

Ladder-and-platform metal-organic hosts: molecular and crystal structure of polymeric and dimeric host complexes incorporating nickel(II) dibenzoylmethanate units connected with 4,4'-bipyridyl

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The molecular structure, conformational features and packing mode of the polymeric $[\text{Ni}(\text{bipy})(\text{DBM})_2]_n$ complex (bipy = 4,4'-bipyridyl, DBM = dibenzoylmethanate), which is a 'soft' metal-organic sorbent suitable for gases and volatile organics, are reported.

In the search for new practically useful sorbents, we have developed supramolecular materials based upon modified metal dibenzoylmethanates (DBMs).^{1–5} We utilised a general strategy^{6–8} to enhance the inclusion affinity of known molecular hosts by linking them with 4,4'-bipyridyl (bipy). Connecting flat metal DBM units with bipy produces oligomeric and polymeric materials with very strong inclusion affinity and good prospects as storage matrices and microporous sorbents.^{9,10} A distinguishing feature of these materials is the 'soft' architecture of their supramolecular framework that is apparent in the easy conversion among many possible structures on response to external stimuli, an important characteristic attributed to the 'third generation' of host metal-organic frameworks.^{11,12}

The $[\text{Ni}(\text{bipy})(\text{DBM})_2]$ complex forms inclusions with all sorbates tried.¹⁰ We characterised inclusion compounds of this complex with 13 organic solvents, which fall into seven structural types and demonstrated the ability of the complex to absorb significant quantities of xenon and methane.¹⁰ It is believed that the complex has a polymeric structure in all inclusions it forms with a ladder-and-platform motif previously developed for organic molecules,^{13–15} as shown schematically in Figure 1. Presumably, the parallel packing of 1D polymeric chains of the complex is conducive to more effective packing because of their interdigitation, yet leaving some space between DBM fragments of adjacent chains for guest species.

We attempted to elucidate the actual structure of the complex, but we failed to form crystals suitable for single-crystal XRD analysis. The structure proposed, as shown in Figure 1, was based on indirect observations, as well as on an analogy with a zinc(II) analogue of the complex.^{9,10} The zinc(II) analogue $[\text{Zn}(\text{bipy})(\text{DBM})_2]_n$ forms highly crystalline inclusion materials, many of which were studied to an atomic resolution. Unfortunately, the zinc complex does not absorb gases and thus is of less practical interest.

Here we report two crystal structures, polymeric $[\text{Ni}(\text{bipy})(\text{DBM})_2]_n \cdot 2n(\text{DMF})$ **1** and dimeric $[\text{Ni}_2(\text{bipy})\text{Py}_2(\text{DBM})_4] \cdot 2(\text{bipy}) \cdot 2\text{Py}$ **2** (DMF = dimethylformamide; Py = pyridine). In spite of the poor quality of the crystals studied, the results provide the first direct structural information on the $[\text{Ni}(\text{bipy})(\text{DBM})_2]$ materials and unambiguously elucidate the molecular structure and crystal packing in the materials.

Yellowish green crystals of **1** were obtained by heating $[\text{Ni}(\text{bipy})(\text{DBM})_2]$ ¹⁰ powder (0.2 g) in DMF (20 ml) at ~110 °C for one day followed by very slow (3 K h^{–1}) cooling to room temperature. The inclusion formed as agglomerates of presumably prismatic crystals, which decomposed in air with greening. A suitable sample found after several crystallizations was instantly cooled down to –100 °C and studied.[†] A dark green crystal of **2** was chipped out of a shapeless crystalline aggregate after slow evaporation (three months) of a solution prepared by combining solutions of $\text{Ni}(\text{DBM})_2$ ¹⁶ (0.25 g, 0.5 mmol) in Py (8 g) and bipy (0.4 g, 2.5 mmol) in Py (6 g). The bulk solid was not a single phase. The crystal piece was cooled and studied at –100 °C to prevent decomposition.[‡]

The results of this work confirm the polymeric structure and ladder-and-platform geometry previously suggested for the $[\text{Ni}(\text{bipy})(\text{DBM})_2]$ complex. The molecular structure of the nickel complexes found in the two studied structures is shown in Figure 2. The nickel atom is *trans* coordinated by four O atoms of two chelating DBMs in the equatorial plane and two N atoms of pyridyl/pyridine ligands coordinated axially. The linear polymer is believed to retain this structure in all inclusion materials of the complex studied previously. The dimer may be considered as a fragment of the polymer cleaved with Py ligands that are chemically similar to bipy. Chemical similarity of the closest coordination environment around Ni^{II} in the two

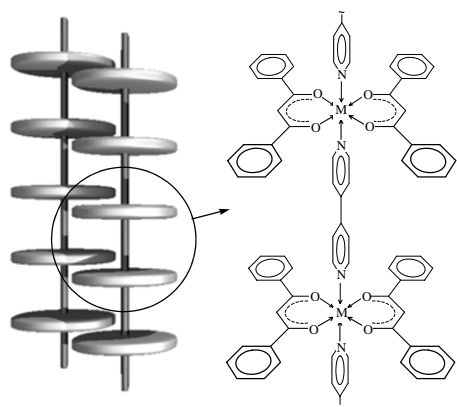


Figure 1 Expected molecular structure and packing motif of the polymeric $[\text{Ni}(\text{bipy})(\text{DBM})_2]_n$ complex.

[†] Crystal data for **1** at 173 K: $\text{C}_{46}\text{H}_{44}\text{N}_4\text{NiO}_6$, $M = 807.6$, monoclinic, $a = 12.661(2)$, $b = 11.320(2)$, $c = 27.735(5)$ Å; $\beta = 100.91(1)^\circ$, $V = 3903(1)$ Å³, space group $C2/c$ (no. 15), $Z = 4$, $d_{\text{calc}} = 1.374$ g cm^{–3}, $\mu(\text{MoK}\alpha) = 0.55$ mm^{–1}, 13882 reflections collected, 2643 unique ($R_{\text{int}} = 0.096$), which were used in the solution and refinement (281 parameters). The final R -values were 0.118 (all data) and 0.096 [for 2096 intense ($I > 2\sigma_I$) data].

For **2** at 173 K: $\text{C}_{110}\text{H}_{88}\text{N}_{10}\text{Ni}_2\text{O}_8$, $M = 1795.3$, triclinic, $a = 10.731(3)$, $b = 14.203(3)$, $c = 16.852(3)$ Å; $\alpha = 98.52(1)^\circ$, $\beta = 107.10(1)^\circ$, $\gamma = 109.43(1)^\circ$, $V = 2227(1)$ Å³, space group $P\bar{1}$ (no. 2), $Z = 1$, $d_{\text{calc}} = 1.339$ g cm^{–3}, $\mu(\text{MoK}\alpha) = 0.49$ mm^{–1}, 26398 reflections collected, 11417 unique ($R_{\text{int}} = 0.052$), which were used in the solution and refinement (534 parameters). The final R -values were 0.111 (all data) and 0.058 [for 6839 intense ($I > 2\sigma_I$) data].

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 223335 and 223336. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

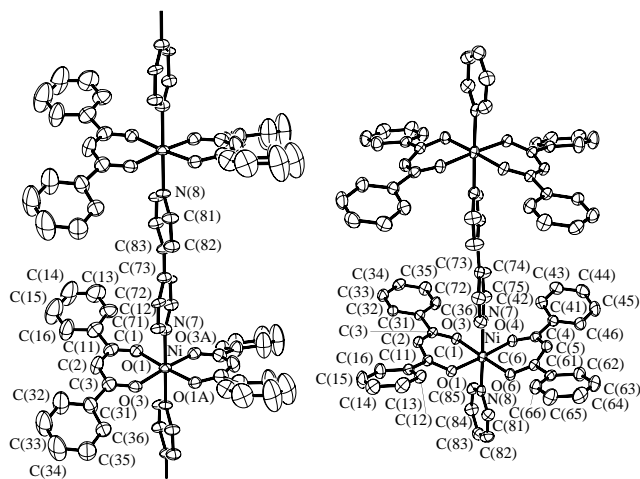


Figure 2 Molecular structure of the $[\text{Ni}(\text{bipy})(\text{DBM})_2]_n$ polymer as found in **1** (two monomeric units are shown) (left) and of the $[\text{Ni}_2(\text{bipy})\text{Py}_2(\text{DBM})_4]$ dimer as found in **2** (right). H atoms are not shown. Selected bond distances (Å): for **1**: Ni–O(1) 2.018(5), Ni–O(3) 2.032(5), Ni–N(7) 2.117(8), Ni–N(8') 2.119(7); coordination angles within 87.2–92.3°; for **2**: Ni–O(1) 2.024(2), Ni–O(3) 2.009(2), Ni–O(4) 2.037(2), Ni–O(6) 2.031(2), Ni–N(7) 2.118(2), Ni–N(8) 2.102(2); coordination angles within 88.0–91.8°.

structures studied allows us to speculate what changes this coordination environment may undergo.

As a new result, a remarkable flexibility of the complex is demonstrated. The flexibility comes not only from conformational freedom of phenyl and pyridyl rings, but the chelating fragments of the DBMs strongly deviate from the equatorial planes of the complex. Therefore, the whole geometry differs significantly from that of the solid model shown in Figure 1. In **1**, two chelating semi-rings $[\text{O}(1)–\text{C}(1)–\text{C}(2)–\text{C}(3)–\text{O}(3)]$ and the opposite one] are twisted with respect to each other by 16.5° while in **2** they are bent on the same side to form a dihedral angle of 42.4° with each other. Such great distortions demonstrate that the molecule easily undergoes drastic changes in geometry while the linear core comprising nickel atoms connected by bipy spacers at a distance of 11.3 Å remains very stable.

The observed deviations explain colour changes (yellowing or greening) in the host material upon sorption of various guests¹⁰

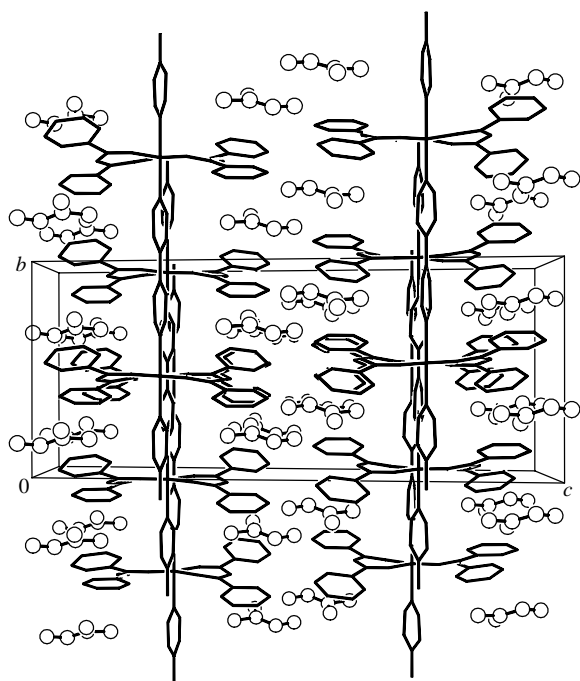


Figure 3 Crystal packing in **1**. For clarity, the host is outlined by sticks while the guest is shown by balls.

as a result of distortion of the coordination environment of the Ni^{II} centre caused by the sorption. In other words, colour changes are a consequence of the high ‘adaptability’ of the complex to the included sorbates.

Both compounds reveal a van der Waals type of crystal structures and belong to the group of ‘soft’ supramolecular materials.¹⁷ Host molecules are aligned parallel while the guest species fill the residual pocket space between DBM fragments. The crystal packing of **1** is shown in Figure 3. Four host chains run through the unit cell along the crystallographic axis *b*. Chains adjacent to the axis *a* are displaced from each other by half a *b*-translation and interdigitate, thus forming a layer. Guest species reside between these layers inserting their most hydrophobic parts in the host pockets. There is a weak π – π interaction between antiparallel carboxy groups of adjacent guest molecules at a distance of 3.17 Å. In the crystal structure of **2**, the guest bipy species reside between two $\text{Ni}(\text{DBM})_2$ fragments of the host dimer while the guest Py species are located in cavities formed by the shallow pockets between DBM and Py ligands.

Note that similar coordination polymers with smaller ‘platforms’, including acetylacetonate,^{18,19} hexafluoroacetylacetonate,²⁰ picrate²¹ and thenoyltrifluoroacetate^{22,23} bischelates connected by 4,4'-bipyridyl spacers have been reported earlier. Like in **1**, these crystal structures reveal a parallel arrangement of polymeric chains but most of them are guest-free. Only coordination polymers of Cu^{II} (ref. 22) and Mn^{II} (ref. 23) thenoyltrifluoroacetates form 1:2 inclusion compounds with DMF and acetone, respectively. The guest species are included and form van der Waals contacts only with each other and with the host and presumably can be replaced with other solvent molecules. In an overall comparison of the structures, the sorption ability seems to be directly defined by the size of the ‘platforms’ and the utilization of even bigger bischelatate units may lead to a new family of sorbents with an enhanced sorption capacity.

In conclusion, this study elucidates important structural properties of the ‘soft’ metal-organic polymeric sorbent $[\text{Ni}(\text{bipy})(\text{DBM})_2]_n$. The material combines robustness and stability of the central $(-\text{Ni}-\text{bipy}-)_n$ core along with the flexibility of DBM ligands. This characteristic gives, on the one hand, thermal and chemical stability, and, on the other hand, high adaptability as it easily transforms into supramolecular architectures.

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