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N vs. O Linkage and σ vs. π Bonding in Transition-Metal Complexes of N_2O and NCO^-

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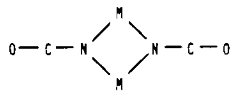
The geometries of NCO^- coordinated to transition metals range over N linkage, end-to-end bridge, N bridge, and possibly O linkage. The linkage in the "only" known complex containing coordinated N_2O, $[Ru(NH_3)_5N_2O]^{2+}$, is still unsettled. We have examined the linkage and mode of bonding of NCO^- and of N_2O to ML_5 fragments by fragment analysis of molecular orbital calculations. Various features of the interaction between the fragments indicate that (a) N-linkage complexes are more stable than O-linkage complexes and (b) σ bonding is the dominant factor in the metal to ligand bond. Our results also suggest that other transition-metal complexes of N_2O, such as $[Os(NH_3)_5N_2O]^{2+}$, should be stable.

Introduction

The cyanate anion (OCN^-) has been found to coordinate to transition metals in a variety of models.[1] There are plentiful examples of the N-bridged variety, **1**,[2] and some examples of the (predominantly N-linked) end-to-end bridge, **2**.[2g,3] As a nonbridging ligand, OCN^- in general coordinates to transition metals through the N atom.[4] Oxygen-bonded cyanates have mostly been claimed for complexes of metals in higher oxidation states;[5] however, no unambiguous evidence to confirm their structure yet exists. Even though OCN^- has not been as common an ambidentate ligand as SCN^-, the existence of an O-bonded cyanate complex has been an often-debated issue for many years.[1] Except in the case of interaction with other ligands,[4f] the OCN^- fragments in the transition-metal complexes are usually linear, but the angle between the metal and the ligand ($\angle MNC$) depends on several factors: packing in the solid state, counterions, and possible steric and trans effects of other ligands.[6]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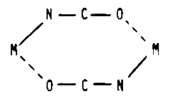
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Although different transition-metal complexes of N_2O have been hinted at as intermediates in chemical reactions and synthesis,[7] at present the "only" known complex containing N_2O is (dinitrogen oxide)pentaammineruthenium(II), $[Ru(NH_3)_5N_2O]^{2+}$.[8] Because of the instability of this ion, the accurate structure determination of it was not attainable.[8c,e] Some evidence indicated that N_2O was bonded to ruthenium through its terminal N atom.[8,9] Other interpretations based on force constant calculations suggested N_2O to be bonded via the O atom.[8d,e] The linkage of N_2O in $[Ru(NH_3)_5N_2O]^{2+}$ is still a controversial issue.[10]

In order to understand the bonding in the complexes of N_2O and NCO^-, we set out to analyze the electronic structure of ML_5XYZ, where M = Co, Ru, Os, L = NH_3, and XYZ = N_2O or NCO^-. The calculations carried out were of the extended Hückel type.[11,12] Details are given in the Appendix. Our argument will be based on the fragment analysis through a formalism[13] that partitions the molecular species into ML_5 and XYZ. Although the systems we studied were suggested by our interest in the linkage in $[Ru(NH_3)_5N_2O]^{2+}$, many of the conclusions we drew, based on symmetry, should carry over to M = any transition metal, L = any σ donor, and XYZ = any linear triatomic with 16 valence electrons. Other trends based on numerical results of our calculations could be extrapolated to predict bonding of ML_5XYZ in general.

Figure 1 presents the computed energy levels of some linear triatomics side by side with the estimated energies of the d orbitals of Mo, Ru, Os, and the first transition series. Similar diagrams were used in studies of the coordination modes of diatomic ligands in transition-metal complexes and on metal surfaces.[14,15] Figure 1 shows that there are symmetry restrictions that make the general features of the interaction independent of the variations of the metal and of the ligands. On the other hand, there is a wide range of relative energies of ligand and metal orbitals, which causes the magnitude of interaction to change from one case to another.

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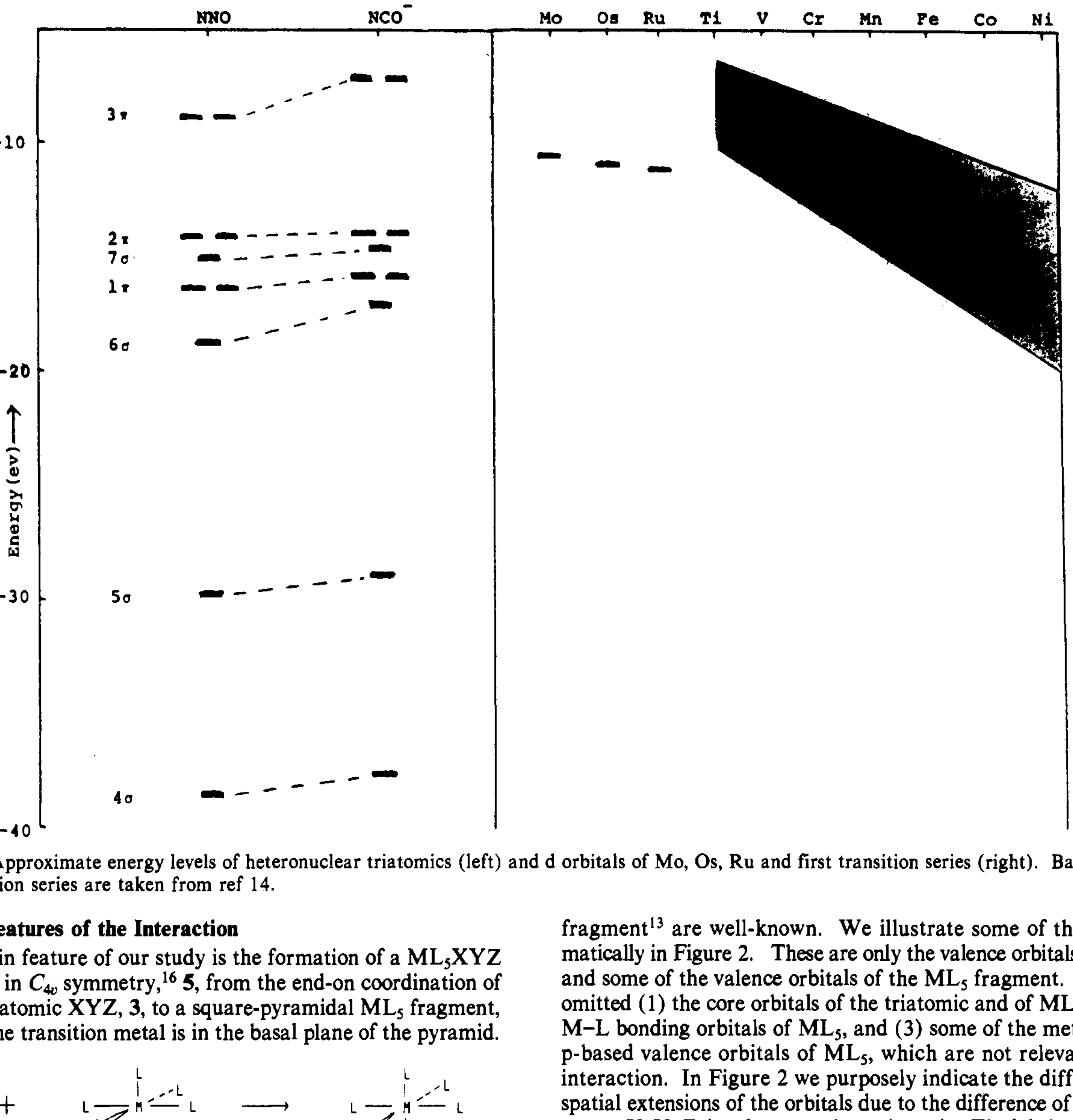
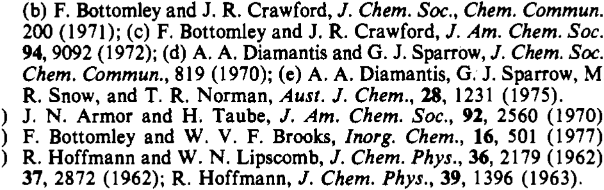


Figure 1. Approximate energy levels of heteronuclear triatomics (left) and d orbitals of Mo, Os, Ru and first transition series (right). Bands of the first transition series are taken from ref 14.

General Features of the Interaction

The main feature of our study is the formation of a ML_5XYZ compound in C_{4v} symmetry,[16] **5**, from the end-on coordination of a linear triatomic XYZ, **3**, to a square-pyramidal ML_5 fragment, **4**, where the transition metal is in the basal plane of the pyramid.



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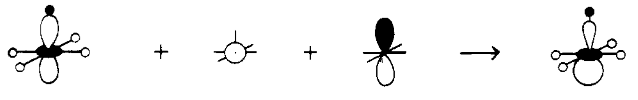
The orbitals of the triatomic[17] and the square-pyramidal ML_5 fragment[13] are well-known. We illustrate some of them schematically in Figure 2. These are only the valence orbitals of XYZ and some of the valence orbitals of the ML_5 fragment. We have omitted (1) the core orbitals of the triatomic and of ML_5, (2) the M–L bonding orbitals of ML_5, and (3) some of the metal s- and p-based valence orbitals of ML_5, which are not relevant in the interaction. In Figure 2 we purposely indicate the difference in spatial extensions of the orbitals due to the difference of the three atoms, X, Y, Z, in a heteronuclear triatomic. The labels of orbitals of the triatomic are based on the $C_{\infty v}$ symmetry in the linear XYZ and the C_{4v} symmetry in ML_5XYZ. The orbitals of ML_5 are referred to by their metal d character and the C_{4v} symmetry of the complex.

In the discussion of the interaction of the two fragments, the following orbitals can further be omitted: (1) the $b_1(x^2 - y^2)$ and $b_2(xy)$ orbitals of ML_5, because in the triatomic there is no orbital of b_1 and b_2 symmetry that will interact with them; (2) the higher 8σ, 9σ, and the lower 4σ, 5σ, and 1π orbitals of the triatomic, because Figure 1 and our calculations show that these orbitals are either too high or too low in energy to interact significantly with orbitals of the ML_5 fragment.

We thus are left with $e(xz,yz)$, $a_1(z^2,s,z)$, $a_1(z^2)$, and $a_1(z^2,s)$ orbitals of ML_5 to interact with the $e(2\pi)$, $e(3\pi)$, $a_1(6\sigma)$, and $a_1(7\sigma)$ orbitals of the triatomic.

The highest lying $a_1(z^2,s,z)$ orbital of ML_5 has been analyzed before.[13] It is a metal (z^2)–ligand σ antibonding, namely z^2–λL combination, **6**, further mixing with metal s and *z* orbitals. The important feature is that the metal *z* mixes in the phase relation shown in **7**. The resulting orbital, **8**, shaped by this hybridization, shows a reduction of the electron density in the apical ligand and



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(16) The results of our studies indicate that the linear mode of bonding of N_2O or NCO^- to $M(NH_3)_5$ is the stable one.

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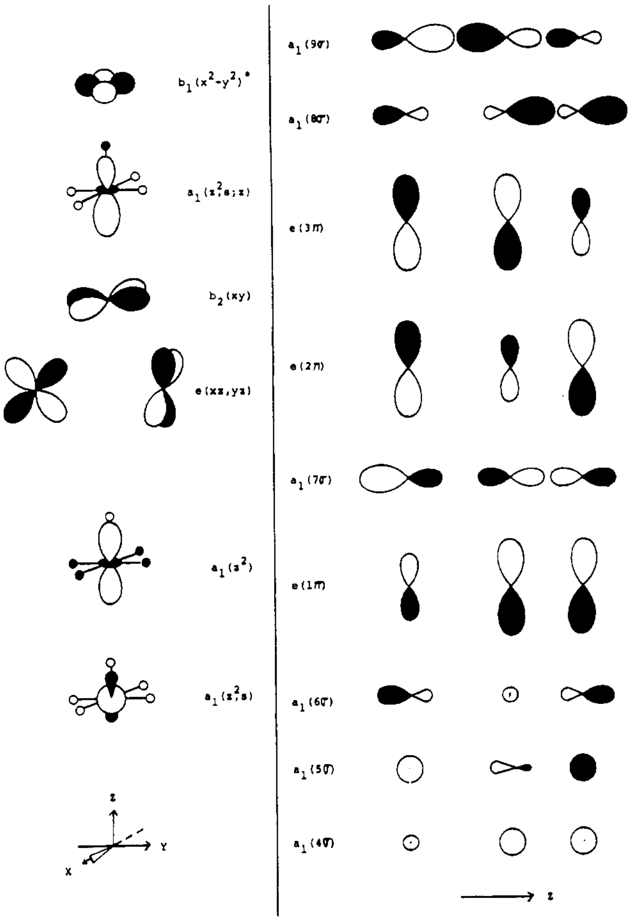
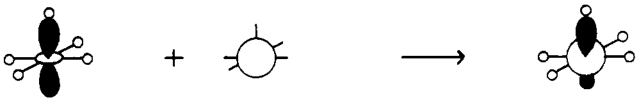


Figure 2. Schematic drawing of some valence orbitals of square-pyramidal ML_5 (left) and a linear heteronuclear triatomic (right). Orbitals are given in order but not on any energy scale.

an increase of the spatial extension of the orbital away from the five ligands and toward the site below the basal plane. A second beneficial consequence of mixing z is that it allows some metal–basal ligand π bonding. This is clearly seen in Figure 3a. The lower $a_1(z^2)$ orbital of ML_5 is a metal (z^2)–ligand σ-bonding, $z^2 + \lambda L$ combination and is shown in Figure 3b. The lowest $a_1(z^2,s)$ orbital of ML_5 is metal (z^2)–basal ligand σ bonding and metal (z^2)–apical ligand σ antibonding, **9**, with some mixing of metal s orbital. The mixing in s is in the phase relation shown in **10**. The resulting orbital, **11**, shows significant reduction of electron density toward the site below the basal plane. When the amount of mixing in s is large, the orbital can even become metal–apical ligand σ bonding, energetically lower than $a_1(z^2)$. This case for $a_1(z^2,s)$ of $Ru(NH_3)_5^{2+}$ is shown in Figure 3c.



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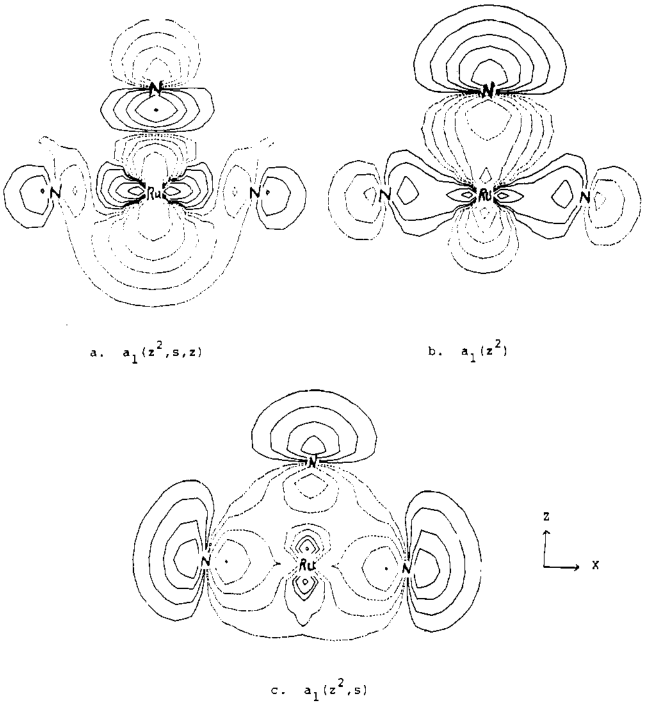
The strength of the symmetry-allowed interactions between the remaining fragment orbitals depends on the amount of overlap between the orbitals and the compatability of the orbital energies. These factors will vary with metal, triatomic, other ligands, and the separation of M–X. Our calculations indicate the following in the systems we studied here:

(1) Among the interaction of e orbitals, on the basis of the compatibility of orbital energies, only the interactions between $e(3\pi)$ of XYX and $e(xz,yz)$ of ML_5 are significant enough to be considered.

(2) For the interaction of a_1 orbitals, according to the degree of the extensions of the electron density toward the site below the basal plane, $a_1(z^2,s,z)$ of ML_5 is the orbital that strongly interacts with $a_1(6\sigma)$ and $a_1(7\sigma)$ of a triatomic approaching this site. $a_1(z^2)$ and $a_1(z^2,s)$ of ML_5 only mix in the resulting orbitals through secondary interactions.



a. $a_1(z^2,s,z)$ b. $a_1(z^2)$

c. $a_1(z^2,s)$

Figure 3. Contour diagrams of the three high-lying occupied a_1 orbitals of square-pyramidal $Ru(NH_3)_5^{2+}$. The scale of the drawing is set by the Ru–N distance of 2.144 Å.

To illustrate the relations between the energies of the fragment orbitals and the composite orbitals, the interaction diagram of $Ru(NH_3)_5^{2+} + N_2O \rightarrow [Ru(NH_3)_5NNO]^{2+}$ from our calculation is shown on the left side of Figure 4. In Figure 4 the $e(3\pi) \pm e(xz,yz)$ bonding and antibonding orbitals are referred to as e and e*. We use i, j, k, l, m (in increasing energy order) to distinguish the five a_1 molecular orbitals that are pertinent to our discussion here.

Bonding Modes of $M(NH_3)_5$ and NCO^- or N_2O

In analyzing the bonding of fragments to form the molecule, we can use three criteria as indicators.

(1) Stabilization Energy E_{st}. This is defined as the difference between the sum of the total energy of the fragments, E_{frag}, and the total energy of the composite molecule, E_{mol}:

$$E_{st} = \sum_{frag} E_{frag} - E_{mol}$$

E_{st} can also be separated into stabilization energies due to σ and π bonding, $E_{st,\sigma}$ and $E_{st,\pi}$, which are defined as

$$E_{st,\sigma} = \sum_{frag} \sum_{i} \epsilon_{i\sigma,frag} - \sum_{i} \epsilon_{i\sigma,mol}$$

$$E_{st,\pi} = \sum_{frag} \sum_{i} \epsilon_{i\pi,frag} - \sum_{i} \epsilon_{i\pi,mol}$$

where $E_{st} = E_{st,\sigma} + E_{st,\pi}$ and $\epsilon_{i\sigma,frag}$, $\epsilon_{i\pi,frag}$, $\epsilon_{i\sigma,mol}$, and $\epsilon_{i\pi,mol}$ are the ith σ- and π-orbital energies of the fragments and the molecule, respectively.

(2) Number of Electrons That Flow from One Fragment to Another, e(donor → acceptor). The electrons mainly flow from the highest occupied orbitals of the donor fragment to the lowest unoccupied orbitals of the acceptor fragment. This number can also be separated into the number of π electrons flowing from a π-donor fragment, e_π(donor → acceptor), and the number of σ electrons flowing from a σ-donor fragment, e_σ(donor → acceptor).

(3) Reduced Overlap Population, Op. Op(M–X) between atoms M and X measures the electron density in the M–X bond. It is an indication of the bond order and can also be used to evaluate the strength of the bond.

Table I. Stabilization Energy, Electron Flow, and Overlap Population

R(M-X), Å	mol species[a]	ΔE, eV[b]	E_{st}, eV[c]	$E_{st,\pi}$, eV[c]	$E_{st,\sigma}$, eV[c]	$e_\pi(M \rightarrow L)$[d]	$e_\sigma(L \rightarrow M)$[d]	Op(M-X)[e]
1.943	Co-NCO$^-$	−0.43	−1.56	0.38	−1.94	0.04	0.47	0.42
	Co-OCN$^-$		−1.13	0.31	−1.44	0.02	0.34	0.30
1.94	Ru-NCO$^-$	−0.41	−1.62	0.24	−1.85	0.10	0.38	0.44
	Ru-OCN$^-$		−1.21	0.26	−1.47	0.03	0.37	0.31
1.943	Co-NNO	−0.57	−1.67	0.093	−1.76	0.10	0.43	0.46
	Co-ONN		−1.12	0.28	−1.40	0.02	0.32	0.31
1.94	Ru-NNO	−0.71	−2.03	−0.28	−1.74	0.32	0.36	0.52
	Ru-ONN		−1.32	0.19	−1.50	0.08	0.26	0.33
1.94	Os-NNO	−0.95	−2.29	−0.49	−1.80	0.50	0.36	0.58
	Os-ONN		−1.34	0.22	−1.56	0.16	0.28	0.35
2.04	Ru-NCO$^-$	−0.39	−1.46	0.16	−1.62	0.06	0.35	0.39
	Ru-OCN$^-$		−1.08	0.16	−1.24	0.02	0.23	0.27
2.04	Ru-NNO	−0.56	−1.70	−0.12	−1.57	0.22	0.32	0.50
	Ru-ONN		−1.14	0.10	−1.25	0.06	0.24	0.29
2.04	Os-NNO	−0.75	−1.91	−0.35	−1.56	0.36	0.33	0.50
	Os-ONN		−1.16	0.14	−1.30	0.10	0.24	0.30
1.84	Ru-NN		−3.88	−1.35	−2.53	0.92	0.43	0.72
1.77	Ru-NO$^+$		−6.98	−4.73	−2.25	2.44	0.40	0.90

[a] Legend: Ru = Ru$(NH_3)_5{}^{2+}$; Os = Os$(NH_3)_5{}^{2+}$; Co = Co$(NH_3)_5{}^{3+}$. [b] $\Delta E = E$(N-bonded isomer) − E(O-bonded isomer). [c] E_{st} = stabilization energy = $[E(M) + E(L)] - E(ML)$ (M = metal fragment = $M(NH_3)_5$, L = XYZ or XY); $E_{st,\pi} = E_{st}$ due to π bonding; $E_{st,\sigma} = E_{st}$ due to σ bonding. [d] $e_\pi(M \rightarrow L)$ = number of π electrons flowing from $M(NH_3)_5$ to XYZ or XY; $e_\sigma(L \rightarrow M)$ = number of σ electrons flowing from XYZ or XY to $M(NH_3)_5$. [e] Op(M-X) = reduced overlap population between metal and the linked atom X in XYZ or in XY.

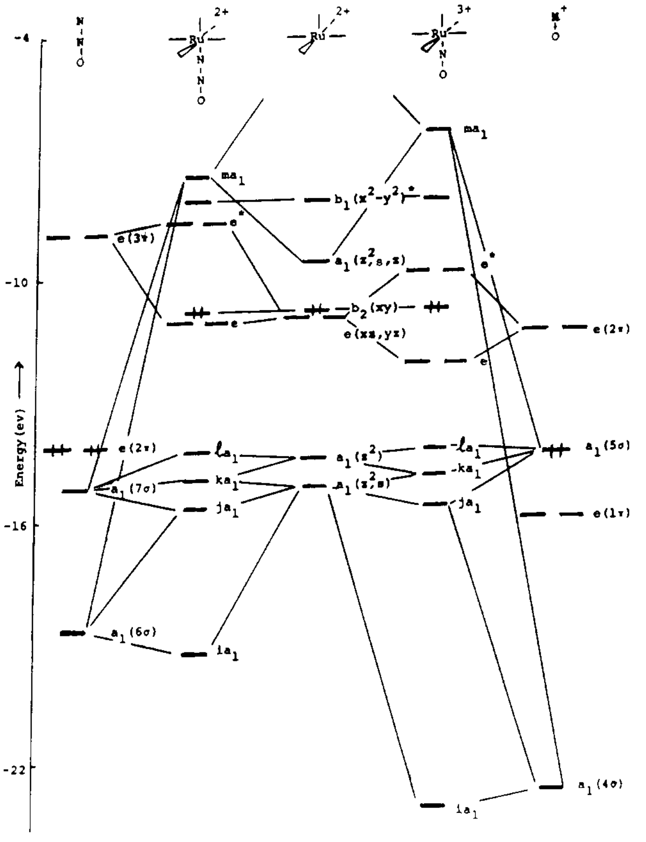


Figure 4. Interaction diagrams for square-pyramidal $Ru(NH_3)_5{}^{2+}$ (middle) interacting with N_2O (extreme left) and NO^+ (extreme right).

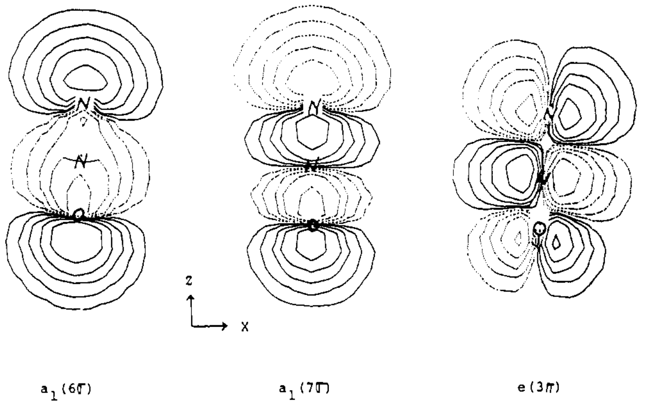


Figure 5. Contour diagrams of e(3π), $a_1(7\sigma)$, and $a_1(6\sigma)$ of N_2O. The scale of the drawing is set by the distances of N–N = 1.129 Å and N–O = 1.188 Å.

Some of the results of our calculations are summarized in Table I. A few trends can be observed from these results. First, in comparing the results for pairs of N- vs. O-linked complexes, on the basis of the values of the stabilization energy, the number of electrons flowing between the fragments, and the reduced overlap population of the M–O or M–N bond, we observed that the N-linked isomers are always more stable then their O-linked counterparts. These results can be explained in terms of the spatial extension of the relevant orbitals of the triatomics, NCO^- or N_2O. Because of the difference of electronegativities of N and O, the spatial extensions of orbitals on the N side of NNO or NCO^- are always larger than those of the O side. This phenomenon has been schematically shown in Figure 2. In order to illustrate this picture more explicitly, we also present the contour diagrams for e(3π), $a_1(7\sigma)$, and $a_1(6\sigma)$ orbitals of N_2O in Figure 5. Larger spatial extension at the N side for the orbitals of the triatomic, particularly for e(3π) and $a_1(7\sigma)$, leads to larger overlap with the orbitals of ML_5 and a larger amount of electron flow between fragments. Thus the bonds for N-linked complexes are stronger. This trend can be used to explain why most complexes of NCO^- prefer an N linkage.[2,4] It agrees with the refutations of some proposed structures of the O-linked complex of NCO^-.[5a] It also suggests that one should accept with caution the proposed structures of the O-linked complexes of NCO^-[5,18] and N_2O,[8d,e] in particular those structures deduced from analogies between the complexes of NCO^- and NCS^-. In contrast to the relation between N and O, the electronegativity of S is less than that of N, and the spatial extension at the S side in the e(4π) and $a_1(9\sigma)$ orbitals of SCN^- is larger, instead of smaller, than that at the N side.[19] Any

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(18) $Mo(NCO)_6{}^{3-}$ has been claimed to be O bonded.[4c] Our calculations (with R(M–N) = R(M–O) = 1.94 Å, and the six NCO^- ligands linearly bonded to Mo in an octahedron) gave the difference of stabilization energies of the two linkage isomers ΔE = −2.84 eV, in favor of N-bonded $Mo(NCO)_6{}^{3-}$.

(19) See our discussion of complexes of SCN^- and $N_3{}^-$ (to be submitted for publication).

(20) Only $Mo(NCO)_6{}^{3-}$ was studied.

observations related to the linkage drawn from the analogy between O in OCN^- and S in SCN^- can very easily lead to wrong conclusions.

The second but more significant trend we can observe from Table I is that, for all the complexes of triatomics we studied here and elsewhere,[19] the π-electron contribution to the bonding is relatively small. This is more clearly demonstrated by comparison with results of some analogous but "genuine" π-bonding complexes of diatomics given at the bottom of Table I. Compared with that for the complexes of the diatomics, the number of π electrons that flow from metal to ligand, which measures the π back-bonding of the metal, is 1 or 2 orders of magnitude smaller in the complexes of triatomics. The stabilization energies due to the π bonding in the complexes of triatomics either are very small or show destabilization (either $E_{st,\pi}$ = a small negative number or $E_{st,\pi}$ = positive). The origin of the difference between the bonding in the complexes of diatomics and triatomics can be deduced from a comparison of some typical interaction diagrams. For this purpose we present the interaction diagrams of

$$Ru(NH_3)_5^{2+} + NO^+ \rightarrow [Ru(NH_3)_5NO]^{3+}$$

$$Ru(NH_3)_5^{2+} + N_2O \rightarrow [Ru(NH_3)_5NNO]^{2+}$$

side by side in Figure 4.

The coordination modes of diatomic ligands in transition-metal complexes have been discussed by Hoffmann, Chen, and Thorn.[14] Those orbitals of the diatomic relevant to the bonding, i.e. $e(2\pi)$, $a_1(5\sigma)$, and $a_1(4\sigma)$, are analogous to the $e(3\pi)$, $a_1(7\sigma)$, and $a_1(6\sigma)$ orbitals of the triatomic we discuss here. Figure 4 shows that the general features of the interaction between a ML_5 fragment with a 10-electron diatomic and with a 16-electron triatomic are the same, namely (1) the $e(xz,yz)$ orbitals of ML_5 interact with the lowest unoccupied $e(\pi)$ orbitals of the ligand to produce the bonding e orbitals and antibonding e* orbitals and (2) the $a_1(z^2,s,z)$ orbital of ML_5 interacts strongly with two higher lying occupied $a_1(\sigma)$ orbitals of the ligand. The resulting MO's will be perturbed further by the $a_1(z^2)$ and $a_1(z^2,s)$ orbitals of ML_5, finally leading to the five molecular orbitals, ia_1, ja_1, ka_1, la_1, and ma_1, of the complexes. The quantitative features of the two kinds of interactions, however, do show significant differences. For the complexes of the diatomic, because the energy of the empty $e(2\pi)$ orbital of the diatomic is lower than that of the occupied $e(xz,yz)$ orbitals of ML_5, the interaction between the orbitals produces a higher unoccupied antibonding orbital and a lower occupied bonding orbital. The net effect is π back-bonding, in which electrons flow from metal to ligand, leading to stabilization of the complexes. The situation for the complexes of a triatomic is quite different. The energy of the empty $e(3\pi)$ orbital of the triatomic is higher than that of the occupied $e(xz,yz)$ of ML_5. Interactions between these orbitals either are too small or produce bonding and antibonding orbitals both higher than $e(xz,yz)$. This leads either to insignificant π back-bonding or sometimes to destabilization.

Table II. Extended Hückel Parameters

orbital		H_{ii}, eV	exponents[a]	
			1	2
H	1s	−13.60	1.30	
C	2s	−21.4	1.625	
	2p	−11.4	1.625	
N	2s	−26.00	1.95	
	2p	−13.40	1.95	
O	2s	−32.3	2.275	
	2p	−14.8	2.275	
Mo	3d	−10.50	4.540 (0.58979)	1.9010 (0.58979)
	4s	−8.34	1.96	
	4p	−5.24	1.90	
Co	3d	−13.18	5.55 (0.55508)	1.90 (0.64609)
	4s	−9.21	2.00	
	4p	−5.29	2.00	
Ru	4d	−11.12	5.380 (0.53427)	2.30 (0.63676)
	5s	−8.60	2.080	
	5p	−3.59	2.040	
Os	5d	−10.946	5.571 (0.63719)	2.416 (0.55980)
	6s	−8.492	2.452	
	6p	−3.479	2.429	

[a] Two Slater exponents are listed for the d orbitals, each followed in parentheses by its coefficient in the double-ζ expansion.

The small π character in the bonding of complexes of the triatomics is also the reason for small reduced overlap population between the metal and the triatomic, Op(M–X), given in Table I. It is also responsible for the relatively weaker M–X bonds and longer M–X bond distances in the complexes of the triatomic in comparison with those of their diatomic counterparts. Our results here suggest that one should be cautious in judging the numerous statements in the literature and textbooks about the "mainly π bonding" character in the coordination of NCO^-, NCS^-, and N_3^- to transition metals, in particular those speculations deduced from the analogy between the complexes of the diatomic and of the triatomic.

The third trend we can observe from Table I is that, at reasonable estimated bond distances of $M(NH_3)_5$ and N_2O, the stability of the $M(NH_3)_5N_2O$ complexes increases in the order M = Co, Ru, and Os. These results suggest that N_2O may form more stable complexes with metals in the third transition series. Some of these complexes may be stable enough for their structure to be determined, which could shed light on the linkage of N_2O complexes.

We also observe the stabilities of the $Ru(NH_3)_5^{2+}L$ and $Co(NH_3)_5^{3+}L$ complexes increase from L = NCO^- to L = N_2O. For the Ru complexes, this trend agrees with the fact that a synthesis has been reported for $[Ru(NH_3)_5N_2O]^{2+}$,[8] but not for $[Ru(NH_3)_5NCO]^+$. Furthermore, a stable Ru complex of NCO^- has been reported, $[Ru(NH_3)_5NCO]^{2+}$, but it is a complex of Ru^{III} rather than of Ru^{II}. For the Co complexes, the differences between E_{st} values of $[Co(NH_3)_5N_2O]^{3+}$ and $[Co(NH_3)_5NCO]^{2+}$ are smaller than the differences (a) between those of Ru–NNO and Ru–NCO^- complexes, (b) among those of different M–NNO complexes, and (c) among those of different M–NCO^- complexes. Even though calculations based on more accurate method may modify our data, our results do suggest that $[Co(NH_3)_5N_2O]^{3+}$ and $[Co(NH_3)_5NCO]^{2+}$ could have the same stability within 1 order of magnitude. However, because of some problems of synthesis or kinetic reasons, no stable $[Co(NH_3)_5N_2O]^{3+}$ has been observed yet.

In summary, our studies indicate the following for the coordination of N_2O and NCO^- to ML_5:

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(22) "Table of Interatomic Distances and Configuration in Molecules and Ions", Chemical Society, London, 1958, M45.

(23) Based on crystal structure of $[Ru(NH_3)_5NO]Cl_3 \cdot H_2O$: F. Bottomley, *J. Chem. Soc., Dalton Trans.*, 1600 (1974).

(24) N–N = 1.115 Å is averaged from the values ranging from 1.106 to 1.124 Å for different transition-metal dinitrogen complexes (R. B. Davies, N. C. Payne, and J. A. Ibers, *Inorg. Chem.*, **8**, 2719 (1969); *J. Am. Chem. Soc.*, **91**, 1240 (1969); I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 6512 (1969)) and the value of 1.0976 Å for gaseous dinitrogen (P. G. Wilkinson and N. B. Houk, *J. Chem. Phys.*, **24**, 528 (1956)).

(25) A. F. Wells, "Structural Inorganic Chemistry", 4th ed., Oxford University Press, New York, 1975, p 745.

(26) Based on geometry of gaseous N_2O: F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th ed., Wiley, New York, 1980, p 423.

(27) Based on crystal structure of $[Co(NH_3)_5N_3](N_3)_2$: G. J. Palenik, *Acta Crystallogr.*, **17**, 360 (1964).

(28) Ru–N_2 = 1.84 Å, based on the crystal structure of $[Os(NH_3)_5N_2]Cl_2$: J. E. Fergusson, J. L. Love, and W. T. Robinson, *Inorg. Chem.*, **11**, 1663 (1972).

(29) Ru–NH_3 = 2.144 Å based on the crystal structure of $[Ru(NH_3)_6]I_2$: H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

(30) Os–NM_3 = 2.14 Å based on the crystal structure of $[Os(NH_3)_5N_2]Cl_2$ in ref 28.

Table III. Bond Lengths and Bond Angles

mol species	bond length, Å and bond angle, deg	ref
OH^-	O-H = 0.971	21
OH_2	O-H = 0.959, ∠HOH = 104.5	21
NH_3	N-H = 1.015, ∠HNH = 107	22
NO^+, N_2	N-O = 1.172, N-N = 1.115	23, 24
CO, CN^-	C-O = 1.15, C-N = 1.155	25
NNO	N-N = 1.129, N-O = 1.188	26
NCO^-	N-C = 1.18, C-O = 1.20	25
$Co(NH_3)_5{}^{3+}XYZ$ (XYZ = NNO, ONN, NCO^-, OCN^-)	$Co-NH_3$ = 1.96, Co-X = 1.943	27
$Ru(NH_3)_5{}^{2+}XY$ (XY = NO^+, N_2, CO, CN^-)	$Ru-NH_3$ = 2.077, Ru-X = 1.77	23
$[Ru(NH_3)_5N_2]^{2+}$	$Ru-NH_3$ = 2.144, $Ru-N_2$ = 1.84	28
$Ru(NH_3)_5{}^{2+}XYZ$ (XYZ = NNO, ONN, NCO^-, OCN^-)	$Ru-NH_3$ = 2.144, Ru-X = 1.94, 2.04	29
$Os(NH_3)_5{}^{2+}XYZ$ (XYZ = NNO, ONN)	$Os-NH_3$ = 2.14, Os-X = 1.94, 2.04	30
$Mo(XYZ)_6{}^{3-}$ (XYZ = NCO^-, OCN^-)	Mo-X = 1.96	18

(1) On the basis of the spatial extensions of the fragment orbitals relevant to the bonding, N-linkage complexes are more stable than their O-linkage counterparts.

(2) On the basis of the compatibility of the energies of the fragment orbitals relevant to the interaction, the bonding is accomplished mainly through σ bonding, with donation of electrons from the σ orbital of the ligand to the metal. There is a very small amount or no π back-bonding.

(3) Complexes of N_2O and metals in the third transition series, such as $[Os(NH_3)_5N_2O]^{2+}$, may be stable.

In conclusion, we might note the future directions in which our present work will be extended. The immediate extension, which is already under way, is to study[19] the coordination of NCS^- and $N_3{}^-$ to transition metals. The problems are similar to those of this study except that the variation of ∠MXY, which is insignificant here,[16] will be a dominant variable. A further extension would be to study the bonding of ML_nXYZ (n = 3, 4, 5) in different geometries, with different coordinations and for different electron counts of the metal. A similar qualitative discussion for diatomic ligands has been given before.[13,14] We would like to investigate those features that are unique to the triatomic ligands.

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Appendix

The $M(NH_3)_5XYZ$ or $M(NH_3)_5XY$ calculations that underlie the arguments used in this paper are of the extended Hückel type[11] with "weighted" H_{ij}'s.[12] The metals, M, studied are Mo,[20] Co, Ru, and Os. The triatomic ligands, XYZ, investigated are N_2O and NCO^-. The diatomic ligands, XY, investigated are NO^+, N_2, CO, and CN^-. The atomic basis sets included single Slater-type functions for all orbitals except the metal d orbitals. The parameters for the elements used are listed in Table II. The parameters of main-group elements, and of Co and Mo, are standard ones taken from earlier work.[11] The H_{ii}'s of Ru and Os are obtained from quadratic charge iteration on $Ru(NH_3)_6{}^{2+}$ and $Os(NH_3)_6{}^{2+}$ by us.

When the triatomic ligands are linearly bound to $M(NH_3)_5$, the geometry of $M(NH_3)_5XYZ$ is chosen to have pseudo-C_{4v} symmetry. In the study of the variation of the angle ∠MXY in the bent $M(NH_3)_5XYZ$, the MXY bond is bent in the "staggered conformation" (i.e., ∠MXY is bent in a plane that bisects the two perpendicular $M(NH_3)_3$ planes of the square-pyramidal $M(NH_3)_5$). The bond lengths and bond angles used are given in Table III. The bond lengths in the ligands, and the metal-to-NH_3 distances, are experimental ones. For the M–X distances, experimental values are used whenever they are available. For the complexes with no experimental M–X distances available, we presented the calculated results at two estimated M–X distances (M–X = 1.94 and 2.04 Å) to indicate that our discussion and conclusion are valid within a range of plausible M–X distances.

Registry No. N, 17778-88-0; O, 17778-80-2; $[Ru(NH_3)_5N_2O]^{2+}$, 25069-25-4.