Bond Stretch Isomerism Still Elusive in Linear Trimetallic Complexes. DFT Calculations on Co₃(dipyridylamine)₄Cl₂

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The concept of bond stretch isomerism, first introduced by Hoffmann,¹ was defined by Parkin as "the unusual phenomenon whereby molecules differ only in the length of one or more bonds".^{2a,b} It has been specified later on that this definition is restricted to isomers of the same spin state.^{2c} This should be translated in terms of potential energy surface by the presence of two distinct minima separated by a significant energy barrier. Several examples of bond stretch isomers had been characterized since the early 1970s, but it was demonstrated later on that most of the reported cases, if not all, were no more than crystallographic artifacts.² Recently, a series of very careful structure determinations have led to what was presented as the first unambiguous example of a molecule satisfying Parkin's definition of bond stretch isomers.³ The reported isomers, of formula Co₃(dpa)₄Cl₂ (dpa = dipyridylamine), belong to a family of complexes where the pyridyl ligands are organized in a spiral conformation around a linear Co_3^{6+} chain axially coordinated to Cl, Cl (1, 2), Cl, BF₄ (3), and BF₄, BF₄ (4). Abstracted from their crystal environment, molecules 1 and 2 correspond to the same formula and to similar structures (Figure 1). The reported differences mainly affect the interatomic distances along the Cl-Co-Co-Co-Cl axis. Isomer 1 is characterized by a crystallographic 2-fold axis containing the central cobalt atom (space group *Pnn2*). This implies a perfect equivalence among the Co-Co distances (2.3178 Å), the Co-Cl distances (2.520 Å), and the two sets of Co_{term}-N bonds (1.990 Å, av). Isomer 2 crystallizes in the space group P4/n with the 4-fold axis collinear with the trinuclear metal axis. It is characterized by markedly different metal-metal distances: Co(1)-Co(2) = 2.459 Å; Co(2)-Co(3) = 2.285 Å. The two Co-Cl distances are similar (2.353 and 2.386 Å), but considerably shorter than those for 1. The two sets of Co_{term} -N bond lengths are also significantly distinct (Co(1)–N = 2.125 Å, Co(3)–N = 1.965 Å) (Figure 2A). Note that complexes 3 and 4 are geometrically similar to isomers 2 and 1, respectively.

The purpose of this work was to use the methods of computational chemistry to characterize on the potential energy hypersurface of the isolated $Co_3(dpa)_4Cl_2$, the two minima distinctive of bond stretch isomerism. All calculations were carried out by means of gradient-corrected DFT calculations.⁴ Geometry optimization processes were carried out on $Co_3(dpa)_4$ - Cl_2 , starting from the structures observed for **1** and **2**, slightly modeled for **1** in order to ensure a strict equivalence between the four pyridyl ligands. A similar equivalence is imposed to **2** by the crystal space group. The constraints imposed to the optimization processes of **1** and **2** were those of the symmetry point groups D_4 and C_4 , respectively. Both symmetry groups prescribe the equivalence of the four ligands, but point group D_4 imposes in addition the identity of the two Co–Co and of the two Co–Cl



Figure 1. XMol (Minnesota Supercomputer Center, Inc., 1995) representation of the $Co_3(dpa)_4Cl_2$ molecule, in the symmetric conformation resulting from the DFT geometry optimization.



Figure 2. Selected structural parameters obtained from DFT geometry optimization (above, in roman) and from X-ray characterization^{3b} (below, in italics). (A) Symmetric form, complex **1**. (B) Nonsymmetric form, complex **2**. In the DFT optimization process, the metal–metal distances (starred) have been kept frozen at their experimental values.

bonds. The geometry optimized, assuming the D_4 constraints, is displayed in Figure 2A and compared to the structural parameters observed for 1. The distances computed for Co–Co, Co–Cl, and Co–N agree with the observed ones within 0.025 Å. A slightly larger discrepancy occurs for the C–N distances, overestimated by 0.02–0.04 Å. In probable relation with this overestimation, the torsional angle N–Co(1)–Co(1')–N, which measures the spiral character of the pyridyl ligands, is computed

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⁽⁴⁾ All calculations have been carried out with the ADF program.⁵ We used the local spin density approximation characterized by the electron gas exchange (X α with $\alpha = 2/3$) together with Vosko–Wilk–Nusair⁶ parametrization for correlation. Becke's nonlocal corrections to the exchange energy and Perdew's nonlocal corrections to the correlation energy8 have been added. For first-row atoms, a 1s frozen core was described by means of a single Slater function. For cobalt and chlorine, the frozen core composed of the 1s to 2sp shells was also modeled by a minimal Slater basis. Two sets of atomic basis functions were used to describe the valence electrons.⁹ Double- ζ Slater basis sets, referred to as BS1, were used for all geometry optimization processes. A single-point calculation was then carried out at the optimal geometries using for the valence electrons a more extended basis set referred to as BS2. For hydrogen, chlorine, and first-row atoms, BS2 is of triple-ζ quality and completed by a polarization function For cobalt, the 3s and 3p shells are described by a double- ξ basis; the 3d and 4s shells by a triple- ξ basis and the 4p shell by a single orbital. No f-type polarization function is added. The geometry optimization processes were continued until all of the three following convergence criteria were fulfilled: (i) the difference in the total energy between two successive gradient optimization cycles is less than 0.001 harrees; (ii) the difference in the *norm of the gradient* between two successive cycles is less than 0.01 hartree. $Å^{-1}$; (iii) the maximal difference in the Cartesian coordinates between two successive cycles is less than 0.01

to be 54.5°, compared to an average experimental value of 46.9°. Despite those differences, it is clear that the conformation of minimal energy—within the constraints of the D_4 point group displayed in Figure 2A can be identified as the structure of isomer 1.

The optimization carried out starting from the experimental geometry of the unsymmetrical isomer 2 failed to define a conformation of minimal energy distinct from that of Figure 2A. At the end of the optimization process, the unconstrained metalmetal distances were 2.325 and 2.313 Å, respectively. Similarly, the final Co-Cl distances were 2.477 and 2.476 Å. The most important discrepancies noticed with respect to the structure of Figure 2A concerning the Co–N and the C–N bond lengths are less than 0.015 Å, that is of the order of magnitude of computational uncertainty.⁴ The final energy computed with BS1 was identical to that obtained from structure 1 within 1.0 kcal mol^{-1} .

To trap a possible energy minimum in the region of the hypersurface corresponding to the unsymmetrical structure of complex 2, another geometry optimization was carried out, still starting from the experimental geometry, but with the metalmetal distances of 2.459 and 2.285 Å-and only those distancesfrozen during the whole optimization process. The resulting structure is displayed in Figure 2B and compared to the experimental geometry reported for 2. Apart from the Co-Co distances, the most important geometrical changes observed from X-ray diffraction with respect to the symmetrical structure concern the cobalt-chlorine bonds, shortened by 0.15 and 0.17 Å, and the Co(1)-N distances, stretched by 0.13 Å on average. Similar trends are obtained from the constrained geometry optimization, but the magnitude of the computed changes is smaller: $\Delta_{Co(1)-N}$ = +0.05 Å; $\Delta_{\text{Co(1)-Cl}} = -0.10$ Å; $\Delta_{\text{Co(3)-Cl}} = -0.02$ Å (Figure 2). The total energy associated with that structure is higher than that of the symmetrical complex, but the difference is weak: +4.2 kcal mol⁻¹ with BS1; +6.7 kcal mol⁻¹ with BS2.⁴ However, when the constraints imposed on the metal-metal distances are lifted, the geometry of the complex evolves toward that of the symmetric isomer and eventually converges toward a structure that cannot be distinguished from that of Figure 2A.

The ground-state electronic configuration of the Co₃(dpa)₄Cl₂ complex was found identical for all considered geometries. The neutral tricobalt complex is a paramagnetic molecule with one unpaired electron. In the symmetrical isomer, the semi-occupied molecular orbital (SOMO) belongs to the A_2 representation of the D_4 point group and corresponds to a combination which is nonbonding between cobalt atoms, but σ -antibonding between terminal cobalt and chlorine.

It is interesting to notice that an exchange between the SOMO and either the HOMO, with b_2 symmetry, or the HOMO-1 (e symmetry) generates two doublet excited states with very low energy. A geometry optimization has been carried out on each of those states with BS1 and completed with a single-point calculation of the energy with BS2, at the optimized geometries. Point group D_4 has been assumed. The relative energies with respect to the ${}^{2}A_{2}$ ground state are +0.24 eV for the ${}^{2}E$ state and +0.35 eV for the ${}^{2}B_{2}$ state.¹⁰ It could therefore be tempting to assign the observed bond stretch isomerism to a change in the electronic configuration of the complex. However, such a change has not been evidenced from the calculations. Moreover, both low-lying excited states are obtained by the transfer of one additional electron to the Co-Cl antibonding orbital with a₂ symmetry. This induces a substantial increase of the Co-Cl bond lengths (2.62 Å and 2.64 Å in the ${}^{2}E$ and ${}^{2}B_{2}$ states, respectively)

which seems difficult to correlate with any of the experimental geometries. It should be noted that in the ground state of both the symmetrical and the unsymmetrical forms, the energy gap separating the HOMO from the metal-metal σ -antibonding LUMO remains rather large ($\sim 1 \text{ eV}$) which makes unprobable the existence of a low-lying quartet state. In that respect, the present calculations on the isolated molecule do not support the interpretation of the electronic structure of 2 proposed by Yang et al. in their preliminary report.¹¹ A highly temperaturedependent magnetic moment, rising to $\mu_{\rm eff} \approx 2.6~{\rm BM}$ at 200 K had been observed by those authors and attributed to a spin crossover Co^{II}N₄Cl chromophore coupled to a diamagnetic dimer.

We conclude this preliminary study by asserting that according to the DFT calculations, the *isolated* Co₃(dpa)₄Cl₂ does not display a double energy minimum, but a flat potential ground-state hypersurface and two very low-lying, low-spin excited states. Should it be inferred that the tricobalt complex does not display bond stretch isomerism? The answer is ambiguous, because of the phenomenological character of Parkin's definition. As a consequence, the *molecular scale* at which the double minimum is expected to appear remains unspecified. Is it restricted to the isolated complex or should it include its immediate environment or even account for the complete crystal field? If the latter interpretation is retained, one should consider that the different crystal environment of isomers 1 and 2 and related compounds might be sufficient to induce the observed structural disparities. It should be noted that the Co-Co bond alternation observed in 2 implies the mixing between the filled Co–Co-bonding MO and an orbital with σ -antibonding metal character, namely, the relatively high-lying LUMO (a₁ symmetry). Moreover, as originally highlighted by Hoffmann,1 the existence of a double energy minimum for the bond stretch isomers implies either an avoided crossing or a real state crossing as a function of the geometrical change. In the present case, the state crossing, either real or avoided, should involve a state in which the metal-metal antibonding LUMO is partly or fully populated. Further calculations are being carried out to check whether the unsymmetrical arrangement of the two sets of four Co(dpa)₂ monomers in the crystal structure of 2 is capable of generating the above-mentioned prerequisites.

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