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Crystal Structure of N,N-bis-(3-Carbomethoxy-5-methyl-pyrazol-1-ylmethyl)aniline

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Abstract: The tripodal ligand N,N-bis-(3-carbomethoxy-5-methylpyrazol-1-yl)methyl aniline (**2**) has been prepared by the condensation of aniline with two equivalents of N-hydroxymethyl[3-carbomethoxy-5-methyl]pyrazole. The molecule consists of two structurally analogous 3-carbomethoxy-5-methylpyrazol-1-ylmethyl moieties, which adopt a transoidal conformation via a central aniline ring, suggesting that this tripodal ligand is highly flexible and could accommodate many metals by coordination.

Keywords: Structure, tripod, pyrazole, tridentate, flexible ligand.

Introduction

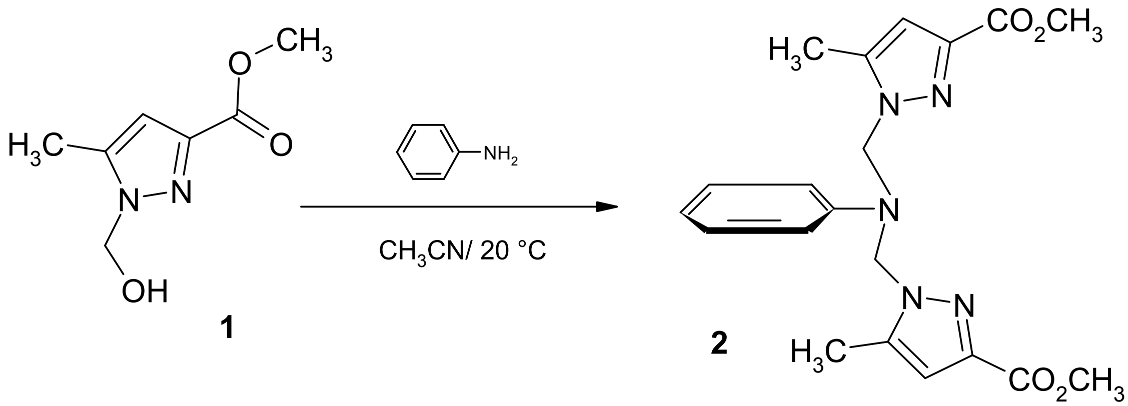
Polydentate pyrazole compounds are known and are particularly interesting as promising ligands for the building of polynuclear complexes as models for bioinorganic systems [1], as well as for the discovery of new catalyst precursors [2]. We are currently working on the synthesis and coordination of monotripodal nitrogen ligands, such as N,N-bis-[(3,5-dimethyl-1-pyrazolyl)methyl]alkylamines [3], to gain insight into the coordination behaviour of larger ligand systems containing both nitrogens of the pyrazolyl groups as potential N-donor atoms, and a delocalised π-conjugated spacer such as an aryldiamine. This research effort is directed towards the preparation of new mixed-valence transition metal complexes for catalysis, and the study of electronic communication [4,5]. The X-ray structure of the N,N-bis-(3-carbomethoxy-5-methylpyrazol-1-ylmethyl) aniline (**2**) was determined to establish its spatial conformation in the free state before coordination to metals.

Results and Discussion

*Synthesis of the tripodal ligand **2**.*

The title compound **2**, which possesses three nitrogen donor sites, was synthesised using literature methods [3,6,7,8]. Thus, the compound was easily prepared from the condensation of 2 equivalents of N-hydroxymethyl-[3-carbomethoxy-5-methyl]-pyrazole (**1**) with one equivalent of aniline under mild conditions (room temperature, atmospheric pressure, 7 days), using anhydrous acetonitrile as solvent (Scheme 1). The yield was good (94%) and compound **2** was recrystallized from dichloromethane/ether.

Scheme 1



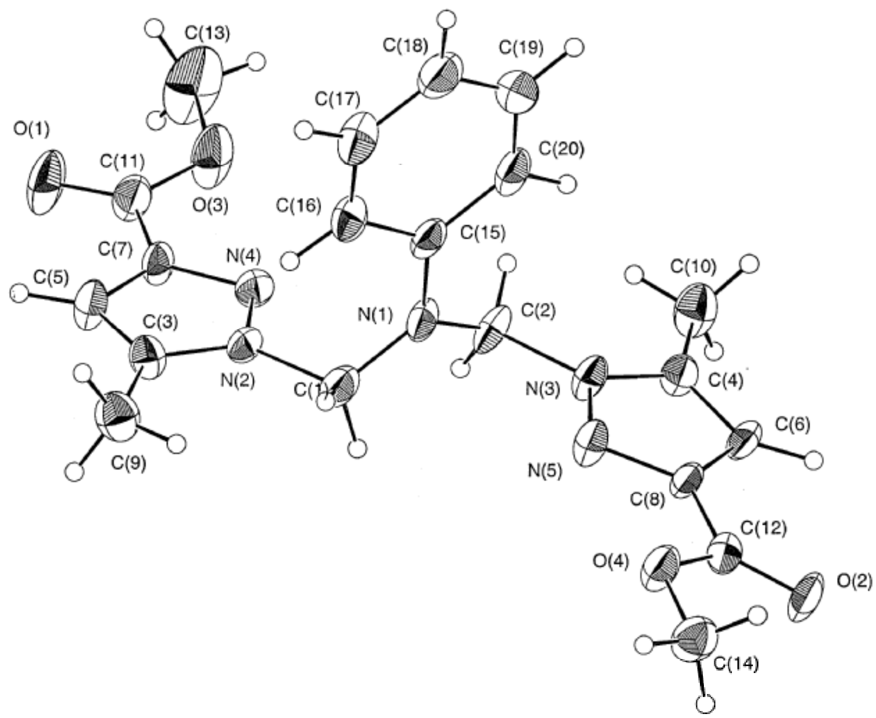
*Crystallographic study of tripodal ligand **2***

The X-ray data for the crystal of the title molecule were collected using graphite-monochromatized Mo Kα radiation at 298 K. The structure was solved by direct methods and refined by full-matrix least-squares with an anisotropic temperature factor for the non-hydrogen atoms. The hydrogen atoms are localised on the difference Fourier map and adjusted to 0.97 Å to bonded atoms. The molecular structure of the title compound is shown in Scheme 2, together with the atomic labelling scheme.

The molecule consists of two 3-carbomethoxy-5-methylpyrazol-1-ylmethyl moieties, which are structurally analogous, and which adopt a transoidal conformation via a central aniline ring suggesting that this tripodal ligand is highly flexible and could accommodate many metals for coordination.

Interestingly molecule **2** has one pseudo C_2 symmetry axis which is formed by the phenyl ring and amine nitrogen centres (N1-C15-C18), so each pyrazole ring is the symmetrical counterpart of the other one. The same observation can be made for the rest of molecule **2** (for example C1 and C2). The electrostatic spatial intermolecular repulsion between N4 and N5 is probably responsible of this general transoidal disposition. These data led us to note the basic character of N4 and N5.

Scheme 2: Molecular structure of the title compound with atom labelling. Thermal ellipsoids are drawn at the 50% probability level.



The N5-C8 bond length is 1.335(5) Å, suggesting that the 3-carbomethoxy-5-methylpyrazole group of compound **2** is less conjugated. This could be due to the electronic attraction of the CO_2CH_3 group. The same observation is valid for the N=N bonds; for example the N2=N4 bond length is 1.353(4) Å. The refinement of the structure has been realized using suitable crystallography programs [11-14]. Table 1 summarises the crystal and experimental data. Selected bond distances and bond angles are listed in Tables 3 and 4, respectively.

Table 1: Crystal and experimental data of tripodal ligand **2**.

Formula: $C_{20}H_{23}N_5O_4$	Radiation: Mo K_α
Formula weight = 397.43	λ = 0.71073 Å
Crystal system: triclinic	μ (Mo K_α) = 0.93 cm^{-1}

Space group: P $\bar{1}$	$2\theta_{max}$ = 64 °
a = 6.624(1) Å	*T* = 298K
b = 12.315(2) Å	Block of white crystals
c = 12.770(2) Å	near prismatic form 0.16, 0.17, 0.20 mm
α = 85.39(1)°	*R* = 0.041 (on F)
β = 83.09(2)°	*R*w = 0.068 (on F^2)
γ = 78.54(1)°	$(\Delta P)_{max}$ = +0.81
V = 1011.8(3)$Å^3$	$(\Delta P)_{min}$ = -0.88
Z = 2	No. of refl. measured = 8258
D_x = 1.305 g/cm^3	No. of refl. used = 1656
Transmission min = 0.667	No. of parameters = 265
Transmission max = 0.986	goodness-of-fit = 0.583

F (000) = 420

Measurement- Kappa CCD – Nonius Diffractometer

Program system: MaXus

Absorption correction : Sortav

Molecular Graphics : ORTEP

Table 2: Selected Fractional Atomic Coordinates and U(iso)

Atom	**x/a**	**y/b**	**z/c**	**U(iso)**
O1	-0.0007(4)	0.2792(3)	0.69695(19)	0.079(2)
O3	-0.1013(4)	0.3459(2)	0.5409(2)	0.0840(18)
N1	0.4611(4)	0.2487(2)	0.23541(19)	0.0482(16)
N2	0.4449(4)	0.1756(2)	0.41638(18)	0.0401(14)
N4	0.2481(4)	0.2309(2)	0.43834(19)	0.0431(15)
C1	0.5254(5)	0.1555(3)	0.3053(3)	0.0500(19)
C3	0.5425(5)	0.1409(3)	0.5052(2)	0.0466(18)
C5	0.4013(5)	0.1760(3)	0.5878(2)	0.051(2)
C7	0.2231(5)	0.2313(3)	0.5435(2)	0.0441(18)
C9	0.7600(5)	0.0792(3)	0.5014(3)	0.062(2)
C11	0.0323(5)	0.2866(3)	0.6023(3)	0.054(2)
C13	-0.2885(8)	0.4112(7)	0.5927(4)	0.132(4)
C15	0.5511(5)	0.3428(3)	0.2293(2)	0.0426(18)
C16	0.7019(5)	0.3506(3)	0.2943(2)	0.050(2)
C17	0.7921(5)	0.4428(3)	0.2861(3)	0.063(2)
H5	0.418(4)	0.172(3)	0.659(3)	0.054114
H6	0.270(4)	0.192(2)	-0.158(3)	0.048953

T. factor of the form: exp[-2pi^2U], U=U(iso) or 1/3 SUM(i)SUM(j){U(ij)*astar(i).astar(j).a(i).a(j).cos(ij)}

Table 3: Selected bond distances (Å) of tripodal ligand **2**.

Atom	Atom	Distance	Atom	Atom	Distance
O1	C11	1.201(5)	N2	N4	1.353(4)
O3	C11	1.323(5)	C15	C20	1.399(6)
N1	C1	1.424(5)	C15	C16	1.395(6)
N1	C15	1.398(5)	C4	C6	1.359(6)
N2	C3	1.370(5)	C3	C5	1.360(6)
N5	C8	1.335(5)	N4	C7	1.334(5)
C3	C9	1.487(6)	C5	C7	1.399(5)
C17	C18	1.376(7)	C7	C11	1.462(6)
C19	C20	1.365(7)	C4	C6	1.359(6)
C15	C20	1.399(6)	C3	C5	1.360(6)

Table 4: Selected bond angles (°) of tripodal ligand **2**

Atom	Atom	Atom	Angle
C1	N1	C2	116.8(4)
C1	N1	C15	121.3(4)
C2	N1	C15	121.3(4)
N4	N2	C3	112.9(3)
N5	N3	C4	112.8(3)
N2	N4	C7	103.8(3)
N3	N5	C8	104.3(3
N2	C3	C5	105.6(4)
N2	C3	C9	122.9(4)
C5	C3	C9	131.5(4)
C3	C5	C7	106.0(4)
N4	C7	C5	111.7(4)
N4	C7	C11	122.7(4)
N5	C8	C6	111.3(4)
N5	C8	C12	123.0(4)
O1	C11	O3	123.1(4)
O1	C11	C7	123.6(4)

Conclusions

We report the easy synthesis of tridentate pyrazolic derivative ligands to establish the structure of one tripodal ligand of this class. We are now investigating whether this mono-tripodal class could display some biological activity and we are extending this synthesis to some bis-tripodal class compounds which are suitable bridging ligands as models of molecular wires.

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Experimental

General

The NMR spectrum was recorded for a $CDCl_3$ solution on a Bruker AM 200 spectrometer working at 200.13 MHz. The chemical shifts are reported in δ values. The melting point was measured on an Electrothermal apparatus and is uncorrected. Reagents and solvents were purchased from commercial suppliers.

Synthesis of N,N-bis-(3-carbomethoxy-5-methylpyrazol-1-ylmethyl)aniline (**2**)

Compound **2** was prepared by the addition of aniline to compound **1** [1] according to a reported procedure [7]. Thus aniline (0.465 g, 5 mmol) was added to a solution of the substituted hydroxymethylpyrazole (1.7 g, 10 mmol) in acetonitrile (35 mL) and the mixture was stirred at 20 °C for a week. The residue was precipitated by addition of cold water, purified by washing with hexane and then dried under vacuum, to afford the title compound as a pure white solid (1 g, 94%) which was recrystallized from dichloromethane/ether; M.p. 124-126 °C; IR (KBr, υ cm^{-1}): 3200 (CH, aromatic), 2920 (CH), 1730 (C=O), 1600 (C=C), 1490 (C=N), 1460, 1420, 1230; ^{1}H-NMR: ppm: 7 (m, 5H, C_6H_5), 6.5 (s, 2H, pyrazolyl-$H^{4,4'}$), 5.65 (s, 4H, NCH_2N), 3.9 (s, 6H, OCH_3), 2.05 (s, 6H, pyrazole-CH_3); MS (Calc. for $[C_{20}H_{23}N_5O_4]^+$: 397); Found $[M]^+$ (m/z): 397; 366; 293; 271; 257; 140; 105; 82; 77. Elemental analysis Calc. (Found) for $C_{20}H_{23}N_5O_4$: C 60.45 (60.48); H 5.79 (5.81); N 17.63 (17.56%).

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Sample Availability: Available from the authors.