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Synthesis, crystal structure and photo-induced isomerization of [*N*,*N*'-bis(4-fluorobenzylidene)ethylenediamine]bromo(triphenylphosphine)copper(I)



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ABSTRACT

The title Schiff base complex is a model compound for photoisomerization reactions which occur in photobiological processes such as vision. The Schiff base ligand and the complex have been prepared in a onepot synthesis. In the crystal structure of the complex, copper has a distorted tetrahedral coordination. Photochemical investigations in solution reveal time-resolved spectroscopic changes that are interpreted in terms of a transformation from *E* to *Z* configuration of the C=N bonds of the coordinated Schiff base ligand. Application of multivariate curve resolution and non-linear least squares curve fitting to the spectroscopic profiles provides a rate constant of 0.11 min⁻¹ for the photoisomerization and a quantum yield of 0.246.

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1. Introduction

Schiff-base metal complexes are of interest in inorganic chemistry and have been studied extensively; the Cambridge Structural Database (version 5.34, November 2012) [1] contains over 70 entries having the Schiff base skeleton shown in Scheme 1 with any substituents allowed on the aromatic rings but none on the aliphatic chain, and has over 1300 metal complexes of such ligands. Complexes of transition metal ions with bidentate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems and represent interesting models for metalloenzymes that catalyze the reduction of nitrogen and oxygen [2]. Schiff-base metal complexes have industrial, antifungal and biological applications [3]. The steric, electronic, and conformational effects imparted by the coordinated ligands play an important role in modifying the properties of their metal complexes. A thorough understanding of these effects will serve as the basis for a rational design of complexes with specific and predictable properties. Although reports on $[Cu^{I}(N_{4})]$ complexes are numerous [4], little

work is related to copper(I) complexes with mixed ligands, Cu(NN)XY [5,6]. Photochemical *Z/E* isomerizations of C=C [7] and N=N [8] double bonds have been investigated thoroughly, but only limited information is available on photoisomerization of C=N double bonds [9]. Multivariate curve resolution-alternating least squares (MCR-ALS) has already been applied to very diverse second-order calibration problems, as for example, series of titrations, chromatographic runs, or kinetic data [10–13]. We report here the synthesis, structural characterization, and photo-induced *E/Z* isomerization of (fb₂en)bromo(triphenylphosphine)copper(I) (1) (Scheme 1), where fb₂en is the ligand *N,N'*-bis(4-fluorobenzylidene)ethylenediamine.

2. Experimental

2.1. Materials and physical measurements

All chemicals used were purchased from commercial sources and used as received without further purification. The infrared spectrum was obtained with a Shimadzu IR-435 spectrophotometer using a KBr pellet. The room-temperature visible absorption spectrum was recorded with a Shimadzu 160 spectrophotometer. NMR spectra were recorded on a Bruker AW spectrometer



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Scheme 1. Synthesis of [CuBr(fb₂en)(PPh₃)] (1).

operating at 400 MHz. A high-pressure mercury lamp with grating monochromator was used in the photoisomerization study. Singular value decomposition (SVD), multivariate curve resolution and non-linear least squares curve fitting were performed with MATLAB version 7.0.

(60 mg, 0.23 mmol) in acetonitrile (5 ml) was added to the above solution, which was stirred for an additional 20 min. Slow evaporation of the solvent under vacuum gave the title compound (**1**) as yellow crystals: yield 136 mg, 85%. IR (KBr pellet, 400–4000 cm⁻¹) 1620 (C=N). UV [chloroform; λ_{max} in nm (log ε in L mol⁻¹ cm⁻¹)]: 274 (6.44), 295 (6.47), 379 (6.59). ¹H NMR (CDCl₃) 3.86 (s, 4H, NCH₂ CH₂N); 7.02–7.75 (m, 23H, ArH); 8.61 (s, 2H, 2CH=N).

2.2. Synthesis of [CuBr(fb₂en)(PPh₃)] (1)

At ambient temperature, a chloroform solution (5 ml) of ethylenediamine (14 mg, 0.23 mmol) was added to 4-fluorobenzaldehyde (57 mg, 0.46 mmol) in chloroform (10 ml) with stirring. After half an hour, a mixture of CuBr (30 mg, 0.23 mmol) and PPh₃

2.3. X-ray diffraction analysis

Single-crystal diffraction for (1) were measured at 150 K on a Bruker smart 1 K CCD diffractometer with Mo K α radiation



Fig. 1. Molecular structure of (1) with 40% probability displacement ellipsoids and atom labels.

 Table 1

 Selected bond lengths (Å) and angles (°) for complex 1.

Cu–Br	2.4789(3)	Cu-P	2.2048(5)
Cu-N(1)	2.1322(14)	Cu-N(2)	2.0912(15)
Br-Cu-P	117.682(15)	Br-Cu-N(1)	107.24(4)
Br-Cu-N(2)	99.22(4)	P-Cu-N(1)	117.69(4)
P-Cu-N(2)	125.10(4)	N(1)-Cu-N(2)	84.07(6)



Fig. 2. UV–Vis absorption spectroscopic changes for 0.10 mM (1) in chloroform with UV irradiation. From a to q, each irradiation time is 2 min, total 40 min.



Scheme 2. Photoisomerization mechanism of (1) in chloroform.

(0.71073 Å); absorption corrections were based on repeated and symmetry-equivalent data. The structure was solved by direct methods and refined on all unique F^2 values, with anisotropic displacement parameters and with constrained riding isotropic H atoms.

Yellow block crystal, $0.34 \times 0.34 \times 0.30$ mm; $C_{34}H_{29}BrCuF_2N_2P$, M = 678.0; monoclinic, space group $P2_1/c$, a = 19.1663(18), b = 13.2456(13), c = 11.9120(11)Å, $\beta = 90.004(2)^{\circ}$, V = 3024.1(5)Å³, Z = 4. 26681 reflections measured, 7368 unique, $R_{int} = 0.0274$, 6178 reflections with $F^2 > 2\sigma$, data 99.9% complete to $\theta = 26^{\circ}$. 370 refined parameters, R [F, $F^2 > 2\sigma$] = 0.0252, R_w [F^2 , all data] = 0.0629, goodness of fit = 1.01 on F^2 , final difference map extremes +0.39 and -0.32 eÅ⁻³. Programs were Bruker SMART, SAINT and SADABS for data collection and processing, SHELXTL for structure solution, refinement and graphics [14–16].

3. Results and discussion

3.1. Crystal structure of [CuBr(fb₂en)(PPh₃)] (1)

Compound (1) is a copper(I) complex with a distorted tetrahedral coordination geometry for the N₂PBr donor set (Fig. 1). Selected bond lengths and angles are given in Table 1. The distortion from ideal tetrahedral geometry is due mainly to the restricted bite angle of the chelating Schiff base ligand: the N(1)-Cu-N(2) angle is only $84.07(6)^{\circ}$ while other angles range from $99.22(4)^{\circ}$ to 125.10(4)°. There is also a twisting distortion, with a dihedral angle of 83.7° (ideal 90°) between the CuN₂ and CuBrP planes. The Cu-Br bond length of 2.4789(3) Å in (1) is somewhat greater than those in closely related copper(I) complexes with N-bidentate, Br and PPh₃ ligands, for example 2.4400(5) Å in [CuBr(ca₂en)(PPh₃)] [17] and 2.3812(3) Å in [CuBr(bipy)(PPh₃)] [18]. The Cu-P distance of 2.2048(5) Å agrees well with those in related complexes [5]. The internal geometry of the ligands is unremarkable. The CuNCCN chelate ring has approximately a twist conformation with atoms C(8) and C(9) on opposite sides of the CuN_2 plane, and this ligand as a whole is bowed, with a dihedral angle of 44.7° between the two aromatic rings. There is intramolecular π -stacking of one of the Schiff base benzene rings (containing C(1)) and one of the phosphine phenyl rings (containing C(29)), with a centroid ... centroid



Scheme 3. Photoisomerization mechanism of the ligand in chloroform.

distance of 3.596 Å, an interplanar distance of approximately 3.38 Å, and a dihedral angle of 1.9° between the rings. The phosphine has approximately the form of a three-bladed propeller, the dihedral angles between pairs of rings being 69.3°, 71.0° and 75.3°. There are no unusually short intermolecular contacts, the most significant probably being a CH··· π interaction between C(9)–H(9A) and the Schiff base ligand ring containing C(1), with CH···centroid = 2.57 Å and an angle of 150° at H(9A); this and a symmetry-related interaction link pairs of molecules into centrosymmetric dimers. The Br atom forms its shortest contacts of 3.83–4.00 Å with H atoms of neighbouring molecules, in addition



Fig. 3. Expanded ranges of isomerization spectra of (1) in chloroform solution starting with the pure *EE* isomer at 293 K.

to a 2.86 Å intramolecular Br \cdots H contact to the ring containing C(1). This ring and a symmetry-equivalent also have mutual F \cdots H contacts of 2.51 Å.

3.2. Photoisomerization of (1)

The spectrum of the free ligand shows two major peaks at 251 and 301 nm, identified as characteristic $\pi \to \pi^*$ and $n \to \pi^*$ absorption bands, and the spectrum of the Cu(I) complex shows two major peaks, one at 295 nm that is related to a ligand-centred transition of the coordinated *E* isomer of fb₂en in solution, and another at 379 nm which is identified as MLCT. On irradiating a chloroform solution of (1) with a high-pressure mercury lamp, the absorption maximum of complex (1) at 295 nm decreases in intensity and that at 379 nm increases, with an isosbestic point at 354 nm (Fig. 2). The shift indicates the transformation from *E* to *Z* configuration of the C=N bonds of the coordinated ligand in solution (Scheme 2).

The isosbestic point in Fig. 2 indicates that an equilibrium is established in solution; no other molecules are involved the photoisomerization process. The mechanisms of photo-induced E/Z isomerization of C=N bonds have been extensively investigated over the last four decades [19–22]. The mechanism for the photochemical interconversion of imine diastereomers has been considered in terms of either a planar inversion mechanism or a rotation mechanism. The rotation or torsion mechanism involves twisting about the C=N double bond. In order to bring about this change in geometry, there must be a reduction in the double bond character of the imine bond in the transition state relative to the ground state. If four substituent groups on the double bonds in the ligand are all different, there are four isomers, *viz.* (*EE*), (*EZ*), (*ZE*), and (*ZZ*),



Fig. 4. Expanded ranges of isomerization spectra of: (a, b) 1,4-di(4-alkoxyphenyl)butadiene in degassed toluene solution [23,24]; (c) *N*,*N*-bis(4-dimethylaminobenzylidene)1,2-diaminopropane in chloroform starting with pure *EE* isomers at 293 K.



Fig. 5. The concentration profiles of EE (A) and ZZ (B) isomers of (1) in chloroform (MCR-ALS (), and fitted exponential functions (solid lines)).

but here we have only three, (EE), (EZ = ZE), and (ZZ) (Scheme 3). The reaction $EE \leftrightarrow ZZ$ does not pass through the EZ isomer, as is shown by the spectra in Fig. 3. In this photoisomerization an iso- sbestic point is observed at 354 nm (i.e. the EE-ZZ spectra cross-over). In contrast to this the cross-overs of the reaction spectra induced by direct irradiation range from 305 nm (the crossover of the *EE*–*EZ* spectra) to 307 nm (Fig. 4(d)). This behaviour is caused by the three-component reaction sequence $EE \leftrightarrow EZ \leftrightarrow ZZ$ [23-25].

3.3. Kinetic constant and quantum yield

As with any other resolution method, the aim of MCR-ALS is the optimal decomposition of a data matrix D into the product of two small matrices, C and S^{T} . This decomposition is the result of the validity of the Beer-Lambert law for absorption measurements. $D = CS^{T} + E$, D is the original measurement and contains as rows the absorption spectra measured as a function of the reaction time. The matrices *C* and *S*^T contain, as columns, the kinetic profiles of the compounds involved in the process and, as rows, their related spectra, respectively. E is the error-related matrix. Decomposition of the D matrix is achieved by iterative optimization under suitable constraints for C and S^{T} . Spectra profiles were evaluated using MCR-ALS, and the best MCR-ALS results were obtained by assuming two components for (1) defined by applying the constraints of non-negativity (for both concentrations and signals), unimodality of the concentrations, and closure (the sum of the concentrations of the isomers). Under such conditions, a lack of fit of 0.33% was obtained for (1). The calculated concentration profiles are shown in Fig. 5 for (1). Kinetic constants were evaluated using non-linear least-squares curve fitting by the MATLAB program toolbox using the concentration profiles and definition of exponential function (fitted exponential curve shown in Fig. 5 with solid lines). For (1) the obtained kinetics constant value is 0.11 min^{-1} (RMSE = 6.9×10^{-4}) (RMSE is root mean squares of errors).

Quantum yield is a useful parameter to indicate the efficiency of a photochemical reaction; it is defined as the number of probe molecules undergoing a specific chemical reaction divided by the number of photons absorbed. The quantum yield of photoisomerization can be calculated from the observed first-order rate constant, where a specific form of quantum yield, ϕ based on firstorder kinetics, is indicated in Eq. (1) [26]

where $I_{0,\lambda}$ is the incident light intensity at a specific wavelength $(E l^{-1} s^{-1})$. According to the data provided by the Southern New England Ultraviolet Company, intensity at 350 nm is 3.11×10^{-6} (24 W) E l⁻¹ s⁻¹, ε_{λ} = molar absorptivity of compound at 350 nm, and l = cell path length (1 cm). The quantum yield value obtained for (1) is 0.246.

4. Conclusion

The Schiff base ligand fb2en forms the distorted tetrahedral copper(I) complex (1) with a small bite angle for the bidentate ligand. The crystal structure shows an *EE* configuration for the Schiff base ligand. Photoisomerization leads to a ZZ configuration in solution, as indicated by time-resolved analysis of spectra, which also provides a quantum yield and rate constant.

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Appendix A. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 658010 for (1). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033: e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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