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N-Oxides in Metal-Containing Multicomponent Molecular Complexes

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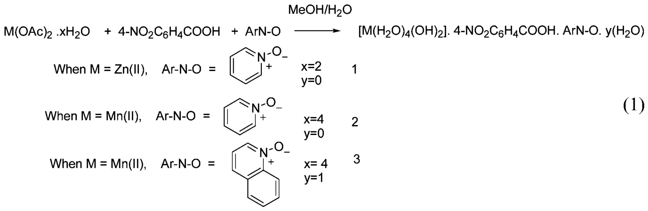
Syntheses and structures of three-component rare cocrystals of 4-nitrobenzoic acid, aromatic *N*-oxides, and aqua complexes of manganese and zinc and their transformation to metal complexes as well as coordination polymers are presented.

N-Oxides are used for oxidation of various organic substrates, and such oxidations are generally facilitated by metal complexes.[1] Metal complexes having *N*-oxide ligands also have great value as magnetic materials.[2] The *N*-oxides show interesting host−guest chemistry with various hosts[3] such as calixarenes, cyclodextrin, and dihydroxybenzene, and there is ample scope to understand host−guest chemistry of *N*-oxides. The aromatic *N*-oxides also form metal complexes easily upon reaction with metal carboxylates and other salts.[2] However, *N*-oxides along with carboxylic acids are not studied as molecular complexes with metal hydroxides. Recently, a hexaaquacobalt complex having bipyridine *N*-oxide has appeared in the literature.[5] Such multiple-component molecular crystals are expected to throw light on the nucleation process of metalloorganic hybrid complex formation as well as on the role of intermolecular hydrogen-bonding interactions in the synthesis of coordination polymers. With this objective, we have studied three-component molecular complex formations between metal hydroxyl complexes, *N*-oxides, and carboxylic acids.

Molecular complexes of *N*-oxides such as pyridine or quinoline *N*-oxide, 4-nitrobenzoic acid, and metal hydroxides are formed upon reaction of the corresponding *N*-oxide and 4-nitrobenzoic acid with metal acetates in aqueous methanol (eq 1). This hydrolytic reaction is highly substrate-dependent, and we could get such three-component molecular complexes only from 4-nitrobenzoic acid out of several aromatic acids such as benzoic acid, methylbenzoic acids (all three isomers), 2-nitrobenzoic acid, etc. However, the reaction of 4-nitrobenzoic acid with manganese(II) actetate and pyridine *N*-oxide in dry methanol leads to coordination polymers (Scheme 1). The reaction procedures for the preparation of a molecular complex or the coordination polymers are very simple, and these complexes can be prepared by mixing the three reactants in dry methanol or aqueous methanol (10%) and stirring at ambient temperature (48 h for the molecular



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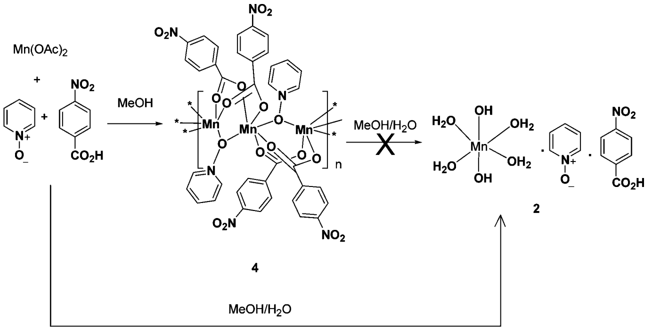
Scheme 1



complex and 2 h for coordination polymers). There is near-quantitative desired product formation in these reactions. The coordination polymer **4** upon dissolution in aqueous methanol and standing for 48 h does not give compound **2**. Thus, compound **2** is not formed by hydrolysis of coordination polymer **4**. However, it may be formed by hydrolytic cleavage of a dinuclear aqua-bridged complex that is generally formed upon reaction of manganese(II) or zinc(II) acetate with various aromatic acids. The crystal structures of each of the complexes **1**−**3** are shown in Figure 1a−c along with some of the selected hydrogen bonds contributing to the packing pattern of the complexes. In each case, the *N*-oxides as well as carboxylic acids are hydrogen-bonded to aqua and hydroxyl ligands. The important hydrogen-bond interactions are listed in Table 1.

It is interesting to note the differences in weak interactions in the crystal structures of these molecular complexes. In the case of **1** and **2**, when pyridine *N*-oxides are there in the lattice, the nitro group of 4-nitrobenzoic acid and the N−O group of *N*-oxides are involved in hydrogen bonding to the aqua ligands of the metal ion and the carboxylic group is involved in C−H···O interactions. However, in the case of **3**, the carboxylic group of 4-nitrobenzoic acid and the N−O group of quinoline *N*-oxide are involved in hydrogen bonding with the aqua ligands of the manganese(II) complex. The thermogravimetric study shows that complexes **1**−**3** undergo dehydration and lose weight corresponding to the six water molecules in the case of **1** and **2** and the seven in the case of **3** in the temperature range of 50−110 °C. These dehydration processes can be attributed to the formation of coordination polymers having structural features similar to those of coordination polymer **4**; see comparisons of IR spectra with an authentic sample of the coordination polymer prepared by an alternative route.

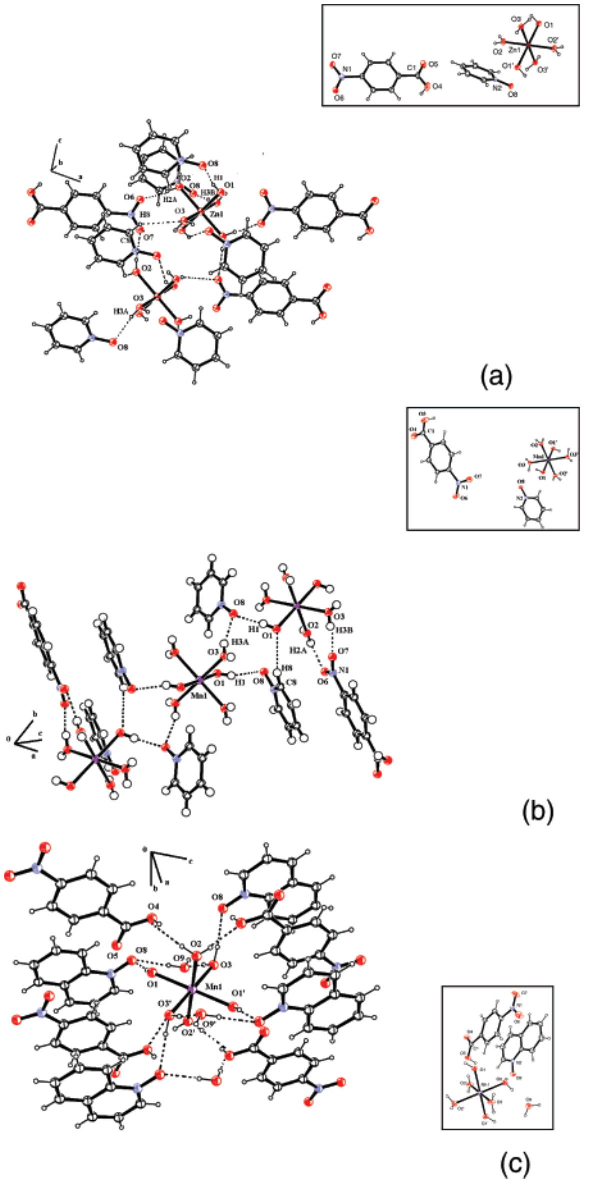


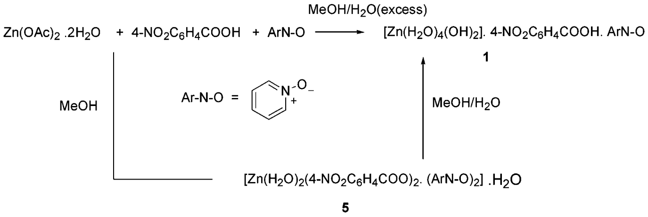
Figure 1. Hydrogen-bonding interactions in the lattice of molecular complexes (a) **1**, (b) **2**, and (c) **3** (drawn with 20% thermal ellipsoids). Insets are the molecular complexes.

An aqua-bridged benzoate complex is generally formed from the reaction of benzoic acid with manganese(II) acetate, and such a complex is isolated as a stable product by adding a N-donor ligand such as pyridine during the reaction.[4] Further evidence to the hydrolytic cleavage of low-nuclearity complexes comes from the control reaction of zinc(II) acetate dihydrate with 4-nitrobenzoic acid and pyridine *N*-oxide. When this reaction was carried out for 2 h and the solvent was evaporated, an intermediate mononuclear complex **5** could be isolated (Scheme 2). This suggests that there is a competition between water molecules to replace the *N*-oxide ligands and also the carboxylate ligands. Over the course of time, these ligands come out of the coordination sphere, facilitating the formation of a neutral molecular complex **1**. Furthermore, the short-range interactions between the *N*-oxide and 4-nitrobenzoic acid keep them apart as noncoordinating under ambient conditions. The same reaction upon continuation for 48 h in aqueous methanol gave compound **1**. The mononuclear complex formed is found to be diaquadi-4-nitrobenzoatodipyridine *N*-oxide zinc(II) monohydrate (**5**; Scheme 2). This complex has hexacoordination with two monodentate carboxylate groups and two *N*-oxide ligands. Each identical pair of ligands is in the trans disposition to each other. We have characterized this compound by crystallography also. The complex has a two-dimensional, infinite chain-like structure growing through the O−H···O interaction between aqua ligands and the water molecules of crystallization along the *b* and *c* crystallographic axes. The complex upon redissolution in aqueous methanol and stirring for further 2 days gives molecular complex **1**.

Table 1. Hydrogen-Bond Geometries in the Complexes

D−H···A	d_{D-H} (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	∠D−H···A (deg)
For 1				
O1−H1···O8	0.82	2.05	2.84(3)	163.38
O2−H2A···O6 [$x, -1 + y, z$]	0.82	1.81	2.62	170.88
O2−H2B···O7	0.80(3)	2.02(3)	2.82(3)	171.39
O3−H3A···O8 [$x, -1 + y, z$]	0.82	1.98	2.73(19)	153.84
O3−H3B···O8 [$-x, -^1/_2 + y, ^1/_2 - z$]	0.84(4)	1.89(4)	2.73(2)	173.07
C8−H8···O3	0.93	2.37	3.28(3)	166.25
For 2				
O1−H1···O8 [$1 - x, -^1/_2 + y, ^1/_2 - z$]	0.82	1.92	2.72(2)	163.5
O2−H2A···O6 [$x, -1 + y, z$]	0.82	1.81	2.62	173.18
O2−H2B···O7	0.79(4)	2.01(4)	2.79(3)	171.69
O3−H3A···O8	0.82	2.06	2.86(2)	163.79
O3−H3B···O7 [$1 - x, 1 - y, 1 - z$]	0.64(4)	2.05(4)	2.68(3)	168.08
C8−H8···O1	0.93	2.41	3.32(2)	165.31
For 3				
O1−H1···O8 [$1 + x, y, z$]	0.82	1.94	2.76	170.18
O3−H3A···O9	0.82	1.87	2.68	173.10
O9−H9B···O4 [$1 + x, -1 + y, z$]	0.88	1.98	2.85	171.33
O9−H9A···O8 [$1 - x, -1 - y, -z$]	0.84	1.98	2.81	170.73

Scheme 2



Because the *N*-oxides have a polar N−O bond and the carboxylic acid has an acidic COOH group, it is expected that they form cocrystals among themselves. We have prepared cocrystal **6** of quinoline *N*-oxide with 4-methylbenzoic acid. The 1:1 cocrystal has the structure shown in Figure 2. The cocrystal **6** is stabilized by extensive hydrogen-bonding interactions such as O2−H2···O3 ($d_{D\cdots A}$, 2.565 Å; ∠D−H−A, 169.30°), C13−H13···O1 ($d_{D\cdots A}$, 3.37 Å; ∠D−H−A, 150.97°), and C14−H14···O3 ($d_{D\cdots A}$, 3.45 Å; ∠D−HA, 154.05°). The formation of this kind of cocrystal suggests that there is a synergic effect in the zinc and manganese aromatic carboxylate complexes to dissociate, and the stability of such complexes is dependent on the solvation versus stability of molecular complexes such as **1**. These competitive effects lead to the facile attack of water on any transient complex formed during the reaction of metal acetate with *N*-oxide and aromatic carboxylic acid, to give molecular complexes such as **1**−**3**. It is important to note that the formation of molecular complexes of metal hydroxides with carboxylic acids suggests the coexistence of an acid and a base in a crystal lattice, and this is interesting because in conventional chemistry an acid would react with a base and vice versa and the two components in the molecular complexes should have led to some other neutral compounds.

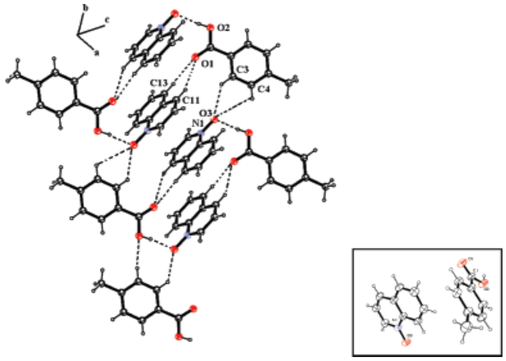


Figure 2. Hydrogen bonds in the structure of cocrystal **6** of quinoline *N*-oxide with 4-methylbenzoic acid (drawn with 20% thermal ellipsoid). The inset is the structure of the cocrystal.

However, we have not come across such reactions, and crystals are stable at ambient temperature for at least a month without any degradation. The stability may be attributed to the packing effect resulting from the weak interactions among the nitro, N−O, and coordinated water molecules, as illustrated in Figure 1. The existence of the cocrystals of manganese/zinc hydroxyl complexes with free carboxylic acids and *N*-oxides is unlikely in conventional acid−base chemistry and happens purely in the solid state, which can be attributed to a packing effect. At this stage, it may be mentioned that during the determination of the structures the H atoms, except those attached to the O atoms, were placed at their calculated positions and refined in the isotropic approximation; however, the H atoms attached to the O atoms of the hydroxyl and carboxylic acid groups, which could not be located in the difference Fourier maps, were placed at the calculated positions and refined with an isotropic approximation. Thus, their location does not reflect the concept of acid and base in a quantitative manner but refers to the packing pattern only. In solution chemistry, such an association is not necessarily observed; the ^{1}H NMR spectra of the zinc compound **1** in solution give the signal of the parent compounds without any change in the chemical shift. It may be mentioned that the basicity of metal hydroxide in a confined medium is important because Zn^{II}-bound OH$^-$ in carbonic anhydrase is a nucleophile in the reaction with carbon dioxide.[6]

In conclusion, molecular complexes having multicomponent complexes, namely, *N*-oxide, metal hydroxide, and carboxylic acid, are characterized by crystallography, which opens an extra dimension to the supramolecular chemistry of *N*-oxides, and these may be considered to be intermediates for the synthesis of *N*-oxide-bridged coordination polymers.

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Supporting Information Available: Crystallographic details of the compounds in the form of CIF files, spectroscopic data, and a crystallographic table. This material is available free of charge via the Internet at http://pubs.acs.org.

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