Metal−Metal Bond Length Variability in Co₃(dipyridylamide)₄Cl₂: Bond-Stretch Isomerism, Crystal Field Effects, or Spin Transition Process? A DFT Study

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Abstract: The unprecedented structural behavior of Co₃(dipyridylamide)₄Cl₂, characterized in two crystalline forms in which the tricobalt framework is either symmetric or highly nonsymmetric at room temperature is investigated by means of gradient-corrected DFT calculations. The isolated molecule is assigned a single energy minimum associated with a low-spin (doublet) electronic configuration. The optimal geometry closely reproduces the X-ray structure observed for the isomer displaying equivalent metal−metal distances. However, the ground-state potential energy surface is extremely shallow with respect to a distortion of the Co₃ framework. A "weak" distortion, similar to that observed for the unsymmetrical complex at low temperature ($\Delta d_{Co-Co} = 0.08$ Å at 110 K) induces a destabilization of 1.1 kcal·mol⁻¹ only. The distortion observed at room temperature ($\Delta d_{Co-Co} = 0.17$ Å) destabilizes the isolated complex by 4.2 kcal·mol⁻¹. These results are rationalized in terms of the "three-electron three-center" concept applied to the σ-bonding electrons of the cobalt framework. A phenomenological model based upon the Heisenberg Hamiltonian successfully reproduces the calculated potential energy curve and assigns the relative stability of the symmetric structure to local forces (Pauli repulsion, ligand bite, etc.) distinct from delocalized σ bonding. In view of these results, the two structures characterized from X-rays cannot be termed "bond-stretch isomers" according to the strict definition given by Parkin. To investigate the origin of the distorted form, an electric field was applied to the isolated molecule, but it did not shift the equilibrium position toward asymmetry, despite a strong polarization of the electron density. Finally, the quartet state of lowest energy (⁴A state) has an optimal structure that is distorted and that reproduces most of the distinctive features observed in the nonsymmetric structure. Despite the high relative energy calculated for this quartet state, we assign the occurrence of the nonsymmetric form and its extreme variability with temperature to a progressive population of this excited state as temperature increases.

1. Introduction

Neutral Mᴵᴵᴵ₃(dpa)₄L₂ and Mᴵᴵ₃(dpa)₄LL′ molecules, in which dpa is the anion of di-(2-pyridyl)amine, have been reported with various metals of the first and second transition rows (M = Cu, Ni, Co, Rh, Ru, and Cr).[1−5] The metal atoms in these complexes form a linear chain that is extended on each side by the axial ligands, which may be single halogen atoms (L = Cl⁻, Br⁻)[3,6] or molecular anions such as BF₄⁻,[3c] NCS⁻, CN⁻, and N(CN)₂⁻.[7] A dicationic complex with acetonitrile as axial ligand[8] has been reported. The four nonplanar dpa anions form an helicoidal structure spiraling around the chain of metal atoms (Figure 1). The cobalt, and to some extent, the chromium complexes belonging to that series of compounds share a structural variability that affects primarily the metal framework and that seems unprecedented in coordination chemistry.[3,5] The most extensively documented case concerns Co₃(dpa)₄Cl₂, which is able to exist with either a symmetrical (s) Co₃ chain or an unsymmetrical (u) one, depending only on the crystal form in which it is found.[3d,9] The temperature dependence of the main interatomic distances is also extremely unusual, especially for the u form.[10] The s structure appears relatively stable in the investigated temperature range (20 K < θ < 298 K) despite a rather large distortion of the Co−Cl distances (0.063 Å) occurring at low temperature in response to a weak interaction with a CH₂Cl₂ molecule in the crystal. In strong contrast with

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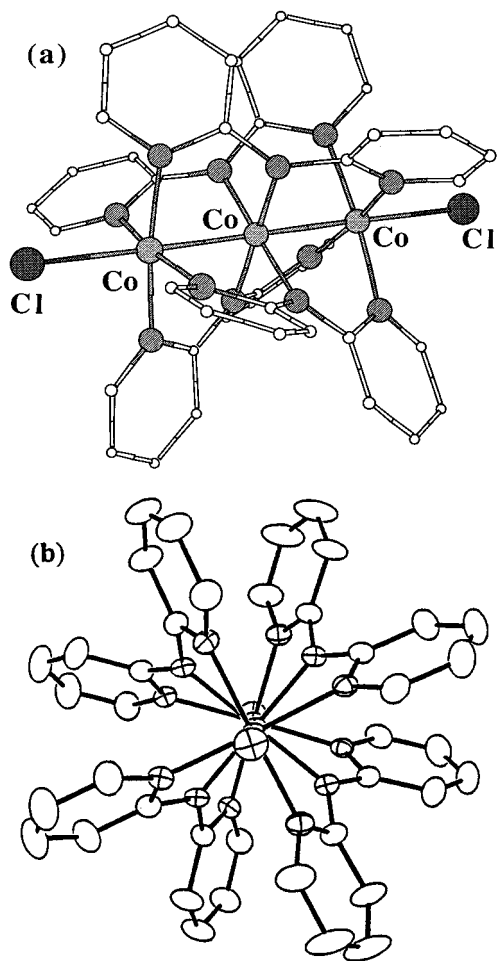
Figure 1. (a) XMOL view of *s*-Co₃(dpa)₄Cl₂: gray circles, Co, Cl, and N atoms; white circles, carbon atoms. (b) View of the same molecule looking down the Co₃ axis (reprinted from ref 10 with permission).

this behavior, the structural environment of the terminal metal atom taking part in the "long" Co−Co bond of the u form is strongly dependent on the temperature. The Co−Co bond length itself decreases by 0.086 Å between 298 K and 20 K, and the whole complex tends to become "less unsymmetrical" at low θ.[10] NMR spectra observed in CD_2Cl_2 solution between 183 and 303 K are consistent with a symmetric conformation in the whole temperature range.[11] Magnetic susceptibility measurements carried out with the two crystal forms have shown that both the s and the u isomers are in an $S = 1/2$ ground state at low temperature, but exhibit gradual spin crossover at higher temperature.[10] Similar investigations carried out on Co₃(dpa)₄-Br₂ indicate that the structural and magnetic behavior of the dibromo compound closely parallels that of the dichloro analogue.[6]

This highly unusual structural behavior is not easily interpretable and raises the question of the nature of the metal−metal bond in such complexes. The abundant structural documentation gathered on Co₃(dpa)₄Cl₂ seems relevant to Parkin's definition of bond stretch isomerism: "the unusual phenomenon whereby molecules differ only in the *length* of one or more bonds".[12] The point is not so clear however, because the structural difference between the s and the u forms has not yet been

assigned a definite electronic origin. In a previous theoretical study dedicated to this molecule, the ground state of an isolated Co₃(dpa)₄Cl₂ was shown to be low-spin ($S = 1/2$) and symmetrical.[13] The optimal geometry obtained from DFT calculations reproduces with an excellent accuracy the structural data obtained for the s form at room temperature. However, calculations were unable to characterize a second energy minimum that could be correlated with the unsymmetrical structure. The hypothesis of bond stretch isomerism was also challenged by the magnetic measurements. The occurrence of a gradual spin crossover from a doublet to a quartet state as temperature increases suggests that the promotion of an electron to an empty orbital with metal−metal antibonding character could weaken the average Co−Co bond order and possibly increase the trend toward symmetry breaking.[9] In such a case, the s and the u forms of Co₃(dpa)₄Cl₂ should be termed spin state isomers rather than bond stretch isomers.[14] However, this rationalization is not quite satisfactory, because it does not provide any explanation (i) to the behavior of the s form, which also exhibits spin crossover, but remains symmetric over the whole range of investigated temperatures; and (ii) to the persistence of a small, but significant asymmetry in the Co−Co bond lengths of the u complexes below 110 K, even though the interpretation of magnetic measurements suggests that only the doublet ground state is populated at this temperature.[10]

We intend to further investigate, by means of DFT calculations, a hypothesis suggested by the shallowness of the potential energy curve of the doublet ground state with respect to the symmetry breaking of the metal framework. This shallowness had been evidenced in our previous work by constraining the metal framework to undergo the strong distortion observed in the u form at room temperature.[13] It will be shown in the present study that the "small" distortion observed at low temperature can be induced using a minimal amount of energy. The smoothness of the ground-state potential energy of the neutral form will be rationalized and reproduced within the model designed by one of us to analyze the trend of three-electron three-center systems, such as H₃, Li₃, Na₃, or the allyl radical either toward bond length identity, or toward symmetry breaking.[16] Two hypotheses will, therefore, be considered to explain the occurrence of a stable u form with temperature-dependent geometry: (i) the small distortion observed at low temperature might originate either in the electric field, or in the nonbonding contacts generated by the crystal environment, and be enhanced at higher θ by the progressive population of the high spin state-(s); or (ii) the small distortion itself should be assigned to a weak population at low θ of the proper high spin state.

2. Computational Details

All calculations performed on Co₃(dpa)₄Cl₂, on (Co₃(dpa)₄-Cl₂)⁺, and on the Co₂(HN−CH−NH)₄ model molecule have been carried out using the formalism of density functional theory (DFT) within the generalized gradient approximation (GGA), as implemented in the ADF program.[17] The formalism is based upon the local spin density approximation characterized by the electron gas exchange (Xα with $\alpha = 2/3$) together with Vosko−Wilk−Nusair[18] parametrization for correlation. Nonlocal corrections due to Becke for the exchange energy[19] and to Perdew for the correlation energy[20] have been added. For first-row

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Table 1. Selected Bond Lengths (Å) Computed for $Co_3(dpa)_4Cl_2$ in the s and u Forms, as for $[Co_3(dpa)_4Cl_2]^+$ in Its Symmetric Ground State, and Compared to the Averaged Values Observed at Various Temperatures[a]

	$Co_3(dpa)_4Cl_2$ (s form) doublet ground state				$Co_3(dpa)_4Cl_2$ (u form), doublet ground state				$Co_3(dpa)_4Cl_2$, quartet state	$[Co_3(dpa)_4Cl_2]^+$, symmetric	
	calc 1[b] BS I	calc BS II	exp 20 K	exp 298 K	calc 2 BS I	calc 3 BS I	exp 20 K	exp 298 K	calc BS I	calc BS I	exp 100 K
Co(1)−Co(2)	2.325	2.325	2.34	2.3369	2.300[d]	2.285[d]	2.3035	2.299	2.303	2.323	2.3168
Co(2)−Co(3)	2.326	2.325	2.34	2.3369	2.385[d]	2.459[d]	2.3847	2.471	2.414	2.323	2.3289
Co(1)−Cl(1)	2.496	2.468	2.508	2.4881	2.522	2.510	2.428	2.434	2.466	2.370	2.350
Co(3)−Cl(2)	2.499	2.468	2.445	2.4881	2.479	2.424	2.440	2.363	2.416	2.370	2.376
Co(1)−N	1.967	1.977	1.962[c]	1.997[c]	1.962	1.955	1.978[c]	1.978[c]	1.957	1.972	1.975[c]
Co(3)−N	1.967	1.977	1.987[c]	1.997[c]	1.972	1.995	2.040[c]	2.119[c]	2.105	1.972	1.979[c]
Co(2)−N	1.885	1.902	1.904[c]	1.907[c]	1.887	1.880	1.901[c]	1.909[c]	1.893	1.878	1.869[c]
ΔE	0.0				+1.11	+4.16			+18.3		
				Relative Energies in the Presence of an Electric Field (see text)							
ΔE	0.0				+0.09[e]						
					+0.96[f]						

[a] Relative energies (ΔE, kcal·mol^{-1}) for the s and u forms of neutral $Co_3(dpa)_4Cl_2$ are displayed for a noninteracting molecule and in the presence of an electric field. [b] Calculation carried out with the constraints of the C_4 symmetry point group. [c] Average. [d] Fixed distances. [e] Plus charge facing the long Co−Co bond. [f] Minus charge facing the long Co−Co bond.

atoms, the 1s shell was frozen and described by a single Slater function. For cobalt and chlorine, the frozen core composed of the 1s and 2sp shells was also modeled by a minimal Slater basis. For all nonmetal atoms, the Slater basis set used for the valence shell is of double-ζ quality without polarization functions.[21] The 3s, 3p, and 4s shells of cobalt are described by a double-ζ Slater basis; the 3d shell, by a triple-ζ basis; and the 4p shell, by a single function. This will be referred to as basis set I. The ground state of $Co_3(dpa)_4Cl_2$ has also been optimized using basis set II, in which the Slater basis describing the valence set of all nonmetal atoms and the 4s shell of cobalt are triple-ζ and augmented, except for cobalt, with one polarization function, either of p type for hydrogen or of d type for the other atoms. The calculations on $Co_3(dpa)_4Cl_2$, which is an open-shell system, have been carried out using the unrestricted formalism. Molecular bonding energies are reported with respect to an assembly of neutral atoms assumed to be isolated and in their ground state. The geometry optimization processes have been carried out by minimizing the energy gradient by the BFGS formalism[22] combined with a DIIS-type convergence acceleration method.[23] The optimization cycles were continued until all of the three following convergence criteria were fulfilled: (i) the difference in the total energy between two successive cycles is <0.001 hartree; (ii) the difference in the norm of the gradient between two successive cycles is <0.001 hartree·Å^{-1}; (iii) the maximal difference in the Cartesian coordinates between two successive cycles is <0.01 Å.[24]

3. $Co_3(Dpa)_4Cl_2$ "In the Gas Phase": Structure at Equilibrium and Imposed Distortion

3.1. Optimal Geometry of an Isolated Molecule. The s form of $Co_3(dpa)_4Cl_2$ belongs to the D_4 symmetry point group if a

perfect identity is assumed between the environments of the terminal cobalt atoms. Breaking the symmetry of the metal framework lowers the molecular symmetry to C_4. For technical reasons, the geometry optimization of the s isomer was carried out first with the constraints of the D_2 point group and with basis set I. Then a new optimization process was carried out using the same basis set, starting from the average experimental structure observed for the u form at room temperature[3c] and assuming the constraints of the C_2 point group. The optimization process slowly went back to a molecular structure very close to D_4 symmetry and to a value of the bonding energy equivalent to the results obtained with the initial constraints, the differences being of the order of the convergence criteria. The s form was then reoptimized with basis set II and with the D_2 constraints. Table 1 reports some important geometrical parameters of the structure at equilibrium in comparison with the structures obtained from X-ray diffraction on s-$Co_3(dpa)_4Cl_2$·CH_2Cl_2 at 20 K and at 298 K.[10] The total bonding energies and the complete list of Cartesian coordinates obtained from the calculations carried out with BS I and BS II are provided as Supporting Information.

The extension of the basis set hardly modifies the metal−metal and the metal−nitrogen bond lengths, which are found to be in excellent agreement with experiment (Table 1, Figure 2A). A similar agreement was noted in our previous work[13] concerning the Co−Cl bond length (2.503 Å as calculated with BS I and the D_2 symmetry constraints,[13] 2.496/2.499 Å with the same basis set and the C_2 constraints (Table 1), and 2.4881 Å as observed at 298 K). However, nonnegligible modifications of this distance have been obtained since then from an extension of the basis set on the computational side and from temperature effects and intermolecular interactions on the experimental side. In fact, Clérac et al. have shown that above 165 K, symmetric interactions are present in the crystal of s-$Co_3(dpa)_4Cl_2$·CH_2-Cl_2 between both chlorine atoms of the complex and interstitial CH_2Cl_2 molecules. Then a phase transition occurs in the crystal and only one Cl···dichloromethane interaction is observed at lower temperature. This induces a significant asymmetry in the

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A neutral, *s*-form

**B** neutral, *u*-form

C cation, symmetric
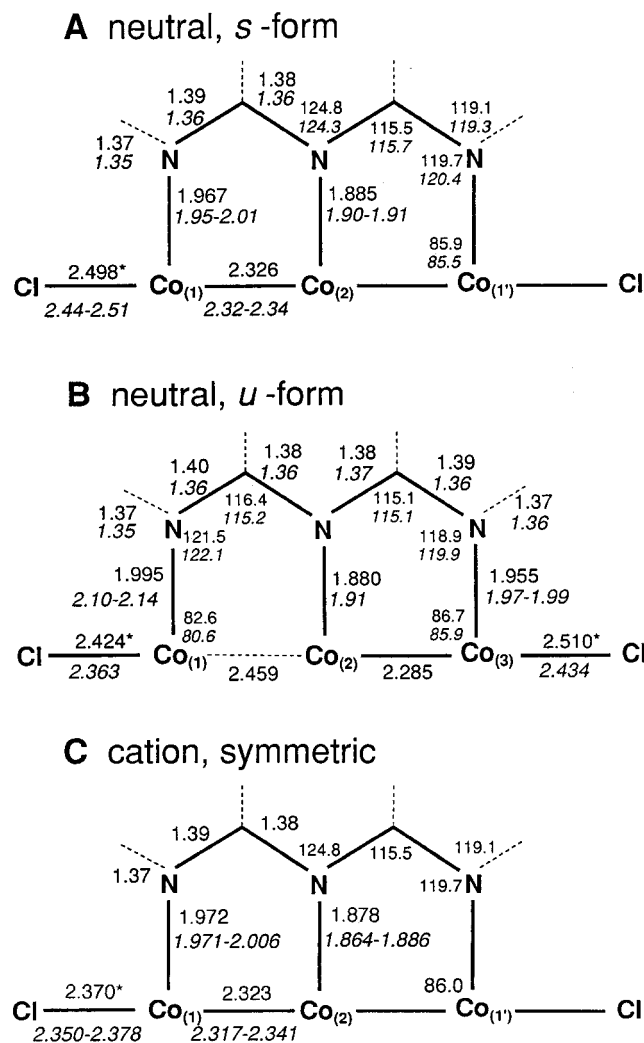
Figure 2. Selected structural parameters obtained from DFT geometry optimization with basis set I (above, in roman) and from X-ray characterization[3c,10] (below, in italics): (A) s form; (B) u form, room temperature; in the DFT optimization process, the metal−metal distances have been imposed and kept frozen; (C) closed-shell cation. The Co−Cl bond lengths optimized with basis set I (starred) are decreased by ∼0.04 Å when the basis set of chlorine is supplemented with a polarization function (basis set II).

Co−Cl distances: at 20 K, the length of the Co−Cl bond undergoing the interaction (2.508 Å) experiences little change with respect to its value at 298 K (2.4881 Å), but the length of the Co−Cl bond now free of interaction is significantly reduced to 2.445 Å.[10] This value should be preferably compared to the Co−Cl bond length calculated for an isolated molecule, and the bond distance of 2.50 Å obtained with basis set I now appears to be somewhat too long. The admixtion of a polarization function on chlorine restores the agreement with a calculated bond length of 2.468 Å (Table 1, basis set II). Because of the large size of the complex and of the reduced symmetry, all subsequent geometry optimizations have been carried out with basis set I, but the overestimation of the Co−Cl bond lengths due to basis set effects (∼0.035 Å) should be kept in mind.

3.2. Electronic Structure and Bonding in the Ground State. The nature and the sequence of the frontier orbitals of $Co_3(dpa)_4Cl_2$ is quite in agreement with the orbital scheme displayed and analyzed by Clérac et al.[15] The d atomic orbitals of the cobalt atoms give rise to 15 molecular orbitals, which can be separated into 5 sets: one set with σ character, two with

Scheme 1
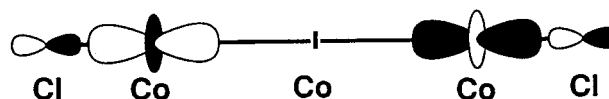
π, and two with δ character. Each set contains three MOs, which can be characterized as bonding (b), nonbonding (nb), and antibonding (ab), respectively. Each Co^{II} atom contributes seven valence electrons to be accommodated in these MO combinations. An analysis of the Kohn−Sham frontier orbitals shows that the b, nb, and ab combinations associated with the two π sets and with one δ set are all fully occupied. The three MOs of the second δ set remain formally unoccupied and take part in the donation interactions originating in the dpa ligands. The 18 electrons accommodated into the six π and the three δ MOs do not take part in any metal−metal interaction, either bonding, or antibonding. They can be considered as localized on individual metal atoms. The three remaining metal electrons are accommodated into the σ set: an electron pair occupies the σ-bonding orbital, rather deep in energy, whereas the unpaired electron occupies the nb combination, nonbonding with respect to the metal framework, but σ-antibonding between the terminal cobalts and the axial chlorine ligands (Scheme 1). Finally, the σ−ab combination represents the LUMO of the symmetric form, which is separated from the occupied set by a relatively large energy gap (1.1 eV).[25] The bonding in the metal framework is therefore exclusively due to the three σ electrons, which are delocalized over the metal framework. As for the π system of the allyl radical and for the valence orbitals of alkali or coinage metal trimers, the σ orbital set of $Co_3(dpa)_4Cl_2$ provides the typical example of a three-electron three-center system.[16,26−28]

3.3. Attempting to Model the u Form of $Co_3(dpa)_4Cl_2$. Much effort has been devoted to the quest of a second energy minimum to be associated with the distorted structures and which would substantiate the hypothesis of bond-stretch isomerism for $Co_3(dpa)_4Cl_2$. Despite the presence of low-lying, low-spin excited states resulting from the transfer of one electron from either the δ^* or the π^* orbitals to the partly occupied σ−nb orbital combination,[13] no state crossing has been evidenced along the Δd_{Co-Co} coordinate measuring the magnitude of symmetry breaking in the Co_3 framework. These states are not likely to be thermally populated, because the transfer of one more electron to an orbital with Co−Cl σ^* character would stretch the cobalt−chlorine bonds by ∼0.1 Å, a trend that is not observed when temperature increases.[10] Still more surprising is the relatively high energy (>15 kcal·mol^{-1}) calculated for the lowest states associated with $S = 3/2$ or $S = 5/2$, despite the spin-crossover behavior documented for $Co_3(dpa)_4Cl_2$ in the crystal[10] and in solution.[11] It is clear that the high energy

(25) Because the calculation has been carried out within the spin-unrestricted formalism, the LUMO corresponds to the α spin orbital with σ−ab character. The associated β spin orbital is still higher in energy. Note that this orbital ordering is obtained for the ground state, symmetric conformation. Assuming a distorted geometry with stretched Co(3)−N bonds as in the u conformation yields as the LUMO an orbital with Co(3)−N π^* character (see section 5.3).

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calculated for the lowest quartet and sextet states is a direct consequence of the large energy gap separating in the isolated symmetric molecule the highest occupied orbitals from the σ^* LUMO.[29,30]

A possible clue for reconciling the observed and calculated structures could be the metastability of the ground-state structure, induced by an extreme flatness of the potential energy surface with respect to a distortion of the nuclear framework. To check this hypothesis, two more optimization processes have been carried out, still on a single molecule of $Co_3(dpa)_4Cl_2$, but with constraints imposed on the Co−Co bond lengths. In calculation 2, the Co−Co distances have been kept fixed at 2.300 and 2.385 Å, respectively, which are the distances observed in u-$Co_3(dpa)_4$-$Cl_2·2CH_2Cl_2$ at 20 K.[10] In calculation 3, a more severe distortion has been imposed on the metal framework, with Co−Co distances of 2.285 and 2.459 Å, similar to those reported for the u complexes at room temperature.[3c,10] The Co−Cl and Co−N distances optimized in calculations 2 and 3 are reported in Table 1, and the complete sets of Cartesian coordinates are provided, with the total energies, as Supporting Information. Figure 2B provides a comparison between the geometrical parameters computed assuming $\Delta d_{Co−Co} = 0.174$ Å and those observed for the u form at room temperature. Calculations 2 and 3 show that breaking the symmetry of the metal framework induces a distortion in the Co−Cl bond lengths: the Co−Cl bond facing the strong Co−Co bond is slightly stretched, whereas the opposite axial coordination is strengthened. The difference in the bond distances obtained from calculation 3, $\Delta d_{Co−Cl} = 0.086$ Å, closely parallels the amplitude of the distortion observed at 298 K (0.071 Å). The calculated value of $\Delta d_{Co−Cl}$ declines to 0.043 Å for a slight distortion of the metal framework. The comparison with the experimental structure at 20K is difficult, because the observed Co−Cl distances are almost identical ($\Delta d_{Co−Cl} = -0.012$ Å, Table 1) and the influence of intermolecular interactions, as in the s complex, cannot be excluded. Contrary to the case of axial coordination, the influence of symmetry breaking on the calculated equatorial bond lengths remains very limited. The calculated difference between the Co−N bond lengths in terminal positions amounts to 0.01 Å in the slightly distorted form and to no more than 0.04 Å in the highly distorted structure. This is in strong contrast with the experimental results,

which display at room temperature and even at 20 K a stretching of the Co(3)−N distances surrounding the weakly bound cobalt atom[10] (Table 1). The extension of the distortion to the coordination sphere of the weakly bound cobalt atom, and possibly the distortion of the metal framework itself, could therefore be tentatively assigned to the progressive population of a high spin state as temperature increases.

3.4. Ground-State Structure and Potential Energy Curve of $[Co_3(dpa)_4Cl_2]^+$. Unconstrained geometry optimization and geometry optimizations with imposed distortions of the metal framework have been carried out on $[Co_3(dpa)_4Cl_2]^+$ with the same strategy as that used for the neutral complex. A diamagnetic ground state was assumed, following the indications of the magnetic susceptibility measurements at low temperature.[15] The unconstrained geometry optimization yields an s-type complex with structural parameters in excellent agreement with the low-temperature crystal structure reported by Clérac et al.[15] The calculated Co−Co bond lengths (2.323 Å) are identical to those calculated for the neutral species. The observed distances comprise between 2.317 and 2.341 Å, depending on the temperature, and are also very close to the Co−Co distances observed for the s form of $Co_3(dpa)_4Cl_2$. The Co−N bond lengths, observed as calculated, are also quite similar to those of s-$Co_3(dpa)_4Cl_2$. By contrast, a contraction of the Co−Cl bonds amounting to 0.13 Å is calculated, and a bond shortening of the same order is observed (Table 1 and Figure 2C). This decrease of the Co−Cl bond lengths is easily explained by the depopulation of the Co−Cl σ-antibonding SOMO of the neutral complex and validates the description of the frontier orbitals proposed for $Co_3(dpa)_4Cl_2$.

At variance with the neutral complex, the cationic form does not exhibit any trend toward structural or crystallographic variability.[15] It was therefore interesting to check whether this increased stability of the s form could be correlated with a steeper aspect of the potential energy curve with respect to a distortion of the Co_3 framework. Constrained geometry optimizations, therefore, have been carried out on $[Co_3(dpa)_4Cl_2]^+$ assuming, as for the neutral molecule, weak and strong distortions of the metal framework corresponding to $\Delta d_{Co−Co} = 0.085$ Å and 0.174 Å, respectively. As shown in Figure 3, the potential curve obtained for the cation is somewhat steeper than that for the neutral system, with relative energies of $+1.4$ kcal·mol^{-1} for the weak distortion, and $+4.7$ kcal·mol^{-1} for the strong distortion. However, the calculated difference does not seem sufficient to explain the distinct structural behavior of the two species.

4. Modeling the Bonding in Co₃(Dpa)₄Cl₂ with the Heisenberg Hamiltonian

4.1. The Heisenberg Hamiltonian Applied to Three-Electron Three-Center Systems: Energy Decomposition and Interpretation. Since the early 1970s, the three-electron three-center problem has been the subject of qualitative discussions in relation to the more general problem of Hartree−Fock instability.[26,31] It was concluded that the structure of real or hypothetical systems, such as H₃, Cu₃, alkali trimers, or the allyl radical, resulted from a delicate balance between opposite trends leading either to symmetry adaptation, as in the allyl radical, or to symmetry breaking, as in the hydrogen trimer. The more recent controversy about the origin of the electronic force

(29) Single-point DFT/B3LYP calculations have been carried out on the doublet ground state (s and u forms) and on the lowest quartet states of $Co_3(dpa)_4Cl_2$, using the Gaussian-98 package.[30] The geometries taken for these calculations were those optimized with the ADF package using the BP86 functional (Table 1). The standard LANL2MB basis sets have been used for all atoms. Convergence of the SCF iterations was exceedingly difficult to obtain for all considered states. The total energies are as follows: ^2A, symmetric, -2638.42037 hartrees; ^2A, nonsymmetric ($\Delta d_{Co−Co} = 0.174$ Å), -2638.40286 hartrees; and ^4A, nonsymmetric ($\Delta d_{Co−Co} = 0.111$ Å), -2638.37976 hartrees. The energy difference between the lowest doublet and the lowest quartet is 0.04061 hartree, that is, 25.4 kcal·mol^{-1}. Given the relatively poor quality of the LANL2MB basis set and the lack of geometry reoptimization, it can be concluded that the order of magnitude of the doublet-quartet energy separation obtained with the BP86 functional (18.3 kcal·mol^{-1}, Table 1) is not basically modified by the present calculations.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. M.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(31) (a) Paldus, J.; Cizek, J. *J. Polym. Sci.* **1970**, *C29*, 199. (b) McKelvey, J. M.; Berthier, G. *Chem. Phys. Lett.* **1976**, *41*, 476. (c) McKelvey, J. M.; Hehre, W. J. *Mol. Phys.* **1973**, *25*, 983. (d) Paldus, J.; Veillard, A. *Mol. Phys.* **1978**, *35*, 445. (e) Martin, R. L.; Davidson, E. R. *Mol. Phys.* **1978**, *35*, 1713. (f) Fukutome, H. *Int. J. Quantum Chem.* **1981**, *20*, 955.
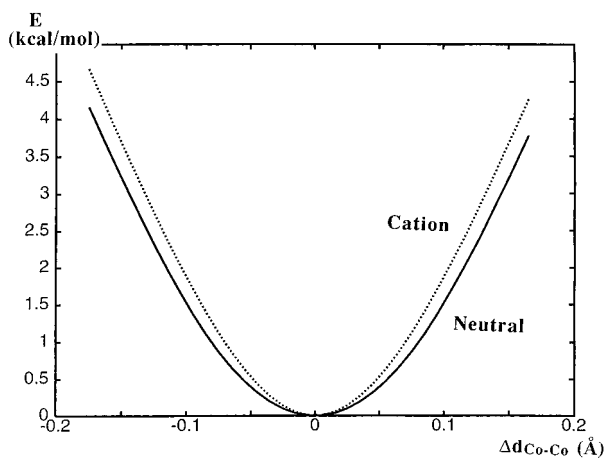
Figure 3. Potential energy curve (eV) of neutral $Co_3(dpa)_4Cl_2$ (solid line) and of $[Co_3(dpa)_4Cl_2]^+$ as a function of the metal−metal bond length distortion Δd_{Co-Co} (Å).

governing the geometry of conjugated systems[27] has given a quantitative support to these discussions. New methods were derived that allow the separation of the contribution of resonance, or delocalization energy from that of σ bonding, Pauli repulsion, and other effects involving only two consecutive atoms. Shaik et al. have expressed the respective contributions of these terms by means of valence bond state correlation diagrams.[27] These authors concluded that the π system of allyl is basically unstable with respect to a Kekulean distortion and that the observed molecular symmetry proceeds from local forces and primarily from the σ framework.[27] Malrieu came to a similar conclusion by analyzing the three-electron three-center systems by means of a Heisenberg model introducing only two-center interactions.[16] If $\mathscr{R}_{AB}(r)$ is defined as a scalar function of nuclear coordinates expressing the local forces acting between atoms A and B and $g(r)$ as the energy term associated with the electron delocalization occurring in the singlet state, the solutions stemming from the Heisenberg model for the triplet and the singlet states of a two-electron dimer have the following energies:[16]

$$E^T = \mathscr{R} \qquad (1)$$

$$E^S = \mathscr{R} - 2g \qquad (2)$$

In practice, g will therefore represent half of the singlet−triplet energy difference, which can be calculated on the dimer by means of any convenient method, whereas $\mathscr{R}$ will be identified with the energy calculated for the triplet state of the dimer.

Extending the model to a symmetric trimer with no terminal-to-terminal interaction ($g_{12} = g_{23} = g$; $\mathscr{R}_{12} = \mathscr{R}_{23} = \mathscr{R}$; $\mathscr{R}_{13} = g_{13} = 0$) yields as the lowest root a doublet state with energy

$$E_{trimer} = 2\mathscr{R} - 3g \qquad (3)$$

The condition ensuring the stability of the symmetric structure at a given internuclear distance with respect to a dimer and a separate monomer will be

$$2\mathscr{R} - 3g < \mathscr{R} - 2g \qquad \text{i.e.,} \quad \mathscr{R} - g < 0 \qquad (4)$$

Between symmetry conservation and dissociation, the trimer is offered a third possibility, which is bond distortion, or symmetry breaking. Let us assume that the r_0 bond lengths of the symmetric trimer are modified by $\pm dr$ to give the system with broken symmetry. According to eq 3, the trend, or the reluctance, toward distortion will be determined by the local curvature of
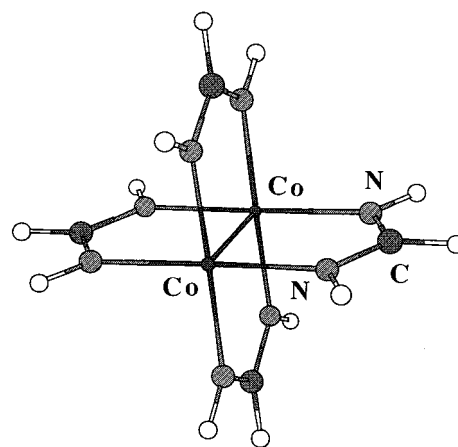
Figure 4. Representation of the lantern-type cobalt formamidinate molecule $Co_2(HN-CH-NH)_4$.

the $\mathscr{R}$ and g functions at $r = r_0$

$$\Delta(2\mathscr{R}) = \mathscr{R}(r_0 + dr) + \mathscr{R}(r_0 - dr) - 2\mathscr{R}(r_0) = 2\frac{\partial^2\mathscr{R}}{\partial r^2}dr^2 \qquad (5)$$

$$-\Delta(3g) = -1.5[g(r_0 + dr) + g(r_0 - dr) - 2g(r_0)] = -3\frac{\partial^2 g}{\partial r^2}dr^2 \qquad (6)$$

In all of the investigated cases, and particularly for the allyl radical, the curvature of $\mathscr{R}$ was positive, which means that the local forces tend to keep the system symmetric. This is in agreement with the message delivered by Shaik et al. telling that delocalized π systems, such as the allyl radical, may well be unstable or metastable species that are locked by the σ framework into symmetric geometries.[27] As a matter of fact, the influence of delocalized electrons with respect to symmetry breaking is not easily defined. Except for H_2, the curvature of $g(r)$ is extremely shallow, sometimes locally negative (as for Li_2, Na_2), but most often it is very slightly positive, which confirms the diagnosis of metastability for the delocalized electron system.

4.2. Application to $Co_3(dpa)_4Cl_2$. $Co_3(dpa)_4Cl_2$ presents the typical example of a three-electron three-center system, and the formalism exposed above is quite relevant to this complex. The delocalized system is composed of the three electrons accommodated in the σ−b and σ−nb orbital combinations. Contrary to allyl, but similar to Cu_3 and alkali trimers, there is no framework reducible to local bonds, and the "local forces" acting on the cobalt atoms and to be accounted for by the $\mathscr{R}$ function are the Pauli repulsion but also the reaction force assigned to the bite of the equatorial ligands. A delicate problem then consisted of modeling a dimer of Co^{II} that could be considered to be a precursor of $Co_3(dpa)_4Cl_2$ electronically, topologically, and sterically. We eventually selected the tetraformamidinate, lantern-type complex $Co^{II}_2(HN-CH-NH)_4$ (Figure 4). The dimeric framework is composed of two d^7 cobalt atoms linked by a single σ bond and the equatorial environment of each metal atom can be considered as similar to that of $Co_3(dpa)_4Cl_2$, despite the planarity of the formamidinate ligand. The equilibrium Co−Co distance calculated for $Co_2(HN-CH-NH)_4$ was $r_0 = 2.362$ Å, a distance intermediate between the short and the long Co−Co bonds in u-$Co_3(dpa)_4Cl_2$ at 20 K, which is in agreement with the hypothesis of bond length variations of $\pm dr$ in the distorted trimer. The energies of the singlet and triplet
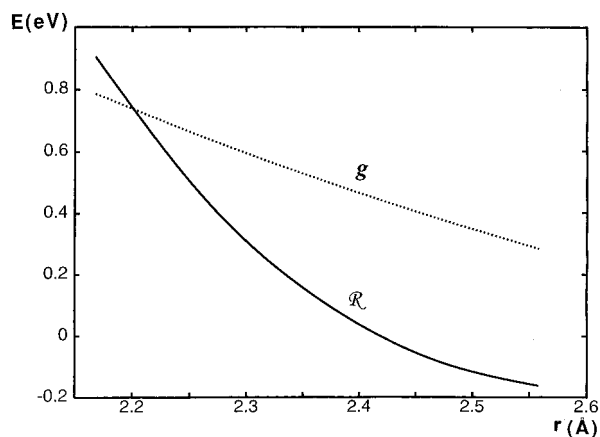
Figure 5. Repulsive energy parameter $\mathscr{R}$ and effective exchange term g (cf eqs 1, 2) in the cobalt formamidinate molecule $Co_2(HN-CH-NH)_4$. The variations of $\mathscr{R}$ are represented with respect to an arbitrary origin. All values are in eV.

states of $Co_2(HN-CH-NH)_4$ have been calculated with respect to the metal—metal σ bond at r_0, $r_0 \pm 0.1$ Å, and $r_0 \pm 0.2$ Å. The functions $\mathscr{R}(r)$ and $g(r)$ deduced from these values are displayed in Figure 5.

These curves are very similar to those obtained by Malrieu for the other three-electron three-center systems, except for H_3: $\mathscr{R}(r)$ is characterized by a positive curvature, whereas $g(r)$, also positively curved, is however, very close to a straight line. According to eqs 5 and 6, the energy term associated with delocalized interactions would make the system metastable, but the positive curvature of $\mathscr{R}(r)$ constrains the trimer to remain symmetric. However, some hints suggest that the preference for symmetry is weak, if not borderline. First, the curvature of $\mathscr{R}$, which measures the reluctance of the system to distort, is much more shallow than for the allyl radical and should rather be compared to the curvatures obtained for the alkali trimers. This should be easily explained by the lack of a localized bonding framework, even though the effect of the ligand bite contributes to the increase of the curvature in the vicinity of the optimal ligand conformation.[32] Then, the contribution of the g function, also displaying a very slightly positive curvature, tends to oppose the trend toward symmetry adaptation and to still flatten the global potential curve. A quantitative estimate of the reluctance toward distortion by means of eqs 5 and 6 gave the following energy differences in favor of the s form:

$$\Delta E = \Delta(2\mathscr{R}) - \Delta(3g) = +0.662 - 0.097 =$$
$$+0.56 \text{ kcal·mol}^{-1} \text{ with } dr = 0.05 \text{ Å} \quad (7)$$

$$\Delta E = \Delta(2\mathscr{R}) - \Delta(3g) = +2.908 - 0.419 =$$
$$+2.59 \text{ kcal·mol}^{-1} \text{ with } dr = 0.10 \text{ Å} \quad (8)$$

Considering the simplicity of the Heisenberg model and the differences in the ligand bite between formamidinate and dpa,[32] the order of magnitude calculated for ΔE reproduces appreciably well the relative energies calculated for the u form of the real system with calculations 2 ($dr = 1/2 \Delta d_{Co-Co} = 0.0425$ Å, $\Delta E = +1.11$ kcal·mol⁻¹) and 3 ($dr = 0.087$ Å, $\Delta E = +4.16$ kcal·mol⁻¹) (Table 1). It should finally be mentioned that an increased stability of the symmetric form was predicted by Shaik and Bar[28a] for the 2-electron/3-center systems, exemplified by H_3^+ and the allyl cation. Shaik and Bar conclude that this

behavior is likely to be general, mainly due to the delocalization of the electrostatic interaction, which favors the symmetric system.[28] The results obtained for $[Co_3(dpa)_4Cl_2]^+$ (Figure 3) seem to agree with this prediction, even though the difference with the potential energy surface of the neutral complex appears to be borderline.

5. Tracking the Origin of the Observed Bond Length Variability

5.1. Three Hypotheses. The quite unusual behavior of neutral $Co_3(dpa)_4Cl_2$ and other $Co_3(dpa)_4LL'$ complexes has been extensively documented by the group of Cotton and Murillo.[3,5−11] From the experimental investigations carried out on the various crystalline forms of $Co_3(dpa)_4Cl_2$ and $Co_3(dpa)_4Br_2$ and from the calculations reported above on the former complex, three hypotheses can be proposed:

(i) $Co_3(dpa)_4Cl_2$ is an illustration of the concept of bond stretch isomerism, as initially proposed by Stohrer and Hoffmann[33] and later formalized by Parkin;[12,14]

(ii) The ground state of an isolated molecule of $Co_3(dpa)_4$-Cl_2 corresponds to the s form, but the potential energy curve is extremely shallow and a small perturbation originating in the crystal environment may induce a distortion of the metal framework; or

(iii) the distortion of the metal framework in the u form should be assigned to the partial population of a high spin state (spin crossover system). The population of this high spin state increases with temperature, but the effect of spin crossover should already exist at 20 K to explain the persistence of a distortion at this temperature for some of the u compounds.[9,10]

It seems that the first hypothesis can be ruled out in view of the calculations reported here. The strict definition of bond stretch isomerism proposed by Hoffmann and Parkin implies the existence of a double minimum on the potential energy surface of the investigated compound associated with a specific spin multiplicity.[12,14,32] In the present case, no energy minimum corresponding to a doublet spin state could be found for the unsymmetrical conformation. However, the shape of the single-minimum potential energy surface appears to be extremely shallow with respect to a s → u distortion. Two types of interactions with the crystal can be thought of: (i) an asymmetric interaction along the Cl−Co−Co−Co−Cl axis with another $Co_3(dpa)_4Cl_2$ molecule or with a cocrystallized solvent molecule, or (ii) the response of $Co_3(dpa)_4Cl_2$ to an electric field induced by the crystal environment. Asymmetric hydrogen bonding between CH_2Cl_2 and one axial chlorine ligand was evidenced in s-$Co_3(dpa)_4Cl_2$·CH_2Cl_2 below 165 K.[10] This interaction is sufficient to induce a significant asymmetry in the Co−Cl bonds, but it does not affect the symmetry of the metal framework. In view of this negative result, we instead investigated the influence of an electric field on the structure of $Co_3(dpa)_4Cl_2$.

5.2. The Ground-State Structure of $Co_3(dpa)_4Cl_2$ Undergoing an Electric Field. The energies associated with the structures optimized for the symmetric and for the slightly nonsymmetric ($\Delta d_{Co-Co} = 0.085$ Å) forms of $Co_3(dpa)_4Cl_2$ have been recomputed in the presence of an electric field. The field was generated by two point charges of $+1$ e and -1 e, both located along the axis of the metal framework, and taken at 3.0 Å from the closest chlorine atom in the s form, that is, at 15.659 Å from each other. Two energy values were calculated for the u form, corresponding to opposite orientations of the electric field. In all cases, the application of the field resulted in a

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(32) The framework of the dpa ligand is expected to be more rigid than formamidinate because of the aromatic rings and should contribute more firmly to keep the system symmetric.

(33) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779, 1661.

decrease of the total energy by ∼32.5 kcal·mol^{-1}. Removing the constant energy shift due to the attraction between the point charges (21.2 kcal·mol^{-1}) leaves an important stabilization energy (∼11.3 kcal·mol^{-1}) that should be assigned to the polarization of the molecular electron density induced by the field. The importance of this polarization appears from the point charge separation that affects equivalent atoms of the s form undergoing the field: -0.79 e and -0.24 e for the Cl atoms (-0.55 e for the unperturbed molecule) and $+0.74$ e and $+0.58$ e for the terminal Co atoms instead of $+0.66$ e. The strong perturbation generated by the electric field is, however, unable to stabilize the u form. In both orientations of the field, the slightly unsymmetrical conformation remains higher in energy than the s form by a fraction of kcal.mol^{-1} (Table 1). This response of the isolated molecule to an external perturbation, therefore, makes less probable the hypothesis of a geometric deformation induced by the crystal forces, despite the very shallow potential curve displayed in Figure 3.

5.3. The ⁴A State of Lowest Energy. The quartet state of lowest energy obtained when assuming the experimental u conformation as a starting geometry originates in a one electron transfer from the doubly occupied δ*(ab) orbital to a Co—N antibonding MO centered on the weakly attached cobalt atom. Both MOs belong to the B representation of the C_4 point group and the third SOMO (the σ—nb orbital) belongs to A; the lowest quartet state is, therefore, a ⁴A state. At variance with the situation in all investigated doublet states, the asymmetry of the highest SOMO is sufficient to retain the system in the initially postulated distorted conformation. The main geometrical features of the fully optimized u structure associated with the ⁴A state are displayed in Table 1. The calculated bond lengths are quite reminiscent of the experimental structure reported for the u form at room temperature. More specifically, the metal—chlorine distance is shorter on the weakly bonded metal atom ($\Delta d_{\text{Co—Cl}} = 0.05$ Å), and the metal—nitrogen distances on the same Co atom are longer by 0.147 Å than on the other terminal cobalt (observed difference at room temperature, 0.141 Å[10]). This remarkable feature, characteristic of the u structure, could not be reproduced in any of the other investigated geometries (Table 1). It should be specifically associated with a partial population of one Co—N π* orbital localized on a single metal atom because of the framework distortion and lowered in energy below the Co—Co—Co σ* orbital by the stretching of the affected C—N bonds. As far as the structure is concerned, the observed variability of the geometry between 20 and 298 K could, therefore, be explained in terms of a progressive population of the quartet state with increasing temperature, assuming that the spin crossover process is already active at very low temperature. This hypothesis, proposed to explain the slight distortion already observed at 20 K in the coordination sphere of Co(3),[10] could find some support in the high value of 2.85 μ_B measured for the effective magnetic moment of u-Co₃(dpa)₄Cl₂ at 10 K.[10] The problem remaining to be solved comes from the very high energy value calculated for the quartet state, $+18.3$ kcal·mol^{-1} with respect to the doublet ground state of the symmetric conformation. This high excitation energy appears to be consistent with the SOMO-LUMO gap of ∼1 eV obtained in all DFT calculations carried out on the ground state of tricobalt complexes in the present work. The order of magnitude of the doublet-quartet energy separation is not appreciably modified when single-point calculations are carried out on these two states with the hybrid B3LYP functional.[29,30] The calculated singlet—quartet energy gap is hardly compatible with the spin crossover behavior of the Co₃(dpa)₄Cl₂ complexes

reported in solution[11] and in the crystal.[10] The most probable explanation is a systematic error made in the comparison of states having different spin multiplicities,[34] and other methodological approaches are clearly needed to solve this problem. However, DFT optimization is known to provide correct geometries for the states of lowest energy associated with each spin multiplicity. In view of the experimental and theoretical results, we therefore propose to assign the occurrence of u-Co₃(dpa)₄Cl₂ to a partial and progressive population of the excited ⁴A state.

A similar spin crossover behavior has, however, been documented in the s forms of Co₃(dpa)₄Cl₂ and Co₃(dpa)₄Br₂ without any significant symmetry breaking of the nuclear framework, even at room temperature.[9,10] In the case of Co₃-(dpa)₄L₂·C₆H₁₂ (L = Cl, Br), however, an important stretching of the symmetric metal—metal bond (0.043 Å for Co₃(dpa)₄-Cl₂, 0.064 Å for Co₃(dpa)₄Br₂) has been observed as temperature increases from 120 to 295 K.[7,9] These observations can be rationalized in the context of a competition between two different high-spin states, namely the above-described ⁴A state yielding a nonsymmetric conformation, and a ⁴B state resulting from a δ* → σ* one-electron transfer. The latter state is indeed the lowest quartet when a symmetric Co₃ framework is assumed. A progressive population of the ⁴B state would therefore account for the symmetric elongation of the delocalized metal—metal bond.

Conclusion and Summary

Co₃(dpa)₄LL′ complexes represent rare examples of stable three-electron three-center systems, a concept that was best illustrated up to now by the allyl radical. As for the allyl radical and for other, transient representatives of this category, such as the H + H₂ system, alkali, or coinage metal trimers, the structure of the tricobalt complexes in their ground state results from a delicate balance between localized and delocalized interactions. Local forces, acting between two consecutive metal atoms, are globally repulsive at a Co—Co distance of 2.3–2.4 Å. However, the positive curvature of the local potential with respect to the bond distance shows that these forces tend to oppose a distortion of the metal framework. The delocalized σ bond ensures the cohesion of the system, but the curvature of the bond energy function, also very slightly positive, would favor such a distortion. In a context somewhat different from that of the allyl radical due to the absence of localized bonds, the energy of the delocalized σ bond is large enough to keep the system stable, but the symmetry of the framework is an effect of the local repulsion. Resulting from this balance of forces, the potential energy curve of Co₃(dpa)₄Cl₂ presents a single minimum with a geometry very close to that of the observed symmetric structure, but this curve is extremely shallow with respect to a distortion of the metallic framework. The hypothesis of bond-stretch isomerism, which had been proposed to explain the characterization of a nonsymmetric structure in a different crystal environment, can therefore be ruled out, because it would require the existence of a double minimum on the potential energy curve associated with the low-spin ground state. Two conjectures could therefore explain the occurrence of the nonsymmetric structure: (i) a nonsymmetric crystal field could be sufficient to cause an important shift of the framework geometry, or (ii) the progressive population of a low-energy, high-spin excited state associated with a nonsymmetric equilibrium structure could induce a temperature-dependent distortion of the framework.

(34) Caballol, R.; Castell, O.; Illas, F.; Malrieu, J. P.; Moreira, I. P. R. *J. Phys. Chem. A* **1997**, *101*, 7860.

The application of an electric field oriented along the Co$-$Co$-$Co axis was not sufficient to stabilize the distorted conformation, however. Furthermore, symmetric cobalt frameworks have been characterized with axial ligands interacting nonsymmetrically with the crystal environment.[10] The second hypothesis, therefore, becomes most probable and is compatible with the observed spin crossover behavior and with the unusual variability of the nonsymmetrical geometry with temperature. Moreover, the geometry optimized for the quartet state lowest in energy starting from a distorted structure (^{4}A) remains nonsymmetric and closely reproduces the structure observed for *u*-Co$_3$(dpa)$_4$Cl$_2$ at room temperature. A quartet state belonging to a different representation of the C_4 group (^{4}B) is the lowest high-spin state when a symmetric conformation is assumed. The occurrence of the u and s structures characterized for Co$_3$(dpa)$_4$L$_2$ molecules could therefore be explained by a competition between excited states with different equilibrium conformations, gradually populated as temperature increases. Further theoretical work is needed, however, to explain or to correct the high relative energy computed for the quartet states, hardly compatible with spin crossover, and resulting from an overestimation of the HOMO$-$LUMO gap.

Supporting Information Available: Complete list of Cartesian coordinates and bonding energies for Co$_3$(dpa)$_4$Cl$_2$ and [Co$_3$(dpa)$_4$Cl$_2$]$^+$ as optimized in the various considered conformations. This material is available free of charge via the Internet at http://pubs.acs.org.

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