ν(C=N)	$\nu_s(COO^-)$	ν(Bi—O)
$H_3Dcp \cdot H_2O$, **1**	3228–3436	1696	—	1494	—	—
$K_3Dcp \cdot H_2O$	—	—	1676	1566	1360	—
$Bi_2(Dcp)_2 \cdot 4H_2O$, **3**	—	—	1620	1550	1343	528
2,3-H_2pzdc, **2**	—	1717	—	1578	—	—
K_2pzdc[10]	—	—	1621	1598	1390	—
Bi(2,3-Hpzdc)$_3 \cdot 2H_2O$, **4**	—	1723	1617	1570	1363	532
Bi(2,3-Hpzdc)$_2$OH, **5**	—	1639	1598	1553	1366	530

geometries[12] and a vanadyl(IV) complex characterized by a square pyramidal coordination[13] have already been described in the literature. The ability of the trianion of **1** to form dinuclear complexes in the presence of ancillary ligands like CO, PPh_3 and 1,5-cyclooctadiene has also been established in a series of anionic complexes of Rh^I and Ir^I. [14] Further examples of bridging Dcp^{3-} anions were observed in chromate(III) complexes containing acetylacetonate or diamine-*N*,*N*′-dicarboxylate ligands.[15,16] In the absence of any crystal structure data on the new Bi complex with 3,5-H_3Dcp, only hypotheses can be formulated about the coordination around Bi. For the compound that is initially obtained in the hydrated form, it can be speculated that two water molecules coordinate each Bi atom together with two nitrogen atoms and two oxygen carboxylate atoms belonging to two different ligand molecules, resulting in a coordination number of 6 for each metal atom. The obtention of this dinuclear complex with a bridging trianionic ligand could result from the strongly favoured structure that is achieved: aromaticity of the pyrazole rings is retained, and five- and six-membered rings are formed in the plane containing the pyrazole rings and the Bi atoms. Complexation of Bi^{III} by the nitrogen lone pair of the pyrazole ring can be taken as responsible for the enhanced acidity of the neighbouring pyrazolic hydrogen, and consequently account for the formation of the trianionic species. The equilibrium is also shifted by the extremely low solubility of compound **3**.



3

Tris(2,3-hydrogenpyrazinedicarboxylato)bismuth(III) dihydrate: Bi(2,3-Hpzdc)$_3 \cdot 2H_2O$, 4. The infrared spectrum of the free acid **2** exhibits absorption bands between 2500 and 3267 cm^{-1} (2500, 2609, 2837, 3267 cm^{-1}) that are typical of hydrogen bonded carboxylic groups. Similar absorption bands appear in the IR spectrum of complex **4**. In the IR spectrum of the anhydrous compound **4a**, these bands appear at 2526, 2643, 2896 and 3431 cm^{-1}. An additional sharp intense band occurs at 3558 cm^{-1}, which corresponds to the free carboxylic acid. The bands centred at 1717–1754 cm^{-1} in the IR spectrum of the free acid **2** can be assigned to stretching vibrations of the carboxyl group. The related vibrations in the Bi complex **4** are centred at 1723 cm^{-1}. It is concluded that each ligand molecule has one carboxylic function and coordinates to the metal ion through an oxygen atom of the carboxylate group. The values associated with the stretching vibrations of the carboxylate group in **4** are similar to those obtained in the analogous potassium salt.[10]



4a

The NMR spectra of complex **4a** and ligand **2** have been recorded in DMSO-d$_6$. The ^{1}H NMR spectrum of complex **4a** gives two signals at 13.24 and 8.96 ppm. The signal at 13.24 ppm, corresponding to the carboxylic proton, appears as a broad single line with the same chemical shift as the carboxylic proton of the free ligand. The signal at 8.96 ppm is characteristic of the heterocyclic protons. The ^{13}C NMR spectrum is characterized by three lines at 167.30, 146.60 and 144.65 ppm. They can be assigned to the carboxylic group and the quaternary and tertiary carbon atoms, respectively. The resonance line associated with the quaternary carbon atoms is broadened due to the presence of bismuth atoms in their close neighbourhood.

Hydroxobis(2,3-hydrogen pyrazine dicarboxylato)bismuth(III): Bi(2,3-Hpzdc)$_2$OH, 5. The infrared spectrum of the Bi(2,3-Hpzdc)$_2$OH compound is in agreement with the one reported in the literature.[8] The band assigned to the stretching vibrations of the carboxylic group in the IR spectra of the ligand has shifted towards lower frequencies owing to a possible interaction between the carboxylic function and the hydroxyl group coordinated with the Bi atom. The difference of 232 cm^{-1} between the asymmetric (1366 cm^{-1}) and symmetric (1598 cm^{-1}) stretching modes indicates an unsymmetrical monodentate coordination of the carboxylate group. The vibrations found in the 530 cm^{-1} region are assigned to the Bi—O(H)—Bi bonds. NMR spectra of **5** could not be recorded due to the insufficient solubility of this product in DMSO.

X-Ray photoelectron spectroscopy

The binding energy values measured for carbon [C (1s)], oxygen [O (1s)], nitrogen [N (1s)] and bismuth [Bi (4f) doublet] atoms in the starting ligands, the various complexes and their thermal degradation products are listed in Table 2.

The C (1s) photoelectron spectra of the free ligands and the Bi^{III} complexes display the same general shape, with three major components. The first one (C_I) corresponds to hydrocarbonaceous species, including the heterocyclic CH and the residual surface 'CH_x' contamination; this component was fixed arbitrarily at 284.8 eV as the internal reference for the whole binding energy scale. The highest energy component

Table 2 XPS data

	Binding energy/eV (Relative intensities/%)						
	C (1s)				N (1s)		
Compound	C_I[a] CH_x	C_{II} C=N	C_{III} COO	O (1s) COO	N_I N=C	N_{II} N—H	Bi ($4f_{7/2}$) Bi^{3+}
2,3-H_2pzdc	284.8 (8)	286.3 (63)	289.4 (29)	532.2 (60)–533.7 (40)	400.1 (100)	—	—
Bi(2,3-Hpzdc)$_3$ · $2H_2O$	284.8 (11)	286.2 (63)	289.0 (26)	531.6 (71)–533.0 (29)	400.0 (100)	—	160.0 (100)
Bi(2,3-Hpzdc)$_3$ · $2H_2O$[b]	284.8 (64)	285.9 (25)	288.5 (11)	529.4 (62)–531.1 (38)	present	present	158.7 (100)
3,5-H_3Dcp	284.8 (28)	285.9 (38)	289.2 (34)	531.9 (52)–533.3 (48)	400.0 (50)	401.3 (50)	—
Bi_2(Dcp)$_2$ · $4H_2O$	284.8 (28)	285.9 (41)	288.8 (31)	531.7 (97)–533.5 (3)	400.0 (80)	401.2 (20)	160.1 (100)
Bi_2(Dcp)$_2$ · $4H_2O$[b]	284.8 (59)	285.7 (34)	288.3 (7)	529.5 (58)–531.1 (42)	—	—	158.9 (100)

[a] Fixed arbitrarily at 284.8 eV for use as internal reference. [b] Calcined at 550 °C.

C_{III} corresponds to the carboxylic groups and is slightly shifted downwards (0.4 eV in compounds **3** and **4**) upon coordination with bismuth atoms. The intermediate C (1s) component (C_{II}) can be assigned to the heterocyclic carbon atoms bound to nitrogen. In agreement with the structural composition of the two carboxylic acids concerned, the intensity ratios C_{II}/C_{III} are close to 1.0 in 3,5-H_3Dcp and to 2.0 in 2,3-H_2pzdc. As expected, the E_b values of the C_{II} component are not affected by the formation of complexes.

The N (1s) XPS spectra of free 3,5-pyrazoledicarboxylic acid are characterized by two components of equal intensity, ascribed to the two non-equivalent nitrogen atoms present in this ligand. Coordination with bismuth in the pyrazolate form, as suggested by the infrared data, removes the difference between these nitrogen atoms and the corresponding photoelectron spectrum of complex **3** is essentially restricted to the lower binding energy component (N_I). The same observations have already been made for the $(NBu_4)_2$ [Pd_2(Dcp)$_2$] complex described elsewhere.[17] This E_b value is identical to the one observed in the heteroleptic complexes $(NR_4)_x$[$Ir_2(CO)_4$(Dcp)].[14]

As expected from the structure of ligand **2**, the N (1s) photoelectron spectrum shows only one component, which is unaffected by the formation of complex **4**. As the E_b values for the N—Bi and N=C bonds are rather similar we could not argue for the coordination of the bismuth atom by the nitrogen atoms of the heterocyclic ring.

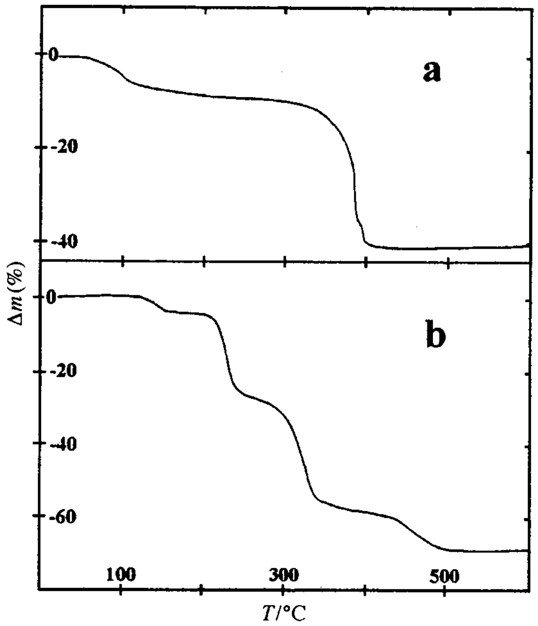


Fig. 1 Thermal degradation curves of (a) Bi_2(Dcp)$_2$ · $4H_2O$, **3**, and (b) Bi(2,3-Hpzdc)$_3$ · $2H_2O$, **4**, under air (heating rate of 10 °C min^{-1})

The Bi (4f) binding energy values in all three complexes appear to be slightly larger (by about 1 eV) than in the calcined samples where Bi is present as Bi_2O_3.

Thermal behaviour of the bismuth complexes and characterization of the degradation products

When heated under air or nitrogen, compounds **3** and **4** decompose into bismuth(III) oxide in two or four successive steps. The formation of α-Bi_2O_3 under these experimental conditions was checked by X-ray diffractometry. Typical thermal degradation curves obtained in air are illustrated in Fig. 1. The 3,5-pyrazoledicarboxylate complex **3** is shown to lose its crystallization water at about 97 °C and the anhydrous compound exhibits an extended stability range up to 385 °C, where it decomposes in one single step into α-Bi_2O_3. The thermal degradation scheme of the 2,3-pyrazinedicarboxylate compound **4** is more complex and shows four successive steps at 143, 231, 327 and 451 °C. The second and third degradation steps are assumed to involve the decomposition of the pzdc ligand into pyrazine and CO_2, as reported previously in the literature for hydrated 2,5-pyrazinedicarboxylate complexes of Cu^{II}, Ni^{II} and Co^{II}, where this evolution occurred in the temperature range 280–315 °C, depending on the transition metal.[18] Similarly, simultaneous formation of CO_2, pyrazine and bipyrazine has been reported in the temperature range 284–325 °C when the bis(pyrazinecarboxylate) complex of Cu^{II} was heated under argon.[19]

The main relevant parameters corresponding to the present work are listed in Table 3, together with the specific surface areas of the Bi_2O_3 residues obtained after calcination of the starting compounds at 500 °C. Values in the range of 0.5 to 0.7 m^2 g^{-1} were observed. These surface areas are similar to those obtained from other carboxylate-type compounds[7] and are slightly larger than those of commercially available Bi_2O_3, which typically displays BET surface areas in the range 0.1–0.2 m^2 g^{-1}.

Although calcination was carried out at 500 °C, that is at a temperature where all the investigated compounds are converted into Bi_2O_3 according to their respective TGA curves,

Table 3 Calculated and experimental weight losses of the complexes heated at 500 °C under air (10 °C min^{-1}) and specific surface areas of the final Bi_2O_3 residues

	Weight loss/%		
Compound	Exptal	Calcd[a]	BET specific surface area/m^2 g^{-1}
Bi(2,3-Hpzdc)$_3$ · $2H_2O$	72.0	68.7	0.65
Bi_2(Dcp)$_2$ · $4H_2O$	40.7	41.5	0.55

[a] Calculated for Bi_2O_3.

the C(1s) photoelectron spectra still reveal the presence of some oxygenated carbonaceous species, which are most probably residual surface amounts of the carboxylate precursor, itself or partially decomposed (Bi/C atomic intensity ratio = 1.3 and 0.8 for the calcined compounds **3** and **4**, respectively).

Experimental

Materials and syntheses

3,5-Pyrazoledicarboxylic acid monohydrate ($3,5\text{-}H_3Dcp \cdot H_2O$), **1**, (Janssen, 97%), 2,3-pyrazinedicarboxylic acid ($2,3\text{-}H_2pzdc$), **2**, (Janssen, 97%) and bismuth(III) nitrate pentahydrate (Fluka, 99%) were used as received. The bismuth content was estimated by complexometric titration with EDTA using xylenol orange as the indicator. C-H-N elemental analysis was carried out at University College, London.

$Bi_2(3,5\text{-}Dcp)_2 \cdot nH_2O$, 3. 3,5-Pyrazoledicarboxylic acid (1.00 g, 5.74 mmol) was dissolved in 25 ml of hot water (55 °C). Successive fractions of solid $Bi(NO_3) \cdot 5H_2O$ (1.857 g, 3.83 mmol) were added to the previous solution, producing a white precipitate. The temperature was kept constant for 19 h. The precipitate was collected by filtration at this temperature, then washed with hot water and diethyl ether. As suggested by the thermogravimetric analysis and the chemical assay of bismuth, the stoichiometry of the collected compound is close to $Bi_2(3,5\text{-}Dcp) \cdot 4H_2O$. Anal. found: Bi, 50.6; H_2O, 8.6; calcd for $Bi_2(3,5\text{-}Dcp)_2 \cdot 4H_2O$: Bi, 52.5; H_2O, 9.0%. Yield: 89%. The compound is insoluble in common organic solvents.

The elemental analysis of the anhydrous product **3a** obtained after heating at 110 °C gave the following results: found: C, 16.03; N, 7.49; H, 0.58; calcd for $Bi_2(3,5\text{-}Dcp)_2$: C, 16.59; N, 7.73; H, 0.28%.

$Bi(2,3\text{-}Hpzdc)_3 \cdot 2H_2O$, 4. 2,3-Pyrazinedicarboxylic acid (1.00 g, 5.95 mmol) was dissolved in 10 ml of water. Four millilitres of a 2 M HNO_3 solution of $Bi(NO_3)_3 \cdot 5H_2O$ (0.9616 g, 1.98 mmol) were added dropwise to the former solution, producing instantaneously a white precipitate. The mixture was maintained at room temperature for 3 days. The precipitate was filtered out, washed with water and diethyl ether, and dried at room temperature. The stoichiometry of the obtained complex is $Bi(2,3\text{-}Hpzdc)_3 \cdot 2H_2O$. Anal. found: C, 29.03; N, 10.86; H, 1.59; Bi, 28.8; calcd for $Bi(2,3\text{-}Hpzdc)_3 \cdot 2H_2O$: C, 28.97; N, 11.26; H, 1.76; Bi, 28.1%. Yield: 80%.

The corresponding anhydrous product $Bi(2,3\text{-}Hpzdc)_3$, **4a**, was obtained after heating at 110 °C. NMR data of **4a** (DMSO-d_6 solutions, δ): ^1H 8.96, 13.24; ^{13}C 144.65, 146.60, 167.30. (The corresponding data of the free ligand **2** are: ^1H 8.84, 13.24; ^{13}C 145.68, 145.35, 166.11.)

$Bi(2,3\text{-}Hpzdc)_2 \cdot OH$, 5. Another Bi complex of pyrazine-2,3-dicarboxylic acid, previously described in the literature but synthesized according to another procedure,[8] was also obtained when the metal was in excess with respect to the diacid (Bi/ligand = 1.5). The stoichiometry of the complex is $Bi(2,3\text{-}Hpzdc)_2 \cdot OH$, **5**.‡

$Bi(NO_3)_3 \cdot 5H_2O$ (6.503 g, 13.41 mmol) dissolved in 15 ml of a 2M HNO_3 solution were added dropwise, at room temperature, to 20 ml of an aqueous solution of 2,3-pyrazinedicarboxylic acid (1.502 g, 8.93 mmol). The white precipitate that formed after 30 min was filtered after 16 h storage at room temperature, washed with water and diethyl ether and dried at room temperature. Anal. found: 24.86; N, 9.67; H, 1.06; Bi, 38.3; calcd for $Bi(2,3\text{-}Hpzdc)_2 \cdot OH$: C, 25.73; N, 10.00; H, 1.26; Bi, 37.3%. Yield: 83%.

Instrumental

Infrared absorption spectra were recorded on a Perkin–Elmer model 1710 spectrophotometer using KBr pellets. ^1H and ^{13}C NMR spectra of the complexes were recorded on a Bruker AM 500 spectrometer equipped with a 5 mm probe. DMSO d_6 was used as both solvent and internal reference (residual proton line at 2.49 ppm, ^{13}C NMR line at 39.5 ppm). The XPS measurements were carried out on an SSI-X-probe (SSX-100/206) spectrometer from Fisons, equipped with an Al X-ray source and connected to an HP 9000/310 computer. The C (1s) photopeak corresponding to the hydrocarbon contamination was fixed at 284.8 eV and used as internal reference for the calibration of the binding energy scale. Analytical photopeaks were Bi ($4f_{7/2}$), N (1s) and O (1s).

Thermogravimetric analysis measurements were performed with a Setaram TGC 85 thermal analyser connected to a Hewlett–Packard 86D computer. The analyses of powder samples (10 mg) were carried out in alumina under air or nitrogen. The heating rate was fixed at 10 °C min^{-1}. The BET specific surface area were measured with a Micrometrics ASAP 2000 instrument and based on krypton adsorption at −196 °C.

Acknowledgements

The authors greatly acknowledge financial assistance from the Belgian National Fund for Scientific Research (FNRS), Brussels. This work was supported by a fellowship allotted to M.W. by the 'Institut pour l'Encouragement de la Recherche dans l'Industrie et l'Agriculture' (IRSIA), Belgium.

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Received in Montpellier, France, 9th February, 1998;
Paper 8/01161C

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‡ $\{Bi[pz(COO)_2](OH)\}_n$ is the stoichiometry suggested by M. Postel and co-workers.[8] However, the calculated and experimental results of their elemental analysis are not in agreement with this hypothesis. For the same product (confirmed by IR analysis), we therefore propose the stoichiometry given here.