for CO on ruthenium, giving values ranging between 0.5 eV and 1.8 eV:[31] there is evidence that the value obtained depends on the surface and on the degree of coverage.[31c] The wide range of estimates makes this an ineffective comparison, but if we take the uppermost value for the work function of ruthenium with CO adsorbed (6.5 eV), this still lies below Plummer's values for the first binding energy of $Ru_3(CO)_{12}$ (6.7 or 7.25 eV depending on calibration procedure).

The first ionization energies of metal cluster compounds are dominated by the electron-withdrawing properties of the ligand. For example, the rhenium halide cluster Re_3Cl_9 has a first ionization energy of 9.15 eV,[1c] which may be compared with a value of 8.45 eV for $H_3Re_3(CO)_{12}$. Cyclopentadienyl ligands on the other hand appear to enhance the electron "richness" of a cluster; for example, $H_4Co_4(\eta\text{-}C_5H_5)_4$ has a first IE of 5.7 eV, which may be compared with a value of 8.9 eV for $Co_4(CO)_{12}$.[32]

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Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; $Co_4(CO)_{12}$, 17786-31-1; $Os_6(CO)_{18}$, 37216-50-5; $H_4Os_4(CO)_{12}$, 12375-04-1; $H_2Os_3(CO)_{10}$, 41766-80-7; $H_3Re_3(CO)_{12}$, 73463-62-4; $H_4Re_4(CO)_{12}$, 60146-15-8.

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Contribution from the Departments of Chemistry, University of Durham, Durham, DH1 3LE, England,
and the University of Perugia, 06100 Perugia, Italy

A Theoretical Investigation of the Ground and Core Hole States of $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$. Models for the Reversible Binding of CO to Cu(I) Complexes

DAVID T. CLARK, ANTONIO SGAMELLOTTI,* and FRANCESCO TARANTELLI

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Nonempirical LCAO-MO-SCF computations have been carried out on the ground and core hole states of $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$ (and the associated fragments) as models for Cu(I) complexes which reversibly bind CO. For the diamino complex, which serves as a model for $[Cu(en)CO]^+$ and $[Cu(hm)CO]^+$, the computations show that a linear ∠Cu-C-O arrangement is preferred, the computed coordination energy for carbon monoxide being −8.1 kcal mol^{-1}. The bond overlap populations suggest that for both $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$ (which serves as a model for $[Cu(dien)CO]^+$ and $[Cu_2(hm)_3(CO)_2]^{2+}$) the CO bond length should be somewhat shorter than for the free ligand, as is observed experimentally. For the isolated ions, the ΔSCF calculations suggest significant shifts between the core levels for the model systems; however, the lattice potential in the solid state reduces the computed shifts somewhat.

Introduction

The study of the interaction of small molecules with crystallographically oriented metal surfaces has been an area of expanding activity on both experimental and theoretical fronts in recent years.[1] The importance of such studies derives from the fundamental insight they provide for model systems for heterogeneous catalysis, and such studies have received considerable impetus in recent years from developments in instrumental surface science.[1,2]

An area of equal importance is that encompassed by the activation of small molecules by complex formation in homogeneous media, and of particular interest is the reversible fixation of small molecules.[3] Such studies are of relevance to homogeneous catalysis and its synthetic applications as well as the specialized field of bioinorganic chemistry.[4]

While the focus of interest of both theoretical and experimental surface science studies has naturally been in the area of relevance to heterogeneous catalysis,[1,2] the very significant advances which have been made in recent years in the reversible binding of small molecules to metal complexes suggests that the time is opportune to investigate such systems by using techniques which have proved so successful in the heterogeneous catalysis field.

A significant fraction of the published literature in the past few years has detailed studies on the interaction of simple molecules such as carbon monoxide with both simple crystal and polycrystalline metal surfaces, and the mode of bonding of chemisorbed CO on a variety of metals is now reasonably well understood.[5] Comparatively few studies of this genre have been made, however, with transition metals at the end of the first-row series (viz., Cu and Zn) although such elements are of considerable importance in bioinorganic chemistry.[4]

Recently, however, data have become available on simple copper(I) complexes which reversibly bind CO in homogeneous media.[6] The complexes which have been isolated by Floriani and co-workers[6] are of two structural types, and a remarkable feature is the relative stability toward dissociation of the complexes in the solid state. As has previously been pointed out, prior to the work by Floriani and co-workers copper(I) carbonyls, although of considerable interest, had largely remained, because of their lability and propensity for disproportionation, chemical curiosities.[7,8] The possibility of employing Cu(I) mediated transfer of CO to organic substrates[9]

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*To whom correspondence should be addressed at the University of Perugia.

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and the general bioinorganic interest, however, makes the detailed study of CO complexes of copper(I) of more than usual interest.

The complexes described by Floriani et al. fall into two broad structural classes. The first[6b–d] exemplified by $[Cu(en)CO(BPh_4)]$ exhibits a roughly planar coordination of the nitrogen ligands and carbon monoxide, with carbons of one of the phenyl residues occupying two further sites in a pseudo-trigonal-bipyramidal arrangement. The second class[6a,c] typified by $[Cu(dien)CO](BPh_4)$ and $[Cu_2(hm)_3(CO)_2](BPh_4)_2$ shows a pseudotetrahedral arrangement around the copper, with the nitrogen ligands occupying three sites and the CO ligand in the fourth position. The most remarkable aspect of these structure is the linearity of the ∠Cu–C–O moeity and the fact that the two structural types span the shortest C–O bond length and the longest Cu–C bond length in the few examples which have been described in the literature.[6b]

For the systems in the second category, the high relative stability of the complexes has been ascribed to a variety of electronic effects; however, no attempt has previously been made to investigate prototype model systems theoretically. The factors which are thought to be important[6a] include highly basic nitrogens as donor atoms and the polydentate nature of the ligands and the polarizability and low nucleophilicity of the counterion. In the case of the bidentate nitrogen ligand complexes, the role of the counterion is of crucial importance and the rather specific orientation of the phenyl substituent to provide an overall trigonal-bipyramidal arrangement is one manifestation of this.

It is interesting to contrast the rather strong binding of CO in the solid state for these complexes, involving as they do the interaction of a Cu(I) d^{10} system with the carbon monoxide, with the generally held view in heterogeneous catalysis that the interaction of CO with d^{10} metals is weak.[1,2]

Previous studies have shown[1,2,10] the considerable insight into structure and bonding both in metal carbonyls and for CO chemisorbed on metal surfaces provided by high-energy photoelectron spectroscopy (ESCA) studies, and it is therefore of interest to consider the possibility of applying this technique to the Cu–CO complexes.

In this paper, therefore, we describe the results of ab initio LCAO–MO–SCF calculations on both the ground and core hole states of model systems for the reversible coordination of CO to copper(I). As models we have considered $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$ with geometries derived from X-ray crystallographic studies of $[Cu(en)CO(BPh_4)]$[6d] and $[Cu(dien)CO](BPh_4)$,[6a] respectively. The objectives of this study may be considered as follows: (i) to investigate the nature and energetics of the interaction between Cu(I) and CO in these systems as models for those which have been experimentally characterized; (ii) to investigate core ionization phenomena in the model systems by means of ΔSCF computations to provide data for direct comparison with experimental data when these become available.

Theoretical Considerations

(a) Model Systems. The computational expense dictated that for the two structural types the simplified model systems encoded only the essential features. Thus as a model for the $[Cu(en)CO]^+$ system we have taken $[Cu(NH_3)_2CO]^+$ with the Cu–N and ∠Cu–C–O bond length and angle being directly transcribed from the experimental data. The crystallographic data confirm that the interaction with the tetraphenylborate anion is essentially Coulombic in nature, and, although this is important in describing the solid state structure, it is not germane to the discussion of the interaction between Cu(I) and carbon monoxide. The Coulombic interaction is however important in discussing the likely solid-state ESCA spectra, and this will be considered in some detail in a later section. So that the nature of the interaction between CO and Cu(I) could be investigated, computations have been carried out on $[Cu(NH_3)_2]^+$ and CO at the geometries appropriate to the model system. The near linearity of the ∠Cu–C–O arrangement observed experimentally has been subjected to investigation in this work by use of the MERGE facility in the ATMOL[11] suite of programs. The experimental geometry may be described in terms of a plane passing through the two nitrogens and the carbon of the CO ligand, with the copper displaced slightly above the plane and the oxygen slightly below the plane, the experimental ∠Cu–C–O bond angle being 178.3° (viz., the oxygen is displaced slightly upward toward the plane from the exactly linear arrangement). Computations were carried out for ∠Cu–C–O bond angles of 180, 200, and 220° (viz., displaced downward from linearity by 1.7, 21.7, and 41.7°, respectively), and 160 and 140° (viz., displaced upward by 18.3 and 38.3°).

It seems reasonable that the important feature as far as the nitrogen ligand is concerned is the appropriate spatial arrangement, and it may therefore be argued that NH_3 substituents at the appropriate positions will reflect rather well the interactions involved between ethylenediamine and the copper.

As a model for $[Cu(dien)CO]^+$ we have taken the experimental Cu–N and ∠Cu–C–O geometries, the diethylenetriamine ligand being simulated by three NH_3 substituents. So that the interaction between the copper and the CO ligand could be investigated, computations were also carried out on the fragments, viz., $[Cu(NH_3)_3]^+$ and CO.

(b) Computational Details. Calculations have been carried out on both the ground and Cu_{2s}, Cu_{2p}, C_{1s}, and O_{1s} core hole states by the ΔSCF formalism. The computations were performed with the use of the ATMOL3 program package[11] implemented on the Rutherford IBM 370/195 computer.

The basis set employed may be described as follows.

(i) For copper the basis consisted of a [5s,3p,2d] contraction of a primitive (12s,7p,5d) Gaussian set. The exponents and contraction coefficients for this set were defined in the following manner. The s,p basis set was derived from that described for copper by Roos et al.,[12] the final two s functions of lowest exponents being replaced with two less diffuse functions of exponents 0.32 and 0.08, as suggested in ref 12 for use in molecular calculations. The basis has been augmented with a p-type function to allow for representation of the 4p orbital.[13] The d functions of ref 12 have been replaced by those optimized by Hay[14] (thus introducing an extra d function), the remaining contraction coefficients being taken from ref 12 as the largest atomic eigenvector coefficients.

(ii) For the first-row atoms, Dunning's [4s,2p] contractions[15a] of (9s,5p) primitive sets[15b] were employed, while for hydrogen the corresponding 2s contraction of the 4s primitive set was taken (scale factor 1.2).

For the largest system studied, namely, $[Cu(NH_3)_3CO]^+$ with a basis of 92 contracted functions, integral evaluation took 43 min of CPU time while the SCF computation which took

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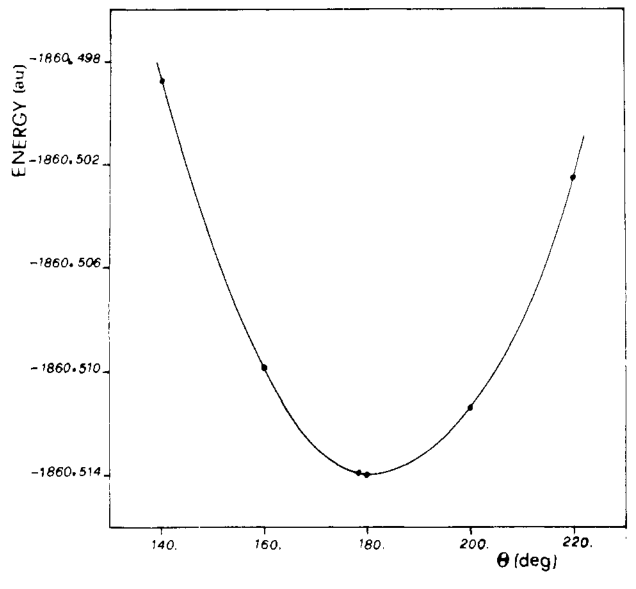

Figure 1. Total energy as a function of the ∠Cu–C–O angle for $[\mathrm{Cu(NH_3)_2CO}]^+$. (Angles of less than 180° correspond to displacement of oxygen upward toward the plane of the carbon and nitrogen atoms.)

Table I. Energetics of CO and NH_3 Coordination for the Ground and Core Hole States of $[\mathrm{Cu(NH_3)_2}]^+$ and $[\mathrm{Cu(NH_3)_3}]^+$

process	E, kcal mol^{-1}
$[\mathrm{Cu(NH_3)_2}]^+ \xrightarrow{\mathrm{CO}} [\mathrm{Cu(NH_3)_2CO}]^+$	−8.1
$[\mathrm{Cu(NH_3)_2}]^+ \xrightarrow{\mathrm{NH_3}} [\mathrm{Cu(NH_3)_3}]^+$	−15.3
$[\overset{*}{\mathrm{Cu}}\mathrm{(NH_3)_2}]^+ \xrightarrow{\mathrm{CO}} [\overset{*}{\mathrm{Cu}}\mathrm{(NH_3)_2CO}]^+$	−27.5 (Cu_{2s}), −27.9 (Cu_{2p})
$[\overset{*}{\mathrm{Cu}}\mathrm{(NH_3)_2}]^+ \xrightarrow{\mathrm{NH_3}} [\overset{*}{\mathrm{Cu}}\mathrm{(NH_3)_3}]^+$	−61.2 (Cu_{2s}), −61.3 (Cu_{2p})
$[\mathrm{Cu(NH_3)_2}]^+ \xrightarrow{\overset{*}{\mathrm{C}}\mathrm{O}} [\mathrm{Cu(NH_3)_2}\overset{*}{\mathrm{C}}\mathrm{O}]^+$	73.0 (C_{1s}), 83.9 (O_{1s})
$[\mathrm{Cu(NH_3)_3}]^+ \xrightarrow{\mathrm{CO}} [\mathrm{Cu(NH_3)_3CO}]^+$	−2.1
$[\overset{*}{\mathrm{Cu}}\mathrm{(NH_3)_3}]^+ \xrightarrow{\mathrm{CO}} [\overset{*}{\mathrm{Cu}}\mathrm{(NH_3)_3CO}]^+$	−12.4 (Cu_{2s}), −13.8 (Cu_{2p})
$[\mathrm{Cu(NH_3)_3}]^+ \xrightarrow{\overset{*}{\mathrm{C}}\mathrm{O}} [\mathrm{Cu(NH_3)_3}\overset{*}{\mathrm{C}}\mathrm{O}]^+$	57.5 (C_{1s}), 67.5 (O_{1s})

~1.25 min/cycle were complete in 57 min.

Core-hole-state calculations were carried out with use of the LOCK directive, and, as a typical example, convergence to a given hole state was complete in ~30 min, starting from the vectors appropriate to the ground-state system. In the particular case of the Cu_{2p} core hole states, convergence was sometimes a problem; however, with appropriate manipulation of ther level shift parameters convergence was obtained in all cases. Relaxation energies were computed by reference to Koopmans' theorem.

Results and Discussion

(a) Ground States. (i) $[\mathrm{Cu(NH_3)_2CO}]^+$. The experimental data[6b] indicates a ∠Cu–C–O bond angle very close to 180° (178.3°), and computations on the total energy as a function of angle provide the data given in Figure 1. As we have previously noted, there is a degree of asymmetry consequent upon the fact that the copper is displaced slightly above and the oxygen slightly below the plane encompassing the two nitrogens and the carbon of the carbon monoxide ligand. The energetic preference for the essentially linear arrangement is confirmed, and it is clear that displacement of the oxygen away from the plane is energetically less expensive than the displacement toward and above the plane. It is interesting to compare the energies for displacement from linearity by a given extent for this system to that for the prototype NiCO system ($^3\Delta(d^9)$ and $^1\Sigma(d^{10})$) which has previously been described.[16] For a displacement of 20° from linearity, the energy rises by 2.6 and 1.6 kcal mol^{-1} for the upward and downward motion, respectively, in the $[\mathrm{Cu(NH_3)_2CO}]^+$ system. This compares very favorably with the energy required for distortion of the ∠Ni–C–O system for the comparable d^{10} configuration of ~0.74 kcal mol^{-1} for a 17° displacement. This contrasts with the situation for the $^3\Delta(d^9)$ state of NiCO, where a comparable displacement is predicted to give rise to a small energy lowering of 0.81 kcal mol^{-1}.

The coordination energy of CO computed as the energy difference between $[\mathrm{Cu(NH_3)_2CO}]^+$ and $[\mathrm{Cu(NH_3)_2}]^+$ and CO is −8.1 kcal mol^{-1} which would seem to be a fortuitously good figure, consistent with the reversibly bound nature of the CO ligand in the solution phase (kinetic factors will almost certainly dominate considerations of stability of the solid state complex). (Correlation energy differences are of course likely to be of considerable importance in dictating the overall energetic preference, and the discussion of the energetics presented here is therefore at a relatively crude level.) It is interesting to compare this energetic preference for the coordinated CO species with that computed for the $^1\Sigma(d^{10})$ NiCO system.[16] The energetic preference in this case is significantly higher (ΔE −53.4 kcal mol^{-1}).

(ii) $[\mathrm{Cu(NH_3)_3CO}]^+$. The computations on $[\mathrm{Cu(NH_3)_3CO}]^+$ and on $[\mathrm{Cu(NH_3)_3}]^+$ allow interesting comparisions to be drawn and the relevant data are displayed in Table I.

The total energies again predict that CO should be bound to $[\mathrm{Cu(NH_3)_3}]^+$, the binding energy being −2.1 kcal mol^{-1}. Since the total energies are so large and the differences so small, the most that can be said from this data alone is that it is not unreasonable that CO should be reversibly bound to both $[\mathrm{Cu(en)}]^+$ and $[\mathrm{Cu(dien)}]^+$.

The data also allow an intersting comparison to be drawn between the relative affinities of $[\mathrm{Cu(NH_3)_2}]^+$ for NH_3 and CO as ligands. The energetic preference computed for NH_3 is −7.2 kcal mol^{-1} compared with CO, and it seems likely, in view of the small geometry changes which have not properly been taken into account in this estimate, that this figure represents a lower bound to the energetic preference. This also points to one of the obvious difficulties in the isolation of these complexes, namely, competition for sites between CO and stronger donors.

It is of interest at this stage to briefly survey the corresponding data for the core ionized species, which will be discussed in somewhat more detail in a later section. Considering first the Cu_{2s} core-ionized species for $[\mathrm{Cu^*(NH_3)_2CO}]^+$ (where an asterisk indicates a core hole on the starred atom), the coordination energy for either CO or NH_3 is now significantly increased (ΔE −27.5 and −61.2 kcal mol^{-1}, respectively) consequent upon the strong electron demand of the core hole located on the copper. A similar trend is apparent for $[\mathrm{Cu(NH_3)_3}]^+$ where the creation of a core hole increases the CO affinity to −12.4 kcal mol^{-1}. Closely similar data are evident for the Cu_{2p} hole states. By contrast, creation of a core hole on the carbon monoxide ligand (thus suppressing donor capability) leads to a substantial energetic preference for the

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Table II. Population Analysis for $[Cu(NH_3)_2CO]^+$, $[Cu(NH_3)_3CO]^+$, and Their Fragments

	gross atomic charges		
species	Cu	NH_3	CO
$[Cu(NH_3)_2]^+$	0.93	0.035	
$[Cu(NH_3)_2CO]^+$	0.88	0.035	0.050
$[Cu(NH_3)_3]^+$	0.96	0.013	
$[Cu(NH_3)_3CO]^+$	0.98	0.010	−0.010

	gross atomic charges	
species	C	O
CO (a)[a]	0.21	−0.21
CO (b)[a]	0.20	−0.20

	changes in bond overlap population[a,b]		
process	Δ (Cu-N)	Δ (Cu-C)	Δ (C-O)[c]
$[Cu(NH_3)_2]^+ \xrightarrow{CO} [Cu(NH_3)_2CO]^+$	−0.003	0.054	0.065
$[Cu(NH_3)_3]^+ \xrightarrow{CO} [Cu(NH_3)_3CO]^+$	−0.008	0.033	0.057
$[Cu(NH_3)_2CO]^+ \xrightarrow{NH_3} [Cu(NH_3)_3CO]^+$	−0.023	−0.021	−0.018

[a] CO charges and bond overlap populations computed at the equilibrium geometry appropriate to (a) $[Cu(NH_3)_2CO]^+$ and (b) $[Cu(NH_3)_3CO]^+$. [b] CO bond overlap population: (a) 0.60; (b) 0.59. [c] With respect to CO at the appropriate bond length.

dissociated species for both $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$. This provides yet another example of the large change in potential energy surface associated with going from ground to core hole states.[17]

(b) Population Analysis. As a crude estimate of the overall electron distributions, Mulliken population analyses may be used. The relevant data are displayed in Table II. The analyses show that the description of these systems in terms of Cu(I) is entirely reasonable. On going from $[Cu(NH_3)_2]^+$ to the carbon monoxide complex, there is a small decrease in positive charge on the copper while for the $[Cu(NH_3)_3]^+ \rightarrow [Cu(NH_3)_3CO]^+$ system there is a small computed increase. Whereas in the case of the diamino complex the CO overall carries a small defect in terms of electron density, for the triamino complex there is overall a small negative charge on the CO ligand. The individual gross atomic populations give charges of 0.11 and 0.09 for the carbon atom in the diamino and triamino complexes, respectively, compared with the free ligand charge of 0.20. The corresponding data for oxygen are −0.06 and −0.10 for the complexes and −0.20 for the free ligand. This suggests substantial π interaction via the $2\pi^*$ orbital of the CO ligand, which increases as the number of nitrogen ligands increases.

Considering the changes in bond overlap populations, the calculations suggest an increased C–O bond overlap for both complexes compared with the isolated ligand. Since the comparison is in each case with the ligand at the *same* bond length, this may be taken as a direct indication that the C–O bond length should be shorter than for the free ligand, in the order diamino < triamino complex, in agreement with the experimental data.[6a,b] This is of more than trivial interest since the Cu–C bond lengths might lead one to suspect that the reverse would be true. It is unfortunately difficult to compare the Cu–C bond overlaps directly since the distances are different, however it is of interest to note that, despite the shorter distance, the bond overlap is smaller for the triamino complex. This perhaps points to one of the deficiencies of a Mulliken population analysis, since the orbitals involved are of disparate size. For example, the radical maxima for the 3d orbital in Cu^+ is ~0.6 au[18] from the nucleus; however, the orbital has a very long tail. By comparison for the first-row atoms involved, viz., C, N, and O, the radial maxima for the 2s and 2p valence orbitals are typically in the range 0.8–1.2 au.[18] It is clear therefore that there are likely to be considerable difficulties consequent upon the equipartition of overlap densities when Cu–N and Cu–C bond lengths in the range 3.4–3.9 au are considered.

(c) Core Hole States. A considerable literature now exists[1,2,10] documenting ESCA investigations on the core-hole-state spectra of CO chemisorbed on metals, on metal carbonyls, and on complexes of Cu(I) and Cu(II). It is therefore of considerable interest to investigate the likely core-hole-state spectra for the copper complexes which reversibly bind carbon monoxide on the basis of the theoretical investigation of the model systems described in this work.

We consider first the calculated "isolated ion" binding and relaxation energies before briefly considering the likely spectral features for the solid state.

As we have previously noted, computations have been carried out on the Cu_{2s}, Cu_{2p}, C_{1s}, and O_{1s} core hole states, and comparison with Koopmans' theorem allows estimates to be made of relaxation energies. The relevant data are displayed in Table III.

Although the basis sets are of double-ζ quality, absolute binding energies are still slightly overestimated. Thus for CO we have previously investigated[19] in some detail the basis set dependence of both absolute and relative binding energies and for double-ζ quality basis sets both are well described. It has also been shown[19a] that the dependence of both absolute and relative computed binding and relaxation energies is not significantly influenced by the bond length. For the sake of completeness, however, comparisons of C_{1s} and O_{1s} binding energies have been made with respect to the free ligand at the appropriate geometry. For comparison purposes, the absolute binding and relaxation energies computed with the ΔSCF formalism employing the same basis set but including polarization functions[19b] are 299.1, 543.5, 10.5, and 18.9 eV, respectively for the C_{1s} and O_{1s} hole states of carbon monoxide.

Several comparisons are of interest for the copper core levels. Thus in going from $[Cu(NH_3)_2]^+$ to $[Cu(NH_3)_2CO]^+$ the calculated shifts are ~0.8 eV to lower binding energy for both the 2s and 2p hole states, the shifts being dominated by the changes in relaxation energy which amount to ~2.0 eV. It is instructive to compare these shifts and changes in relaxation energies with those involved in the transformation $[Cu(NH_3)_2]^+ \rightarrow [Cu(NH_3)_3]^+$. A greatly increased shift to lower binding energy is predicted in this case (~2 eV), the relaxation energy contribution being a much smaller component (~0.6 eV) of this overall shift. For the CO complex of $[Cu(NH_3)_3]^+$, the shifts with respect to the parent system are calculated to be much smaller than those for the diamino complex (0.4 vs. 0.8 eV); however, the differences in relaxation energies are comparable (~2.0 eV).

A comparison of the two model systems for $[Cu(en)CO]^+$ and $[Cu(dien)CO]^+$ shows a predicted shift for the isolated ions of 1.5 (2s level) and 1.7 eV (2p level), with the tridentate nitrogen ligand complex having the lower binding energy. Approximately a third of these shifts originates on differences in relaxation energies.

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Table III. Binding and Relaxation Energies (in eV) for the Core Hole States of $[Cu(NH_3)_2CO]^+$, $[Cu(NH_3)_3CO]^+$, and Their Fragments

	core level							
	Cu_{2s}		Cu_{2p}		C_{1s}		O_{1s}	
species	BE	RE	BE	RE	BE	RE	BE	RE
$[Cu(NH_3)_2]^+$	1072.5	15.4	953.7	16.1	300.0[a]	10.3[a]	543.9[a]	18.9[a]
$[Cu(NH_3)_2CO]^+$	1071.7	17.4	952.9	18.0	303.5	11.4	547.9	19.7
$[Cu(NH_3)_3]^+$	1070.6	16.0	951.7	16.6	300.1[b]	10.3[b]	543.9[b]	18.9[b]
$[Cu(NH_3)_3CO]^+$	1070.2	18.0	951.2	18.7	302.7	11.6	546.9	19.9

[a] CO core level computed at the geometry appropriate to $[Cu(NH_3)_2CO]^+$. [b] CO core level computed at the geometry appropriate to $[Cu(NH_3)_3CO]^+$.

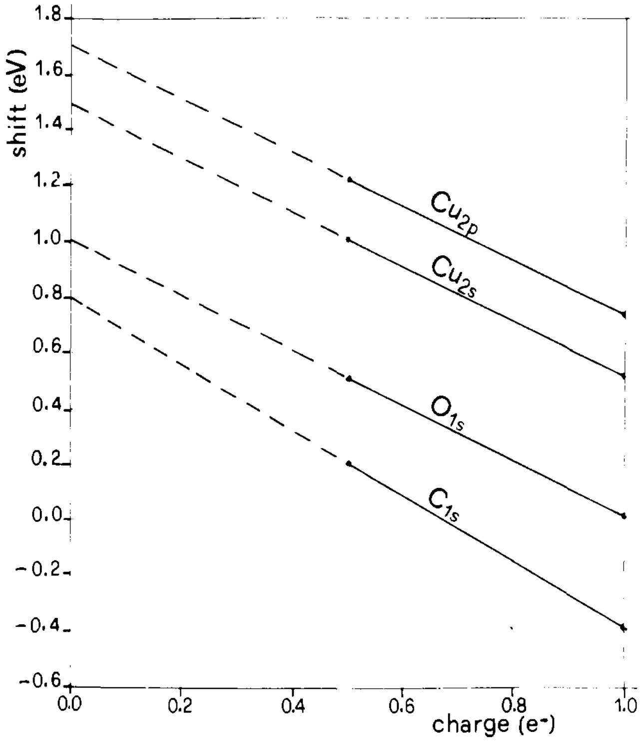

Figure 2. Plot of lattice potential modified binding energy shifts for Cu_{2s}, Cu_{2p}, C_{1s}, and O_{1s} core levels between $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$ as a function of charge on the boron atom in the $(BPh_4)^-$ counterion.

Before considering the likely effect of lattice potentials in the solid state of these complexes in moderating these shifts, we may briefly consider core ionization in the carbon monoxide ligand. A significant feature of previous theoretical studies of prototypes for the interaction of CO with transition metals is the relativey small shift predicted for the ligand core levels for linearly (180°) bonded systems.[16,20] The interesting feature, as far as the present data are concerned, is the substantial computed shifts for both the C_{1s} and O_{1s} core levels. Thus comparing $[Cu(NH_3)_2CO]^+$ with $[Cu(NH_3)_3CO]^+$, the computed shifts are 0.8 and 1.0 eV to lower binding energy for the C_{1s} and O_{1s} levels, respectively. The relaxation energy term in each case plays a relatively minor role in these shifts (~0.2 eV). Compared to the free ligand, the computations suggest a substantial shift to higher binding energy. Thus for $[Cu(NH_3)_2CO]^+$ with respect to CO, the computed shifts are 3.5 and 4.0 eV for the C_{1s} and O_{1s} levels, respectively; the comparable figures for the $[Cu(NH_3)_3CO]^+$ complex being 2.6 and 3.0 eV, respectively. Since the relaxation energies are uniformly larger for the complexes compared with the free ligand, the relaxation contributions to the shifts are actually negative. A similar situation has previously been discussed theoretically in considering HCO^+ and CH_3CO^+.[21]

A comparison may be drawn of the C_{1s} and O_{1s} level shifts (with respect to the free ligand) in the series XCO with X as the following substituents:[21,22] X = H^+, CH_3^+, $[Cu(NH_3)_2]^+$, $[Cu(NH_3)_3]^+$, and BF_3. The computed shifts for the C_{1s} level are 10.9, 8.1, 3.5, 2.6, and 2.5 eV respectively, while for the O_{1s} level the corresponding shifts are 10.3, 7.3, 4.0, 3.0, and 2.5 eV. From this it can be seen that, in terms of the overall electron perturbation to the ligand (at least as far as the core levels are concerned), $[Cu(NH_3)_3]^+$ as a substituent is somewhat comparable to BF_3, which would seem to be not unreasonable.

The data discussed thus far pertain to the isolated ions, whereas experimental data will refer to the Fermi level of the condensed phase. As such a comparison needs to take into consideration two dominant effects: the first being differences in lattice potential, the second being differences in extramolecular relaxation energies.

The crystallographic data for the two systems on which the theoretical models are based show close similarities.[6] Thus both $[Cu(en)CO(BPh_4)]$ and $[Cu(dien)CO](BPh_4)$ have monoclinic crystal structures with four molecules per unit cell of very comparable dimensions (*a*, *b*, and *c* are 10.30, 12.23, and 18.39 Å for $[Cu(en)CO(BPh_4)]$ and 14.83, 18.74, and 9.60 Å for $[Cu(dien)CO](BPh_4)$. The differences in relaxation energies for the same core levels of the two models studied in this work are small, and since extramolecular contributions to relaxation energies[23] are typically < 10% of the total, it would seem unlikely that such contributions could give rise to shifts of more than ~0.1 eV. The close similarities in lattice sites would tend to reinforce this, and the main difference is therefore to be expected from the nearest-neighbor lattice potentials. For $[Cu(en)CO(BPh_4)]$ the distances between the Cu, C, and O nuclei and the boron, which carries a significant proportion of the overall negative charge, are[6d] 8.05, 8.5, and 9.3 au, respectively. If the full negative charge were located on boron, this would lead to negative lattice potential contributions to the shifts of 3.4, 3.2, and 2.9 eV, respectively. For $[Cu(dien)CO](BPh_4)$, the corresponding distances are 11.3, 13.3, and 14.7 au,[6a] with corresponding lattice potential for unit charge on boron of 2.4, 2.0, and 1.9 eV for Cu, C, and O, respectively. It is evident from this that the shifts expected for the solid state will be significantly modified with respect to the free ions. As a crude estimate of the likely solid-state shifts, Figure 2 gives a plot of lattice potential modified shifts vs. the charge on boron (over the range 1.0–0.5 for the negative charge on boron). The crystallographic data indicates discrete $(BPh_4)^-$ ions, so that a charge of 0 corresponds to the free ion shifts while $q = -1$ corresponds to the tetraphenylborate anion with the negative charge localized on boron. In previous

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investigations of lattice potentials on shift phenomena,[24] it has been shown that shifts are dominated almost entirely by nearest-neighbor interactions, and it is likely therefore that the estimates provided in Figure 2 will be useful as semiquantitative guides to the interpretation of the experimental data when these become available. The solid lines correspond to the typical range of charges on boron that might be expected for tetraphenylborate anion; the dotted lines then providing extrapolation of these shifts to those for the free ion. A charge of 0 on boron could also hypothetically correspond in the extreme to a completely delocalized system. In which case, if the charge were equally spread over the phenyl groups, each carbon would have a charge of ~0.04 electrons; as a matter of interest, if this were the case (we should emphasize that such a charge distribution would be completely unrealistic), the potentials provided by the phenyl ligands would still produce a small lattice potential shift for the Cu core levels of ~0.5 eV between $[Cu(NH_3)_2CO]^+$ and $[Cu(NH_3)_3CO]^+$, such that the computed solid state shift would be reduced to 1.0 eV for the Cu_{2s} level. For the sake of comparison, the total charges on boron and on the phenyl groups in the tetraphenylborate anion derived from CNDO/2 computations are 0.16 and 0.21 electrons, respectively.

It seems clear therefore that the likely solid-state shifts between $[Cu(en)CO(BPh_4)]$ and $[Cu(dien)CO](BPh_4)$ will be relativey small.

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Registry No. $[Cu(NH_3)_2CO]^+$, 60927-79-9; $[Cu(NH_3)_3CO]^+$, 60927-78-8.

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Contribution from the Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637

The Band Intensity/Frequency Factored Force Field Method for the Quantitative Determination of Bond Angles in Transition-Metal Carbonyls

JEREMY K. BURDETT[1]

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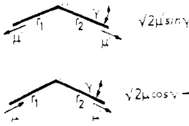
Use of carbonyl-region IR intensities and the frequency factored force field (F^4) is an established method for calculating CMC bond angles in metal carbonyls. Some of the critieria for accurate structure determination are examined. For all species the better the agreement between observed and calculated frequencies of the $M(^{12}CO)_x(^{13}CO)_{y-x}$ fragment with use of the F^4, the closer the calculated angle is to reality. The use of harmonic force constants to describe real (i.e., anharmonic) "CO stretching" vibrations does not give good results. For ternary systems the presence of oscillators with similar frequencies and dipole moment derivatives in addition to the carbonyl groups (e.g., $Mo(CO)_5N_2$) led to unreliable results due to vibrational coupling. For square-pyramidal (C_{4v}) $M(CO)_5$ and distorted tetrahedral (C_{2v}) $M(CO)_4$ molecules, the factors determining the phase relationship between the two a_1 modes are described. The most serious restriction on the use of the method, however, is that the bond dipole moment derivative may not lie parallel to the bond direction.

Introduction

In recent years[2-8] the intensities of carbonyl stretching vibrations and the force constants of the frequency factored force field (F^4)[9-12] have been extensively used to determine quantitatively the bond angles in transition-metal carbonyl fragments trapped in matrices and other stable carbonyls in solution. This is a particularly useful method in those circumstances where more conventional structural methods such as X-ray crystallography are inappropriate. This is most obviously true for reactive molecules trapped in low-temperature matrices.[6,7] In the form usually used, the IR absorption intensity corresponding to a normal mode Q_i, proportional to $(\partial\mu/\partial Q_i)^2$ where μ is the molecular dipole moment, is written in terms of contributions from CO bond dipole moment derivatives (μ') pointing along the bond. This is shown in **1** for the simple case of the bent dicarbonyl. Measurement of the *relative* intensity of symmetric and antisymmetric stretching



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