

Inter-ligand interactions and the selective formation of the unusual metal–N3(adenine) bond in ternary copper(II) complexes with *N*-benzyliminodiacetato(2–) ligands

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Abstract

A novel mixed-ligand copper(II) complex with *N*-(*p*-methoxybenzyl)-iminodiacetato(2–) ligand (MOBIDA) and adenine (AdeH) of formula [Cu(MOBIDA)(AdeH)(H₂O)] · H₂O has been obtained. Its crystal structure reveals the selective formation of a rare Cu–N3(AdeH) bond, closely related to those reported by first time for compounds of general formula [Cu(B)(AdeH)(H₂O)] · H₂O, with B = *N*-benzyl- or *N*-(*p*-methylbenzyl)-iminodiacetato(2–) ligands. Appropriate structural comparison reveals that the copper(II) coordination by less basic N3 heterocyclic donor of the nucleobase is controlled by a molecular recognition process involving the formation of an intra-molecular inter-ligand N7(imidazole-like)–H ··· O(carboxyl) bond and the inter-molecular inter-ligand π, π -stacking interaction between six membered rings of benzyl (MOBIDA) and AdeH. This stack generates multi-stacked infinite chains along the *b*-axis of the crystal.

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1. Introduction

Recent advances on mixed-ligand metal complexes involving nucleobases are discussed on the basis of inter-ligand interactions [1–3]. In this connection, non-substituted adenine (AdeH) has proved to be a versatile ligand [4] and its coordinating ability seems mainly controlled by the basicity order of its N donor atoms (N9 > N1 > N7 > N3 > N6-exocyclic). Surprisingly, in a recent report we have shown three new modes of Cu(II)–AdeH coordination by N7, N3 or bridging μ -N3, N7 in *N*-substituted iminodiacetato (*N*-R-IDA = R-N(CH₂CO₂[–])₂), where R is an alkyl, benzyl or phenethyl substituent, respectively. The origin of the bridging μ -N3, N7-(AdeH) di-copper(II) mode remains unclear, but

the selective AdeH–Cu(II) coordination by N7 or N3 seem to be rationalised by appropriate cooperation of both intra- and inter-molecular inter-ligand interactions [3]. In this connection, two compounds [Cu(*N*-alkyl-IDA)(AdeH)(H₂O)] · H₂O (type I) have a Cu–N7(AdeH) bond with an intra-molecular inter-ligand N9(imidazole-like)–H ··· O(carboxyl) interaction as well as significant, nearly anti-parallel, AdeH–AdeH π, π -stacking interaction which forms “pairs of molecules”. In clear contrast, two compounds [Cu(*N*-(benzyl-like)-IDA)(AdeH)(H₂O)] · H₂O (type II) exhibit an unexpected Cu–N3(AdeH) bond with an intra-molecular inter-ligand N6(exocyclic)–H ··· O(carboxyl) bond, displaying alternating benzyl–AdeH inter-molecular/inter-ligand π, π -interactions in multi-stacked infinite complex chains. These later cases concern to *N*-benzyl- and *N*-(*p*-methylbenzyl)-IDA derivatives of type II (here after compound 1 and 2, respectively). The formation of a single metal–N3(AdeH) bonds is rare enough so that

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before the knowledge of these type II cases, only other two examples were known in a nickel(II) [5] and a palladium(II) [6] derivatives.

2. Results and discussion

Using closely similar experimental methods to those reported previously [3] we have prepared three new compounds of type II with *N*-(*p*-methoxy-benzyl)iminodiacetato(2−) (MOBIDA) and its *p*-fluoro-(FBIDA) or *p*-nitro-(NBIDA) chelating ligand analogues. The analytical, thermal, spectral and magnetic properties of these compounds 3–5, respectively, are consistent with those of the closely related compounds 1 and 2 [3]. Until the present no structural results of 4 and 5 are available, and this report mainly deals with the molecular and crystal structure of 3 which is discussed in terms of inter-ligand interactions and the molecular recognition relevance.

Crystal data for [Cu(MOBIDA)(AdeH)(H₂O)]·H₂O(3): C₁₇H₂₂CuN₆O₇, formula weight 485.95; orthorhombic system, space group Pbca; *a* = 8.436(1) Å, *b* = 14.000(1) Å, *c* = 33.692(2) Å, $\alpha = \beta = \gamma = 90^\circ$, *Z* = 8; *T* = 293(2) K, solved and refined by direct methods (on *F*²) from 4764 reflections for 280 parameters to final *R*1 [*I* > 2σ(*I*)] = 0.057, *wR*2 = 0.096 and *GOF* = 0.932 indices.

The new compound 3 exhibit a typical 4 + 1 copper(II) coordination, with a *mer*-tridentate IDA-like conformation, the AdeH ligand in the *trans*-site to the Cu–N(MOBIDA) bond and one aqua apical ligand (Fig. 1 and Table 1). Certainly, the most striking structural feature is the formation of the Cu–N3(AdeH) coordination bond which is reinforced by the intra-molecular inter-ligand N9(imidazole-like)–H···O(carboxyl) bond (2.87(1) Å, 120°). The *mer*-tridentate MOBIDA conformation offers two possibilities of building up this intra-molecular H-bonding interaction and both ‘right-handed’ and ‘left-handed’ isomers are indeed present in the crystal with a ‘racemic’ equimolar ratio. In addition, complex molecules recognise themselves forming multi- π,π -stacked chains, extending along the *b*-axis, which connect inter-molecularly the six-membered rings of one AdeH ligand (A6) and one *N*-(*p*-methoxybenzyl)-MOBIDA arm of the next complex unit (Fig. 1). The crystal is built by means of many H bonding interactions. Particularly, the N9(imidazole-like)–H(AdeH) bond is involved in a bifurcate H-interaction (intra-molecularly with O11 and inter-molecularly with O22ⁱ; symmetry code *i* = *x* + 1, *y*, *z*). In addition, both H atoms of the N(6)H₂ exocyclic AdeH group interact with N7ⁱⁱⁱ and N1ⁱⁱⁱ atoms of adjacent nucleobases from two anti-parallel chains (symmetry codes: *ii* = *x* − 1/2, −*y* − 1/2, −*z*; *iii* = *x* + 1/2, −*y* − 1/2, −*z*). Consequently, each multi- π,π -stacked chain is linked to other three in such a way that a supra-molecular 2D

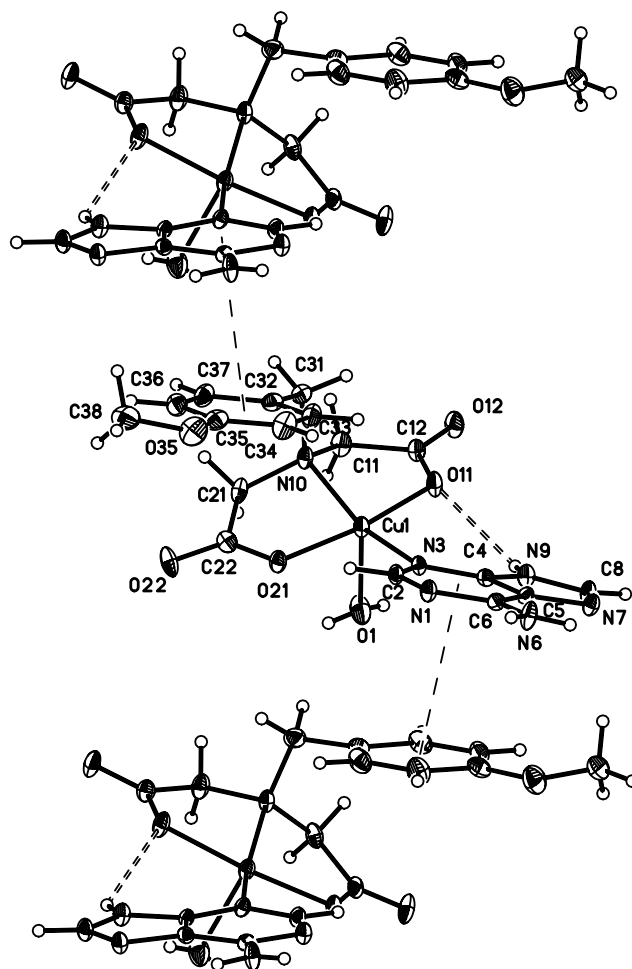


Fig. 1. Three complex units of [Cu(MOBIDA)(AdeH)(H₂O)]·H₂O (3) in a multi-stacked chain showing the *intra*-molecular inter-ligand N6–H(exocyclic)···O(carboxyl) hydrogen bond (open dashed lines) and the *inter*-molecular π,π -stacking interactions between six-membered aromatic rings of MOBIDA and AdeH ligands from adjacent complex molecules (non-coordinated water omitted).

structure results, lying parallel to the plane *ab*. These macro-molecular layers are superimposed along the *c*-axis, connected by H-bonds involving hydrogen atoms from the aqua ligand and non-coordinated water molecule with water or carboxyl O acceptors (Fig. 2). The crystal of compound 3 is remarkably similar to that of

Table 1
Coordination bond distances (Å) in compounds of type II, with general formula [Cu(*N*-benzyl-like)(AdeH)H₂O]·H₂O, and parameters for copper(II) polyhedron distortion

Compound	1 [3]	2 [3]	3
Cu–N(amine)	2.012(3)	1.98(2)	2.007(4)
Cu–O(carboxyl)	1.937(2)	1.96(1)	1.936(3)
Cu–O(carboxyl)	1.943(2)	1.99(1)	1.936(4)
Cu–N(AdeH)	1.981(3)	1.88(1)	1.993(4)
Cu–O(aqua)	2.303(3)	2.27(1)	2.284(4)
τ %	17.35	14.47	20.80
<i>T</i> (tetragonality)	0.86	0.86	0.86

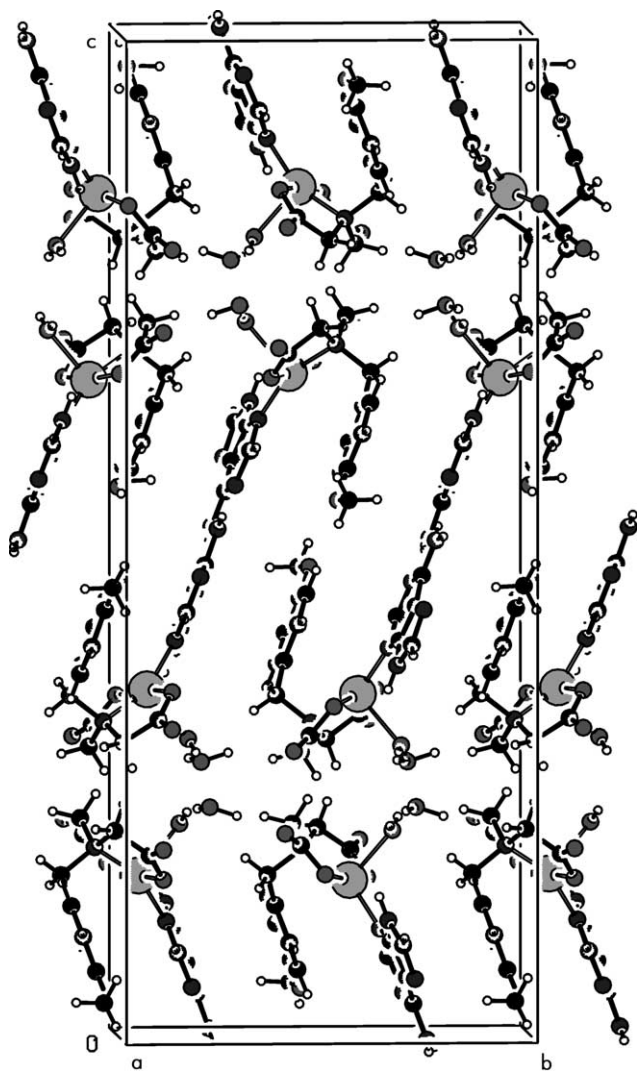


Fig. 2. Fragments of four π,π -stacked chains of compound 3 connected by hydrogen bonds. The two central chains correspond to the same 2D supra-molecular structure extending parallel to the ab -plane. This framework connects up and down with other two by H-bonds involving water molecules.

compound 1 (both have the same space group) but differs in non-relevant supra-molecular details from that of compound 2. Compounds 1–3 exhibit the same molecular recognition phenomena concerning the binding mode between AdeH and the (*N*-benzyl-like)-copper(II) chelate (via the formation of a Cu–N3(AdeH) bond and a intra-molecular inter-ligand N9–H–O(carboxyl) interaction) as

Table 2

Parameters for (benzyl-like)/AdeH inter-molecular inter-ligand π,π -stacking interactions in compounds $[\text{Cu}(\text{N-benzyl-like})(\text{AdeH})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (type II) between six-membered aromatic rings of the benzyl-like arm (B6 or I ring) and the AdeH (A6 or J ring)

Compound	1 [3]	2 [3]	3
Ring I and J	B6/A6	B6/A6	B6/A6
Averaged π,π -stacking distance (Å)	3.4(1)	3.5(1)	3.4(1)
$d(\text{C}_1\text{--}\text{C}_j)$ (Å)/ α (°)	3.53/6.24	3.65/3.41	3.54/7.47
$d(\perp \text{C}_1\text{--}\text{C}_j)$ (Å)/ β (°)	3.42/15.8	3.46/15.3	3.44/8.73
$d(\perp \text{C}_1\text{--}\text{C}_j)$ (Å)/ γ (°)	3.46/14.4	3.53/18.6	3.50/13.74

For significance of symbols see [3].

well as building up inter-molecular multi- π,π -stacked chains. Additional information on the properties of compounds 3–5 or the structure of compound 3 have been submitted as Supplementary material and it can be obtained from the authors (structure and properties) or from the appropriate deposited structural files (see Table 2).

Crystallographic data for the structural analysis of compound 3, $[\text{Cu}(\text{MOBIDA})(\text{AdeH})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$, has been deposited with the Cambridge Crystallographic Data Centre CCDC No. 188262.

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