pressure the concentration of CO in solution was taken to be 4.64 mM.[27]

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Registry No. **1**, 61114-07-6; **1**·*p*-NC(C_6H_4)NC, 71171-29-4; **1**·*p*-NO_2(C_6H_4)NC, 71171-30-7; **1**·P(OC_6H_{11})$_3$, 71171-31-8; **1**·P(OBu)$_3$, 71171-32-9; **1**·P(O-*p*-C_6H_4Cl)$_3$, 71171-33-0; **1**·CO, 61128-83-4; **1**·P(OC_6H_5)$_3$, 71194-22-4; **1**·P(O-*p*-$C_6H_4CH_3$)$_3$, 71171-22-7; **1**·P(O-*o*-$C_6H_4CH_3$)$_3$, 71194-23-5; **1**·P(*p*-C_6H_4Cl)$_3$, 71194-24-6; **1**·P(*p*-$C_6H_4CH_3$)$_3$, 71171-23-8; **1**·P(C_6H_5)$_3$, 71171-24-9; **1**·P(*o*-$C_6H_4OCH_3$)$_3$, 71171-25-0; **1**·P(*o*-$C_6H_4CH_3$)$_3$, 71171-26-1; **1**·$(CH_3)_2N(C_6H_5)$, 71171-27-2; **1**·py, 66069-81-6; **1**·4-$(CH_3)_2$N(py), 71171-12-5; **1**·4-CH_3O_2C(py), 71171-13-6; **4**, 64783-09-1; **4**·*p*-NC(C_6H_4)NC, 71171-14-7; **4**·*p*-NO_2(C_6H_4)NC, 71171-15-8; **4**·P(OC_6H_{11})$_3$, 71171-16-9; **4**·P(OBu)$_3$, 71171-17-0; **4**·P(O-*p*-C_6H_4Cl)$_3$, 71171-18-1; **4**·CO, 71171-19-2; **4**·P(OC_6H_5)$_3$, 71171-20-5; **4**·P(O-*p*-$C_6H_4CH_3$)$_3$, 71171-21-6; **4**·P(O-*o*-$C_6H_4CH_3$)$_3$, 71171-03-4; **4**·P(*p*-C_6H_4Cl)$_3$, 71171-04-5; **4**·P(*p*-$C_6H_4CH_3$)$_3$, 71171-05-6; **4**·P(C_6H_5)$_3$, 71171-06-7; **4**·P(*o*-$C_6H_4OCH_3$)$_3$, 71171-07-8; **4**·P(*o*-$C_6H_4CH_3$)$_3$, 71171-08-9; **4**·$(CH_3)_2N(C_6H_5)$, 71171-09-0; **4**·py, 66070-14-2; **4**·4-$(CH_3)_2$N(py), 71171-10-3; **4**·4-CH_3O_2C(py), 71171-11-4; **8**·CO, 71170-93-9; **8**·*p*-NO_2(C_6H_4)NC, 71170-94-0; **9**·CO, 71194-20-2; **9**·*p*-NO_2(C_6H_4)NC, 71170-95-1; **11**·CO, 71170-96-2; **12**·$(ClO_4)_2$, 71170-98-4; **12**·CO, 71170-99-5; **12**·*p*-NO_2(C_6H_4)NC, 71171-00-1; **13**·ClO_4, 71171-01-2; **13**·CO, 71171-02-3; **14**·ClO_4, 71171-35-2; **14**·CO, 71171-36-3; **15**·CO, 71171-37-4; **15**·*p*-NO_2(C_6H_4)NC, 71171-38-5; **16**, 71170-91-7; **17**, 71170-92-8.

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Relative Stability of Bent and Linear Coordination of the Nitrosyl Ligand in Nitrosylpentaamminecobalt(III), $Co(NH_3)_5NO^{2+}$. An ab Initio Investigation

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The stability of the complex $Co(NH_3)_5NO^{2+}$ is investigated within the ab initio SCF framework, as a function of the angle at which the nitrosyl is coordinated. We find, in agreement with experiment, that the most stable conformer is one in which the nitrosyl bends in such a manner as to eclipse an equatorial ammonia ligand. In the implementation of an energy decomposition scheme, this is interpreted as the result of enhanced electrostatic and charge-transfer interactions attendant upon bending of the nitrosyl. The preference of an eclipsed conformer to its staggered counterpart is found to be principally due to its more favored electrostatic interaction. Other topics discussed include the length of the M-N bond in relation to other nitrosyl complexes, the origin of the large trans effect, and orbital correlations as one forms the total complex as a composite of the monomers $Co(NH_3)^{3+}$ and NO^-.

Introduction

The coordination of the nitrosyl ligand to metals of the first and second transition series is currently the subject of intense research interest in both structural and interpretive inorganic chemistry. Much of this interest spawns from the first confirmation by Ibers et al.[2a,b] of a bent coordination mode for the binding of the nitrosyl ligand to a transition metal. Since this original finding a large host of nitrosyl complexes, both bent and linear in their coordination, have been prepared and structurally characterized. Frenz and Ibers[2c] have collated these data, segregating the complexes into three classes. There is the class, denoted as linear nitrosyls, in which the M-N-O bond angle is very nearly equal to 180°. By contrast, there is a second, structurally distinct group of nitrosyls whose M-N-O angle is in the vicinity of 120°. Intermediate between these extremes, there is a third class of complexes with an angle in the region of 150°. In addition to the apparent parameter of the metal–nitrosyl bond angle, there are other structural features which distinguish the classes one from the others. The average M–N bond length in the linear complexes is 1.71 Å as compared with an average of 1.89 Å for the bent complexes.[2] The N–O bond length, on the other hand, is somewhat shorter in bent complexes (an average of 1.13 Å as compared with 1.17 Å in linear complexes). Bent, octahedral complexes are also known to exhibit large trans effects, the lengthening of the trans, axial M–L bond being far more pronounced than it is for linear nitrosyl complexes.[2,3] A final interesting structural characteristic of bent nitrosyls is that they most often eclipse one of the equatorial M–L bonds even in situations where the equatorial ligands are all identical.

The earliest qualitative interpretations of the bimodality of the nitrosyl ligand were predicated on the formal assignments of NO^+ in linear complexes and NO^- in bent complexes.[4] Concordant with these assignments are the interpretations of the nitrosyl ligand as a three and a one electron donor in the linear and bent complexes, respectively. Such an interpretation of the binding is now generally regarded as an oversimplification in that the evidence now suggests that the NO is essentially neutral for either binding modality. Nonetheless, this view is of heuristic value in that many of the binding characteristics outlined above are successfully predicted.[2]

The current tools of vogue which have been extensively applied to this problem are "Walsh type diagrams".[5-7] Such studies have successfully predicted when a nitrosyl ligand will be bent. In addition, Hoffmann et al.,[7] in particular, have been able to interpret many suubstituent effects on the coordination of the nitrosyl ligand. The computations presented in evidence of the interpretations have, in general, been at the extended Hückel level.[6d,7]

Our approach to the problem is considerably less global than that of many other workers. Rather than treating nitrosyl coordination in a general, intuitively motivated fashion, we have chosen to examine in somewhat more detail, using ab initio MO techniques, the nature of the nitrosyl ligand in a single, well-characterized complex. The particular complex chosen for study was the dipositive cation $Co(NH_3)_5NO^{2+}$, a complex whose structure has been determined by Ibers and co-workers.[3] This is an exemplary complex of the bent class of molecules. Concordant with its 119° M–N–O bond angle, it has a M–N bond length of 1.87 Å and exhibits a large trans effect. In the notation of Enemark and Feltham,[5] this is a $\{CoNO\}^8$ complex; i.e., there are totally eight electrons in the d shell of the metal and the π^* orbitals of the ligating nitrosyl. Complexes with six or fewer electrons in this manifold are expected to be linear, electrons occupying the nonbonding xy orbital (z axis being that of the nitrosyl) and the symmetric admixtures of the metal π orbitals with the nitrosyl π^* orbitals. Bent nitrosyls are destabilized in this regime due to reduced metal-to-ligand, π back-bonding in the plane defined by the metal–nitrosyl linkage.[5,7] Addition of two more electrons to form $\{MNO\}^8$ complexes radically changes the picture. The next lowest lying levels are the π^* orbitals of the nitrosyl ligand. If the nitrosyl bends, one of the π^* orbitals is allowed to mix with the vacant d_{z^2} orbital of the metal thereby stabilizing the complex. In linear complexation such interaction is symmetry forbidden. Consequently, on addition of the seventh and eighth electrons to the d–π^* manifold, bending of the nitrosyl is observed.

The intent of the present study was a qualitative differentiation of the bonding between the observed bent $Co(NH_3)_5NO^{2+}$ complex and the hypothetical analogue in which the nitrosyl is coordinated linearly. Rather than view the binding from a one electron, orbital energy point of view, we wished to interpret the differences in the binding based on the physically motivated interaction energy analysis of Morokuma and Kitaura.[8] Within this analysis, the interaction energy between the conjugate monomers is separated into the components: electrostatic (ES), charge transfer (CT), polarization (PL), exchange (EX), and residual mixing (MIX) term. The electrostatic term represents the classical electrostatic interaction between the electronic clouds of the conjugate monomers. The charge-transfer component is the stabilization provided by intermolecular excitations between the occupied levels of one monomer and the vacant levels of the other. The polarization component is the result of intramolecular excitations in the monomers induced by their being brought into the presence of one another. The exchange term arises both from the exchange of the electrons in accord with the Pauli prinicple and from the nonorthogonality of the monomeric wave functions. The latter term generally dominates, making the exchange component repulsive. The MIX term arises from the synergic character of the polarization and charge-transfer component. For further details regarding the decomposition scheme, the reader is referred to the definitive papers.[8] The energy decomposition analysis should provide evidence for the qualitative differences in the nature of the binding of nitrosyl ligand in its two coordination modes. We also analyzed the molecular orbitals of the complex in terms of the monomeric orbitals, affording us the opportunity to check the insight of earlier workers with our somewhat more definitive, numerical results.

A price must be paid for the services of the decomposition scheme. First, the molecule must be split into the fragment monomers: $Co(NH_3)_5{}^l$ and NO^m where $l + m = +2$. A priori it is certainly not evident as to how one ought best to partition the electrons between the fragments. This question is necessarily returned to shortly. In addition the decomposition approach necessitates the use of a single configuration wave function. As a consequence the use of a CI wave function is precluded: hence, we cannot expect our absolute energies to be correct, particularly since both the linear and bent complexes have a number of low-lying excited states implicating the desirability of CI. It should be emphasized that our interest was not in determining an accurate energy separation between the bent and linear conformers of the complex but rather in discriminating qualitatively the factors which influence the binding. The restriction of a single configuration also limits the treatment of the linear complex in that two electrons are being placed in a degenerate pair of orbitals. The ground state would hence be expected to be a triplet. Nonetheless, to ensure that both the linear and bent complexes were treated on an equal footing (single configuration RHF), an excited singlet state of the linear complex was examined. The effect that this will have on the qualitative conclusions will be considered later.

As an additional interpretive aid, we also examined the orbitals of the complex in a basis of fragment molecular orbitals. This allows us to determine the degree of interaction or mixing between the metal and nitrosyl orbitals. Thereby it should provide a barometer by which to judge the insight of earlier workers regarding the significance of various metal–ligand interactions.

We will give special emphasis to the consideration and rationalization of each of the structural characteristics which make this a representative molecule of the class of strongly bent nitrosyl complexes. Such considerations at the more rigorous ab initio level should lead to new insights into the problem of a nitrosyl binding in general.

Computational Details

All geometries studied were derivatives of the experimental determination of Ibers et al.[3] As a simplification we assumed that all the N–Co–N angles were 90° (all experimental values

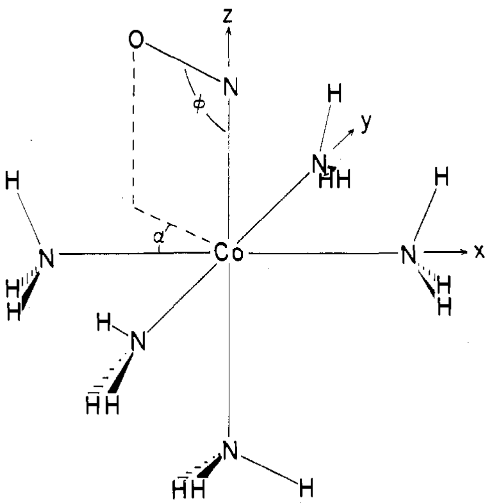

Figure 1. Geometry of the $Co(NH_3)_5NO^{2+}$ cation (see ref 3). The angle ϕ was varied from the experimental value of 119° to 180°. The angle α is 0 for the eclipsed and 45° for the staggered conformation. Regardless of the angle ϕ, the complex is of C_s symmetry, though for a linear nitrosyl (ϕ = 180°) it would be C_{4v} save for the slight perturbation of the axial ammonia ligand.

are within 2° of this, though slight deviations do exist), and that the equatorial N–Co bond lengths were the average (1.981 Å) of the experimental values. Each ammonia was assumed to have the N–H bond length of 1.0124 Å and the H–N–H angle of 106.67° with its C_{3v} axis lying on a N–Co bond. The ammonia molecules were arranged in the manner shown in Figure 1. The remainder of the experimental parameters were taken unchanged in the calculations: the axial N–Co length = 2.220 Å, the nitrosyl N–Co length = 1.871 Å, and the N–O length = 1.154 Å. Calculations were performed for values of the Co–N–O angle, ϕ, in Figure 1 of 119 (experimental angle), 150, and 180°. For $\phi \neq 180°$, both the eclipsed (α = 0) and staggered (α = 45°) conformers were considered.

The calculations performed were ab initio SCF calculations with split valence basis functions. The basis functions for the cobalt were the (11/6/4) set of Veillard, Roos, and Vinot[9] contracted to [5/3/2]; the 4-31G basis with standard parameters[10] was used for the first-row atoms.

Calculations reported here are, unless otherwise noted, single determinant closed-shell SCF calculations. As an interpretive aid we also performed calculations in which the ammonia ligands were represented by fractional charges. Previously we introduced this molecular representation as a simplifying model in solution-phase calculations.[11] Its virtues and limitations have been discussed elsewhere and will not be reiterated here. A priori one might not expect it to be an excellent representation in the present application, since charge delocalization from the cationic metal to the ammonia ligands would be anticipated to be a significant stabilizing contribution. As an empirical result one finds, however, that the calculations employing fractional charges yield results concordant with the qualitative conclusions drawn from the full ab initio results. In light of this fact, the approximation is of utility, not only because of its economic benefits but also because of the more facile interpretation of its wave function. The fractional charges employed were those which reproduce the calculated dipole moment of the ammonia monomer ($q_N = -1.2552$, $q_H = +0.4184$).

The two electron integrals for the full ab initio computations were evaluated by using the program MOLECULE.[12] These integrals were then interfaced with a modified version of the GAUSSIAN 70[13] program capable of handling the 124 contracted basis functions and of performing energy decomposition analyses.

Table I. Energy Decomposition for the Interaction $Co(NH_3)_5{}^{3+} + NO^- \rightarrow Co(NH_3)_5NO^{2+}$

geometry		interaction energy, kcal/mol					
ϕ, deg	E/S[a]	ΔE	ES	EX	PL	CT	MIX
		Full Calculation					
180		−366.5	−367.9	+80.9	−126.9	−26.7	+74.1
119	E[b]	−408.9	−435.6	+130.9	−67.6	−42.1	+5.5
119	S	−402.9	−416.7	+118.2	−75.8	−36.9	+8.3
		Fractional Charge Calculation					
180		−463.6	−421.3	+58.1	−166.6	−57.1	+123.3
150	E	−533.1	−447.5	+67.5	−129.1	−71.0	+47.1
150	S	−530.8	−432.5	+68.0	−144.4	−70.0	+47.6
119	E	−547.7	−493.5	+109.3	−81.7	−106.2	+24.4
119	S	−546.4	−472.1	+98.4	−101.2	−72.3	+0.8

[a] E and S denote eclipsed ($\alpha = 0°$) and staggered ($\alpha = 45°$) conformers, respectively. [b] The total energy of the complex for this geometry is −1788.664 224 hartree, whereas the energies for $Co(NH_3)_5{}^{3+}$ and NO^- are −1659.080 709 and −128.931 890 hartree, respectively.

Results and Discussion

It was earlier noted that the energy decomposition scheme necessitated viewing the complex as a composite of the monomers $Co(NH_3)_5{}^l$ + NO^m ($l + m = +2$). This requires an initial apportionment of the electrons between the two fragments. In most of the calculations, the complex was split into a tripositive cobalt pentaammine fragment and the nitrosyl anion ($l = +3$, $m = -1$). The principal reason for this division was that appropriating more electrons to the metal fragment fills the d_{z^2} orbital: as the interaction of this orbital and the π^* orbitals of the nitrosyl is forbidden to mix by symmetry, such a configuration cannot lead smoothly to the low-lying states of the linear complex (those having π^{*2} character). A second, subsidiary reason for this partitioning of the electrons is that it is consistent with the formal assignment of electrons in the more stable bent conformer.

The partitioning of the electrons may seem, and indeed is, arbitrary. Nonetheless, it is felt that any partitioning of electrons is reasonable if (a) it smoothly yields (i.e., avoids any forbidden orbital crossings) the ground states of the molecules under study and (b) it provides insight regarding the interaction of the fragments. On the basis of these criteria, we feel that it is heuristically useful to view nitrosyl ligation in terms of an anionic NO. Nonetheless, wherever possible we have made an effort to identify conclusions which are dependent on this division of electrons. We have tried to indicate how these conclusions would be transformed to a different perspective of the interaction which would result from a different initial assignment of the electrons.

The results of the energy decomposition for the interaction $Co(NH_3)_5{}^{3+} + NO^- \rightarrow Co(NH_3)_5NO^{2+}$ are shown in Table I. Results for both the fully ab initio and for calculations employing the fractional charge representation of the ammonia ligands are displayed. In agreement with experiment we find the bent (ϕ = 119°), eclipsed (α = 0°) conformer of the nitrosyl to be the most favored structure. In the fully ab initio calculations, it is 42 kcal/mol more stable than the linear conformer and 6 kcal/mol lower in energy than the bent, staggered (α = 45°) structure. These numbers, particularly the energy spread between the bent and linear conformers, are not intended as quantitative estimations but rather merely as indications that the correct experimental trends are picked up at this single configurational level of treatment.

As alluded to previously, one factor influencing the total energy of the linear conformer is our use of a single determinant, $XX\alpha\beta$, wave function for the valence electronic configuration (in C_{4v} notation which the axial ammonia breaks

Table II. Energy of the States Obtainable from the $(e_{x,y})^2$ Configuration in the C_{4v} Symmetry

states		energy
$^1A_1$	$(XX + YY)\alpha\beta$	K_{XY}
$^1(A_1 + B_1)$	$XX\alpha\beta$ $YY\alpha\beta$	0.0 (ref)
$^1B_1$	$(XX - YY)\alpha\beta$	$-K_{XY}$
$^1B_2$	$XY(\alpha\beta - \beta\alpha)$	$-K_{XY} - \Delta^a$
$^1B_1 + {}^3A_2$	$XY\alpha\beta$	$-2K_{XY} - \Delta$
$^3A_2$	$XY(\alpha\beta + \beta\alpha)$ $XY\ \alpha\alpha$ $XY\ \beta\beta$	$-3K_{XY} - \Delta$

[a] $\Delta = J_{XX} - J_{XY} - 2K_{XY}$.

to only a very small extent): . . . $(3a_1)^2(2e)^4(3e)^2$. This is, of course, not the lowest energy solution; indeed, it is not even of C_{4v} symmetry. Nonetheless, it is the lowest energy, single configuration wave function whose nitrosyl parentage is appropriate for the ground state of the bent complex. Consequently, it should provide the closest analogue for comparison with bonding in the bent conformer. Still, we felt it appropriate to make an estimate of how far this closed-shell singlet is above the true ground state. In Table II are shown the energies—assuming frozen orbitals—of a number of states resulting from placing two electrons in a pair of degenerate orbitals, X and Y. Calculating K_{XY} from the orbitals of the $XX\alpha\beta$ singlet (fractional charge representation of the ammonias), we estimate the $^1B_1$ $(XX - YY)\alpha\beta$ state to be 11.0 kcal/mol below the $XX\alpha\beta$ state. Generalized restricted Hartree–Fock calculations for the $^1B_2$, $XY(\alpha\beta - \beta\alpha)$, and $^3A_2$, $XY\alpha\alpha$, states place them 10.3 and 26.0 kcal/mol, respectively, below the $XX\alpha\beta$ singlet. Hence the ground state for the hypothetical linear complex is a triplet lying 26 kcal/mol below the state assumed in this work. Hence our calculations would still suggest that the bent adduct is the more stable but now only by 16 kcal/mol.

In light of the above noted results, brief discussion seems required regarding the utility of energy decomposition for a state of the linear adduct 26 kcal/mol above its true ground state. From a comparison of our calculated value of K_{XY} coupled with the predictions of Table II and the RHF results cited above, it is evident that the principal difference in the states arises from varying coupling of the electrons and does not reflect differences in the orbitals themselves or in the binding of the nitrosyl.

Indeed, the orbitals in question are principally nitrosyl π^* in character. As a consequence, one might view the ground state of the linear complex as arising from interaction of the ground-state $^3A_2$ (in C_{4v} notation) nitrosyl anion with the cobalt center while the $XX\alpha\beta$ state considered here arises from the $XX\alpha\beta$ state of the nitrosyl anion (keep in mind that the $XX\alpha\beta$ state of the nitrosyl will lead to the ground state of the bent conformer). We feel that it is reasonable to expect that the actual character of the nitrosyl-metal binding will be little different in these two cases. Hence conclusions based on the $XX\alpha\beta$ state should be applicable to the ground state by a shift in the reference energy of the nitrosyl monomer, as a qualitative, interpretive tool. In the discussions which follow all references to relative energies will be based on the full calculations. On the other hand, all discussions concerning the nature of the orbitals themselves will be derived from the fractional charge model calculations.

We would now like to return to the focal point of the paper, that being the differences in the binding in the linear and bent complexes. From Table I it is evident that electrostatic and charge-transfer energies are primarily responsible for the greater stability of the bent modality. The significance of the electrostatic interaction deserves particular emphasis in that it is a contribution which has been generally neglected by earlier workers. This result may be rationalized in terms of a simple electrostatic potential picture. The electrostatic potentials at the site of the Co nucleus were calculated by using the NO^- monomeric wave function. At an angle ϕ of 90, 119, and 180°, respectively, one obtains potentials of −173.93, 173.96, and −157.4 kcal/mol. The fact that the minimum in the electrostatic potential map is not at $\phi = 180°$ is not altogether unexpected. Indeed, very similar results have been found for other diatomic molecules of first-row atoms.[14,15] Kollman[15] has suggested that the minimum in the electrostatic potential map will not be along the molecular axis if the diatomic has more than ten valence electrons, i.e., if one occupies the $\pi^*(2\pi)$ level. Our finding of the significant difference in electrostatic interaction between bent and linear coordination is, therefore, consistent with existing evidence for other systems, even though it has not been recognized in this context.

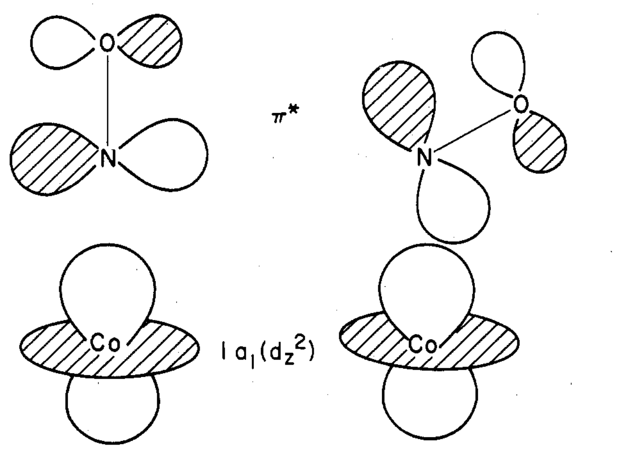

Figure 2. The importance of the charge-transfer interaction is illustrated here. In the linear complex the highest occupied orbital of the nitrosyl anion (2π) and the lowest vacant orbital of the $Co(NH_3)_5^{3+}$ monomer ($1a_1$) are orthogonal. In the bent complex one expects large mixing of the orbitals and consequently a significant charge-transfer contribution.

Our finding of a significant difference between linear and bent coordination in the charge-transfer interaction is a confirmation of a previously proposed suggestion.[7b] Hoffmann has correctly pointed out the significance of the charge transfer from the π^* orbital of the NO^- to the lowest vacant $1a_1$ (d_{z^2}) orbital of $Co(NH_3)_5^{3+}$. As is shown in Figure 2, this is expected to be a significant stabilizing interaction for the bent conformation. For linear coordination, on the other hand, these two orbitals are orthogonal and such an interaction is forbidden by symmetry. The importance of the charge transfer from the π^* orbital of the nitrosyl to the d_{z^2} orbital of the $Co(NH_3)_5^{3+}$ is dramaticalty reflected in the coefficients of the complex wave function in the basis of the monomer molecular orbitals. These coefficients for both the linear and the bent complexes in the fractional charge representation are collated in Tables III–V. As a visual complement of these tables, the orbital interactions for the linear and the strongly bent (ϕ = 119°), eclipsed conformers are shown in Figure 3 and 4, respectively. It is clear that the π^* and the $1a_1$ (d_{z^2}) orbitals strongly interact in the bent complexes resulting in a significant stabilization of the highest occupied orbital (6a′ for 119E and 7a′ for 119S). This same interaction is forbidden in a linear complex. It is also interesting to note that in the linear complex the σ molecular orbitals of the nitrosyl do not mix strongly with the vacant $1a_1$ (d_{z^2}) orbital of the cobalt. From Figure 3 it is evident that the reason for this is that their eigenvalues are too widely spaced, resulting (in a perturbation sense) in a large denominator in the mixing coefficient. It is interesting to note (see Table III) that for the linear complex charge

Table III. Coefficients of the Valence Orbitals for the Linear Complex[a]

complex MO	orbital energy[b]	coefficients
		Occupied
$1a_1$	−1.823	1.000[1σ(NO)]
$1b_2$	−1.313	1.000[$1b_2$(Co)]
$1e(d_{xz})$	−1.310	1.001[$1e(d_{xz})$(Co)]
$1e(d_{yz})$	−1.310	1.001[$1e(d_{yz})$(Co)]
$2a_1$	−1.197	0.878[2σ(NO)] − 0.439[3σ(NO)] + 0.146[$2a_1$(Co)] − 0.322[$3a_1$(Co)]
$3a_1$	−0.957	0.821[3σ(NO)] + 0.310[2σ(NO)] − 0.276[$1a_1$(Co)] + 0.280[$2a_1$(Co)] − 0.558[$3a_1$(Co)]
2e[c]	−0.954	0.995[1π(NO)]
2e[c]	−0.857	0.985[1π(NO)] + 0.175[2π(NO)]
3e[c]	−0.598	0.976[2π(NO)] + 0.251[2e(Co)] − 0.152[3e(Co)]
		Vacant
$4a_1$	−0.419	0.925[$1a_1$(Co)] − 0.236[3σ(NO)] − 0.181[2σ(NO)] + 0.127[$2a_1$(Co)] − 0.120[$3a_1$(Co)] + 0.363[4σ(NO)] + 0.516[5σ(NO)]
$1b_1$	−0.401	0.997[$1b_1$(Co)]
3e[c]	−0.171	0.908[2π(NO)] − 0.154[1π(NO)] − 0.419[2e(Co)] − 0.177[3e(Co)]

[a] C_{4v} notation used even though (due to axial NH_3) complex is rigorously only of C_s symmetry. [b] In hartrees. [c] The eigenvalues of these e orbitals are split due to use of the single determinant wave function (see text for discussion).

Table IV. Coefficients for the Valence Orbitals for the Bent (φ = 119°), Eclipsed (α = 0) Complex[a]

complex MO	orbital energy	coefficients
		Occupied
1a′	−1.985	1.000[1σ(NO)]
2a′	−1.293	0.952[2σ(NO)] + 0.180[3σ(NO)] − 0.122[$1a_1$(Co)]
3a′	−1.085	0.775[1π(NO)] + 0.507[3σ(NO)] − 0.236[2σ(NO)] − 0.180[$1a_1$(Co)]
1a″	−1.070	0.998[$1b_2$(Co)]
4a′	−1.062	0.706[1e(Co)] + 0.486[3σ(NO)] + 0.442[1π(NO)] − 0.108[2σ(NO)] + 0.131[$1a_1$(Co)]
2a″	−1.053	0.909[1e(Co)] + 0.370[1π(NO)]
5a′	−1.007	0.619[3σ(NO)] − 0.675[1e(Co)] + 0.398[1π(NO)]
3a″	−0.980	0.921[1π(NO)] − 0.402[1e(Co)]
6a′	−0.710	0.698[2π(NO)] + 0.605[$1a_1$(Co)] − 0.205[3σ(NO)] − 0.164[1e(Co)] − 0.149[2σ(NO)]
		Vacant
7a′	−0.311	0.739[$1a_1$(Co)] − 0.627[2π(NO)] + 0.219[$2a_1$(Co)]
4a″	−0.261	0.974[2π(NO)] − 0.113[1π(NO)]
8a′	−0.184	0.993[$1b_1$(CO)]

[a] See Table III for notation and units.

transfer into the $2a_1$ (Co 4s) and $3a_1$ (Co $4p_z$) orbitals is more facile than that into the lower lying $1a_1$ (d_{z^2}) level. In a perturbation sense, this must be an overlap effect attributable to the more diffuse nature of the valence s and p orbitals.

One may be disconcerted by the fact that PL is shown to strongly favor the linear binding while the mixing contribution is also large, favoring bent coordination. These two factors are, in fact, closely related. The fact that polarization favors the linear form is reasonable as one suspects that the cationic cobalt center will have a greater polarizing influence on the σ framework of the nitrosyl when the three centers are collinear. The magnitude of this enhanced polarization appears to be an artifact of our calculation, however. We did not find nearly the extent of polarization in our true wave function as in the wave function neglecting exchange between the two monomers (from which the polarization energy was calculated). The consequence of this overestimate of the polarization interaction for the linear binding is an unrealistically large mixing term. One may, in this particular case, get a more reasonable and useful measure of the significance of polari-

Table V. Coefficients for the Valence Orbitals for the Bent (φ = 119°), Staggered (α = 45 °) Complex[a]

complex MO	orbital energy	coefficients
		Occupied
1a′	−1.985	1.000[1σ(NO)]
2a′	−1.292	0.951[2σ(NO)] + 0.183[3σ(NO)] + 0.121[$1a_1$(Co)]
3a′	−1.083	0.785[1π(NO)] + 0.483[3σ(NO)] − 0.234[2σ(NO)] + 0.172[$1a_1$(Co)] + 0.123[$1b_2$(Co)]
4a′	−1.068	0.971[$1b_2$(Co)] + 0.122[1e(Co)] − 0.161[3σ(NO)]
5a′	−1.062	0.711[1e(Co)] − 0.197[$1b_2$(Co)] + 0.117[$1a_1$(Co)] + 0.481[3σ(NO)] + 0.404[1π(NO)] − 0.106[2σ(NO)]
1a″	−1.048	0.892[1e(Co)] + 0.403[1π(NO)]
6a′	−1.008	0.619[3σ(NO)] − 0.669[1e(Co)] + 0.415[1π(NO)]
2a″	−0.980	0.907[1π(NO)] − 0.434[1e(Co)]
7a′	−0.708	0.695[2π(NO)] + 0.611[$1a_1$(Co)] − 0.211[3σ(NO)] − 0.167[1π(NO)] − 0.148[2σ(NO)]
		Vacant
8a′	−0.311	0.742 [$1a_1$(Co)] − 0.628[2π(NO)] + 0.221[$2a_1$(Co)]
3a″	−0.268	0.973[2π(NO)] − 0.110[1π(NO)]
4a″	−0.182	0.995[$1b_1$(Co)]

[a] See Table III for notation and units.

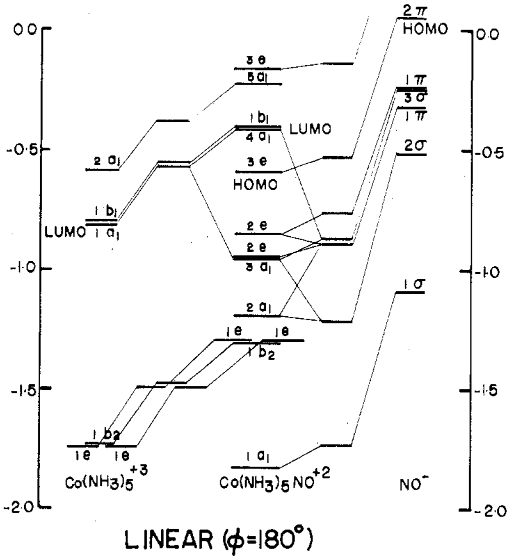

Figure 3. Orbital correlation diagram for the linear complex in the fractional charge representation. At the extreme left and right of the figure one has the orbitals of the $Co(NH_3)_5{}^{3+}$ and NO^- monomers, respectively. These orbitals are then brought into the presence of the electrostatic field of the conjugate monomer. As one expects, the NO^- orbitals are greatly stabilized by the presence of the $Co(NH_3)_5{}^{3+}$ cation while the metal orbitals are raised in energy by the presence of the anion. The orbitals of the total complex are here correlated with all monomer orbitals whose mixing coefficients are greater than 0.3. The unit of the eigenvalues is the hartree. The orbitals for both $Co(NH_3)_5{}^{3+}$ and $Co(NH_3)_5NO^{2+}$ are designated by C_{4v} notation even though rigorously they are only of C_s symmetry.

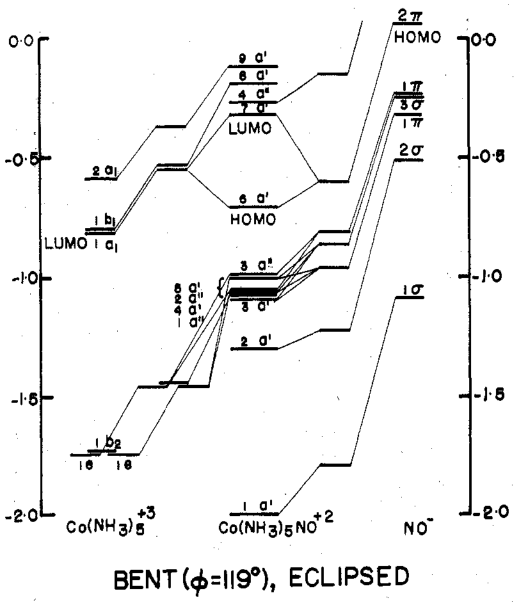

Figure 4. Orbital correlation for the bent ($\phi = 119°$), eclipsed conformer of the complex. The total complex orbitals are characterized by their C_s symmetry notation. Otherwise notation is the same as in Figure 3.

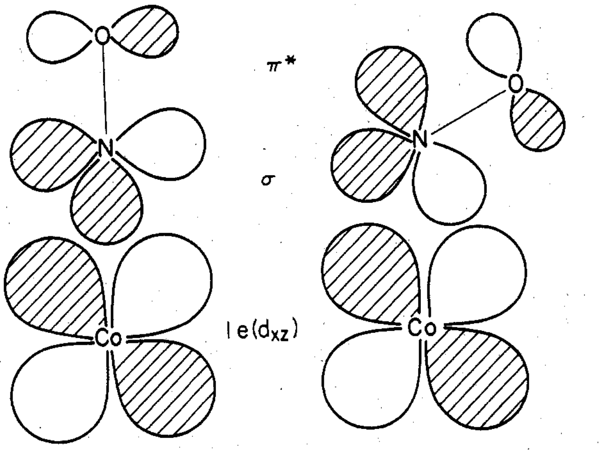

Figure 5. Schematic illustration of the rationale for increased exchange repulsion on bending. It is clear that one has increased overlap between the $2\pi(\pi^*)$ and σ (an N lone pair in a localized orbital sense) orbitals of the nitrosyl and the 1e orbital of the cobalt.

zation by summing the pure polarization and the mixing terms. If this is done, one finds little difference between the linear and bent complexes. In fact, the bent moiety is now slightly favored (−62.1 kcal/mol as compared with −52.8 kcal/mol); one is cautioned not to interpret this as a pure polarization effect, however, as the mixing term also includes charge-transfer effects. The crucial point to be made is that the polarization and mixing terms are not nearly so critical as they at first might appear.

The exchange repulsion also favors a linear structure. This result may be intuitively rationalized as the result of increased overlap between both the π^* and (in a localized orbital sense) the N lone pair with the occupied 1e (d_{xz} and d_{yz}) levels of the cobalt. This situation is illustrated in Figure 5. We shall return to this point in a later discussion.

Summarizing our comparison between the linear and the bent complex, we may say the following. There are two terms which are essential to the preferential stability of the bent form of the complex, these being the electrostatic and charge-transfer interactions. These two terms are sufficiently large such that the destabilization due to exchange repulsion is overwhelmed.

Table VI. Energy Decomposition for the Interaction $Co(NH_3)_5^+ + NO^+ \rightarrow Co(NH_3)_5NO^{2+}$[a]

	linear	119E[c]
ΔE	b	−74.4
ES	+45.7	+46.6
EX	+77.9	+69.8
PL	−49.1	−55.1
CT	−95.0	−113.9
MIX	b	−21.8

[a] All calculations reported here are in kcal/mol and employed the fractional charge representation of the ammonia ligands.
[b] These numbers would not be of significance as this does not represent the ground-state complex. In fact, we had difficulty in obtaining convergence for the excited state. [c] Bent ($\phi = 119°$), eclipsed conformer.

At this point we must again consider the degree to which this analysis was dependent on the initial division of electrons. Once again, it should be noted that other reasonable separations of the electrons (e.g., $Co(NH_3)_5^+$, NO^+, or $Co(NH_3)_5^{2+}\cdot$ + NO·) cannot lead to the lowest lying manifold of states for the linear conformer. Nonetheless, it would be appealing if the results for the present division could be understood also in terms of an alternate electron appropriation. In Table VI are displayed the decomposition results for the interaction of $Co(NH_3)_5^+$ and NO^+. These monomers result from the transfer of a pair of electrons from the π^* orbital of the nitrosyl to the d_{z^2} orbital of the cobalt center. First it should be noted that the salience of the charge-transfer contribution is unaltered by this division. Now one merely has the reverse processes of those discussed above. For the bent complex, one has the facile transfer from the $1a_1$ (d_{z^2}) orbital to the π^* level of the nitrosyl while in the linear complex this pathway is symmetry forbidden and the principal charge-transfer process is from the 1e (d_{yz}) level of the cobalt to the nitrosyl π^*. It will be noted that the electrostatic interaction is no longer significantly different between the linear and bent modalities. Indeed, the ES interaction is now somewhat less destabilizing in the linear mode than in its bent counterpart. In light of the earlier discussion on the electrostatic interaction, this should not be a surprising result. The two electrons which we removed from the π^* orbital were the electrons responsible for the fact that the minimum in the electrostatic potential was off of the molecular axis. This does not necessarily imply that our earlier conclusion regarding the importance of the ES interaction is not valid. Instead what we may say is that by placing this last critical pair of electrons in the $Co(NH_3)_5^+$ monomer, we have destabilized the linear moiety as a result of exchange interaction. The critical interaction which is responsible for the relative destabilization is clearly between the now filled $1a_1$ (d_{z^2}) orbital and the σ (N lone pair) orbitals of the nitrosyl. Bending of the nitrosyl clearly relieves this strain since the π^* orbital is no longer occupied.

We may now generalize our earlier conclusions at this point. Regardless of the choice of monomers there will always be two terms favoring the bent modality of nitrosyl bonding. The first of these will always be change transfer as this is dependent only on the symmetries of the $1a_1$ and the π^* orbital and not on which of the two is initially occupied. The second factor will be either electrostatic or exchange depending on how one partitions the electrons. If one appropriates the electrons to the π^* orbital, then the enhanced off-axis electrostatic potential of the nitrosyl will favor bending, while if one starts with the electrons in the d_{z^2} orbital of the cobalt, the resulting exchange repulsion will disfavor the linear mode.

We now turn to the second of the questions which we intend to address: why it is that the bent nitrosyl eclipses one of the equatorial ligands? On first consideration one might suspect

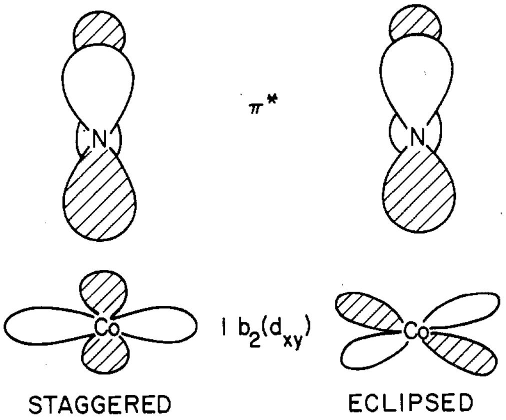

Figure 6. Schematic illustration of the prinicipal difference between staggered and eclipsed conformers. In the staggered configuration the $1b_2$ orbital of the $Co(NH_3)_5^{3+}$ is of the same symmetry as the occupied $\pi^*(2\pi)$ orbital (as well as the σ orbitals and 1π orbital), shielding it from the stabilizing influence of the Co nucleus.

the staggered conformation to be the more stable form, using a steric crowding argument as a rationale. Indeed, if one checks Table I, one does find greater exchange repulsion for the eclipsed conformer. More than compensating for this effect, however, is a 19 kcal/mol difference in the electrostatic interaction favoring the eclipsed configuration. This is perhaps not an intuitively obvious result and is therefore deserving of more detailed comment.

The critical factors differentiating between eclipsed and staggered configurations are the symmetries of the occupied d_{xy} ($1b_2$) orbital and the vacant $d_{x^2-y^2}$ ($1b_1$) orbitals. In the eclipsed form ($\alpha = 0$) the d_{xy} orbital is antisymmetric (a″) with regard to reflection in the lone symmetry plane (*xz* plane in Figure 1) while the $d_{x^2-y^2}$ is symmetric (a′). In the staggered complex ($\alpha = 45°$) these two orbitals reverse symmetries, the d_{xy} becoming a′ with respect to the symmetry plane (the plane defined by the NO group and the *z* axis) while the $d_{x^2-y^2}$ is of a″ symmetry. All other valence orbitals of an eclipsed conformer may be correlated with an orbital of the same symmetry in the staggered complex and should be nearly independent of rotation. It is obvious upon study of Tables IV and V that the actual character of all the orbitals including the d_{xy} is changed only slightly upon rotation of an eclipsed conformer to a staggered form. This is not a surprising result, since the overlap between the d_{xy} orbital and the a′ orbitals of the nitrosyl is not very large even though it is, in the staggered form, of the proper symmetry. As a result one finds that the mixing between these orbitals (see Table V) is not large. This does not preclude this orbital from having a significant effect on the electrostatic interaction, however. The extra a′ orbital in the staggered form shields the a′ electrons of the nitrosyl ligand (most of the nitrosyl density is of a′ symmetry) from the stabilizing influence of the cobalt nucleus. This effect is schematically illustrated in Figure 6 where for simplicity only the d_{xy} orbital and the occupied π^* orbital of the nitrosyl are shown. In simplest terms one may say that if all other factors were equal the nitrosyl ligand would prefer to bend in the nodal plane of the d_{xy} orbital.

Capsulizing the above discussion we conclude that a reduced electrostatic interaction results from a rotation away from an eclipsed conformation. This effect is determined by the symmetry of the d_{xy} orbital, and is large enough to more than compensate for reduced exchange upon rotation away from an eclipsed conformer.

At this point one may wish to consider alternate initial assignments of electrons in analogy to our earlier discussion. In this case one would expect that removing electrons from the π^* orbital and placing them in the $1a_1$ (d_{z^2}) would only cloud the central issue. The ES would still favor the eclipsed conformer, though to a much weaker extent. The remainder of the difference between the conformers would then be spread among the other terms. The key factor, which was clear most likely to an exaggerated extent in the calculations reported here, is that the electrons of a′ symmetry in the nitrosyl are stabilized more by the cobalt nucleus in the eclipsed coordination mode. This is due to the shielding of these electrons by the $1b_2$ (d_{xy}) orbital in the staggered conformer.

The next question to consider is the origin of the large trans influence of the nitrosyl ligand in this, a representative bent nitrosyl complex. This effect has previously been ascribed to the formal negative charge on the nitrosyl ligand, analogy being drawn to the similar effect in other anionic ligands such as the ethoxy ion.[2,16] This interpretation is consistent with correlations which have been found between the trans influence and electronegativity of the directing ligand.[17] Other interpretations of the trans influence have been based on the σ-donor ability of the ligand as well as the overlap of the directing ligand's σ orbitals with those of the metal.[17] Each of these factors is, quite obviously, a measure of the extent of interaction between the ligand and metal orbitals. The greater this interaction is, the more significant will be the labilizing effect on the conjugate trans ligand. In this view, it is notable (see Tables III and IV) that the nitrosyl ligand interacts much more strongly with the $1a_1$ (d_{z^2}) orbital of the cobalt when coordinated in its bent modality. As alluded to earlier this is the result of the relative energy spacings between the d_{z^2} orbital on the metal and the σ and π orbitals on the nitrosyl and not the overlap between these same orbitals. The critical point is that the energy matching between the π^* and d_{z^2} orbital is considerably more favorable than that between the nitrogen lone pair and the d_{z^2} orbital. This results, in the parlance of earlier workers, in the nitrosyl ligand being a better σ donor (through its π^* orbital) in its bent coordination mode than it is when coordinated linearly. It might be argued that our interpretation is dependent of the particular eigenvalue orderings found here; however, evidence does exist to indicate that ordering is of considerable generality. Manoharan and Gray, using SCCC–MO computations, examined a series of linear, pentacyanonitrosyl complexes.[18] For each complex, the d_{z^2} orbital was found to lie somewhat above the π^* orbital of the nitrosyl. Such an ordering would seem to preclude the possibility of strong interaction between the σ orbitals (which are, of course, considerably lower in energy than the π^* orbitals) and the metal d_{z^2}. As a consequence one would not expect, and indeed does not find, a large trans effect in these molecules.[19]

The last characterizing feature of bent nitrosyl which deserves brief comment here is their longer M–N bond length in comparison with linear complexes. This has traditionally been accepted as evidence of multiple bond formation in the latter case.[2] Concordant with formal assignment of a positive charge on the nitrosyl is this multiple character (σ donation from N to the metal and synergic back-donation from the metal to the π^*) in the M–N bond. This is contrasted with the binding in bent complexes in which a single dative bond from a sp^2 hybridized orbital of the nitrosyl N to the metal is formulated. As we have studied only a single complex, and that at only one M–N separation, it is difficult to address this question. Some comments are in order, however, as our calculations are not fully consistent with the interpretation just outlined. In particular, it seems reasonable that the dative bond formed between the π^* orbital of the nitrosyl and the d_{z^2} orbital of the metal in the linear binding modality will be far more stabilizing than the analogous bond formed between the nitrogen lone pair and the d_{z^2} orbital in a linear complex. In addition our calculations (see Tables III–V) indicate that

Table VII. Total Atomic Populations for $Co(NH_3)_5{}^{3+}$, NO^-, and $Co(NH_3)NO^{2+}$ (119E)[a]

	population		
ligand	$Co(NH_3)_5{}^{3+}$	NO^-	$Co(NH_3)NO^{2+}$
Co	25.198		25.293
NH_3-1[b]	9.752		9.857
N	8.098		8.080
H[c]	0.552		0.592
NH_3-2,4	9.750		9.849
N	8.096		8.079
H	0.551		0.590
NH_3-3	9.750		9.859
N	8.095		8.092
H	0.552		0.589
NH_3-5	9.797		9.904
N	8.096		8.081
H	0.551		0.608
NO		16.000	15.391
N		7.371	7.061
O		8.629	8.330

[a] Bent ($\phi = 119°$), eclipsed conformer. [b] Equatorial ammonia ligands are numbered 1–4, 1 being the ligand eclipsed by the nitrosyl. Ammonia no. 5 is the axial ligand. [c] Hydrogen populations are averaged over the ammonia ligand.

the interaction between the d_{xz} and d_{yz} orbitals of the cobalt with the π^* orbitals of nitrosyl are very modest in comparison with the σ interactions, implicating their lesser significance in the binding. These calculations are, therefore, not consistent with an interpretation of nitrosyl binding which infers greater bonding in the linear mode.

We are now left with the chore of explaining the longer M–N bond length without resorting to bond strength or bond multiplicity arguments. Our results are certainly not conclusive in this regard; however, it is interesting that the bent complex is found to have a larger exchange repulsion than that of the linear complex. This is explicable in terms of the expected overlap between the π^* orbital and the Co d_{xz} orbital of the 1e pair. This situation is illustrated in Figure 5. This destabilizing four-electron interaction buffers against too close of an approach of the nitrosyl ligand to the cobalt center. This interaction is considerably more moderate for a linear complex. Indeed in an $\{MXY\}^6$ complex, this repulsion would be entirely absent enabling a closer approach of the nitrosyl (this of course would also result in increased σ donation and π back-donation). It is notable that this interpretation of the difference in the M–N bond lengths does not implicate a greater bond strength or multiplicity for either modality and is therefore consistent with the fact that only relatively modest variations in the NO bond length are observed.[2]

Most of the above discussion has skirted the issue of the electronic configuration of the complex; i.e., we have not directly addressed the question of how many electrons are formally associated with the nitrosyl ligand. A possible clue in this regard, though certainly not a definitive answer, is provided by a Mulliken population analysis at the equilibrium conformation. These results are presented in Table VII. The most apparent conclusion is that the cobalt center is not nearly so positive as its formal, Co(III) designation would imply. This is not unexpected in light of the basic, σ-donor ability of the ammonia ligands. It is interesting that the charge on the cobalt is only slightly altered upon interaction of the pentacoordinate fragment with the nitrosyl even though the anionic ligand, NO^-, donates a charge of 0.61 e. Clearly the influence of the nitrosyl, a strong σ donor, is to moderate the donor capabilities of the ammonia ligands. It is notable that the nitrosyl ligand, even though it donated a majority of its excess charge, is left with a significant charge of −0.39 e, this in a complex whose overall charge is +2. This result is in accord with the heuristic interpretive value of assuming an anionic ligand in bent nitrosyl complexes. Of course, firm evidence for such an interpretation would necessitate finding a partial positive charge on the nitrosyl ligand in a linear complex. It should be emphasized that such a result would not be found on Mulliken analysis of the linear modality of $Co(NH_3)_5NO^{2+}$. Indeed one would find the nitrosyl to be even more negative than in the bent structure, this the result of its less facile charge transfer into the d_{z^2} orbital, the lowest lying vacant orbital of the cobalt. The situation could be quite different in a complex whose ground state was linear, e.g., a $\{MNO\}^6$ complex. In such an instance one expects the highest occupied orbital of the complex to be due to the e level on the metal and not the π^* orbital of the nitrosyl. The net charge on the nitrosyl ligand would then be determined by the relative importance of σ donation from NO to the metal and back-donation from the Co e levels to the π^*-acceptor orbitals of the nitrosyl. We will refrain from conjecture as to possible results except to note that a more positive nitrosyl than that found here seems likely.

Concluding Remarks

We have approached the question of the binding of a nitrosyl ligand in a metal complex from a quite specific point of view treating only a single complex. The results and implications of this study are, however, of more general applicability. As an example, for the present complex we found two contributions to be of primary importance for the stability of the bent complex, these being the charge-transfer and electrostatic interactions. Both of these contributions were dependent on the occupancy of the π^* orbital of the nitrosyl monomer. If one were to treat a complex with fewer electrons, the bent complex would be greatly destabilized and one would expect the linear geometry to be the equilibrium conformer. This is, of course, found to be the case.

We also feel that our explanation for the nitrosyl's preference of an eclipsed conformer in this molecule is of more general validity. This feature, the eclipsing of a bent nitrosyl with an equatorial ligand, is common to most complexes, both six-coordinate, octahedral and five-coordinate, square-pyramidal species.[2,3,20] Most notable are examples such as nitrosyl ($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)cobalt(II)[20b] and bis(dimethyldithiocarbamato)nitrosylcobalt,[20h] in which the four equatorial ligands are nearly identical precluding the control of the d_{xz}, d_{yz} (e) orbitals in determining the relative stability of staggered and eclipsed conformers.[7a] It ought to be noted that *trans*-(chloronitrosyl)bis(ethylenediamine)cobalt(III) is anomalous in this regard, the nitrosyl being staggered between the two diamines.[20e] Our argument, emphasizing the electrostatic interaction preference for the eclipsed conformer, was dependent only on the symmetry of the d_{xy} orbital. As this orbital will be occupied for any bent nitrosyl complex (regardless of whether it is octahedral or pentacoordinate, square pyramidal) this interaction should be operative. As noted earlier, the exchange interaction will tend to favor staggered conformers; hence there may be cases, as noted above, in which the preferred structure has the nitrosyl staggered between equatorial ligands.

The large trans effects observed for linear complexes were also explicable in terms of the present calculations. Once again the critical factor was the occupancy of the nitrosyl π^* orbital coupled with the relative spacing of the orbitals. As such, linear complexes (which contain fewer electrons) would not be expected to exhibit large trans effects.

The calculations reported here imply a partial negative charge on the nitrosyl ligand in the equilibrium conformer of the complex. This result is in accord with a qualitative, intuitive interpretation in which a formal negative charge is assigned the nitrosyl ligand in bent complexes.

At this point, several of the limitations of the present calculations should be emphasized. We were interested in making qualitative, physically oriented conclusions regarding the nature of the bonding in $Co(NH_3)_5NO^{2+}$. As the single configuration wave functions employed did faithfully reproduce the experimental structural tendencies, we feel that they were useful as a basis of qualitative discussions. We do not claim that the present results give quantitative energy separations. Indeed, the plethora of low-lying excited states—as suggested by the number of bound virtual orbitals as well as by the black color of the complex—would suggest that any attempts at a more quantitative treatment would necessitate inclusion of CI. Similarly, correlation effects would be critical if a description of the absorption spectrum of the complex were desired. These, however, were not the intent of the present study.

We feel that the insights provided by this work are both significant and typical of what might be attained by application of ab initio techniques to this type of problem. It should be noted that the energy analyses presented here are not possible with empirical wave functions. We also feel that the fractional charge simulation of dipolar ligands has proven itself as a useful qualitative tool in these types of problems.

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Molecular Orbital Analysis of the Metal–Metal Interaction in Some Carbonyl-Bridged Binuclear Complexes

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Molecular orbital calculations performed on *trans*-$[C_5H_5Fe(CO)_2]_2$ and the bridged form of $Fe_3(CO)_{12}$ show that there is apparently no net direct bonding between carbonyl-bridged iron atoms. The metal–metal interaction responsible for the short interatomic distance is better described in terms of multicentered linkages between the metal and the bridging carbonyl ligands. This description is supported by a recent experimental determination of differential electron density.

Introduction

The nature of the metal–metal interaction in diamagnetic binuclear complexes has for some years been the subject of numerous discussions, especially in the case of ligand-bridged systems.[1-3] When spin coupling between the metal atoms is required from the magnetic behavior of the complex, either a direct metal–metal bond[6] or a superexchange mechanism via the bridging ligands[8] can be invoked. However, qualitative considerations based upon molecular orbital symmetry have raised ambiguity about the nature of the metal–metal interaction since it was not possible according to these discussions to distinguish unequivocally between M–M direct bonding and indirect spin coupling through the bridging ligands.[1-3] It seems that these considerations have been already substantiated by a molecular orbital calculation on $Co_2(CO)_8$.[4] However, on the basis of structural data which associate the setting up of a spin-coupling interaction to a dramatic decrease of the M–M distance, Dahl et al.[6,7] were led to postulate the existence of a distinct metal–metal bond. These data were obtained on phosphorus-[6] and sulfur-bridged[7] complexes. Parameter-free molecular orbital calculations later performed on several P-, S-, N-, and As-bridged complexes with pseudobioctahedral