



to be  $54.5^\circ$ , compared to an average experimental value of  $46.9^\circ$ . 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 metal–metal 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.<sup>4</sup> The final energy computed with BS1 was identical to that obtained from structure **1** within 1.0 kcal mol<sup>-1</sup>.

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 metal–metal distances of 2.459 and 2.285 Å—and only those distances—frozen 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:  $\Delta_{\text{Co(1)-N}} = +0.05$  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<sup>-1</sup> with BS1; +6.7 kcal mol<sup>-1</sup> with BS2.<sup>4</sup> 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  $\text{Co}_3(\text{dpa})_4\text{Cl}_2$  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  $\sigma$ -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  ${}^2A_2$  ground state are +0.24 eV for the  ${}^2E$  state and +0.35 eV for the  ${}^2B_2$  state.<sup>10</sup> 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  $a_2$  symmetry. This induces a substantial increase of the Co–Cl bond lengths (2.62 Å and 2.64 Å in the  ${}^2E$  and  ${}^2B_2$  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  $\sigma$ -antibonding LUMO remains rather large ( $\sim 1$  eV) which makes improbable 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.<sup>11</sup> A highly temperature-dependent magnetic moment, rising to  $\mu_{\text{eff}} \approx 2.6$  BM at 200 K had been observed by those authors and attributed to a spin crossover  $\text{Co}^{\text{II}}\text{N}_4\text{Cl}$  chromophore coupled to a diamagnetic dimer.

We conclude this preliminary study by asserting that according to the DFT calculations, the *isolated*  $\text{Co}_3(\text{dpa})_4\text{Cl}_2$  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  $\sigma$ -antibonding metal character, namely, the relatively high-lying LUMO ( $a_1$  symmetry). Moreover, as originally highlighted by Hoffmann,<sup>1</sup> 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  $\text{Co}(\text{dpa})_2$  monomers in the crystal structure of **2** is capable of generating the above-mentioned prerequisites.

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