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1-(2-biphenyl)-3-methyltriazenide-*N*-oxide as a template for intramolecular copper(II)···arene-π interactions

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ABSTRACT

Deprotonated triazene N-oxides are able to chelate metal ions resulting in five-membered rings without carbon atoms. A new ligand 1-(2-biphenyl)-3-methyltriazenide-*N*-oxide (**1**) and its mononuclear Cu(II) complex (**2**) were synthesized to verify the capability of this ligand to promote Cu(II)···arene-π interactions. Ligand **1** and complex **2** have been characterized by elemental analysis, mass spectrometry (ESI(+)-TOF), IR, and UV–Vis spectroscopy. In addition, ligand **1** was characterized by ^{1}H and ^{13}C NMR and complex **2** by X-ray diffraction on single crystal. The crystal structure of complex **2** reveals a distorted tetrahedral geometry of Cu(II) in the first coordination sphere, which expands to a distorted octahedral environment by two symmetrically independent intramolecular metal···arene-π interactions. These interactions are provided by *ortho*-phenyl rings of both triazene *N*-oxide ligands **1**. The aim of this work was to contribute to the architecture of new Cu(II)···arene-π complexes based on the synthesis of appropriated ligand for intramolecular interactions

1. Introduction

Besides the most frequently related copper(I)···arene-π interactions [1–4], copper(II)···arene-π interactions have been recently identified and considered for publication are highlighted as a more rare form of metal···arene-π interaction [5]. This last mode of metal···arene-π interaction can be considered as an extension of a deficient coordination sphere of the copper(II) ion resulting in a consequent increase of its coordination number. The importance of copper(II) in a deficient coordination sphere is its capacity to catalyze reactions, i. e., a regioselective oxygenation reaction at the fourth coordinating pyrrolic double bond [5].

Triazenes, including triazene-*N*-oxides (or triazene 1-oxides), are known as efficient coordinating ligands [6]. They are considered a versatile tool because they are stable, adaptable to numerous synthetic transformations [7] and can evidence a variety of applications [8,9]. In this connection, metal···arene-π complexes of triazenide ligands have received attention in recent years [10–14]. Moreover, triazene-1-oxide complexes show particular interest based on their coordination mode and their ability to chelate metal centers through cis-trans geometry [15,16].

In this report, the synthesis and characterization of a novel triazene N-oxide **1** and its Cu(II) complex **2** are described, as well as the evaluation of metal···arene-π interactions in the complex **2** *cis-bis*[1-(η^6-2-biphenyl)-3-methyltriazenide-*N*-oxide-κ^2N^1,O^4]copper(II). The strategy to promote this kind of interaction was to increase the coordination versatility of triazene-*N*-oxide units including terminal 2-biphenyl substituents, which were geometrically oriented to expand the coordination sphere of the metal center. The obtained complex showed two additional intramolecular Cu(II)···arene-π interactions in the axial direction of the strongly distorted octahedral environment. The complex **2** represents the first report of copper(II) triazenide complexes with expanded coordination sphere through intramolecular Cu(II)···arene-π interactions.

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2. Material and methods

2.1. General remarks

All reagents and solvents used in the study were reagent grade and used without further purification. The employed instruments for the characterization procedures were: Bruker DPX 400 for ^{1}H and ^{13}C NMR spectroscopy; Bruker FT-IR Spectrometer TENSOR-27 for IR spectroscopy using KBr pellets; Shimadzu UV-1650-PC Spectrophotometer for UV–Vis spectroscopy, Bruker Spectrometer Daltonic microTOF-Q with HPLC coupled for ESI(+) TOF/MS; Thermo Finnigan MAT 95 XL 70 eV 200–280 °C for EI/MS spectroscopy; Sand Shimadzu EA 112 microanalysis for C, H, N elemental analysis and a MEL-TEMP II instrument for melting point determination. Crystallographic measurements were carried out at 293(2) K on a Bruker Kappa Apex II-CCD area-detector diffractometer.

2.2. Synthesis of the ligand 1-(2-biphenyl)-3-methyl-triazene-N-oxide (**1**)

A mixture of 2-biphenylamine (1.18 g, 7.0 mmol), 6.0 mL of concentrated H_3CCOOH, 1.0 mL of concentrated HCl and 6.0 mL of H_2O was cooled at 0 °C, and a solution of sodium nitrite (0.48 g, 7.0 mmol) in water (5.0 mL) was added under magnetic stirring. After 20 min stirring at 0 °C, a cold solution of *N*-methylhydroxylamine•HCl (7.0 mmol, 0.59 g) in water (5 mL) was slowly added to the previous reaction mixture. Following 15 min of stirring, the reaction mixture was carefully neutralized at 0 °C by adding small volumes of a cooled aqueous solution of sodium carbonate until pH 7.0. A beige solid precipitate was obtained. This solid product was extracted by ethyl acetate (3 × 50 mL), dried under vacuum and purified by chromatographic column with silica gel (70/230 mesh) using 20% ethyl acetate in hexane as eluent. The purified product was obtained as beige needles. Yield 81% (1.29 g, 5.7 mmol) based on 2-biphenylamine. M.p. 46 °C. **IR** ν_{max}/cm^{-1}, KBr, main signals: 3258 [m, ν(N–H)], 1603 [m, δ(C=C)], 1582 [s, δ(C=C)], 1511 [vs, δ(N–H)], 1407 [s, ν_{as}(N=N)], 1346 [s, ν_s(N→O)], 1220 [vs, ν_s(N–N)], 974 [s, ν(N→O)]. **^{1}H NMR** (400 MHz, $CDCl_3$/TMS) δ/ppm: 10.24 (br, 1*H*, N*H*), 7.51–7.29 (m, 8*H*, Ar*H*), 7.21 (d, *J* = 7.58 Hz, 1*H*, Ar*H*), 7.04 (t, *J* = 7.58 Hz, 1*H*, Ar*H*), 3.86 (s, 3*H*, C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$/TMS) δ/ppm: 137.4 (*Ar*), 136.5 (*Ar*), 130.6 (*Ar*), 129.1 (*Ar*), 128.7 (*Ar*), 128.6 (*Ar*), 128.1 (*Ar*), 127.9 (*Ar*), 122.3 (*Ar*), 114.1 (*Ar*), 49.8 (*C*H$_3$). **UV–Vis** (THF) λ_{max}/nm: 245, 310 ($\varepsilon_{310}/dm^3\ mol^{-1}\ cm^{-1}$ 2.28 × 10^4). **EA** ($C_{13}H_{13}N_3O$, 227,26 g/mol) %: C 68.70 (calc. 68.70), H 5.66 (calc. 5.77), N 18.34 (calc. 18.49). **EI/MS** (m/z): 227.1 (M^+, 12%), 181.1 (1-(2-biphenyl)NN$^+$, 17%), 169.1 (1-(2-biphenyl)NH$_2^+$, 25%), 153.1 (1-(2-biphenyl$^+$, 100%).

2.3. Synthesis of the complex bis{(1-(2-biphenyl)-3-methyl-triazenide-N-oxide)-copper(II)·H$_3$COH} (**2**)

A solution of $Cu(OAc)_2\cdot H_2O$ (40.0 mg, 0.2 mmol) in 4 mL of a methanol-pyridine mixture (1:1) was added under magnetic stirring to a solution of **1** (91 mg, 0.4 mmol) dissolved in 10 mL methanol, which was previously deprotonated with granulated KOH (31 mg, 0.55 mmol). Immediately after, the color of the reaction mixture changed to deep-brown. After 10 min, solid impurities were removed by filtration. Suitable greenish-brown plates with rhombus shape were obtained for X-ray diffraction analysis by evaporation of the solvent mixture after one day. Yield 61% (67 mg, 0.12 mmol, presence of MeOH as crystallization solvate) based on $Cu(OAc)_2\cdot H_2O$. M.p. 135 °C. **IR** ν_{max}/cm^{-1}, KBr, main signals: 1596 [w, δ(C=C)], 1580 [w, δ(C=C)], 1564 [w, δ(C=C)], 1490 [m, δ(C=C)], 1476 [s, δ(C=C)], 1394 [vs, ν_{as}(N=N)], 1232 [vs, ν_s(N–N)], 977 [s, ν(N→O)]. **UV–Vis** (THF) λ_{max}/nm: 245, 310 ($\varepsilon_{310}/dm^3\ mol^{-1}\ cm^{-1}$ 3.24 × 10^4). **EA** ($C_{26}H_{24}N_6O_2Cu$, 516,07 g/mol) %: C 59,85 (calc. 60,51), H 4,72 (calc. 4,69), N 16,05 (calc. 16,29). **ESI(+) TOF/MS** (Collision energy 8 eV, HCOONa, m/z): 1055.2 (2M$^+$ + Na$^+$), 538.1 (M$^+$ + Na$^+$), 516.1 (M$^+$), 289 [1-(2-biphenyl)-3-methyl-triazenide-N-oxide)-copper(II)$^+$].

2.4. Crystal structure determination of $C_{26}H_{24}N_6O_2Cu\cdot CH_3OH$ (**2**)

The X-ray diffraction analysis for complex **2** was carried out using a single crystal fixed on a glass fiber for data collection. Data were collected at 293(2) K on a Bruker APEX II CCD area–detector diffractometer using graphite monochromatized Mo-K$_\alpha$ radiation and *COSMO* program [17].

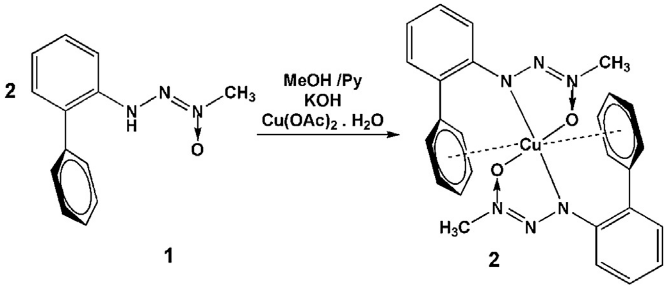
A Gaussian absorption correction was performed on the collected x-ray intensities. The structure was solved by direct methods (*SIR*2004) [18] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms using the *SHELXL*-97 program [19]. Positional parameters of the H atoms bonded to C atoms were obtained geometrically with the C–H distances fixed (0.96 Å for C*sp*^{3} methyl and 0.93 Å for C*sp*^{2} phenyl) and refined as riding on their respective C atoms with $U_{iso}(H) = 1.5U_{eq}(Csp^3$ methyl) and $U_{iso}(H) = 1.2U_{eq}(Csp^2$ phenyl), respectively. The positional parameter for H atom of the hydroxyl group of methanol crystallization solvate was obtained from a difference map and refined with an isotropic displacement parameter. Graphical representations were drawn with the *DIAMOND* software [20].

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The free ligand [Ph(2-Ph)N(H)NN(O)CH$_3$] **1** was obtained by the coupling reaction of the diazonium salt of the 2-biphenylamine and *N*-methyl-hydroxylamine•HCl in an half-diluted acid medium (HCl) and isolated under pH control by extraction. Compound **1** was purified by chromatographic column (yield: 81% based on the *N*-methylhydroxylamine•HCl). The free ligand **1** is soluble in the most common organic solvents such as methanol which facilitates its metal complexation reactions.

Complex {Cu^{II}[(Ph(2-Ph)NNN(O)CH$_3$)]$_2$} **2** was synthesized by the reaction of copper(II) acetate monohydrate with ligand **1** previously deprotonated with a KOH/methanol solution (Scheme 1). The Cu(II) ion is chelated by two deprotonated triazenide-*N*-oxide ligands in form of two five-membered rings including a common vertex occupied by the metal center, which shows a distorted tetrahedral geometry, Cu^{II}(NNNO)$_2$. However, if the metal···arene-π interactions between the *ortho*-phenyl rings of the terminal biphenyl substituents are considered, the Cu(II) coordination geometry expands to distorted octahedral. These phenyl rings are included in the second coordination sphere of the Cu(II) ion and



Scheme 1. Synthesis of complex 2.