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Mononuclear and binuclear cobalt carbonyl nitrosyls: comparison with isoelectronic nickel carbonyls†

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The cobalt carbonyl nitrosyls $Co(NO)(CO)_n$ (n = 4, 3, 2, 1) and $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3, 2) have been studied by density functional theory. The lowest energy structures for the mononuclear derivatives $Co(NO)(CO)_n$ (n = 3, 2, 1) parallel those of the corresponding isoelectronic $Ni(CO)_{n+1}$ derivatives. In addition, a thermodynamically unstable $Co(NO)(CO)_4$ structure is predicted with a bent nitrosyl group. The potential energy surfaces of the binuclear cobalt carbonyl nitrosyl derivatives $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3, 2) are complicated by the similar energies of analogous structures with bridging carbonyl or bridging nitrosyl groups. However, these structures are analogous to those previously predicted for the isoelectronic binuclear nickel carbonyls $Ni_2(CO)_{n+2}$. Thus the lowest energy structures of $Co_2(NO)_2(CO)_5$, $Co_2(NO)_2(CO)_4$, and $Co_2(NO)_2(CO)_3$ have one, two, and three bridging groups, respectively, just like the isoelectronic $Ni_2(CO)_{n+2}$. For $Co_2(NO)_2(CO)_5$ and $Co_2(NO)_2(CO)_4$ the otherwise analogous structures with bridging carbonyl and/or nitrosyl groups are of very similar energies. However, for $Co_2(NO)_2(CO)_3$ there appears to be a particularly stable triply carbonyl bridged structure with an unusually short Co$\equiv$Co distance consistent with the formal triple bond required to give the cobalt atoms the favored 18-electron configuration.

1. Introduction

A number of metal carbonyl nitrosyls are known, and these are isoelectronic with homoleptic metal carbonyl derivatives, particularly for the less oxophilic transition metals with at least six valence electrons. The most extensive such sequence consists of the tetrahedral molecules $Co(NO)(CO)_3 \rightarrow Fe(NO)_2(CO)_2 \rightarrow Mn(NO)_3CO \rightarrow Cr(NO)_4$, which are isoelectronic and isostructural with $Ni(CO)_4$. In this series the neutral NO ligands function as three-electron donors.[1,2] Alternatively and equivalently, the NO group may be considered as the nitrosonium cation, NO^+, isostructural and isoelectronic with a neutral CO group. In either case the M–NO interactions for such three-electron donor NO groups are very similar to the M–CO interactions in analogous metal carbonyl derivatives.[1] Such three-electron donor terminal neutral NO groups are linear, as recognized by an ∠MNO angle close to 180°.

The NO group differs from the CO group in one important respect: a terminal CO group is always linear with an ∠MCO angle close to 180°. However, a terminal neutral NO group can function as a net one-electron donor corresponding to the nitroxyl anion, NO^-, a mode of bonding not possible with the CO group. Such a formal one-electron donor neutral NO group can be recognized structurally by a significantly bent M–NO angle with ∠MNO angles in the range 120° to 140° (Fig. 1). Such bent nitrosyl groups occur most frequently in complexes of the late transition metals[1] since they require the fewest electrons from the external ligands to achieve the favored 18-electron configuration.

A similar dichotomy can potentially occur with bridging nitrosyl groups. Thus neutral bridging μ-NO groups donating three electrons to the pair of metal atoms have structures with coplanar $N(O)M_2$ units similar to BF_3, as recognized by a dihedral ∠MMNO angle close to 180° (Fig. 1). Analogously, one-electron bridging μ-NO groups might be expected with a pyramidal $N(O)M_2$ configuration similar to NH_3 as recognized by dihedral angles around 120° or less.

Cobalt is the transition metal with the most valence electrons, namely nine, to form a stable metal carbonyl

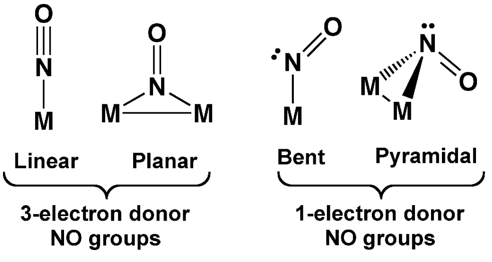

Fig. 1 The various types of terminal and bridging NO groups.

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† Electronic supplementary information (ESI) available: Tables S1–S17: theoretical harmonic vibrational frequencies for the 32 structures of $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3, 2) and $Co(NO)(CO)_m$ (m = 4, 3, 2, 1) using the BP86 and B3LYP method; Tables S18–S49: theoretical Cartesian coordinates for the 32 structures of $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3, 2) and $Co(NO)(CO)_m$ (m = 4, 3, 2, 1) using the BP86/DZP method. See DOI: 10.1039/b908030a

nitrosyl, namely Co(NO)$(CO)_3$ in the series of tetrahedral molecules noted above.[3,4] Thus the series of the mononuclear derivatives Co(NO)$(CO)_n$ (n = 4, 3, 2) and binuclear derivatives $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3, 2) includes the most promising ternary metal carbonyl nitrosyls to exhibit some structures with bent nitrosyl groups. Also of interest in the binuclear derivatives is the relative tendency of CO and NO groups to function as bridges and the possible occurrence of formal four-electron donor CO groups and five-electron donor NO groups in the unsaturated derivatives. In addition, the unsaturated mononuclear Co(NO)$(CO)_n$ (n = 2, 1) derivatives have been generated in argon matrices at 7 K by reactions of laser-ablated cobalt atoms with CO/NO mixtures.[5]

This research uses density functional theory (DFT) to explore the chemistry of the mononuclear and binuclear cobalt carbonyl nitrosyls mentioned above. Also of interest is the comparison of the predicted structures with those found for isoelectronic nickel carbonyls in a previous study.[6]

2. Theoretical methods

Electron correlation effects were considered by employing density functional theory (DFT), which has evolved as a practical and effective computational tool, especially for organometallic compounds.[7–21] Two density functional theory (DFT) methods were used in this study, namely the B3LYP and BP86 methods. The B3LYP method is an HF/DFT hybrid method using Becke's three-parameter functional (B3)[22] and the Lee–Yang–Parr generalized gradient correlation functional (LYP).[23] The BP86 method is a pure DFT method, which combines Becke's 1988 exchange functional (B)[24] with Perdew's 1986 gradient corrected correlation functional (P86).[25] The B3LYP method has been found to be more suitable for the structures and energetics of transition metal systems while the BP86 method usually provides better vibrational frequencies.[26,27]

Double-ζ plus polarization (DZP) basis sets were used for the C, N, and O atoms. They are the Huzinaga–Dunning contracted double-ζ sets[28,29] appended with a set of spherical harmonic d polarization functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_d(O) = 0.85$. For N, there are extra s and p diffuse functions. The Wachters' primitive set[30] augmented by two sets of p functions and one set of d functions and contracted according to Hood *et al.*[31] was used for the cobalt atoms in our loosely contracted DZP basis set, designated (14s11p6d/10s8p3d). For the binuclear cobalt carbonyl nitrosyls $Co_2(NO)_2(CO)_5$, $Co_2(NO)_2(CO)_4$, $Co_2(NO)_2(CO)_3$, $Co_2(NO)_2(CO)_2$, there are, respectively, 316, 286, 256, and 226 contracted Gaussian functions in the present DZP basis set.

The geometries of all structures were fully optimized using the two selected DFT methods. The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates at the same levels. The corresponding infrared intensities were also evaluated analytically. All of the predicted ν(CO) and ν(NO) frequencies discussed in this paper were obtained using the BP86 method, which has been shown to be more reliable than the B3LYP method for such predictions. Complete vibrational frequency data from both the BP86 and B3LYP methods are given in the ESI.† All of the computations were carried out with the Gaussian 03 program[32] in which the fine grid (75, 302) was the default for evaluating integrals numerically and the tight (10^{-8} hartree) designation is the default for the energy convergence. The finer grid (120, 974) was used only for investigating small imaginary vibrational frequencies.[33] All of the predicted triplet structures are found to have negligible spin contamination, *i.e.*, the values of $S(S + 1)$ are very close to the ideal outcome of 2.

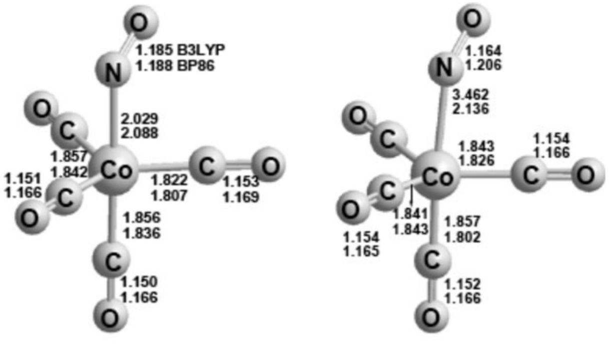
A given $Co_a(NO)_a(CO)_b$ structure is designated as **ab(S or T)-c** where **a** is the number of cobalt atoms (the same as the number of NO groups), **b** is the number of CO groups, and **c** orders the structures according to their relative energies. **S** or **T** refer to singlet and triplet electronic states, respectively. Thus the lowest energy singlet structure of $Co_2(NO)_2(CO)_5$ is designated **25S-1**.

3. Results

3.1 Structures of mononuclear derivatives

3.1.1 Co(NO)$(CO)_4$. Only two structures were found for Co(NO)$(CO)_4$, namely one singlet and one triplet (Fig. 2, Table 1 and 2). The singlet C_s structure **14S-1** is a global minimum with all real vibrational frequencies. This structure has a bent nitrosyl group in an axial position with a predicted Co–N–O angle of 120.1° (BP86) or 119.0° (B3LYP). The cobalt atom in **14S-1** has the favored 18-electron configuration, assuming the bent nitrosyl group to be a formal one-electron donor. The BP86 method also predicts a triplet C_s structure **14T-1** for Co(NO)$(CO)_4$ at 17.1 kcal mol^{-1} above the global minimum **14S-1** with a Co–N–O angle of 135.1°. Attempted optimization of triplet Co(NO)$(CO)_4$ using the B3LYP method led to separation into $^{\bullet}Co(CO)_4$ + NO radicals as indicated by a Co···N non-bonding distance of 3.462 Å in the optimized configuration.

The infrared ν(CO) frequencies (Table 2) of the terminal carbonyl groups fall in the range of 1996 to 2070 cm^{-1} (BP86) for the Co(NO)$(CO)_4$ structure. The typical infrared ν(NO) frequencies of the terminal nitrosyl groups predicted in the Co(NO)$(CO)_4$ molecule are 1693 and 1630 cm^{-1} (BP86) for **14S-1** and **14T-1**, respectively, both corresponding to bent NO ligands. (Table 2).



14S-1 (C_s) **14T-1 (C_s)**

Fig. 2 Optimized structures of Co(NO)$(CO)_4$. The upper distances in the images are B3LYP values and the lower ones are BP86 values.

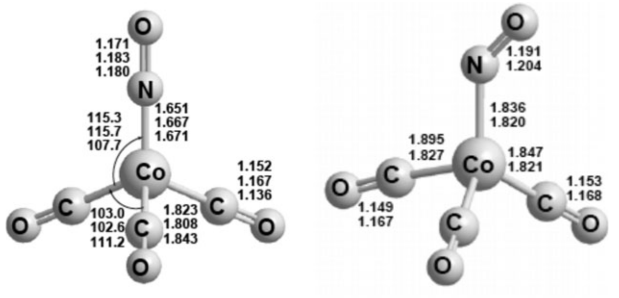
Table 1 The total energies (E, in hartree), relative energies (ΔE, in kcal mol^{-1}), numbers of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized Co(NO)(CO)$_4$ structures

	BP86				B3LYP			
Species	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O
14S-1 (C_s)	1966.482589	0	0	120.1	1966.197178	0	0	119.0
14T-1 (C_s)	1966.455291	17.1	0	135.1	1966.193305	2.4	0	178.2

Table 2 The infrared ν(CO) and ν(NO) vibrational frequencies (cm^{-1}) predicted for the Co(NO)(CO)$_4$, Co(NO)(CO)$_3$, Co(NO)(CO)$_2$, and Co(NO)(CO) structures (infrared intensities in parentheses are in km mol^{-1}; ν(NO) frequencies are in italics)

Species	BP86
14S-1 (C_s)	*1693(734)*, 1996(993), 2002(982), 2005(499), 2064(93)
14T-1 (C_s)	*1630(566)*, 2005(1017), 2009(535), 2012(831), 2070(78)
13S-1 (C_{3v})	*1840(1015)*, 2006(869), 2006(868), 2063(165)
Co(NO)(CO)$_3$ expt.[35]	*1822*, 2047, 2108
13T-1 (C_s)	*1674(702)*, 1990(1040), 1995(768), 2046(262)
12S-1 (C_s)	*1812(976)*, 1976(1145), 2034(279)
Co(NO)(CO)$_2$ expt.[5]	*1788*, 1996, 2071
12T-1 (C_{2v})	*1770(963)*, 1985(1083), 2036(366)
11S-1 (C_s)	*1799(875)*, 1991(556)
Co(NO)(CO) expt.[5]	*1768*, 2001
11T-1 (C_s)	*1757(965)*, 1998(722)

3.1.2 Co(NO)(CO)$_3$. Our research predicts two structures for Co(NO)(CO)$_3$, namely one singlet and one triplet (Fig. 3, Table 2 and 3). Both structures are genuine minima without any imaginary vibrational frequencies. The lowest energy structure predicted for Co(NO)(CO)$_3$ is the experimentally known[34] C_{3v} singlet tetrahedral structure **13S-1**, with the nitrosyl group in the axial position and linear Co–N–O and Co–C–O bonds. The Co–N bond distance and the Co–C bond distances are 1.667 Å and 1.808 Å (BP86) or 1.651 Å and 1.823 Å (B3LYP), respectively, which are close to the experimental values[34] of 1.671 Å and 1.843 Å as well as previously calculated values[5] of 1.665 Å and 1.811 Å, respectively. The N–O and C–O bond distances are 1.183 Å and 1.167 Å (BP86) or 1.171 Å and 1.152 Å (B3LYP), compared with the experimental values[34] of 1.180 Å and 1.136 Å, respectively, as well as previously calculated values[5] of 1.165 Å and 1.154 Å, respectively. Assuming that the nitrosyl ligand is a formal three-electron donor in accord with the linearity of the Co–N–O bond, the cobalt atom in **13S-1** has the favored 18-electron configuration.



13S-1 (C_{3v}) **13T-1 (C_s)**

Fig. 3 Optimized structures for Co(NO)(CO)$_3$. The upper distances are the B3LYP values, the middle (**13S-1**) or lower (**13T-1**) distances are the BP86 values, and the lowest distances in **13S-1** are the experimental values from ref. 34.

The next lowest energy structure of Co(NO)(CO)$_3$ is a triplet C_s structure **13T-1** lying at the relatively high energy of 36.0 kcal mol^{-1} (BP86) or 20.1 kcal mol^{-1} (B3LYP) above the global minimum **13S-1**. The Co–N–O angle in **13T-1** is predicted to be 135.6° (BP86) or 139.9° (B3LYP), suggesting a bent one-electron donor nitrosyl ligand, thereby giving a 16-electron configuration consistent with a triplet electronic state.

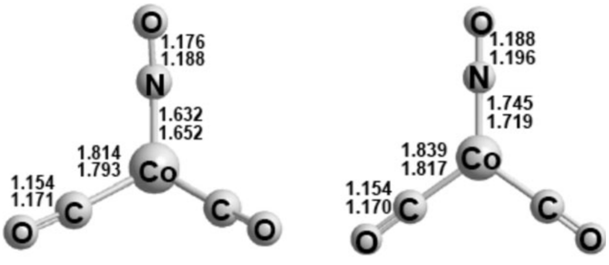
The infrared ν(CO) frequencies (Table 2) of the terminal carbonyl groups fall in the expected range of 1990 cm^{-1} to 2063 cm^{-1} (BP86) for both Co(NO)(CO)$_3$ structures. The infrared ν(NO) frequencies of the terminal nitrosyl groups predicted in these Co(NO)(CO)$_3$ structures are 1840 and 1674 cm^{-1} (BP86) for **13S-1** and **13T-1**, corresponding to a linear terminal NO group and a bent terminal NO group, respectively. (Table 2).

3.1.3 Co(NO)(CO)$_2$. A singlet and a triplet structure were found for Co(NO)(CO)$_2$ at relatively low energies (Fig. 4, Table 2 and 4). The singlet C_s structure **12S-1** is the global minimum with all real vibrational frequencies. The Co–N–O angle in **12S-1** is predicted to be 163.2° (BP86) or 166.8° (B3LYP), which may be considered to be close enough to linearity to regard the nitrosyl group as a three-electron donor. The trigonally coordinated cobalt atom in **12S-1** thus acquires a favored 16-electron configuration.

The triplet C_{2v} planar triangle Co(NO)(CO)$_2$ structure **12T-1** is a genuine minimum with all real vibrational

Table 3 The total energies (E, in hartree), relative energies (ΔE, in kcal mol^{-1}), numbers of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized Co(NO)(CO)$_3$ structures

	BP86				B3LYP			
Species	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O
13S-1 (C_{3v})	1853.168732	0	0	179.9	1852.884628	0	0	179.9
13T-1 (C_s)	1853.111374	36.0	0	135.6	1852.852638	20.1	0	139.9



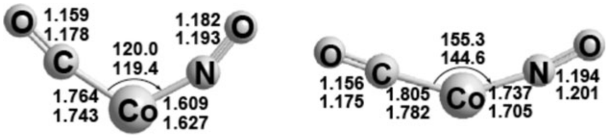
12S-1 (*C_s*) **12T-1** (*C_{2v}*)

Fig. 4 Optimized structures for Co(NO)(CO)$_2$.

frequencies, lying 20.5 kcal mol^{-1} (BP86) or 3.9 kcal mol^{-1} (B3LYP) energetically above the global minimum **12S-1**. The Co–N–O angle is predicted to be linear by both methods used here. The nitrosyl ligand in **12T-1** thus appears to be a formal three-electron donor, thereby giving the cobalt atom a favored 16-electron configuration.

The infrared ν(CO) frequencies (Table 2) of the terminal carbonyl groups fall in the expected region of 1976 to 2036 cm^{-1} (BP86) for both Co(NO)(CO)$_2$ structures. The predicted infrared ν(NO) frequencies of the terminal nitrosyl groups in the Co(NO)(CO)$_2$ structures are 1812 and 1770 cm^{-1} (BP86) for **12S-1** and **12T-1**, respectively, in the region for linear terminal nitrosyl groups (Table 2). Our predicted ν(CO) and ν(NO) frequencies for the lowest lying singlet Co(NO)(CO)$_2$ structure **12S-1** are within 40 cm^{-1} of those assigned to Co(NO)(CO)$_2$ in the low temperature argon matrix studies.[5]

3.1.4 Co(NO)(CO). Two structures were found for Co(NO)(CO), namely one singlet and one triplet (Fig. 5, Table 2 and 5). Both structures are predicted to be genuine minima, having all real vibrational frequencies. The singlet V-shaped C_s structure **11S-1** is the global minimum. The nitrosyl group in **11S-1** is predicted to be slightly bent with a Co–N–O angle of 157.4° (BP86) or 159.0° (B3LYP). The triplet V-shaped C_s structure **11T-1** for Co(NO)(CO) is a local minimum with all real vibrational frequencies, lying 19.5 kcal mol^{-1} (BP86) or 0.3 kcal mol^{-1} (B3LYP) energetically above the global minimum **11S-1**. The Co–N–O angle in **11T-1** was computed to be essentially linear at 171.3° (BP86) or 179.8° (B3LYP). The infrared ν(CO) frequencies (Table 2) of the terminal carbonyl groups are 1991 and 1998 cm^{-1} (BP86) for **11S-1** and **11T-1**, respectively. The infrared ν(NO) frequencies of the terminal nitrosyl groups predicted for the Co(NO)(CO) are 1799 and 1757 cm^{-1} (BP86) for **11S-1** and **11T-1**, respectively (Table 2). These are in the typical region for linear nitrosyl groups despite the somewhat bent Co–N–O angle predicted for **11S-1**.



11S-1 (*C_s*) **11T-1** (*C_s*)

Fig. 5 Optimized structures for Co(NO)(CO).

3.2 Structures of binuclear derivatives

3.2.1 Co$_2$(NO)$_2$(CO)$_5$. Eight energetically low-lying structures (seven singlet and one triplet) were found for Co$_2$(NO)$_2$(CO)$_5$, and they are depicted in Fig. 6. The energies and numbers of imaginary vibrational frequencies of the eight structures are reported in Table 6 and the infrared ν(CO) and ν(NO) frequencies are given in Table 7.

The global minimum for Co$_2$(NO)$_2$(CO)$_5$ is predicted to be either a singly nitrosyl bridged structure **25S-1** or a singly carbonyl bridged structure **25S-2** depending on the method. The BP86 method predicts a C_2 singlet structure **25S-2** as the global minimum with the lowest lying singlet C_1 structure **25S-1** at about 0.5 kcal mol^{-1} higher in energy than **25S-2**. However, the B3LYP method predicts the singlet C_1 structure **25S-1** to be the global minimum with the C_2 singlet structure **25S-2** lying energetically at about 1.9 kcal mol^{-1} above **25S-1**. Thus structures **25S-1** and **25S-2** appear to be essentially degenerate.

The C_1 structure **25S-1** for Co$_2$(NO)$_2$(CO)$_5$ (Fig. 6 and Table 6 and 7) has one bridging nitrosyl group, one terminal nitrosyl group and five terminal carbonyl groups. It is predicted to be a genuine minimum with all real vibrational frequencies. The bridging NO group in **25S-1** exhibits a typical bridging ν(NO) frequency at 1660 cm^{-1}. The Co–Co bond distance in **25S-1** is computed to be 2.581 Å (BP86) or 2.606 Å (B3LYP), consistent with a single bond, giving each of the cobalt atoms the favored 18-electron configuration. For comparison, the doubly bridged Co–Co bond in crystalline Co$_2$(CO)$_8$ [$=$Co$_2$(CO)$_6$(μ-CO)$_2$] is found by X-ray diffraction to be 2.528 Å.[36]

The C_2 structure **25S-2** for Co$_2$(NO)$_2$(CO)$_5$ (Fig. 6 and Table 6 and 7) has one bridging carbonyl group, two terminal nitrosyl groups and four terminal carbonyl groups. This structure has a very small imaginary vibrational frequency at 3*i* cm^{-1} (B3LYP) (Table 6). Following the corresponding normal mode removes the small imaginary vibrational frequency but changes the structure and energy very little. The bridging CO group exhibits a typical ν(CO) frequency at 1881 cm^{-1}. The Co–Co bond distance in **25S-2** of 2.646 Å (BP86) or 2.702 Å (B3LYP) suggests the formal single bond needed to give each of the cobalt atoms the favored 18-electron configuration.

Table 4 The total energies (E, in hartree), relative energies (ΔE, in kcal mol^{-1}), numbers of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized Co(NO)(CO)$_2$ structures

	BP86				B3LYP			
Species	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O
12S-1 (C_s)	1739.773795	0	0	163.2	1739.500360	0	0	166.8
12T-1 (C_{2v})	1739.741196	20.5	0	180.0	1739.494071	3.9	0	180.0

Table 5 The total energies (E, in hartree), relative energies (ΔE, in kcal mol^{-1}), numbers of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized Co(NO)(CO) structures

	BP86				B3LYP			
Species	$-E_{\mathrm{total}}$	ΔE	N_{Imag}	Co–N–O	$-E_{\mathrm{total}}$	ΔE	N_{Imag}	Co–N–O
11S-1 (C_s)	1626.376032	0	0	157.4	1626.112187	0	0	159.0
11T-1 (C_s)	1626.344970	19.5	0	171.3	1626.111675	0.3	0	179.8

A third structure for $Co_2(NO)_2(CO)_5$ (Fig. 6 and Table 6 and 7) is the C_{2v} structure **25S-3**, lying 4.4 kcal mol^{-1} energetically above **25S-1** by both BP86 and B3LYP with all real vibrational frequencies. Structure **25S-3**, like structure **25S-2**, has a bridging carbonyl group, two terminal nitrosyl groups, and four terminal carbonyl groups. However, the arrangements of the terminal nitrosyl groups relative to the Co–Co bond are different in structures **25S-3** and **25S-2**. The predicted Co–Co bond distance in **25S-3** of 2.650 Å (BP86) or 2.698 Å (B3LYP) corresponds to the single bond required by the 18-electron rule, assuming the linear terminal NO group to be a three-electron donor. The bridging CO group in **25S-3** exhibits a typical bridging ν(CO) frequency at 1882 cm^{-1} very close to the bridging ν(CO) frequency of **25S-2**. For comparison the ν(CO) frequencies of the bridging carbonyl groups in $Co_2(CO)_8$ are 1857 and 1868 cm^{-1}.[37]

The fourth energetically low-lying $Co_2(NO)_2(CO)_5$ structure **25S-4** (Fig. 6 and Table 6 and 7) is found to be a transition state with a small imaginary vibrational frequency at 19i (BP86) or 26i cm^{-1} (B3LYP). Following the corresponding normal mode leads to **25S-1**. Structure **25S-4** has a bridging nitrosyl group, one terminal nitrosyl group, and five terminal carbonyl groups and it lies energetically above **25S-1** by 4.5 kcal mol^{-1} (BP86) or 2.1 kcal mol^{-1} (B3LYP). The Co–Co bond distance in **25S-4** of 2.583 Å (BP86) or 2.601 Å (B3LYP) suggests the single bond required to give each of the cobalt atoms the favored 18-electron configuration, assuming that the bridging NO group (as well as the terminal NO group) is a formal three-electron donor. The bridging NO group exhibits a typical bridging ν(NO) frequency at 1667 cm^{-1}.

The C_s singlet $Co_2(NO)_2(CO)_5$ structure **25S-5** (Fig. 6 and Table 6 and 7) is a singly nitrosyl bridged structure lying energetically above **25S-1** by 4.9 kcal mol^{-1} (BP86) or 1.0 kcal mol^{-1} (B3LYP). Structure **25S-5** is a transition state with a small imaginary vibrational frequency at 15i (BP86) or 12i cm^{-1} (B3LYP). Following the corresponding normal mode

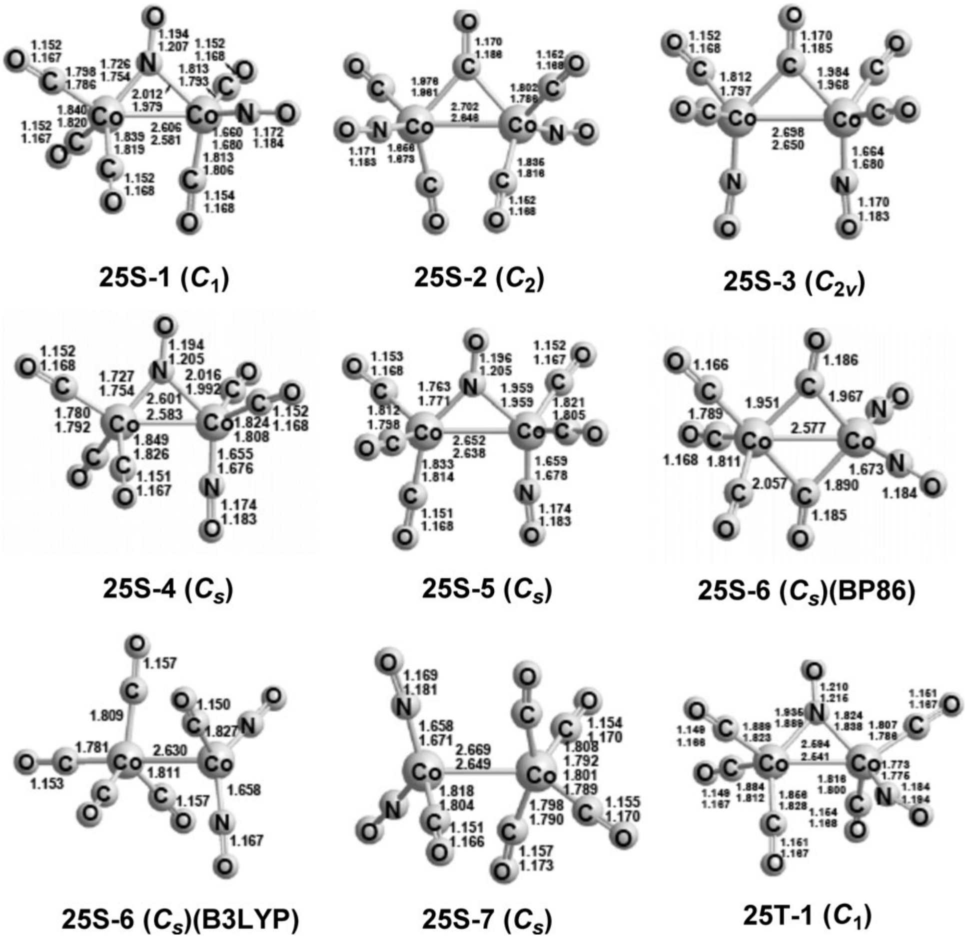

25S-1 (C_1)
25S-2 (C_2)
25S-3 (C_{2v})
25S-4 (C_s)
25S-5 (C_s)
25S-6 (C_s)(BP86)
25S-6 (C_s)(B3LYP)
25S-7 (C_s)
25T-1 (C_1)

Fig. 6 The optimized structures of $Co_2(NO)_2(CO)_5$.

Table 6 The total energies (E, in hartree), relative energies (ΔE, in kcal mol^{-1}), numbers of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized $Co_2(NO)_2(CO)_5$ structures

	BP86				B3LYP			
Species	$-E_{\mathrm{total}}$	ΔE	N_{Imag}	Co–N–O	$-E_{\mathrm{total}}$	ΔE	N_{Imag}	Co–N–O
25S-1 (C_1)	3592.970403	0	0	161.6	3592.401167	0	0	164.7
25S-2 (C_2)	3592.971191	−0.5	0	168.9,168.9	3592.398141	1.9	1(3*i*)	170.2,170.2
25S-3 (C_{2v})	3592.963454	4.4	0	175.7,175.7	3592.394220	4.4	0	175.3,175.3
25S-4 (C_s)	3592.963200	4.5	1(19*i*)	178.8	3592.397829	2.1	1(26*i*)	177.7
25S-5 (C_s)	3592.962566	4.9	1(15*i*)	173.0	3592.399647	1.0	1(12*i*)	172.5
25S-6 (C_s)	3592.960194	6.4	0	172.0,172.0	3592.387990	8.3	0	178.9,178.9
25S-7 (C_s)	3592.953495	10.6	0	174.2,174.2	3592.384478	10.5	0	175.8,175.8
25T-1 (C_1)	3592.928570	26.3	0	148.6	3592.384470	10.5	0	150.4

Table 7 The infrared ν(CO) and ν(NO) vibrational frequencies (cm^{-1}) predicted for the $Co_2(NO)_2(CO)_5$ structures (infrared intensities in parentheses are in km mol^{-1}, ν(NO) frequencies are in italic type, and bridging ν(CO) and ν(NO) frequencies are in bold type)

Species	BP86
25S-1 (C_1)	***1660(480)***, *1814(1064)*, 1990(44), 2000(770), 2007(908), 2023(1375), 2060(266)
25S-2 (C_2)	*1822(1969)*, *1826(39)*, **1881(385)**, 1989(108), 2006(1121), 2024(1403), 2051(4)
25S-3 (C_{2v})	*1790(98)*, *1847(1649)*, **1882(20)**, 1998(0), 2005(1628), 2028(1067), 2055(203)
25S-4 (C_s)	***1667(479)***, *1819(659)*, 1995(18), 2003(1607), 2003(627), 2025(1356), 2059(56)
25S-5 (C_s)	***1657(451)***, *1816(618)*, 1996(107), 2001(704), 2002(1539), 2026(1411), 2057(24)
25S-6 (C_s)	*1812(1071)*, *1840(751)*, **1875(903)**, **1905(373)**, 2001(922), 2012(547), 2058(538)
25S-7 (C_s)	*1822(727)*, *1849(891)*, 1973(1232), 1986(97), 1993(728), 2019(1040), 2057(252)
25T-1 (C_1)	***1611(540)***,*1729(760)*, 1993(5), 2000(733), 2006(1180), 2023(1681), 2055(109)

leads to **25S-1**. The Co–Co bond distance in **25S-5** is predicted to be 2.638 Å (BP86) or 2.652 Å (B3LYP), suggesting the formal single bond required to give both cobalt atoms the favored 18-electron configuration. The bridging NO group exhibits a typical bridging ν(NO) frequency at 1657 cm^{-1}.

The C_s singlet $Co_2(NO)_2(CO)_5$ structure **25S-6** (Fig. 6 and Table 6 and 7) is predicted to be a local minimum with all real vibrational frequencies. This structure, which is predicted to be a doubly carbonyl bridged structure by BP86 or an unbridged structure by B3LYP, lies 6.4 kcal mol^{-1} (BP86) or 8.3 kcal mol^{-1} (B3LYP) energetically above **25S-1**. The Co–Co bond distance in **25S-6** is predicted to be 2.577 Å (BP86) or 2.630 Å (B3LYP), consistent with the formal single bond required to give both cobalt atoms the favored 18-electron configuration. The two bridging CO groups in **25S-6** exhibit typical bridging ν(CO) frequencies at 1875 and 1905 cm^{-1} by BP86.

The energetically highest-lying singlet structure **25S-7** found for $Co_2(NO)_2(CO)_5$, (Fig. 6 and Table 6 and 7) lies 10.6 kcal mol^{-1} (BP86) or 10.5 kcal mol^{-1} (B3LYP) energetically above **25S-1**, with no imaginary vibrational frequencies. Structure **25S-7** is an unbridged structure consisting of a $Co(NO)_2(CO)$ unit and a $Co(CO)_4$ unit joined only by a Co–Co bond. The predicted Co–Co bond distance of 2.649 Å (BP86) or 2.669 Å (B3LYP) suggests the formal single bond needed to give each of the two cobalt atoms the favored 18-electron configuration. The two terminal NO groups exhibit typical terminal ν(NO) frequencies at 1822 and 1849 cm^{-1} by BP86.

A triplet structure **25T-1** was found for $Co_2(NO)_2(CO)_5$, (Fig. 6 and Table 6 and 7) at 26.3 kcal mol^{-1} (BP86) or 10.5 kcal mol^{-1} (B3LYP) above **25S-1**. Structure **25T-1** is a local minimum with all real vibrational frequencies. This structure is a singly nitrosyl bridged structure. The terminal nitrosyl group in **25T-1** is bent with a predicted Co–N–O angle of 148.6° (BP86) or 150.4° (B3LYP), suggesting that the bent NO group is a one-electron donor. The predicted Co–Co bond distance of 2.541 Å (BP86) or 2.594 Å (B3LYP) appears to be a single bond, thereby giving both cobalt atoms the favored 17-electron configuration consistent with a triplet binuclear structure, assuming the bridging NO group is a three-electron donor and the bent terminal nitrosyl group is a one-electron donor. The bridging NO group exhibits a typical bridging ν(NO) frequency at 1611 cm^{-1} by BP86. The bent terminal NO group in **25T-1** exhibits a ν(NO) frequency of 1729 cm^{-1}, which, as expected, is appreciably below the terminal linear ν(NO) frequencies found in the other $Co_2(NO)_2(CO)_5$ structures (Table 7).

3.2.2 $Co_2(NO)_2(CO)_4$.

Five singlet doubly bridged structures (Fig. 7, Table 8 and 9) were found for $Co_2(NO)_2(CO)_4$, including structures with two nitrosyl bridges, structures with two carbonyl bridges, and structures with one carbonyl and one nitrosyl bridge. No unbridged $Co_2(NO)_2(CO)_4$ structures were found at competitive energies.

The global minimum of $Co_2(NO)_2(CO)_4$ is predicted to be a doubly nitrosyl bridged structure **24S-4** or a doubly carbonyl bridged structure **24S-1** depending on the method. Thus the B3LYP method predicts **24S-4** as the global minimum with **24S-1** at ~1.8 kcal mol^{-1} higher in energy than **24S-4**. However, the BP86 method predicts **24S-1** to be the global minimum with **24S-4** lying energetically at ~5.2 kcal mol^{-1} above **24S-1**.

The $Co_2(NO)_2(CO)_4$ structure **24S-1** (Fig. 7, Table 8 and 9) is a singlet (S = 0) electronic state with C_s symmetry and two bridging carbonyl groups. The predicted ν(NO) frequencies are 1813 and 1824 cm^{-1} in a typical region for terminal nitrosyl groups. The bridging carbonyl groups in **24S-1** exhibit bridging ν(CO) frequencies which are relatively high at 1900 and 1910 cm^{-1} but nevertheless 85 cm^{-1} below the lowest terminal ν(CO) frequency (Table 9). The Co=Co bond distance in **24S-1** of 2.508 Å (BP86) or 2.535 Å (B3LYP)

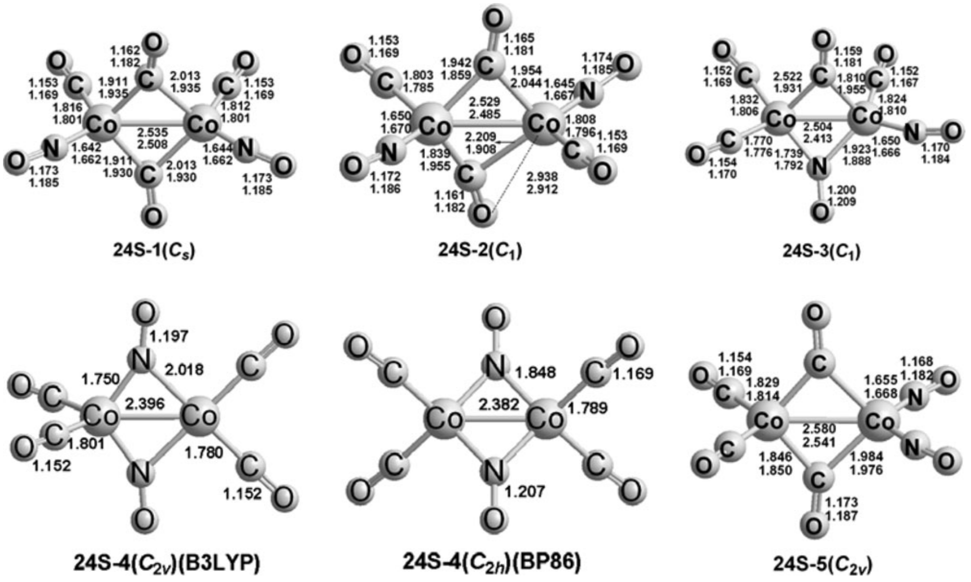


Fig. 7 The optimized structures of $Co_2(NO)_2(CO)_4$.

Table 8 The total energies (E, in hartrees), relative energies (ΔE, in kcal mol^{-1}), numbers of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized $Co_2(NO)_2(CO)_4$ structures

	BP86				B3LYP			
Species	$-E_{total}$	ΔE	N_{Imag}	Co–N–O	$-E_{total}$	ΔE	N_{Imag}	Co–N–O
24S-1 (C_s)	3479.599880	0.0	0	169.8,169.8	3479.029388	0	0	169.7,171.1
24S-2 (C_1)	3479.599399	0.3	0	162.6,165.5	3479.030149	−0.5	0	164.0,168.6
24S-3 (C_1)	3479.595495	2.8	0	166.1	3479.030653	−0.8	0	173.2
24S-4	3479.591530	5.2	0	150.3,131.1	3479.032332	−1.8	0	139.0,139.0
24S-5 (C_{2v})	3479.588518	7.1	0	172.0,172.0	3479.010529	11.8	0	173.8,173.8

Table 9 The infrared ν(CO) and ν(NO) vibrational frequencies (cm^{-1}) predicted for the $Co_2(NO)_2(CO)_4$ structures (infrared intensities in parentheses are in km mol^{-1}, ν(NO) frequencies are italic type, and bridging ν(CO) and ν(NO) frequencies are in bold type)

Species	BP86
24S-1 (C_s)	*1813(1591)*, *1824(707)*, **1900(969)**, **1910(450)**, 1995(765), 2031(707)
24S-2 (C_1)	*1805(2222)*, *1814(64)*, **1902(870)**, **1914(115)**, 2003(1809), 2029(10)
24S-3 (C_1)	***1649(591)***, *1826(1194)*, **1913(569)**, 1988(459), 2008(1592), 2042(405)
24S-4	***1640(1059)***, ***1671(0)***, 1988(0), 1996(1550), 2015(1984), 2045(0)
24S-5 (C_{2v})	*1823(1040)*, *1850(879)*, **1869(936)**, **1887(671)**, 1983(1084), 2028(585)

can be interpreted as the double bond needed to give both cobalt atoms the 18-electron configuration.

The other energetically low-lying structure **24S-2** is a local minimum, lying either 0.3 kcal mol^{-1} above **24S-1** (BP86) or 0.5 kcal mol^{-1} below **24S-1** (B3LYP) so that structures **24S-1** and **24S-2** are essentially degenerate. This is not surprising since structures **24S-1** and **24S-2** differ only in the relative arrangements of the terminal nitrosyl groups, with structure **24S-1** being the *cis* isomer and structure **24S-2** being the *trans* isomer. This **24S-2** structure has two unsymmetrical bridging carbonyl groups and two nearly linear (162.6°/165.5° by BP86 or 164.0°/168.6° by B3LYP) terminal nitrosyl groups. The relatively long Co···O distances of about 2.912 Å (BP86) or 2.938 Å (B3LYP) to the bridging carbonyl groups in **24S-2** and the bridging ν(CO) frequencies at 1902 and 1914 cm^{-1} suggest that they are both two-electron donors. The linear terminal ν(NO) groups exhibit typical terminal ν(NO) frequencies at 1805 and 1814 cm^{-1}. The Co═Co bond distance of 2.485 Å (BP86) or 2.529 Å (B3LYP) can be interpreted as the double bond needed to give both cobalt atoms the favored 18-electron configuration.

A C_1 singlet structure of $Co_2(NO)_2(CO)_4$, namely **24S-3**, lies above **24S-1** by only 2.8 kcal mol^{-1} by BP86 or below **24S-1** by 0.8 kcal mol^{-1} by B3LYP and has all real harmonic vibrational frequencies. Structure **24S-3** has one bridging CO group, one bridging NO group, and one nearly linear (166.1° by BP86 or 173.2° by B3LYP) terminal nitrosyl group. The ν(NO) frequencies at 1649 and 1826 cm^{-1} correspond to the bridging and terminal nitrosyl groups, respectively. The Co═Co bond distance of 2.413 Å (BP86) or 2.504 Å (B3LYP) in **24S-3** is consistent with a double bond, thereby giving each of the cobalt atoms the favored 18-electron configuration.

The fourth $Co_2(NO)_2(CO)_4$ structure **24S-4** is predicted to have two bridging nitrosyl groups exhibiting ν(NO) frequencies in the region typical for bridging nitrosyl groups at 1640 and 1671 cm^{-1}. This structure is predicted to have C_{2h} symmetry using BP86 or C_{2v} symmetry using B3LYP, with all real harmonic vibrational frequencies in each case. The Co═Co bond distance of 2.382 Å (BP86) or 2.396 Å (B3LYP) in **24S-4** is consistent with the double bond required to give both cobalt atoms the favored 18-electron configuration.

The last structure of $Co_2(NO)_2(CO)_4$ is the C_{2v} structure **24S-5** with all real harmonic vibrational frequencies and lying 7.1 kcal mol^{-1} (BP86) or 11.8 kcal mol^{-1} (B3LYP) above **24S-1**. Structure **24S-5** has two bridging carbonyl groups predicted to exhibit ν(CO) frequencies at 1869 and 1887 cm^{-1} (BP86). In **24S-5** one cobalt atom has two terminal carbonyl groups whereas the other cobalt atom has two terminal nitrosyl groups. The Co–Co bond distance of 2.541 Å (BP86) or 2.580 Å (B3LYP) in **24S-5** is consistent with a single bond leading to the favored 18-electron configuration for one cobalt atom but only a 16-electron configuration for the other cobalt atom. The cobalt atom in **24S-5** with a formal 16-electron configuration is probably the one bearing the two terminal carbonyl groups, since a carbonyl group donates one less electron than a neutral nitrosyl group.

3.2.3 $Co_2(NO)_2(CO)_3$.

A total of eight stationary points were found after optimization for $Co_2(NO)_2(CO)_3$ (Fig. 8 and Table 10 and 11), indicating a rather complicated potential energy surface. The global minimum for $Co_2(NO)_2(CO)_3$ is the beautiful triply carbonyl bridged D_{3h} structure **23S-1**. The ν(CO) frequencies at 1921 and 1967 cm^{-1} correspond to the three bridging carbonyl groups. The predicted terminal ν(NO) frequencies for **23S-1** are 1845 and 1854 cm^{-1}. The very short predicted Co≡Co distance in **23S-1** of 2.182 Å (BP86) or 2.191 Å (B3LYP) is consistent with the triply bridged formal triple bond required to give both cobalt atoms the favored 18-electron rare gas configuration.

A C_s structure **23S-2** was found for $Co_2(NO)_2(CO)_3$ with one bridging carbonyl group and one bridging nitrosyl group (Fig. 8 and Table 10 and 11). This structure is a genuine minimum with no imaginary vibrational frequencies and lies 11.0 kcal mol^{-1} (BP86) or 2.6 kcal mol^{-1} (B3LYP) energetically above the global minimum **23S-1**. The Co···O distances of 2.812 Å (BP86) or 2.832 Å (B3LYP) to the bridging carbonyl group in **23S-2** are too long for this carbonyl group to be a four-electron donor. The latter conclusion is also consistent with the normal bridging ν(CO) frequency at 1897 cm^{-1}. The ν(NO) frequencies at 1667 and 1836 cm^{-1} correspond to the bridging and the terminal nitrosyl groups, respectively. The Co≡Co bond distance of 2.358 Å (BP86) or 2.373 Å (B3LYP) in **23S-2** can correspond to the formal triple bond required to give both cobalt atoms the favored 18-electron configuration. The longer Co≡Co triple bond in **23S-2** relative to that in **23S-1** can relate to the presence of only two bridging groups in **23S-2** in contrast to the three bridging groups in **23S-1**. Bridging groups almost invariably reduce metal–metal bond distances.

A second doubly carbonyl bridging $Co_2(NO)_2(CO)_3$ structure **23S-3** with C_1 symmetry and no imaginary vibrational frequencies lie 12.3 kcal mol^{-1} (BP86) or 6.8 kcal mol^{-1} (B3LYP) energetically above the global minimum **23S-1** (Fig. 8 and Table 10 and 11). The ν(CO) frequencies in **23S-3** at 1899 and 1924 cm^{-1} correspond to the two bridging carbonyl groups. The ν(NO) frequencies at 1823 and 1833 cm^{-1} correspond to the two terminal nitrosyl groups. The Co≡Co bond distance of 2.304 Å (BP86) or 2.310 Å (B3LYP) in **23S-3** can correspond to a doubly bridged triple bond giving each cobalt atom the favored 18-electron configuration.

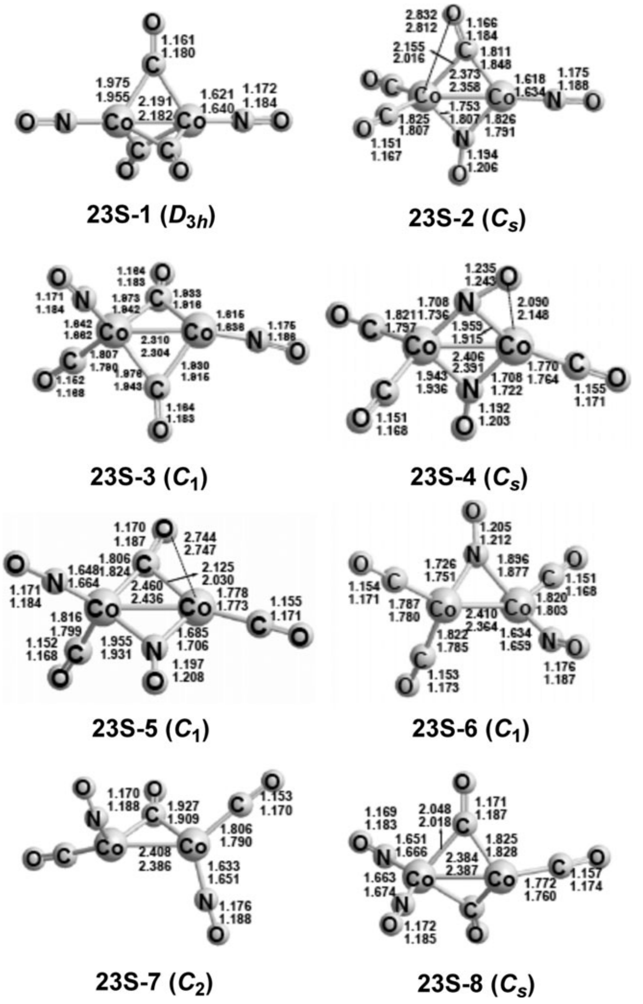

23S-1 (D_{3h})
23S-2 (C_s)
23S-3 (C_1)
23S-4 (C_s)
23S-5 (C_1)
23S-6 (C_1)
23S-7 (C_2)
23S-8 (C_s)

Fig. 8 The optimized structures of $Co_2(NO)_2(CO)_3$.

The next $Co_2(NO)_2(CO)_3$ structure **23S-4** has C_s symmetry without any imaginary vibrational frequencies and lies 16.7 kcal mol^{-1} (BP86) or 1.3 kcal mol^{-1} (B3LYP) energetically above the global minimum **23S-1**. Structure **23S-4** has two bridging NO groups. The very short Co···O distances of 2.148 Å (BP86) or 2.090 Å (B3LYP) to the upper bridging nitrosyl group (Fig. 8) in **23S-4** and the very low bridging ν(NO) frequency at 1497 cm^{-1} (Table 11) suggest that this NO group is a formal five-electron donor. The other predicted ν(NO) frequency is 1693 cm^{-1}, which is consistent with a typical formal three-electron donor. Thus **23S-4** is of interest since it has both three-electron donor and five-electron donor bridging nitrosyl groups. The Co═Co bond distance of 2.391 Å (BP86) or 2.406 Å (B3LYP) in **23S-4** can be interpreted as the formal double bond required to give both cobalt atoms the favored 18-electron configurations.

The next $Co_2(NO)_2(CO)_3$ structure is the C_1 structure **23S-5**, with no imaginary vibrational frequencies and lying 16.9 kcal mol^{-1} (BP86) or 7.2 kcal mol^{-1} (B3LYP)

Table 10 The total energies (E, in hartrees), relative energies (ΔE, in kcal mol^{-1}), numbers of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized $Co_2(NO)_2(CO)_3$ structures

	BP86				B3LYP			
Species	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O	$-E_{\text{total}}$	ΔE	N_{Imag}	Co–N–O
23S-1 (D_{3h})	3366.236952	0	0	180.0,180.0	3365.667589	0	0	180.0,180.0
23S-2 (C_s)	3366.219421	11.0	0	178.3	3365.663379	2.6	0	175.4
23S-3 (C_1)	3366.217326	12.3	0	169.5,174.8	3365.656806	6.8	0	172.4,175.1
23S-4 (C_s)	3366.210403	16.7	0	—	3365.665521	1.3	0	—
23S-5 (C_1)	3366.209963	16.9	0	170.5	3365.656120	7.2	0	172.4
23S-6 (C_1)	3366.201566	22.2	0	155.9	3365.654352	8.3	0	161.0
23S-7 (C_2)	3366.199603	23.4	0	159.5,159.5	3365.648210	12.2	0	160.4,160.4
23S-8 (C_s)	3366.199208	23.8	0	178.7,179.9	3365.631841	22.4	0	179.7,179.8

Table 11 The infrared ν(CO) and ν(NO) vibrational frequencies (cm^{-1}) predicted for the $Co_2(NO)_2(CO)_3$ structures (infrared intensities in parentheses are in km mol^{-1}, ν(NO) frequencies are in italic type, and bridging ν(CO) and ν(NO) frequencies are in bold type)

Species	BP86
23S-1 (D_{3h})	*1845(2361)*, *1854(0)*, **1921(969)**, **1921(969)**, **1967(0)**
23S-2 (C_s)	***1667(495)***, *1836(1361)*, **1897(679)**,1996(945), 2037(679)
23S-3 (C_1)	*1823(1906)*, *1833(487)*, **1899(1033)**, **1924(120)**, 2025(765)
23S-4 (C_s)	***1497(435)***, ***1693(353)***, 2002(826), 2009(1759), 2045(216)
23S-5 (C_1)	***1667(415)***, *1829(1194)*, **1887(563)**, 1999(1679), 2030(290)
23S-6 (C_1)	***1638(490)***, *1795(909)*, 1971(864), 2004(1841), 2033(129)
23S-7 (C_2)	*1795(1573)*, *1807(519)*, **1874(207)**, 2000(1855), 2026(172)
23S-8 (C_s)	*1815(1213)*, *1844(828)*, **1879(954)**, **1900(668)**, 2001(834)

energetically above the global minimum **23S-1**. This structure has one bridging NO group and one bridging CO group. The Co···O distances of about 2.747 Å (BP86) or 2.744 Å (B3LYP) to the bridging carbonyl group in **23S-5** are too long to identify the bridging CO group as a four-electron donor. This is consistent with the normal bridging ν(CO) frequency at 1887 cm^{-1}. The ν(NO) frequencies at 1667 and 1829 cm^{-1} correspond to the bridging nitrosyl group and the terminal nitrosyl group, respectively. The Co=Co bond distance of 2.436 Å (BP86) or 2.460 Å (B3LYP) in **23S-5** is consistent with a formal double bond, giving the "left" cobalt atom the favored 18-electron configuration, and the "right" cobalt atom a 16-electron configuration.

The lowest energy singly bridged structure predicted for $Co_2(NO)_2(CO)_3$ is the C_1 structure **23S-6** with no imaginary vibrational frequencies and lying 22.2 kcal mol^{-1} (BP86) or 8.3 kcal mol^{-1} (B3LYP) energetically above the global minimum **23S-1**. Structure **23S-6** has one bridging NO group. The ν(NO) frequencies in **23S-6** at 1638 and 1795 cm^{-1} correspond to the bridging nitrosyl group and the terminal nitrosyl group, respectively. The Co≡Co bond distance of 2.364 Å (BP86) or 2.410 Å (B3LYP) in **23S-6** can correspond to the singly bridged formal triple bond required to give both cobalt atoms the favored 18-electron configuration.

A higher energy singly carbonyl bridged C_2 structure **23S-7** was also found for $Co_2(NO)_2(CO)_3$ with no imaginary vibrational frequencies and lying 23.4 kcal mol^{-1} (BP86) or 12.2 kcal mol^{-1} (B3LYP) energetically above the global minimum **23S-1**. The ν(CO) frequency at 1874 cm^{-1} corresponds to the bridging carbonyl group. The ν(NO) frequencies at 1795 and 1807 cm^{-1} correspond to the two terminal nitrosyl groups. The Co≡Co bond distance of 2.386 Å (BP86) or 2.408 Å (B3LYP) in **23S-7** is close to that found in the singly nitrosyl bridging structure **23S-6** with a triple bond required to give both cobalt atoms the favored 18-electron configuration.

The last structure predicted for $Co_2(NO)_2(CO)_3$ is the doubly carbonyl bridged C_s structure **23S-8** with no imaginary vibrational frequencies and lying 23.8 kcal mol^{-1} (BP86) or 22.4 kcal mol^{-1} (B3LYP) energetically above the global minimum **23S-1**. The ν(CO) frequencies at 1879 and 1900 cm^{-1} correspond to the bridging carbonyl groups. The ν(NO) frequencies at 1815 and 1844 cm^{-1} correspond to the two terminal nitrosyl groups. The Co≡Co bond distance of 2.387 Å (BP86) or 2.384 Å (B3LYP) in **23S-8** can correspond to the formal triple bond required to give both cobalt atoms the favored 18-electron configuration.

3.2.4 $Co_2(NO)_2(CO)_2$.

Three energetically low-lying structures are predicted for $Co_2(NO)_2(CO)_2$ (Fig. 9 and Table 12 to 13), for which the 18-electron rule predicts a Co≣Co quadruple bond, assuming that both nitrosyl groups are three-electron donors and all of the carbonyl groups are

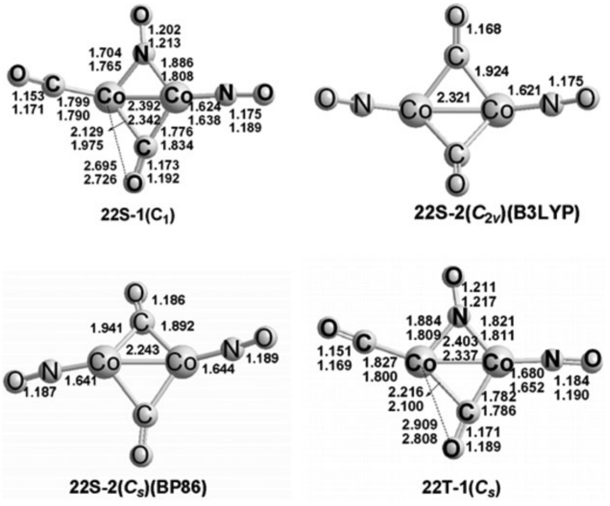


Fig. 9 Optimized structures of $Co_2(NO)_2(CO)_2$.

Table 12 The total energies (E, in hartrees), relative energies (ΔE, in kcal mol^{-1}), number of imaginary vibrational frequencies (N_{Imag}), and angles Co–N–O for the optimized $Co_2(NO)_2(CO)_2$ structures

	BP86				B3LYP			
Species	$-E_{\mathrm{total}}$	ΔE	N_{Imag}	Co–N–O	$-E_{\mathrm{total}}$	ΔE	N_{Imag}	Co–N–O
22S-1 (C_1)	3252.823332	0	0	173.4	3252.278813	0	0	171.9
22S-2	3252.822498	0.5	0	167.5,171.0	3252.271759	4.4	0	169.9,169.9
22T-1 (C_s)	3252.807703	9.8	0	175.1	3252.292087	−8.3	0	174.4

two-electron donors. The two DFT methods disagree on the relative energies of these three structures. Thus the BP86 method predicts **22S-1** to lie below **22T-1** by 9.8 kcal mol^{-1}, whereas the B3LYP method predicts **22T-1** to lie below **22S-1** by 8.3 kcal mol^{-1}.

The C_1 doubly bridged $Co_2(NO)_2(CO)_2$ structure **22S-1** has no imaginary vibrational frequencies and is thus a genuine minimum. Structure **22S-1** has one bridging NO group and one bridging CO group. The ν(NO) frequencies at 1636 and 1826 cm^{-1} correspond to the bridging nitrosyl group and the terminal nitrosyl group, respectively. The Co$\equiv$Co bond distance in the singlet doubly bridged $Co_2(NO)_2(CO)_2$ structure **22S-1** is 2.342 Å (BP86) or 2.392 Å (B3LYP) corresponding to a formal triple bond to give one of the cobalt atoms the favored 18-electron configuration but the other cobalt atom only a 16-electron configuration.

A doubly carbonyl bridged structure **22S-2** is also predicted for $Co_2(NO)_2(CO)_2$ with no imaginary vibrational frequencies and lying 0.5 kcal mol^{-1} (BP86) or 4.4 kcal mol^{-1} (B3LYP) energetically above **22S-1**. Structure **22S-2** has C_s symmetry when optimized by the BP86 method but C_{2v} symmetry when optimized by the B3LYP method. The two NO groups are on opposite sides of the symmetry plane in the BP86 structure but on the same side of the plane in the B3LYP structure. The ν(CO) frequencies at 1884 and 1919 cm^{-1} correspond to the bridging carbonyl groups. The ν(NO) frequencies at 1812 and 1824 cm^{-1} correspond to the linear terminal nitrosyl groups. The Co$\equiv$Co distance of 2.243 Å (BP86) or 2.321 Å (B3LYP) in **22S-2** is slightly shorter than any of the cobalt–cobalt distances in the other doubly bridged structures in this paper and thus could correspond to the formal quadruple bond required to give both cobalt atoms the favored 18-electron configuration.

The C_s triplet structure **22T-1** for $Co_2(NO)_2(CO)_2$ is like the singlet structure **22S-1** in that it has one bridging NO group and one bridging CO group. The ν(NO) frequencies at 1618 and 1817 cm^{-1} correspond to the bridging nitrosyl group and the terminal nitrosyl group, respectively. The Co$\equiv$Co bond distance in **22T-1** is 2.337 Å (BP86) or 2.403 Å (B3LYP), consistent with a formal triple bond corresponding to 17-electron configurations for both cobalt atoms consistent with a dimeric triplet.

Table 13 The infrared ν(CO) and ν(NO) vibrational frequencies (cm^{-1}) predicted for the $Co_2(NO)_2(CO)_2$ structures (infrared intensities in parentheses are in km mol^{-1}, ν(NO) frequencies are in italic type, and bridging ν(CO) and ν(NO) frequencies are in bold type)

Species	BP86
22S-1 (C_1)	***1636(491)***, *1826(1282)*, **1868(745)**, 2007(921)
22S-2	*1812(2450)*, *1824(68)*, **1884(1150)**, **1919(45)**
22T-1 (C_s)	***1618(498)***, *1817(1416)*, **1885(735)**, 2017(1072)

3.3 Thermodynamics.

The CO dissociation energies for the global minima of the mononuclear cobalt carbonyl nitrosyls $Co(NO)(CO)_n$ (n = 4, 3, 2) are listed in Table 14. The dissociation of one carbonyl group from the global minimum of $Co(NO)(CO)_4$ to give $Co(NO)(CO)_3$ is seen to be an exothermic process by 8.4 kcal mol^{-1} (BP86) or 10.1 kcal mol^{-1} (B3LYP). This indicates that the "lone pair" on a one-electron donor bent nitrosyl group can readily displace a carbonyl group to become a linear three-electron donor nitrosyl group (Fig. 1). This is why the reaction of $Co_2(CO)_8$ with NO is observed experimentally[3] to go directly to $Co(NO)(CO)_3$ without any evidence for the formation of an isolable $Co(NO)(CO)_4$ intermediate.

The energies for the subsequent dissociation of carbonyl groups from $Co(NO)(CO)_3$ are all endothermic. The predicted CO dissociation energy from $Co(NO)(CO)_3$ of 42.5 kcal mol^{-1} (BP86) or 34.9 kcal mol^{-1} (B3LYP) is significantly higher than the 27 kcal mol^{-1} experimental[38] CO dissociation energy of the isoelectronic $Ni(CO)_4$.

The dissociation energy of $Co(NO)(CO)_4$ into NO + $Co(CO)_4$ radicals (Table 14) is predicted to be endothermic by 21.6 kcal mol^{-1} (BP86) or 3.1 kcal mol^{-1} (B3LYP). This means that the reverse reaction of $Co(CO)_4$ + NO to give $Co(NO)(CO)_4$ is exothermic. Since CO loss from $Co(NO)(CO)_4$ to give $Co(NO)(CO)_3$ is also exothermic as

Table 14 Bond dissociation energies (kcal mol^{-1}) for the optimized $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3) and $Co(NO)(CO)_m$ (m = 4, 3, 2) structures

Dissociation processes	BP86	B3LYP
$Co(NO)(CO)_4 \rightarrow {}^{\bullet}Co(CO)_4 + NO$	21.6	3.1
$Co(NO)(CO)_4 \rightarrow Co(NO)(CO)_3 + CO$	−8.4	−10.1
$Co(NO)(CO)_3 \rightarrow Co(NO)(CO)_2 + CO$	42.5	34.9
$Co(NO)(CO)_2 \rightarrow Co(NO)(CO) + CO$	44.3	37.4
$Co_2(NO)_2(CO)_5 \rightarrow Co_2(NO)_2(CO)_4 + CO$	27.2	27.1
$Co_2(NO)_2(CO)_4 \rightarrow Co_2(NO)_2(CO)_3 + CO$	22.4	20.8
$Co_2(NO)_2(CO)_3 \rightarrow Co_2(NO)_2(CO)_2 + CO$	54.2	37.7
$Co_2(NO)_2(CO)_5 \rightarrow Co(NO)(CO)_4 + Co(NO)(CO)$	70.1	57.6
$Co_2(NO)_2(CO)_5 \rightarrow Co(NO)(CO)_3 + Co(NO)(CO)_2$	17.5	10.1
$Co_2(NO)_2(CO)_4 \rightarrow 2Co(NO)(CO)_2$	32.8	18.0
$Co_2(NO)_2(CO)_4 \rightarrow Co(NO)(CO)_3 + Co(NO)(CO)$	34.6	20.4
$Co_2(NO)_2(CO)_3 \rightarrow Co(NO)(CO)_2 + Co(NO)(CO)$	54.7	34.5

[a] All results reported refer to the lowest energy structures of reactant and products.

noted above, the known reaction[3] of $Co_2(CO)_8$ with NO to give $Co(NO)(CO)_3$ appears to be favored thermodynamically.

Table 14 also reports some dissociation energies involving the binuclear cobalt carbonyl nitrosyls $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3). In this connection there are at least two different pathways for the dissociation for each binuclear $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3) derivative, namely dissociation of a carbonyl group (eqn (1)) or dissociation into two pairs of mononuclear $Co(NO)(CO)_m$ (m = 4, 3, 2) units (eqn (2)).

$$Co_2(NO)_2(CO)_n \rightarrow Co_2(NO)_2(CO)_{n-1} + CO\ (n = 5, 4, 3) \quad (1)$$

$$Co_2(NO)_2(CO)_n \rightarrow Co(NO)(CO)_m + Co(NO)(CO)_{n-m} \quad (n = 5, 4, 3;\ m = 4, 3, 2) \quad (2)$$

The CO dissociation energies from $Co_2(NO)_2(CO)_n$ to give $Co_2(NO)_2(CO)_{n-1}$ (n = 5, 4, 3) are computed to be much less than those for the dissociation of $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3) into mononuclear fragments $Co(NO)(CO)_m$ (m = 4, 3, 2). This indicates the strength of the cobalt–cobalt interactions in all of these structures.

4. Discussion

4.1 Mononuclear derivatives

The geometrical structures $Co(NO)(CO)_n$ (n = 4, 3, 2, 1) were all fully optimized. For $Co(NO)(CO)_4$ the favored 18-electron configuration requires the nitrosyl group to be a bent one-electron donor. Such a structure, namely **14S-1** (Fig. 2 and Table 1), was found. However, it was found to be thermodynamically unstable with respect to CO dissociation to give the known[3,4] $Co(NO)(CO)_3$ (**13S-1** in Fig. 3 and Table 3), which has a linear formal three-electron donor nitrosyl group and the favored 18-electron configuration. A triplet higher energy structure, namely **13T-1**, was also found for $Co(NO)(CO)_3$ with a bent rather than linear nitrosyl group. The single electron donated by the bent nitrosyl group in **13T-1** gives the cobalt atom a 16-electron configuration, consistent with the triplet spin multiplicity.

The structures predicted for the unsaturated mononuclear cobalt carbonyl nitrosyls $Co(NO)(CO)_n$ (n = 2, 1) are closely related to those previously predicted for the isoelectronic nickel carbonyls[6] $Ni(CO)_{n+1}$. Thus the lowest energy structure for $Co(NO)(CO)_2$, namely **12S-1** (Fig. 4 and Table 4), is trigonal like the previously studied isoelectronic $Ni(CO)_3$. Similarly the lowest energy structure for Co(NO)(CO), namely **11S-1** (Fig. 5 and Table 5), has angular rather than linear coordination of the central cobalt atom, similar to that of the nickel atom in the isoelectronic $Ni(CO)_2$. The infrared ν(CO) and ν(NO) frequencies for $Co(NO)(CO)_n$ (n = 2, 1) predicted in this work are within 40 cm^{-1} of the experimental data from the low-temperature matrix studies.[5]

4.2 Binuclear structures

The binuclear structures $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3, 2) found in this research can be compared with the isoelectronic $Ni_2(CO)_{n+2}$ structures previously studied.[6] However, the $Co_2(NO)_2(CO)_n$ energy surfaces are considerably more complicated since there are two types of ligands (NO + CO) whereas the $Ni_2(CO)_{n+2}$ structures have only carbonyl ligands.

The lowest energy structure previously found by DFT[6] for $Ni_2(CO)_7$ is a singly bridged $Ni_2(CO)_6(\mu\text{-}CO)$ structure and even this structure is barely thermodynamically stable (by only ~1 kcal mol^{-1}) with respect to dissociation to $Ni(CO)_4$ + $Ni(CO)_3$. Similar structures with either a single bridging nitrosyl group (**25S-1**) or a singly bridging carbonyl group (**25S-2**) were found for the isoelectronic $Co_2(NO)_2(CO)_5$ (Fig. 6 and Table 6). The energies of the $Co_2(NO)_2(CO)_5$ structure with the bridging nitrosyl group (**25S-1**) and that with the bridging carbonyl group (**25S-2**) are predicted to be essentially equivalent (within ~2 kcal mol^{-1}), suggesting no significant preference for a bridging nitrosyl group over a bridging carbonyl group for this system. Either of these $Co_2(NO)_2(CO)_5$ structures has modest stability relative to dissociation into $Co(NO)(CO)_3$ + $Co(NO)(CO)_2$ by 10 to 17 kcal mol^{-1} (Table 14) suggesting some stabilization by the nitrosyl ligands with respect to dissociation. The predicted Co–Co single bond distance of 2.67 ± 0.03 Å in the singly carbonyl bridged $Co_2(NO)_2(CO)_5$ structure **25S-2** (Fig. 6) is close to the predicted Ni–Ni single bond distance of 2.70 ± 0.03 Å in $Ni_2(CO)_7$.

The lowest energy structure previously found by DFT[6] for the unsaturated $Ni_2(CO)_6$ is a doubly bridged $Ni_2(CO)_4(\mu\text{-}CO)_2$ structure with an Ni═Ni distance suggesting the formal double bond required by the 18-electron rule. Several similar doubly bridged structures were found for the isoelectronic $Co_2(NO)_2(CO)_4$ with various combinations of nitrosyl and carbonyl groups in the bridges. The energy differences between carbonyl and nitrosyl bridges were relatively small (5 kcal mol^{-1} or less) for these $Co_2(NO)_2(CO)_4$ structures, suggesting a highly fluxional system with interchange of bridging carbonyl and nitrosyl ligands. The predicted Co═Co double bond distance in the lowest energy doubly carbonyl bridged $Co_2(NO)_2(CO)_4$ structure, namely **24S-1** (Fig. 7 and Table 8), is 2.52 ± 0.02 Å, which is reasonably close to the predicted Ni═Ni double bond distance of 2.54 ± 0.02 Å in $Ni_2(CO)_6$.

The only structure previously found by DFT[6] for the unsaturated $Ni_2(CO)_5$ is a triply bridged $Ni_2(CO)_2(\mu\text{-}CO)_3$ structure with a very short Ni≡Ni distance suggesting the formal triple bond required by the 18-electron rule. This $Ni_2(CO)_5$ structure was predicted[6] to be much more stable towards dissociation into mononuclear fragments than the less highly unsaturated structures $Ni_2(CO)_6$ and $Ni_2(CO)_7$. A similar triply carbonyl bridged structure **23S-1** is found for $Co_2(NO)_2(CO)_3$ as the global minimum by both methods (Fig. 8 and Table 10). The predicted Co≡Co triple bond distance of 2.19 ± 0.01 Å in the triply carbonyl bridged $Co_2(NO)_2(CO)_3$ structure **23S-1** (Fig. 8) is essentially identical to the predicted Ni≡Ni triple bond distance[6] in $Ni_2(CO)_5$. Higher energy doubly and singly bridged structures were also found for $Co_2(NO)_2(CO)_3$ for which no $Ni_2(CO)_5$ counterparts were found in the previous work.[6]

Our studies of the binuclear cobalt carbonyl nitrosyls included the even more unsaturated $Co_2(NO)_2(CO)_2$ required by the 18-electron rule to have a Co≣Co quadruple bond if all carbonyl groups are two electron donors and all nitrosyl groups are three-electron donors. Such a high degree of unsaturation was not anticipated in the nickel carbonyl work approximately ten years ago[6] where $Ni_2(CO)_4$ would have been the analogue to $Co_2(NO)_2(CO)_2$. All of the three optimized structures for $Co_2(NO)_2(CO)_2$ have two bridging groups (Fig. 9). The Co···O distances to the clearly unsymmetrical bridging carbonyl groups in **22S-1** and **22T-1** of 2.7 to 2.9 Å and some distortion of this bridging carbonyl group suggest the possibility of a weak cobalt–oxygen interaction. However, such Co···O distances are much longer than the Co–O distances for a true four-electron donor bridging carbonyl group. Also the ν(CO) frequencies of these somewhat unusual bridging carbonyl groups in **22S-1** and **22T-1** are in the normal region. Therefore, these bridging carbonyl groups are probably best considered as a slightly different type of two-electron bridging carbonyl group.

5. Conclusion

The lowest energy structures for the mononuclear derivatives $Co(NO)(CO)_n$ (n = 3, 2, 1) predicted by DFT have linear nitrosyl groups and parallel those of the corresponding isomeric $Ni(CO)_{n+1}$ derivatives. In addition, a $Co(NO)(CO)_4$ structure is predicted with a bent nitrosyl group, namely **14S-1** (Fig. 2). However, this structure is thermodynamically unstable with respect to CO loss to give $Co(NO)(CO)_3$, with concurrent conversion of the bent nitrosyl group to a linear nitrosyl group.

The potential energy surfaces of the binuclear cobalt carbonyl nitrosyl derivatives $Co_2(NO)_2(CO)_n$ (n = 5, 4, 3, 2) are complicated by the similar energies of analogous structures with bridging carbonyl or bridging nitrosyl groups. However, they are analogous to the previously predicted structures[6] of the isoelectronic binuclear nickel carbonyls $Ni_2(CO)_{n+2}$. Thus the lowest energy structures of $Co_2(NO)_2(CO)_5$, $Co_2(NO)_2(CO)_4$, and $Co_2(NO)_2(CO)_3$ have one, two, and three bridging groups, respectively, just like the isoelectronic $Ni_2(CO)_{n+2}$. For $Co_2(NO)_2(CO)_5$ and $Co_2(NO)_2(CO)_4$ the otherwise analogous structures with bridging carbonyl and/or nitrosyl groups are of very similar energies. However, for $Co_2(NO)_2(CO)_3$ there appears to be a particularly stable triply carbonyl bridged structure with an unusually short Co≡Co distance consistent with the formal triple bond required to give the cobalt atoms the favored 18-electron configuration.

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