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N,N,O Ligands Based on Triazoles and Transition Metal Complexes Thereof

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The reaction of 2*H*-benzotriazole (1) with dichloroacetic acid leads to the symmetric bis(2*H*-benzotriazol-2-yl)methane (2c) in 40 % yield. Deprotonation of 2c at the bridging methylene group and subsequent carboxylation with CO₂ yielded the new tripodal *N*,*N*,*O* ligand bis(2*H*-benzotriazol-2-yl)acetic acid Hbbta (3). The sterically less demanding sodium 3,3bis(1*H*-1,2,4-triazol-1-yl)propionate Na[btp] (5) was obtained by saponification of methyl 3,3-bis(1*H*-1,2,4-triazol-1-yl)propionate (4). The heteroscorpionate ligand 3 was treated with [MnBr(CO)₅] and [RuCl₂(PPh₃)₃] to form the manganese tricarbonyl complex [Mn(bbta)(CO)₃] (6) and the air stable ruthenium complex [Ru(bbta)Cl(PPh₃)₂] (7). DFT calculations and the IR spectra of the carbonyl complex 6 reveal ligand 3

Introduction

N,N,O ligands such as bis(1H-pyrazol-1-yl)acetic acids are a versatile class of ligands structurally related to the well-known hydrotris(1H-pyrazol-1-yl)borate (Tp) ligand. Efficient syntheses for achiral, chiral and enantiopure bis(1H-pyrazol-1-yl)acetic acids have been developed over the years since they have been introduced to coordination chemistry in 1999 by A. Otero.^[1] Various transition metal complexes bearing these tripodal, κ^3 -N,N,O-binding ligands indicate binding properties as weak electron-donating ligands, similar to the Tp ligands.^[2,3] Examples for transition metal complexes with manganese and ruthenium are [Mn(bdmpza)(CO)₃] and [Ru(bdmpza)(PPh₃)₃] {bdmpza: bis(3,5-dimethyl-1*H*-pyrazol-1-yl)acetate}.^[4–6] Furthermore, model complexes with biorelevant transition metals such as iron(II) and zinc(II) support the concept of bis(1Hpyrazol-1-yl)acetic acids to be good structural mimics for the active site of metalloenzymes with an 2-His-1-carboxylate motif.^[7-9]

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to be a less electron-donating ligand compared to the bis(1*H*-pyrazol-1-yl)acetic acid Hbpza. In case of the 1*H*-1,2,4-triazole-based ligand **5** formation of coordination polymers were observed as proven by the synthesis of $[Zn(btp)_2]_{\infty}$ (**8**) and $[Mn(btp)_2]_{\infty}$ (**9**). Polymer **8** crystallises in linear chains of zinc atoms bridged by two molecules of ligand **5** each. These polymer chains show an interesting π -stacking interaction between uncoordinated triazole residues of the ligands. Deposition of the coordination polymer on highly ordered pyrolytic graphite (HOPG) was successful and was analysed by scanning tunnelling microscopy (STM). Reaction of Na[btp] (**5**) with MnSO₄·H₂O resulted in a metal organic framework (MOF) [Mn(btp)₂]_{ $\infty}$ (**9**).

Our recent work focuses on derivatives of such N,N,O ligands, to broaden the field of available heteroscopionate ligands with various electronic and steric properties. So far examples of chiral bis(1*H*-pyrazol-1-yl)acetic acids,^[10] 3,3-bis(imidazol-2-yl)propionic acids^[11] or 2-[bis(1*H*-pyrazol-1-yl)methyl]phenolates^[12] have been obtained. Moreover, tricarbonylrhenium complexes are of particular interest as model compounds for radiopharmaceutical applications.^[13]

Introducing triazoles instead of pyrazoles or imidazoles as *N*-donor seems to be one reasonable option to establish a new field of *N*,*N*,*O* heteroscorpionate ligands. To the best of our knowledge, so far mainly bis(1*H*-1,2,4-triazol-1-yl)acetic acids have been applied in coordination chemistry, e.g. in cytotoxic copper(I) complexes or metal-organic frameworks (MOFs).^[14–16]

2*H*-Benzotriazole, which is well known to form a chelating *N*,*N*-donor ligand by reaction with dichloromethane,^[17] offers rather large steric demand but electron deficiency. Therefore, synthesis of bis(2*H*-benzotriazol-2-yl)acetic acid promises to result in an interesting ligand candidate. In contrast, 1*H*-1,2,4-triazole may act as small and sterically nondemanding *N*-donor.

Ligand Design

Reaction of 2*H*-benzotriazole (1) with dichloromethane leads to the three possible isomers bis(1*H*-benzotriazol-1yl)methane (2a), (1*H*-benzotriazol-1-yl)(2*H*-benzotriazol-2yl)methane (2b) and bis(2*H*-benzotriazol-2-yl)methane (2c)

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(Scheme 1).^[17,18] Almost independently from the reaction conditions the synthesis yields a mixture of all three isomers. A reaction with dichloromethane in the presence of KOH and a phase-transfer catalyst for example results in 40% **2a**, 31% **2b** and 6% **2c**.^[18] Isomer **2c** is the isomer required for the synthesis of a symmetric and bulky heteroscorpionate tripodal N,N,O ligand. Therefore, higher amounts of isomer **2c** would be desirable.



Scheme 1. Synthesis of the Hbbta ligand 3.

Instead of reacting 1 with dichloromethane, the reaction with dichloroacetic acid as starting material offers an alternative synthetic pathway. In the presence of K_2CO_3 , KOH and phase-transfer catalyst 2*H*-benzotriazole (1) reacts with dichloroacetic acid to the desired isomer **2c** in yields up to 40% (Scheme 1).

Reaction of **2c** with *n*BuLi in THF leads to a dark blue anion, due to its large delocalized π -electron system. In analogy to the synthesis of Li[bdmpza], that is obtained from the corresponding bis(3,5-dimethyl-1*H*-pyrazol-1-yl)methane,^[1] further reaction with dry gaseous carbon dioxide affords the bis(2*H*-benzotriazol-2-yl)acetic acid (Hbbta) (**3**) after acidic workup. The presence of **3** is clearly indicated by a shift of the bridging CH ¹H NMR signal from δ = 7.43 ppm in **2c** to 8.25 ppm for **3**, as well as the appropriate mass spectrum. The IR resonance at 1763 cm⁻¹ (THF) is assigned to the asymmetric carboxylate vibration. Finally, an X-ray analysis revealed the molecular structure of **3** (Figure 1).

Although, decarboxylation occurs during the reaction of 2H-benzotriazole with dichloroacetic acid, ligand **3** was found to be stable at room temperature as crystalline powder as well as in solution.



Figure 1. Molecular structure of bis(2*H*-benzotriazol-2-yl)acetic acid (3); thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: d(C2-O1) = 1.320(5), d(C2-O2) = 1.179(5), d(C1-N12) = 1.440(5), d(C1-N22) = 1.462(5), $\angle(N12,C1,N22) = 112.2(3)$.

Due to the annelated benzene rings, compound **3** represents a ligand with relatively large steric demand. Díez-Barra and co-workers recently published an interesting pathway to various esters of *N*-heterocyclic 3,3-bis(hetero-aryl)propionic acids, such as methyl 3,3-bis(1*H*-1,2,4-triazol-1-yl)propionate (**4**).^[19] The corresponding acid, 3,3-bis(1*H*-1,2,4-triazol-1-yl)propionic acid or the salt sodium 3,3-bis(1*H*-1,2,4-triazol-1-yl)propionate (Nabtp) (**5**) are obtained by saponification of ester **4** in presence of water and NaOH in THF (Scheme 2). Due to the very good solubility of **5** in water, purification of **5** in the presence of excess base or other inorganic salts proved to be rather difficult.



Scheme 2. Sodium 3,3-bis(1*H*-1,2,4-triazol-1-yl)propionate (Nabtp) (5) obtained by saponification of the ester methyl 3,3-bis(1*H*-1,2,4-triazol-1-yl)propionate (4).

However, saponification with a slight deficit of NaOH yields a mixture of 4 and 5. Ester 4 was removed by washing with chloroform to yield the sodium propionate 5 as a colourless solid. Extracted ester 4 can be recirculated in a second saponification step. The sodium propionate 5 is clearly indicated by the absence of the resonance of the methyl ester at $\delta = 3.71$ ppm in the ¹H-NMR spectra and the asymmetric carboxylate vibration at 1612 cm⁻¹ (methanol). Ligands 3 represents on one side a new and sterically demanding bis(triazolyl)carboxylic acid whereas ligand 5 on the other side is sterically less demanding.

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DFT Calculations

To gather some information about the electronical and coordination properties of the two ligands 3 and 5, DFT calculations were performed. Comparison of the calculated frontier orbitals of 2-methyl-2H-benzotriazole, 1-methyl-1H-1,2,4-triazole and 1-methyl-1H-pyrazole (Table 1) gives information about the donor and acceptor properties of the binding nitrogen sites of 3 and 5. The frontier orbitals of 2methyl-2*H*-benzotriazole are assumed to be comparable to those of the 2H-benzotriazol-2-yl donor in 3, the frontier orbitals of 1-methyl-1H-1,2,4-triazole to those of the 1H-1,2,4-triazol-1-yl donor in 5 and the frontier orbitals of 1methyl-1*H*-pyrazole to those of the 1*H*-pyrazol-1-yl donor in bis(1H-pyrazol-1-yl)acetic acids. The binding behaviour of histidine according to Holm and co-workers is dominated by its frontier orbitals.^[20] Recently, we and others successfully discussed the binding of imidazole- and pyrazolebased N,N,O ligands by means of their frontier orbitals.^[11]

Table 1. Comparison of the Khon–Sham orbitals of 2-methyl-1*H*-benzotriazole, 1-methyl-1*H*-triazole and 1-methyl-1*H*-pyrazole.

2-Methyl-2 <i>H</i> -	1-Methyl-1 <i>H</i> -	1-Methyl-1 <i>H</i> -
benzotriazole	1,2,4-triazole	pyrazole
	· •••	
Ia) LUMO + 1	Ib) LUMO	Ic) LUMO
(-2.0518 eV)	(0.7791 eV)	(– 0.2829 eV)
	200	× DD
IIa) HOMO	IIb) HOMO	IIc) HOMO
(– 5.4827 eV)	(- 6.1943 eV)	(– 5.6571 eV)
·••••	*	2
IIIa) HOMO – 1	IIIb) HOMO – 1	IIIc) HOMO – 1
(– 6.0617 eV)	(– 6.2515 eV)	(– 5.7849 eV)
	00	Sr.
IVa) HOMO – 2	IVb) HOMO – 2	IVc) HOMO – 2
(– 6.7646 eV)	(– 6.9316 eV)	(– 6.3999 eV)

The orbital plots show the capability of **3** to act as π -acceptor (LUMO+1, Table 1, Ia) as well as the pyrazoles (LUMO, Ic) do. Noticeable is the energetically low and strongly delocalised LUMO+1. The orbital plot of the HOMO (IIa) points out the π -donor character of the 1*H*-benzotriazole ligands in accordance to the pyrozoles (IIc). σ -Donor binding properties (HOMO–2, IVa) are provided similar to pyrazoles (HOMO–2, IVc).

Solely the HOMO-1 (IIIa) does not seem to be involved in the interaction between the frontier orbitals and the metal centre. Obviously, all considered orbitals apart from the HOMO-2 show conspicious delocalisation in the aromatic benzene ring. Over all, bis(2*H*-benzotriazol-2-yl)acetic acid should be able to act as σ -donor, π -donor and π acceptor. The π -donor properties may be less distinctive due to the delocalization into the aromatic system. The two possible nitrogen binding sites in **3** do not show up any differences in the orbital plots, due to the molecular symmetry. Coordination towards the metal centre with one of the nitrogen donors will always lead to the same product.

In contrast, ligand **5** shows some differences regarding the two possible N donors. Both can act as π -acceptors (LUMO, Ib) and σ -donors (HOMO, IIb) although coordination will not lead to the same product due to the broken symmetry. N2 has a smaller orbital coefficient in one of the two orbitals suitable for π -donors compared to N4 (IVb, HOMO–2). On the other hand N4 has a total lack of π donors capabilities compared to N2 in IIIb (HOMO–1). In total, due to missing delocalisation, the orbitals of **5** seem to show some similarity to those of the pyrazole donor. Especially N2 can be compared to the nitrogen of a pyrazole-based ligand. But **5** provides two different binding sites, both able to act as as donor and acceptor.

Besides a discussion of the orbital plots, the HOMO-LUMO energy gap allows to estimate further properties based on the concept of chemical hardness. Molecules with a large HOMO-LUMO energy gap are considered to be hard, molecules with a small energy gap are considered to be soft.^[21] Following the calculated orbital energies in Table 1, ligand 3 must clearly be accepted to be the softest of the three ligands discussed here. The low HOMO-LUMO energy gap can be explained by the strongly delocalized structure of 2H-benzotriazole. Due to the DFT calculations performed here and well-known errors of the resulting orbital energies, no further estimations on the reactivity of these ligands towards metal fragments are extracted from these results.^[22] Furthermore, the different coordination properties of the two possible bindings sites N2 and N5 of 1-methyl-1H-1,2,4-triazole cannot be explained by means of the HOMO-LUMO energy gap.

Metal Complexes

Deprotonation of the carboxylate donor allows ligand **3** to react as a monoanionic N,N,O ligand with organometallic precursors such as [MnBr(CO)₅] and [RuCl₂(PPh₃)₃] (Scheme 3).



Scheme 3. Synthesis of $[Mn(bbta)(CO)_3]$ (6) and $[Ru(bbta)Cl-(PPh_3)_2]$ (7).

The facial N,N,O-binding behaviour of ligand 3 is clearly indicated by the IR stretching frequencies of the complex $[Mn(bbta)(CO)_3]$ (6), which is obtained by a reaction of the potassium salt of 3 with [MnBr(CO)₅]. The IR spectrum of complex 3 exhibits a single A' and two close A'' and A' signals [6: \tilde{v} (THF) = 2047, 1963, 1933 cm⁻¹]. This is typical for an unsymmetric "piano stool" carbonyl complex.^[4] An IR signal observed at 1707 cm⁻¹ is assigned to the asymmetric carboxylate vibration. The formation of 6 is backed by the appropriate MH⁺ signal of the FAB mass spectrum. Although the NMR spectra of 6 are broad, complex 6 shows a clear set of signals for the carbonyl residues at δ = 218.3 and 221.0 ppm in the ¹³C{¹H} NMR spectrum. The signal occurring at $\delta = 162.0$ ppm is assigned to the carboxylate donor. Table 2 shows a comparison of the characteristic IR signals of 6 to analogous tricarbonyl complexes, which allows to estimate the electronic properties of $3^{[4]}$

Table 2. IR data of complexes $[MnL(CO)_3]$ with various tripodal ligands.

Ligand L	bbta	bpza ^[4]	bdmpza ^[4]	Tp ^[4]
ṽ [MnL(CO) ₃]	2047, 1963, 1933	2041, 1946, 1925	2036, 1942, 1915	2033, 1930

The IR stretching vibrations at higher wavenumbers indicate in total (σ - and π -bonding as well as π -back bonding) that ligand **3** is a less electron-donating ligand compared to the other ligands. This may be explained by the large delocalized π -electron system of 2*H*-benzotriazole and electron density located at the benzene rings instead of then *N*donor as indicated by the DFT calculations. Therefore, Hbbta may be the *N*,*N*,*O* ligand providing the most electron deficiency at the metal center from this series of ligands, meanwhile providing noticeable steric demand.



Unfortunately, 6 turned out to be rather unstable towards external influences such as heat and light. After some hours at daylight, complex 6 already decomposes to an orange solid. As known from the synthesis of 3, higher temperatures lead to decarboxylation. Therefore, heating of 6 in solution above 40 °C leads to decomposition indicated by the appearance of several signals in the IR carbonyl region (1900–2050 cm⁻¹). Consequently, synthesis of **6** affords temperatures of 30 °C or lower which causes a longer reaction time compared to the synthesis of $[Mn(bpza)(CO)_3]$.^[4] Purification of 6 by means of column chromatography was only successful with stabilized THF as solvent, leading to residues of butylated hydroxytoluene (BHT) in the product. Attempts of an analogous reaction of ligand 3 with [ReBr(CO)₅] instead of [MnBr(CO)₅] failed, probably due to a slower reaction, which leads to decomposition.

To further investigate the steric demand and coordination properties of ligand 3, the ruthenium complex $[Ru(bbta)Cl(PPh_3)_2]$ (7) was synthesized analogously to the preparation of [Ru(bdmpza)Cl(PPh₃)₂].^[5] Reaction of the potassium salt of 3 with [RuCl₂(PPh₃)₃] leads to [Ru(bbta)- $Cl(PPh_3)_2$ (7), a light orange powder, as indicated by the FD mass peak (Scheme 3). It is well known, that in case of sterically less demanding ligands such as bpza, two diastereomers are obtained, while sterically more demanding ligands such as bdmpza lead to just one symmetrical isomer.^[5] The ³¹P NMR spectrum shows only one singlet for the PPh₃ ligands ($\delta = 33.3$ ppm). This suggests that only one isomer was formed by the reaction. This is backed by the absence of more than one set of benzotriazole signals in the ¹³C{¹H} NMR spectrum. An X-ray structure determination doubtlessly reveals the symmetrical structure of 7 (Figure 2).



Figure 2. Molecular structure of [Ru(bbta)Cl(PPh₃)₂] (7); thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: d(C2-O1) = 1.272(6), d(C2-O2) = 1.211(6), d(Ru-N11) = 1.272(6)2.118(4), d(Ru-N21) = 2.182(4), d(Ru-O1) = 2.106(3), d(Ru-C1) =2.4070(16), d(Ru-P1) = 2.3488(18), d(Ru-P2)2.3415(15). = 78.59(16), \angle (N11,Ru,O1) = = 87.54(15). \angle (N11,Ru,N21) 86.53(14), \angle (N21,Ru,O1) \angle (O1,Ru,Cl) 170.34(10), = = \angle (O1,Ru,P1) = 83.82(11), \angle (O1,Ru,P2) = 95.92(11), \angle (N11,Ru,P1) = 91.19(13), \angle (N11,Ru,P2) = 173.10(12), \angle (N11,Ru,Cl) = 86.07(12), \angle (N21,Ru,P1) = 166.24(11),= \angle (N21,Ru,P2) 95.62(12), \angle (N21,Ru,Cl) = 85.11(11). \angle (Cl,Ru,P1) = 103.53(5), \angle (Cl,Ru,P2) = 89.72(5), \angle (P1,Ru,P2) = 95.11(6).

Signals at $\delta = 83.3$ ppm and 164.6 ppm are assigned to the bridging CH and the CO₂⁻ carboxylate donor. Due to the ambient temperature reaction conditions, no decomposition by decarboxylation was observed. The pure compound 7 itself, was found to be remarkably stable against air. No indication of oxidation of the ruthenium centre was notified even after weeks. Due to the stability of complex 7, and the weak electron-donating properties of ligand 3, compound 7 promises to be an interesting precursor for organometallic ruthenium complexes. Further work might focus on ligand exchange reactions with [Ru(bbta)Cl(PPh₃)₂], e.g. the exchange of PPh₃ or Cl by cumulynidene ligands.

In contrast to the potassium salt of 3, reaction of the sodium salt 5 with [MnBr(CO)₅] does not lead to the corresponding manganese tricarbonyl complex. During the reaction in THF a bright-yellow substance precipitates. IR spectra of the reaction mixture shows three carbonyl absorption bands at $\tilde{v} = 2032$, 1936, 1908 cm⁻¹. The lower signals may be in accordance with the expected more electron-donating properties of 5 compared to 3 as shown by the DFT-calculations, but these results have to be interpreted with caution, since the spectra where obtained from the crude suspension of the reaction mixture. Any attempts to purify the obtained insoluble substances failed. Similar formation of insoluble and unisolable products was obsersed by the reaction of 5 with [ReBr(CO)₅] and [RuCl₂(PPh₃)₃]. Reaction of 5 with $Zn(ClO_4)_2$ in methanole immediately precipitates a white powder, too (Scheme 4). IR spectra of this zinc complex 8 show an absorption band assigned to the asymmetric carboxylate vibration at $\tilde{v} = 1634 \text{ cm}^{-1}$, indicating coordination of ligand 5 via the carboxylate donor. NMR spectra in D_2O_2 , in which the obtained zinc complex 8 slowly dissolves, show the resonances of the free ligand 5. Finally, an X-ray structure determination explains the unusual behaviour of 8 (see Figures 3 and 4). Obviously, a linear coordination polymer $[Zn(btp)_2]_{\infty}$ (8) has been formed. Each zinc atom is tetrahedrally coordinated by four ligands, each binding towards the metal centre with the carboxylate group as Odonor or the nitrogen atom at 4-position of the triazole residue as N-donor (Figure 3). The bond lengths are in the typical range for a tetrahedral coordinated zinc centre with *N*,*O*-donor ligands, as comparison with [Zn(bd*t*bpza)Cl] [d(Zn-O): 1.990(2) Å, d(Zn-N): 2.053(2), 2.067(3) Å]

Scheme 4. Formation of a linear coordination polymer $[Zn(btp)_2]_{\infty}$ (8).

shows.^[7] Two ligands act as bridging ligands towards a second metal centre at a time each. This results in a linear alignment of the zinc atomes (see Figures 3 and 4). In total, every zinc atom is connected to two other zinc centres. Each bridge is build up by two ligands. This results in the total formula ratio of Zn/btp = 1:2.



Figure 3. Molecular structure of $[Zn(btp)_2]_{\infty}(\mathbf{8})$; a cutout of a linear chain with three zinc atoms is shown; thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: d(Zn-O1) = 1.9494(11), d(Zn-N13) = 2.0045(13), d(C1-O1) = 1.2745(19), d(C1-O2) = 1.2301(19), $\angle(O1,Zn,O1A) = 100.41(7)$, $\angle(O1,Zn,N13B) = 121.34(5)$, $\angle(O1,Zn,N13C) = 104.48(5)$, $\angle(N13B,Zn,N13C) = 106.02(8)$, d(Zn-Zn) = 6.773 Å, centroid–centroid distance of the triazole rings: 5.043 Å.

This bridging coordination is possible, since every ligand coordinates via the *N*-donor in 4-position of only one of the two triazole rings. The second triazole ring of each ligand is not coordinated to any metal centre and remains free. The two coordinated triazole rings of the two bridging ligands are aligned coplanar to each other (Figure 3). The centroid-centroid distance of these triazole rings is rather large with 5.043 Å. Each chain of the linear coordiation polymer additionally shows interaction with adjacent chains (Figure 4) by a coplanar orientation of the uncoordinated triazole rings (centroid–centroid distance: 3.618 Å).

The short distance of these triazole rings let us assume a π -stacking interaction since a comparison with the centroid–centroid distance in hexagonal graphite shows only a slightly smaller distance (d = 3.354 Å).^[23]

The formation of linear coordination polymers explains the poor solubility of the zinc complex 8. In water or D_2O the compound probably slowly dissociates to give the free ligand and Zn_{aq}^{2+} , which explains the identical NMR spectra of 5 and 8, and crystallizes again as coordination polymer. This coordination behaviour of 5 may also explain the insoluble products obtained by reaction of 5 with other metal salts although the products could not be crystallized so far. It is noteworthy that recently Klein Gebbink and coworkers obtained a linear coordination polymer with the *N*,*N*,*O* ligand 3,3-bis(1-methyl-2*H*-imidazol-2-yl)propionate.^[24]

Recent studies have shown that the real space structure of metal coordination complexes can be investigated by scanning tunnelling microscopy (STM).^[25] Therefore a



Figure 4. Molecular structure of $[Zn(btp)_2]_{\infty}$ (8); thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for better clarity. A cutout of three adjacent linear polymer chains is shown. Centroid–centroid distance of the triazole rings in π -stacking arrangement: 3.618 Å.

 10^{-9} M aqueous solution of **8** was drop coated on highly oriented pyrolytic graphite (HOPG) and investigated by STM in ambient conditions.

 $[Zn(btp)_2]_{\infty}$ (8) was found to form stable, straight lines (Figure 5, a). This can be attributed to a template effect of the substrate, stabilizing the polymer in positions of minimal energy along step edges and subsurface defect lines. As seen in Figure 5 (b) the minimum observed width of the structures is approx. 2.7 nm, roughly the diameter of a double chain. Therefore we have to assume a strong tendency to form clustered chains. This can be attributed to the π -stacking interaction of the non coordinating triazole rings as observed in the crystal structure. The measured periodicity along the chain is 1.5 nm. This is very close to the distance between every 2nd triazole ring. This can be ex-



Figure 5. STM topographies showing a) the aggregation of linear polymer strands on the surface; and b) STM topography indicating a double stranded polymer on the surface.



pected if one considers sticking to the surface with one ring parallel and one perpendicular to the plane. Due to this strong clustering high resolution topography and spectroscopy where not achieved, even while atomic resolution of the graphite background was routinely observed.

Following a procedure similar to the successful synthesis of $[Zn(btp)_2]_{\infty}$ (8), but employing MnSO₄·H₂O instead of Zn(ClO₄)₂, we found the formation of the two-dimensional coordination polymer $[Mn(btp)_2]_{\infty}$ (9). Instead of the split v(C=N) bands we observed in case of $[Zn(btp)_2]_{\infty}$ (8) $[\tilde{v} = 1530 \text{ cm}^{-1} \text{ and } 1513 \text{ cm}^{-1}]$, now only one signal at 1521 cm⁻¹ for v(C=N) is observed in the IR spectrum (KBr) of 9. This can be explained by a closer look at the molecular structure of 9, gained by X-ray structure determination. Three different metal centres coordinate the two triazole donors and the carboxylate functionality each. Hence, all carboxylate and triazol moieties have the same electronic environment. A cutout of the coordination geometry of one manganese atom is shown in Figure 6.



Figure 6. Molecular structure of $[Mn(btp)_2]_{\infty}$ (9); thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for better clarity. A cutout of the surrounding of one manganese ion is shown. Selected bond lengths [Å] and angles [°]: d(Mn-O1) = 2.1297(11), d(Mn-N13B) = 2.2806(13), d(Mn-N23C)= 2.2678(13), d(C1-O1) = 1.2673(18), d(C1-O2) = 1.2371(19), \angle (O1,Mn,O1D) = 180.00, \angle (O1,Mn,N13B) = 88.10(5), \angle (O1,Mn,N23C) = 92.84(5), \angle (N13B,Mn,N23C) = 90.56(5).

The manganese center is octahedrally coordinated by six different ligands. Two ligands are coordinating through the carboxylate functionalities in *trans*-position towards each other. The left coordination sites are occupied by the N-atoms of the 4-position of four triazole rings, belonging to four different btp ligands. Recently, M. Du and S. R. Batten and co-workers reported on the coordination properties of bis(1*H*-1,2,4-triazol-1-yl)acetate (btza).^[16] It is noteworthy, that reaction of Mn(OAc)₂ with Hbtza afforded a coordination polymer [{[Mn(btza)₂(OH₂)₂]·2H₂O}_∞], in which the manganese centers are coordinated by four independent ligands each, two coordinated by the carboxylates and two by the triazole rings. Two further coordination sites have been occupied by additional water molecules. Evidently, by the elongation of the carbon backbone from acetate to pro-

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pionate, a full occupation of the manganese coordination sites by ligands and vice versa becomes possible.

This results in an array of coordination polymer sheets. Within a sheet all the manganese atoms are situated in one plain [d(Mn-Mn) = 8.064, 8.279 and 9.538 Å], shielded by the ligands form above and from below. The top view on such a sheet is given in Figure 7.



Figure 7. Molecular structure of $[Mn(btp)_2]_{\infty}$ (9); hydrogen atoms have been omitted for better clarity. Cutout of a coordination polymer sheet is shown (top view).

Interestingly, no solvent molecules are intercalated into the structures of **9** and **8**, respectively, although incorporated water molecules were observed for the analogous coordination polymers derived from btza.^[16] In coordination polymer [Mn(btp)₂]_∞ (**9**), the stacked sheets are interlocked into each other, leaving no larger spaces within the structure $[d(O2-N11{other sheet}) = 3.512 \text{ Å}]$. A short distance between the uncoordinated carboxylate oxygen atom O2 and C3 of the neighbouring sheet $[d(O2-C3{other sheet}) =$ 3.329 Å] might indicate hydrogen bonds in between the sheets. Figure 8 shows the side view on the arrangement of the polymer sheets in the crystal structure, showing the coordination polyhedra of the manganese atoms.



Figure 8. Molecular structure of $[Mn(btp)_2]_{\infty}$ (9); cutouts of three adjacent coordination polymer sheets are shown (side view, polyhedral representation of the octahedral coordination of the manganese atoms).

Conclusions

In conclusion, the syntheses of **3** and **5** lead to two new ligands with interesting coordination properties. Ligand 3 shows κ^3 -N,N,O-coordination as it is well-known from other tripodal monoanionic N, N, O ligands. Estimation of the electronic properties of 3 via synthesis of the manganese tricarbonyl complex [Mn(bbta)(CO)₃] (7) and DFT calculations show 3 to be a rather weak electron-donating ligand. Furthermore, synthesis of [Ru(bbta)Cl(PPh₃)₂] (6) might enable the future synthesis of various organometallic complexes. In contrast to 3, ligand 5 does not show tripodal binding towards metal centres but prefers the formation of coordination polymers as proven by the synthesis of $[Zn(btp)_2]_{\infty}$ (8) and $[Mn(btp)_2]_{\infty}$ (9). Interestingly, 8 assembles as linear chains of zinc ions, connected by two bridging ligands 5. The chains show interactions via π stacking of the uncoordinated triazole residue. The coordination polymer $[Mn(btp)_2]_{\infty}$ (9) shows two-dimensional polymer sheets.

Experimental Section

General Remarks: All operations regarding manganese carbonyl and ruthenium complexes were carried out under an inert gas atmosphere by using conventional Schlenk techniques. All solvents (analytical-grade purity) were degassed and stored under nitrogen atmosphere. The yields refer to analytically pure substances and were not optimised. IR spectra were recorded by use of a Varian Excalibur FTS-3500 FT-IR spectrometer in CaF₂ cuvets (0.2 mm). ¹H and ¹³C{¹H} NMR spectra: Bruker AC 250 MHz, Bruker DPX300, Bruker DPX400, δ values relative to TMS or the deuterated solvent. Mass spectra were recorded on a modified Finnigan MAT 312 using either EI or FAB technique or on a Jeol JMS-700 using FD technique. Elemental analysis: Euro EA 3000 (Euro Vector) and EA 1108 (Carlo Erba). Chemicals were used as purchased without further purification. Methyl bis(1,2,4-triazol-1-yl)propionate, [MnBr(CO)₅] and [RuCl₂(PPh₃)₂] were synthesized according to literature.[19,26-28]

Synthesis of Bis(2H-benzotriazol-2-vl)methane (2c): 2H-Benzotriazole (11.9 g, 100 mmol), K₂CO₃ (24.9 g, 180 mmol), KOH powder (10.1 g, 180 mmol) and benzyltriethylammonium chloride (1.00 g, 4.39 mmol) are suspended in THF (500 mL). Dichloroacetic acid (6.45 g, 50.0 mmol) is added and the white suspension heated under reflux for 96 h. The solvent is removed in vacuo and the remaining residue dissolved in water (250 mL). The aqueous solution is extracted with ethyl ether $(5 \times 200 \text{ mL})$ and the combined organic layers dried with Na₂SO₄. Evaporation of the ethyl ether at room temperature to approx. 500 mL affords a first fraction of a mixture containing large amounts of the undesirable isomers. Decanting of the diethyl ether solution and evaporation of the remaining diethyl ether affords 2c in colourless crystals; yield 5.01 g (20.0 mmol, 40%); ¹H NMR (250 MHz, CDCl₃, 25 °C): δ = 7.38 and 7.78 $[AA'BB' pattern, {}^{3}J(H,H) = 6.7, {}^{4}J_{H,H} = 3.1 Hz, 8 H, Ar-H], 7.43$ (s, 2 H, CH_{bridge}) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): δ = 71.6 (C_{bridge}), 118.6 (C_{aryl}), 127.6 (C_{aryl}), 145.2 (CN_{aryl}) ppm.

Bis(2*H***-benzotriazol-2-yl)acetic Acid (3):** A solution of **2c** (0.826 g, 3.30 mmol) in dry THF was treated with *n*BuLi (2.10 mL, 1.6 M in *n*-hexane, 3.36 mmol) at -80 °C. The dark blue solution is stirred for 2 h and warmed up to -40 °C. Dry carbon dioxide ist passed

in for a period of 3 h, meanwhile the colour changes from dark blue over dark red to light yellow. The solvent is removed in vacuo and the remaining residue dissolved in water (100 mL) and acidified with diluted HCl to pH = 7. The aqueous phase is extracted with ethyl ether $(2 \times 100 \text{ mL})$ to remove impurities. The aqueous solution is further acidified to pH = 3 and extracted with ethyl ether $(3 \times 200 \text{ mL})$ and the combined organic layers dried with Na₂SO₄ and concentrated in vacuo. The yellowish residue is recrystallised from acetone to yield 3 as colourless crystals; yield 0.243 g (0.826 mmol, 25%); m.p. 151–153 °C (dec.). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.44, 7.90 (AA'BB' pattern, ³J_{H,H} = 3.6, ⁴J_{H,H} = 3.0 Hz, 8 H, Ar-H), 8.25 (s, 1 H, CH_{bridge}) ppm. ¹³C{¹H} NMR (75.5 MHz, [D₆]DMSO, 25 °C): δ = 80.3 (C_{bridge}), 118.3 (CH_{aryl}), 127.8 (CH_{arvl}), 143.9 (CN_{arvl}), 163.3 (CO₂ H) ppm. IR (THF): ṽ = 1763 [s (CO₂H)], 1563 [m (C=N)] cm⁻¹. FD-MS: m/z (%) = 296 (100) [MH⁺], 250 (46) [M⁺ – CO₂]. $C_{14}H_{10}N_6O_2$ (294.27 g mol⁻¹): calcd. C 57.14, H 3.43, N 28.56; found C 57.40, H 3.48, N 28.49.

Synthesis of Sodium 3,3-Bis(1*H*-1,2,4-triazol-1-yl)propionate (5): To methyl 3,3-bis(1*H*-1,2,4-triazol-1-yl)propionate (1.00 g, 4.50 mmol) a solution of pure NaOH (0.090 g, 2.25 mmol, 0.5 equiv.) in water (100 mL) is stirred for 24 h at ambient temperature. The solvent is removed in vacuo at 40 °C and the residue is extracted five times with chloroform to remove not reacted methyl ester and dried in vacuo. The chloroform may be removed in vacuo to recover methyl bis(1,2,4-triazol-1-yl)propionate.

5 was obtaineds as a white powder; yield 0.434 g (1.89 mmol, 84%); m.p. >260 °C (dec.). ¹H NMR (300 MHz, D₂O, 25 °C): δ = 3.61 (d, ³*J*_{H,H} = 7.1 Hz, 2 H, CH₂), 7.27 (t, ³*J*_{H,H} = 7.1 Hz, 1 H, CH_{bridge}), 8.10 (s, 2 H, H_{triazole}), 8.84 (s, 2 H, H_{triazole}) ppm. ¹³C{¹H} NMR (75.5 MHz, D₂O, 25 °C): δ = 40.7 (CH₂), 69.8 (C_{bridge}), 145.2 (C_{triazole}), 152.8 (C_{triazole}), 175.1 (COO⁻) ppm. IR (MeOH): \tilde{v} = 1612 [s (CO₂⁻)], 1511 [m (C=N)] cm⁻¹. FD-MS (after addition of dil. HCl): *m*/*z* (%) = 210 (60) [MH⁺], 140 (10) [M⁺ – tz]. C₇H₇N₆NaO₂ (230.16 gmol⁻¹): calcd. C 36.53, H 3.07, N 36.51; found C 36.86, H 3.16, N 36.86.

Synthesis of $[Ru(bbta)Cl(PPh_3)_2]$ (7): To Hbbta (3) (0.100 g, 0.340 mmol) in dry THF (50 mL) *t*BuOK (0.038 g, 0.339 mmol) was added and the reaction mixture stirred at ambient temperature for 30 min. To the resulting white suspension $[RuCl_2(PPh_3)_3]$ (0.326 g, 0.34 mmol) was added and stirred for additional 2 h and the dark-brown suspension changes colour to orange. The solvent is removed in vacuo and the remaining residue washed with water $(2 \times 10 \text{ mL})$ and little ethyl ether, pentane $(2 \times 10 \text{ mL})$ and methanol $(2 \times 5 \text{ mL})$ to yield 7 as bright orange powder.

Crystallisation from chloroform yields orange crystals suitable for X-ray structure determination.

Yield 0.195 g (0.20 mmol, 59%); m.p. >140 °C (dec.). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 6.7–7.6 (m, 38 H, H_{aryl}), 7.94 (s, 1 H, CH_{bridge}) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C): δ = 83.3 (CH_{bridge}), 118.3 (CH_{aryl}), 120.2 (CH_{aryl}), 127.2 (vt, ³J_{C,P} = 5 Hz, *m*-PPh₃), 127.7 (m, *i*-PPh₃), 129.1 (*p*-PPh₃), 134.9 (vt, ²J_{C,P} = 5 Hz, *o*-PPh₃), 135.1 (d, J_{C,P} = 2 Hz, CH_{aryl}), 135.4 (CH_{aryl}), 145.0 (CN_{aryl}), 146.4 (CN_{aryl}), 164.6 (CO₂⁻) ppm. ³¹P{¹H} NMR (121.5 MHz, CDCl₃, 25 °C): δ = 33.3 (PPh₃) ppm. IR (THF): \tilde{v} = 1967 [s (CO₂⁻)], 1690 [w (CN)] cm⁻¹. FD-MS: *m*/*z* (%) = 954 (5) [M⁺], 662 (44) [MH⁺ – bbta], 262 (50) [(PPh₃)₃]. C₅₀H₃₉ClN₆O₂-P₂Ru (954.37 gmol⁻¹): calcd. C 62.93, H 4.12, N 8.81; found C 62.27, H 4.19, N 8.60.

Synthesis of [Mn(bbta)(CO)₃] (6): To Hbbta (3) (0.294 g, 1.00 mmol) in dry THF (50 mL) *t*BuOK (0.112 g, 1.00 mmol) was added and the reaction mixture stirred at ambient temperature for

30 min. To the resulting white suspension [MnBr(CO)₅] (0.275 g, 1.00 mmol) was added, the reaction mixture heated to 30 °C and controlled by IR on a regular basis. After 72 h the reaction was completed and the solution filtered. The filtrate was concentrated in vacuo and after washing with water $(2 \times 5 \text{ mL})$ and little diethyl ether dried in vacuo to yield 6 as a yellow, light and heat sensitive solid; yield 0.186 g (0.430 mmol, 43%); m.p. >60 °C (slow dec.), >200 °C (fast dec.). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.6– 8.1 (m, broad, 8 H, H_{aryl}), 7.83 (br., 1 H, CH_{bridge}) ppm. ¹³C{¹H} NMR (75.5 MHz, CDCl₃, 25 °C): δ = 80.4 (CH_{bridge}), 115.8 (CHaryl), 120.3 (CHaryl), 129.3 (CHaryl), 131.5 (CHaryl), 144.7 (CN_{aryl}), 146.3 (CN_{aryl}), 162.0 (COOH), 218.3 (CO), 221.0 (CO) ppm. IR (THF): v = 2047 [s (C=O)], 1963 [s (C=O)], 1933 [s (C=O)], 1707 [s (CO₂⁻)] cm⁻¹. FAB-MS: m/z (%) = 433 (25) [MH⁺], 349 (13) [MH⁺ - 3CO] 307 (25) [MH⁺ - 3CO - CO₂]. C₁₇H₉MnN₆O₅ (432.23 gmol⁻¹): calcd. C 47.24, H 2.10, N 19.44; found: Due to the instability of 6 against light and heat, no sample free of a stabilizing agent (BHT) could be purified.

Synthesis of $[Zn(btp)_2]_{\infty}$ (8): To a solution of Nabtp (5) (0.230 g, 1.00 mmol) in methanole (20 mL) a solution of zinc perchlorate hexahydrate (0.186 g, 0.499 mmol) in methanole (10 mL) is slowly added. Immediately, 8 precipitates as a fine white powder. The suspension is stirred for 15 min at ambient temperature, the residue filtered off, washed with methanol and dried in vacuo, to give 8 as a colourless powder.

Crystallisation from water affords colourless blocks suitable for X-ray structure determination.

Yield 0.187 g (0.390 mmol, 78%); m.p. >240 °C (dec.).

IR (KBr): $\tilde{v} = 1634$ [s (CO₂⁻)], 1530 (w) and 1513 [w (C=N)] cm⁻¹. C₁₄H₁₄N₁₂O₄Zn (479.73 gmol⁻¹): calcd. C 35.05, H 2.94, N 35.04; found C 34.78, H 2.93, N 34.78.

Due to the coordination polymer properties of 8 further analystical methods failed. NMR spectra in D₂O show similar resonances as in case of the free ligand 5.

Synthesis of [Mn(btp)_{2]∞} (9): A test tube was charged with btpNa (0.101 g, 0.439 mmol) and MnSO₄ × H₂O (0.037 g, 0.219 mmol), and water (5 mL) was added. The tube was heated at 70 °C for 4 d. After cooling, pale yellow crystals had formed, that were collected, triturated with water (5 × 5 mL), and dried in vacuo at 80 °C to yield 9 a pale yellow powder; yield 0.066 g, 0.141 mmol, 64%; m.p. >311 °C (dec.). IR (KBr): $\tilde{v} = 3436$ (br), 3114 (m), 1621 [s (CO₂⁻)], 1521 [s (C=N)], 1438 (w), 1395 (m), 1340 (w), 1266 (w), 1199 (w), 1131 (m), 1007 (w), 908 (w), 822 (w), 673 (m), 552 (w) cm⁻¹. C₁₄H₁₄MnN₁₂O₄ (469.28 gmol⁻¹): calcd. C 35.83, H 3.01, N 35.82; found C 35.85, H 3.05, N 35.95.

Calculations

All DFT-calculations and full geometry optimizations were carried out by using Jaguar 6.0012^[29] running on Linux 2.4.18–14smp on five Athlon MP 2800+ dual-processor workstations (Beowulf-cluster) parallelized with MPICH 1.2.4. MM+ calculated structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented N31G6* basis set and the BP86 density functional. Orbital plots^[22] were obtained using Maestro 7.0.113, the graphical interface of Jaguar.^[29]

STM Measurements

The STM imaging was carried out under ambient conditions using a home-built, low-drift microscope and RHK100 control electronics. A drop of aqueous 10^{-9} M sample solution was placed onto a freshly cleaved HOPG surface and left to dry. Sections without molecules clearly showed atomic resolution of the underlying

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Table 5. Details of the structure determination for 5, 7, 6 and	Table 3.	Details	of the	structure	determination	for	3,	7, 8	and and	9
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	3	7	8	9
Empirical formula	$C_{14}H_{10}N_6O_2$	$C_{50}H_{39}ClN_6O_2P_2Ru$	C ₁₄ H ₁₄ N ₁₂ O ₄ Zn	C ₁₄ H ₁₄ MnN ₁₂ O ₄
Formula mass /gmol ⁻¹	294.28	954.33	239.87	234.66
Crystal colour/habit	colourless block	red plate	colourless block	colourless block
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c	$P\bar{1}$
a /Å	9.836(3)	18.183(8)	22.8880(11)	7.7640(4)
b /Å	9.7389(15)	10.654(5)	6.1072(2)	8.0636(4)
c /Å	14.726(3)	22.591(6)	13.4816(7)	8.2794(5)
a /°	90.00	90.00	90.00	108.605(3)
β /°	99.220(17)	93.08(3)	92.934(3)	104.916(5)
γ /°	90.00	90.00	90.00	92.918(4)
$V/Å^3$	1392.4(6)	4370(3)	1882.01(15)	469.66(4)
θ /°	2.10-25.91	1.81-25.46	3.43-29.52	2.74-28.99
h	-12 to 12	-21 to 21	-31 to 31	-10 to 10
h	-11 to 11	-12 to 0	-8 to 8	-10 to 10
1	-18 to 18	0 to 27	-18 to 18	-11 to 11
F(000)	608	1952	976	239
Z	4	4	4	1
μ (Mo- K_{α}) /mm ⁻¹	0.101	0.542	1.359	0.757
Crystal size /mm	$0.3 \times 0.25 \times 0.15$	$0.65 \times 0.2 \times 0.18$	$0.12 \times 0.09 \times 0.08$	$0.18 \times 0.18 \times 0.07$
D_{calcd} /g cm ⁻³ , T/K	1.404, 293(2)	1.450, 293(2)	1.693, 150(2)	1.659, 150(2)
Reflections collected	5225	8312	24456	13616
Indep. Reflections	2675	8088	2639	2491
Obs. refl. $(>2\sigma I)$	840	5080	2310	2224
Parameter	203	560	141	142
Weight parameter a	0.0407	0.0736	0.0241	0.0477
Weight parameter b	0	0.0813	2.0966	0.1519
R_1 (obsd.)	0.0545	0.0480	0.0287	0.0278
R_1 (overall)	0.2665	0.1248	0.0371	0.0340
wR_2 (obsd.)	0.0975	0.1219	0.0605	0.0889
wR_2 (overall)	0.1402	0.1484	0.0628	0.0864
Diff. peak/hole /e Å ⁻³	0.189/-0.195	0.725/-0.590	0.400/-0.369	0.414/-0.302

graphite substrate. Typically, tunnelling currents between 10 and 200 pA were employed. The bias voltage was \pm 72.9 mV. The scan frequency was varied between 2 to 5 Hz. Resolution was 256 × 256 points. Manually cut Pt/Ir(10%) tips were used.

X-ray Structure Determinations

Single crystals of **3**, **7**, **8** and **9** were mounted with Paratone-N or glue on a glass fibre. A modified Siemens P4-Diffractometer and a Bruker–Nonius Kappa-CCD and an Enraf–Nonius CAD4 Mach3 diffractometer were used for data collection (graphite monochromator, Mo- K_a radiation, $\lambda = 0.71073$ Å). The structures were solved by using direct methods and refined with full-matrix least-squares against F^2 {Siemens SHELX-97}.^[30] A weighting Scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2Fc^2 + \max(F_o^2, 0)]/3$. Most hydrogen atoms were included in their calculated positions and refined in a riding model. The proton of carboxylic acids (**3**) was found and its coordinates were refined freely. All details and parameters of the measurements are summarised in Table 3. The structure pictures were prepared with the program Diamond 2.1e.^[31]

CCDC-766896 (for 3), -766897 (for 7), -766898 (for 8) and -766899 (for 9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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