EurJIC
European Journal of Inorganic Chemistry

DOI: 10.1002/ejic.201101356

Spectroscopic Evidence in Solid and Solution of a Discrete Copper(I) Tetrahedral Complex Dimer Supported by Supramolecular Interactions

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Keywords: Copper / Self-assembly / Pi interactions / Supramolecular chemistry / NMR spectroscopy

The first study of the self-association of a copper(I) tetrahedral complex ([Cu(*N*-{4-nitrophenyl}pyridine-2-yl-methanimine)(PPh_3)Br]) has been performed. The formation of a discrete dimer supported by supramolecular π–π stacking and C–H···Br interactions was established by X-ray diffraction techniques. 1D- and 2D NMR techniques were used for the structural characterization of this compound in solution. Unexpected ^1H–^1H NOE effects are coherent with the presence of a dimer in solution, whose structure replicates that found in the crystal. Dimerization constants obtained by VT-^1H NMR spectroscopy allowed the determination of the thermodynamic parameters for the self-association process, namely $\Delta S = -0.67 \pm 0.21\,\mathrm{cal\,mol^{-1}\,K^{-1}}$, $\Delta H = -2.00 \pm 0.05\,\mathrm{kcal\,mol^{-1}}$ and $\Delta G(298\,\mathrm{K}) = -1.79\,\mathrm{kcal\,mol^{-1}}$. Consequently, this association process is enthalpy driven.

Introduction

Coordination Cu^I complexes with high π-delocalized ligands have attracted considerable attention because of their interesting photophysical and electrochemical behavior[1] as well as because of their stereochemical versatility in the construction of supramolecular structures.[2] Furthermore, the presence of noncovalent interactions in molecules with extended, fused aromatic systems has also been investigated in relation to several topics including crystal engineering,[3] anti-HIV activity,[4] intercalation of metal complexes into DNA,[5] and structural stabilization in supramolecular chemistry.[6] The role of π–π stacking in aggregations of transition-metal complexes with aromatic ligands has been reported in several papers.[7] However, the simultaneous evidence of a discrete dimer in the solid and in solution is limited.[8] Complexes with Ru^{II},[8] Os^{II},[8a] and Pt^{II}[9] metallic centers are among those that have been studied.

Holdt et al. reported a crystal rearrangement of the first supramolecular column assembly of homoleptic copper(I) complexes governed by π–π stacking interactions, in which the presence of discrete dimers was observed,[10] but to the best of our knowledge, studies on the dimerization of copper(I) complexes in the solid as well as in solution have not been reported.

In this work, we report the synthesis and characterization of a new Cu^I complex, [Cu{*N*-(4-nitrophenyl)pyridine-2-yl-methanimine}(PPh_3)Br], where PPh_3 is triphenyl phosphane. For this complex, we have obtained experimental evidence of the self-association both in solution and in the solid phase by NMR spectroscopy and X-ray diffraction techniques. The dimerization constant (K_D) and thermodynamic parameters for the self-association process were calculated.

Results and Discussion

The complex was prepared by reaction of equimolar amounts of CuBr, PPh_3, and the *N*-(4-nitrophenyl)pyridine-2-yl-methanimine ligand (NN′-NO_2),[11] and it was obtained as a dark purple solid that was crystallized by slow ether diffusion into a dichloromethane solution of the complex. The ^1H NMR spectrum of the complex is consistent with the presence of NN′-NO_2 and PPh_3 coordinated to the metal center. Unequivocal assignment of the proton signals was carried out by the concerted use of 1D (^1H NMR, $\{^1H\}^{13}C$-NMR) and 2D (COSY, HSQC, HMBC) NMR techniques (Table S1, Supporting Information).

The crystallographic structure shows the copper atom to be dicoordinated by the NN′-NO_2 ligand, while PPh_3 and Br complete the coordination sites of the copper(I) in a pseudo tetrahedral arrangement (Figure 1a). Intramolecular bond lengths and angles do not depart significantly

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201101356.

from commonly accepted values.[12] The geometry around the copper atom corresponds to a distorted tetrahedron, elongated along the common bisector of the small (because of chelation) N–Cu–N angle and the sensibly larger P–Cu–Br angle, which presents, as expected, N–Cu coordination distances shorter than the Cu–P and Cu–Br distances (Table S3).

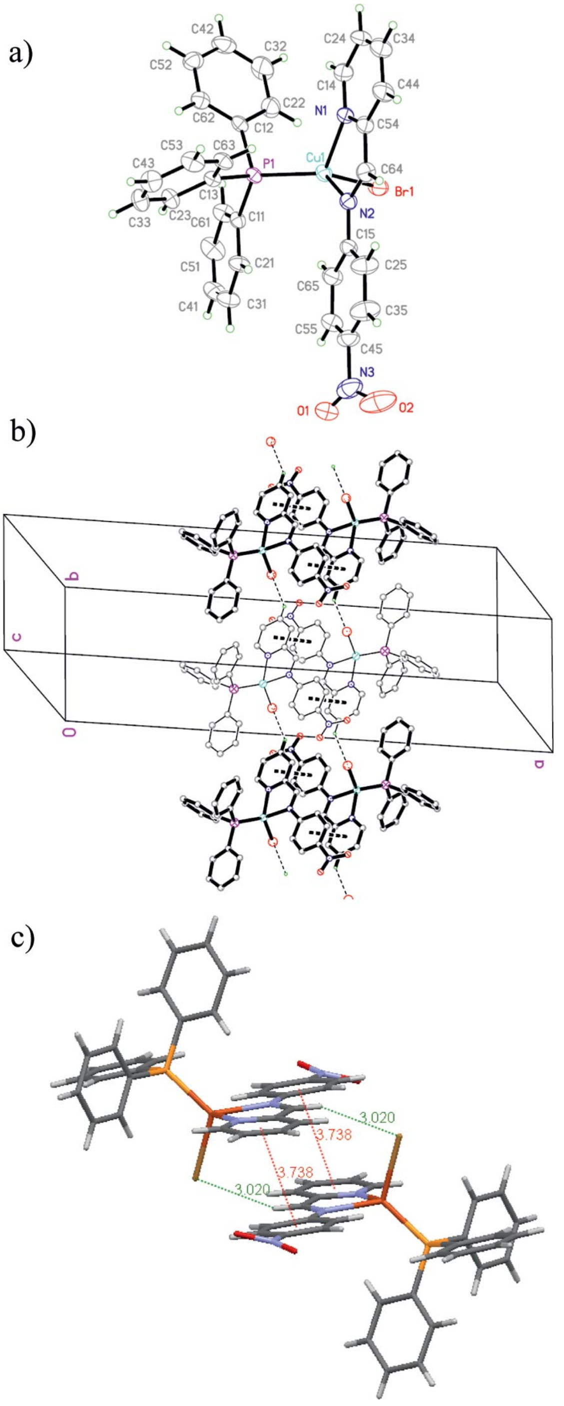

Figure 1. (a) ORTEP view of the [Cu(NN′-NO$_2$)(PPh$_3$)Br] complex. Displacement ellipsoids are drawn at a 50% level. (b) Schematic view of the complex, which shows the linkage of dimers (thick dashed lines) by C–H···Br bonds (thin dashed lines) to form chains along the *b* axis. (c) Scheme showing the way dimers are formed in the solid by π–π interactions around an inversion center.

Intermolecular interactions are also present, the most noticeable are the phenyl/pyridine π–π contacts (Table S4), which define weakly linked centrosymmetric dimeric units. In this dimer, the NN′-NO$_2$ ligands of two different molecules of the complex are placed in an anti-parallel displaced conformation, with centroid–to-centroid distances of 3.738(3) Å between the phenyl and pyridyl rings (Figure 1b and c).

The π–π interactions involving other *N*-phenylpyridin-2-yl-methanimine ligands have been reported, as in the crystal structures of tetracoordinate Hg^{I},[13] Hg^{II}, Zn^{II},[14] and Cu^{I}[15] complexes, whose centroid–to-centroid distances between the phenyl/pyridine rings of neighboring molecules are 3.42, 3.674, 3.601, and 3.8 Å, respectively, similar to that found by us.

Another intermolecular contact is a nonconventional C–H···Br interaction (Table S5), which links the dimeric units through a centrosymmetric pair of (C–H)···Br$_{\text{neighbor}}$ and Br···(H–C)$_{\text{neighbor}}$ interactions, parallel to each other and that define "strips" along the crystallographic *b* axis (Figure 1b).

The behavior of the complex in CDCl$_3$ solution was studied by ^{1}H NMR spectroscopy, which shows a strong dependence of the proton chemical shifts of the ligand with concentration and temperature. Because only narrow signals for all the protons of the NN′-NO$_2$ ligand are observed over the temperature and concentration ranges studied, this equilibrium has a very fast exchange rate relative to the NMR timescale[16] (Figure 2).

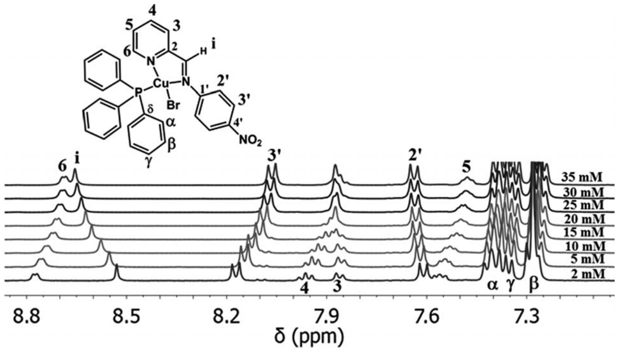

Figure 2. ^{1}H NMR spectra for [Cu(NN′-NO$_2$)(PPh$_3$)Br] in CDCl$_3$ at 298 K as a function of concentration.

The nature of this process was investigated by UV/Vis and NMR spectroscopy. The appearance of new bands was not observed in the UV/Vis spectra when the concentration of the compound was changed. The MLCT band shows a good correlation between absorbance and concentration in chloroform solutions (Figure S1), and $\lambda_{\max}$ values were independent of the concentration in the measured range. These results discard ligand dissociation processes; therefore, the shifting of the proton chemical shift in the NMR spectra can be related to the self-association phenomena. Little changes can be expected in the HOMO and LUMO energies because of noncovalent interactions involved upon dimer formation; however, this fact was not observed in the UV/Vis spectra.

On the basis that this process corresponds to a dimerization supported on π–π stacking interactions, small amounts of benzene were added to the complex solutions, which resulted in significant changes in the proton spectra. Noticeably, as the amount of benzene was increased, the resonance of all the protons of the NN′-NO_2 ligand were shifted upfield. Such behavior suggests an important noncovalent association between benzene and the complex that would explain the increased shielding experienced by the all protons (Figure S2). Thus, the greatest changes in δH^i and δH^3, which are close to the bromine atoms in the dimer, indicate a decrease in the dimerization process by competition with the benzene/complex aggregation process. However, there is not enough evidence to discard the interaction of benzene with the dimer complex.

Dimerization was also confirmed by the presence of NOE correlations, unexpected for a monomolecular species, in the NOESY spectra measured under different experimental conditions. Indeed, NOE effects were observed between the H^4 proton of the pyridine fragment and both the $H^{2'}$ and $H^{3'}$ protons of the 4-nitrophenyl moiety of the vicinal NN′-NO_2 ligands (Figure S3).

Higher order aggregates were discarded on the basis of a very good least-squares fit of the dimer model of Horman and Dreux with the ^{1}H NMR spectroscopic data and the resulting van ’t Hoff plot.

An increase in the concentration of the complex (from 2 to 35 mM) leads to a progressive upfield shift of some protons of the NN′-NO_2 ligand in the spectrum (H^4, H^5, H^6, and $H^{3'}$), which can be accounted for by the shielding of these protons by the aromatic rings of a second NN′-NO_2 ligand coordinated to another complex molecule that forms the dimeric unit in solution, $[Cu(NN'\text{-}NO_2)(PPh_3)Br]_2$. On the contrary, the H^i, H^3, and $H^{2'}$ protons of NN′-NO_2 are shifted downfield as the complex concentration increases (more pronounced for H^i), which could be congruent with the deshielding caused upon metal–ligand coordination. However, this is discarded by the sensitivity of the chemical shift of these protons with complex concentration and rather points to a deshielding effect caused by their interaction with the electronegative bromine of the other complex in the dimer.

Consequently, we estimate then that the Br···H interactions are the consequence of π–π noncovalent associations that lead toward dimerization of the complex by causing an additional stability of the dimer.

These results show a good analogy between the conformations of the dimeric aggregates in the solid and in solution. In the crystal structure of the dimeric unit, the short distances between the bromine atom of one monomer and the H^i, H^3, and $H^{2'}$ protons of the other follow the order 3.020 (H^i), 3.121 (H^3), and 3.550 Å ($H^{2'}$), which agrees with the variation in the downfield chemical shift ($\Delta\delta$) as the concentration increases, namely $H^i > H^3 > H^{2'}$, whose deshielding origin is due to the proximity of bromine.

In this way, the correlation between the crystallographic structure and the NMR findings strongly supports the idea that $[Cu(NN'\text{-}NO_2)(PPh_3)Br]$ dimerizes in solution, in a conformation that resembles the dimeric unit in the crystal, where the interactions responsible for its self-association mainly result from π–π stacking between NN′-NO_2 aromatic rings and (C–H)···Br interactions. Thus, the equation describing the self-association equilibrium is:

$$2[Cu(NN'\text{-}NO_2)(PPh_3)Br] \xrightleftharpoons{K_D} [Cu(NN'\text{-}NO_2)(PPh_3)Br]_2$$

Dimerization constants (K_D) in $CDCl_3$ were determined by the curve fitting method described by Horman and Dreux.[17] Representative K_D values at a given temperature were obtained by averaging the calculated K_D value for each proton of the NN′-NO_2 ligand[18] (Figure 3, Tables S1 and S6).

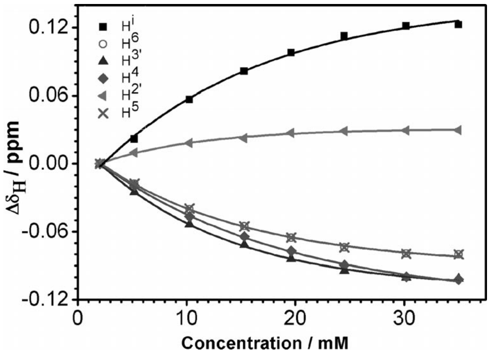

Figure 3. Concentration dependence of the proton chemical shifts for NN′-NO_2 in the complex at 298 K.

The K_D values obtained were in the range 70.4 (220 K) to 21.8 M^{-1} (298 K). These values are comparable to those obtained for the dimerization constants of octahedral ruthenium complexes, $[Ru(bipy)_2(eilatin)][PF_6]_2$ and $[Ru(bipy)_2(isoeilatin)][PF_6]_2$, which are 260 M^{-1} and 34 M^{-1}, respectively, in acetonitrile at 298 K, where the largely fused aromatic rings allow the formation of dimers in solution through π–π stacking.[7a]

On the other hand, for aqueous solutions of square-planar platinum complexes $[Pt(N\text{-}N)_2(L\text{-}S,O)]^+$ (L-S,O = *N*-acyl-*N*′,*N*′-dialkylthioureas and N-N = bipy, phen), K_D values at 298 K have been reported that range from 1.8 to 114 M^{-1}, depending on the nature of the *N*-acyl group and the N-N ligand. In addition, a much larger equilibrium constant was reported for the platinum complex $[Pt(terpy)(CH_3)]Cl$ (terpy = 2,2′:6′,2′′-terpyridine), in the order of 26,000 M^{-1} at 298 K, where instead of dimer formation, highly aggregated species were found to be formed through π–π stacking. In general, dimerization and self-aggregation trends are more favored in square-planar complexes than in octahedral complexes because of the reduced steric hindrance in the apical positions, which allows better interligand π–π stacking, cation–π ligand, and metal–metal interactions.[19]

Although it is difficult to make a comparison among complexes of a different nature, the K_D value found for our complex is relatively high by considering its tetrahedral geometry and also that the NN′-NO_2 ligand does not have an aromatic surface large enough to allow strong π–π stacking; furthermore, there should be a rotational movement of the nitrophenyl moiety to allow the ligand to become flattened and to be able to dimerize.

From the dependence of the K_D values on temperature, the thermodynamic parameters associated with the dimerization of [Cu(NN′-NO_2)(PPh_3)Br] were determined by using van ’t Hoff plots (Table S6 and Figure S4), which correspond to $\Delta G = -1.79\ \text{kcal mol}^{-1}$, $\Delta S = -0.67 \pm 0.21\ \text{cal mol}^{-1}\text{K}^{-1}$, and $\Delta H = -2.00 \pm 0.05\ \text{kcal mol}^{-1}$. The variation in such parameters is consistent with a spontaneous process tending to dimerization, which is enthalpically driven through the formation of both π–π and C–H···Br interactions, despite the entropic cost as the system becomes more ordered.

Conclusions

We carried out the first study of self-association for a tetrahedral copper(I) complex in solution, where both π-stacking and C–H···Br interactions jointly act in a locking way to produce a discrete dimer, whose structure in solution replicates that found in the solid state. The self-association process is enthalpically driven through the formation of both π–π and C–H···Br interactions.

The electronic effect of the *p*-phenyl substituent on the self-association thermodynamics for a related copper(I) complex series is under study in our group, with some interesting results on the effect of intercomplex supramolecular interactions on their properties.

Experimental Section

Material: Pyridine-2-carbaldehyde and 4-nitroaniline were purchased from Merck (Germany). All reactions were carried out under purified nitrogen (99.9%, AGA-Chile S.A.). The solvents were synthesis grade and were used as received. CuBr was prepared as described in the literature.[20]

Instrumentation: ^{1}H, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, ^{1}H–^{1}H 2D-COSY, ^{1}H–^{1}H 2D-NOESY, ^{1}H–^{13}C 2D-HSQC-ed, and ^{1}H–^{13}C 2D-HMBC spectra and the dimerization studies by proton NMR spectroscopy were performed on a Bruker Avance 400 MHz spectrometer (400.133 MHz for ^{1}H, 100.16 MHz for ^{13}C, and 160.984 MHz for ^{31}P) equipped with a 5-mm multinuclear broad-band dual probe head incorporating a *z*-gradient coil. All the measurements were carried out in $CDCl_3$. Chemical shifts were calibrated with respect to the solvent signal (δ =7.26 ppm for proton residual solvent and 77.2 ppm for ^{13}C) and referenced to TMS. ^{31}P{^{1}H} spectra were calibrated with respect to the external pattern H_3PO_4 10%. The X-ray diffraction experiments were performed at room temperature on an Oxford Diffraction Gemini CCD S Ultra diffractometer, with graphite monochromatized Mo-K_α radiation (λ = 0.7107 Å). The structure was solved by direct methods (SHELXS97[21] and refined by least-squares methods on F^2 SHELXL97[21]). The UV/Vis spectra were recorded on a Shimadzu mini-UV 1240 spectrophotometer in chloroform at room temperature. The concentration effect on the spectra was evaluated in the range 2 to 10 mM. Analysis of C, H, and N were performed by using a Fisons element model EA-1108.

Synthesis of *N*-(4-Nitrophenyl)(pyridine-2-yl)methanimine (NN′-NO_2):[22] To a solution of 4-nitroaniline (3.04 g, 22.02 mmol) in CH_2Cl_2 (150 mL) and molecular sieves (15 g, 0.4 nm) was added the pyridine-2-carbaldehyde (2.82 g, 26.28 mmol). The mixture was stirred at 60 °C for 35 h and at room temperature for 3 d and filtered, and the solution was evaporated to dryness under vacuum. The crude NN′-NO_2 ligand was washed with diethyl ether to extract the excess pyridine-2-carbaldehyde to yield a yellow powder. Yield: 51%. ^{1}H NMR ($CDCl_3$, 300 K): δ = 8.75 (d, $J_{H6,5}$ = 4.57 Hz, 1 H, H^6), 8.56 (s, 1 H, H^i), 8.30 (d, $J_{H3',2'}$ = 8.78 Hz, 2 H, $H^{3'}$), 8.20 (d, $J_{H3,4}$ = 7.87 Hz, 1 H, H^3), 7.86 (t, J = 7.55 Hz, 1 H, H^4), 7.44 (dd, J = 5.37, 6.77 Hz, 1 H, H^5), 7.31 (d, $J_{H2',3'}$ = 8.78 Hz, 2 H, $H^{2'}$) ppm. ^{13}C NMR ($CDCl_3$): δ = 163.33 (C^i), 156.86 ($C^{1'}$), 150.01 (C^6), 153.69 (C^2), 145.98 ($C^{4'}$), 136.84 (C^4), 125.91 (C^5), 122.43 (C^3), 125.07 ($C^{3'}$), 121.36 ($C^{2'}$) ppm. UV/Vis (CH_3Cl): λ_{max} (nm) = 301, 332.

Synthesis of [Cu(NN′-NO_2)(PPh_3)Br]: To a solution of CuBr (0.23 g, 1.60 mmol) in acetonitrile (10 mL) was added dropwise PPh_3 (0.42 g, 1.60 mmol) dissolved in acetonitrile (20 mL) to form a white precipitate. The mixture was stirred for 30 min, and the NN′-NO_2 ligand (0.37 g, 1.63 mmol) in an acetonitrile/dichloromethane (1:1) mixture (40 mL) was then added dropwise. The mixture was stirred for 2 h to form a dark purple solution. The solvent volume was reduced, and the solid formed was washed with a mixture of diethyl ether/acetonitrile (9:1). The diffusion of ethyl ether vapor into a concentrated CH_2Cl_2 solution gave dark purple crystals. Yield: 85%. $C_{30}H_{24}BrCuN_3O_2P$ (632.96): calcd. C 56.93, H 3.82, N 6.64; found C 57.00, H 3.88, N 6.19. ^{1}H NMR ($CDCl_3$, 10 mM, 298 K): δ = 8.71 (d, $J_{H6,5}$ = 4.34 Hz, 1 H, H^6), 8.56 (s, 1 H, H^i), 8.09 (d, $J_{H3',2'}$ = 8.90 Hz, 2 H, $H^{3'}$), 7.89 (ddd, $J_{H4,3}$ = 7.54, $J_{H4,5}$ = 8.15, $J_{H4,6}$ = 1.34 Hz, 1 H, H^4), 7.84 (d, $J_{H3,4}$ = 7.54 Hz, 1 H, H^3), 7.59 (d, $J_{2',3'}$ = 8.90 Hz, 2 H, $H^{2'}$), 7.50 (ddd, $J_{H5,4}$ = 8.15, $J_{H5,6}$ = 4.34, $J_{H5,3}$ = 1.05 Hz, 1 H, H^5), 7.36 (6 H, H_α), 7.32 (3 H, H_γ), 7.24 (6 H, H_β) ppm. ^{13}C NMR ($CDCl_3$, 20 mM): δ = 158.71 (C^i), 153.63 ($C^{1'}$), 150.41 (C^6), 149.39 (C^2), 146.84 ($C^{4'}$), 137.54 (C^4), 133.68 (C_α), 129.88 (C_γ), 126.67 (C_β), 127.98 (C^5), 127.98 (C^3), 124.89 ($C^{3'}$), 123.15 ($C^{2'}$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –1.30 ppm. UV/Vis (CH_3Cl): λ_{max} (nm) = 307, 457.

Calculation of K_D: The values of K_D were determined by the method of Horman and Dreux,[17] which relies on the gradual variation in the ^{1}H NMR chemical shifts as a function of concentration at constant temperature. This procedure involves an iterative K_D, by fitting the observed chemical shift (δ_{obs}) of each proton by using the mol fraction of dimer (δ_i) present at each concentration, starting from a reasonable guess of the association constant. The most accurate value of K_D is defined as that which yields the best linear relationship between δ_{obs} and x_i (Figure S5). Once K_D is determined, the chemical shift of each proton for the monomer and dimer can be obtained from the intercept and slope of the plot of δ_{obs} vs. x_i[9a] (Table S1).

VT-NMR Dimerization Experiments: Stock solutions of different complex concentrations (2, 5, 10, 15, 20, 25, 30, and 35 mM) were prepared in flasks of 1 and 2 mL with $CDCl_3$. The proton NMR spectra were recorded each 10 K in the range 220 to 298 K for all solutions. Each measurement was recorded after thermal equilibrium was established (3 min).

CCDC-836091 ([Cu(NN′-NO_2)(PPh_3)Br]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Chemical shifts and self-association constants, crystallographic data, K_D and thermodynamic data, plots of chemical shifts as a function of dimer fraction, van 't Hoff plot, proton and NOESY NMR spectra, and UV/Vis spectra are presented.

Acknowledgments

We are grateful for support from DICYT-USACH, FONDECYT-1101029, MECESUP-0007 for the NMR spectrometer, ANPCyT (project PME 01113) for the purchase of a CCD diffractometer, and the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system.

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Received: December 5, 2011