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

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Received: 13 May 2002; in revised form 9 September 2002 / Accepted: 10 September 2002 / Published: 30 September 2002

**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**

Polycyclic 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-pyrazoly)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 $\pi$-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.

Crystallographic study of tripodal ligand 2

The X-ray data for the crystal of the title molecule were collected using graphite-monochromatized Mo K$\alpha$ 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$_2$CH$_3$ 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.

| Property                  | Value                      |
|---------------------------|----------------------------|
| Formula: $C_{20}H_{23}N_5O_4$ | Radiation: Mo $K_\alpha$ |
| Formula weight = 397.43    | $\lambda = 0.71073$ Å     |
| Crystal system: triclinic  | $\mu (Mo \ K_\alpha) = 0.93$ cm$^{-1}$ |
Space group: \(P \overline{1}\)  
\(a = 6.624(1) \text{ Å}\)  
\(b = 12.315(2) \text{ Å}\)  
\(c = 12.770(2) \text{ Å}\)  
\(\alpha = 85.39(1)^\circ\)  
\(\beta = 83.09(2)^\circ\)  
\(\gamma = 78.54(1)^\circ\)  
\(\Delta P_{\text{max}} = +0.81\)  
\(\Delta P_{\text{min}} = -0.88\)  
\(V = 1011.8(3) \text{ Å}^3\)  
\(Z = 2\)  
\(2\theta_{\text{max}} = 64^\circ\)  
\(T = 298 \text{K}\)  
Block of white crystals  
near prismatic form 0.16, 0.17, 0.20 mm  
\(R = 0.041\) (on \(F\))  
\(R_w = 0.068\) (on \(F^2\))  
No. of refl. measured = 8258  
No. of refl. used = 1656  
No. of parameters = 265  
Transmission min = 0.667  
Transmission max = 0.986  
goodness-of-fit = 0.583  
\(D_x = 1.305 \text{ g/cm}^3\)  
\(F(000) = 420\)  
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: \(\exp[-2\pi^2U]\), \(U=U(iso)\) or \(1/3 \text{SUM}(i)\text{SUM}(j)\{U(ij)\astar(i)\astar(j)a(i)a(j)\cos(ij)}\)
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.

Acknowledgements

Part of the costs of this research was met by the "Programme Thématique d'Appui à la Recherche Scientifique PROTARS N° P1T2/27" Grant from the Ministry of National Education of Morocco, the "Wylaya d'Oujda", to which the authors' thanks are due.

Experimental

General

The NMR spectrum was recorded for a CDCl₃ 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-ylmethy)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, v cm⁻¹): 3200 (CH, aromatic), 2920 (CH), 1730 (C=O), 1600 (C=C), 1490 (C=N), 1460, 1420, 1230; ¹H-NMR: ppm: 7 (m, 5H, C₆H₅), 6.5 (s, 2H, pyrazolyl-H₄,₄'), 5.65 (s, 4H, NCH₂N), 3.9 (s, 6H, OCH₃), 2.05 (s, 6H, pyrazole-CH₃); MS (Calc. for [C₂₀H₂₃N₅O₄]⁺: 397); Found [M]⁺ (m/z): 397; 366; 293; 271; 257; 140; 105; 82; 77. Elemental analysis Calc. (Found) for C₂₀H₂₃N₅O₄: 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.

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